



ENVIRONMENT
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**A Review of the Industrial Uses
of Continuous Monitoring Systems:
Metals Industry Processes**

Environment Agency
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**A REVIEW OF THE INDUSTRIAL USES OF
CONTINUOUS MONITORING SYSTEMS:
METALS INDUSTRY PROCESSES**

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EXECUTIVE SUMMARY.

INTRODUCTION

This report presents the findings of a study into the potential application of continuous monitoring techniques within the UK Metals Industry, with particular reference to:

- The availability of continuous monitoring techniques and equipment;
- Calibration/verification procedures;
- Process operator experience of continuous monitoring.

The range of metals and associated manufacturing processes encountered in the UK Metals Industry is diverse; ranging from large integrated steel works with capacities of over 3 million tonnes/year at a single site, to small non-ferrous metal recycling plants producing around 5 000 tonnes/year of ingot from dross and scrap.

In terms of production output, the UK metals sector is dominated by the iron and steel industry (circa 14.8 mt/y), followed by the primary and secondary aluminium sectors (circa 0.84 mt/y), the copper and brass industry (circa 0.5 mt/y), a variety of other metals, including lead, zinc, magnesium, titanium, nickel and tin, together with small quantities of precious and refractory metals.

This diversity is reflected in the management structures and resources available within the various sectors of the industry to satisfactorily support the maintenance and calibration of continuous monitoring equipment.

SOURCES OF POLLUTION

The principal sources of pollution in those parts of the Metals Industry that are defined in Chapter 2 of the Prescribed Processes Regulations (SI 472) typically include the following:

Releases to air:

- Emissions from smelting of ores (primary metals production), which, depending on the process, typically include a variety of combustion gases, acid gases and metal compounds in the form of particulate, including fume;
- Emissions from melting scrap (secondary metals production), mainly consisting of gases and particulate/fume, with the attendant risk of increased pollution caused by the disassociation of contaminants in the scrap;
- Fume containing metal oxides and other compounds, which are formed during casting, cutting and flame scarfing operations;
- Combustion gases from various heating and heat treatment processes;

- Fugitive windborne dust from stockpiles of raw materials such as ores and coal, together with dust arising during materials handling and movement of vehicles on unmade roads;
- A variety of other sources of atmospheric emissions exist in the Metals Industry, including, for example, oil laden mist from cold rolling operations and emissions from surface treatments, such as pickling of copper with alcohol and pickling of stainless steel with HF/HNO₃ acid.

Releases to water:

The releases to water will depend on the nature of the process but typically include:

- Metals in solution or together with other materials in the form of suspended solids
- Acids/alkalis
- Oils, greases and solvents

Releases to land:

The quantity and characteristics of the process by-products that may be disposed of by landfill vary according to the nature of the processes but typically include:

- Drosses
- Slags
- Sand from casting operations
- Dusts captured by fume cleaning systems

A number of processes related to the Metals Industry, that are outside the "Chapter 2 processes", such as coke oven plant, coated strip products and anode production facilities in the primary aluminium industry, are sources of a variety of organic species, which can be released to air, water and land. Whilst these potential sources of pollution are significant and warrant strict control, they do not form part of the scope of this report.

APPLICATION OF CONTINUOUS MONITORING SYSTEMS

Monitoring of releases is a key element of regulatory control. The Environment Agency expects operators to implement best available techniques for monitoring, which it regards as on-line continuous monitoring methods where they are available, practical and not entailing excessive cost (NEEC) in relation to the process and its environmental impact. The definition of "NEEC" is industry specific and is likely to be the subject of much debate:

The diversity of scale of operation and process technology within the Metals Industry makes it difficult to generalise on the potential application of continuous monitoring systems. The

following observations summarise some of the additional issues that need to be taken into account.

- With the exception of a limited number of continuous processes, such as sinterplant and to a lesser extent primary aluminium potlines and electrolytic copper refineries, the vast majority of processes encountered in the metals industry are either batch processes or involve operating cycles that give rise to variations in release rates. Consequently, care is needed in interpreting the readings of continuous monitors in the Metals Industry and satisfactory regulatory protocols are required where measurements are used as the basis of demonstrating compliance with process authorisations.
- Continuous monitoring instruments need regular servicing to maintain their reliable operation. Many process operators within the metals industry, particularly the smaller operations, do not at present have the resources or expertise to satisfactorily maintain continuous monitoring instruments. Consequently, such operators would need to rely on third parties to maintain and calibrate continuous monitors or, alternatively, train existing staff to perform such tasks.
- Calibration of continuous monitoring systems can be complex and expensive.
- Keeping monitoring instruments operational and calibrated in the harsh environment of the Metals Industry presents a significant challenge.
- Many plants in the Metals Industry are old and suitable locations for monitoring instruments are often unavailable.
- There has been limited encouragement for the indigenous instrument industry in the UK to develop and market continuous monitoring equipment for the Metals Industry Sector. There is a wide selection of monitoring instruments available within the UK, but the majority are manufactured abroad. Importers are well informed but because of the diversity of the Metals Industry and the perceived limited market, the instrument suppliers do not appear to be focusing their sales effort in this sector.

Continuous monitoring of **particulate matter** is well established in the Metals Industry. If, as is sometimes the case, the proportion of polluting substances in a particulate emission is essentially constant (as established by manual measurements during a process cycle and over a period of time), then continuous measurement of particulate concentration is a practical and effective method of monitoring the emission of these substances. Particulate monitors, however, employ indirect methods of measurement and readings outside the calibration conditions may provide little more than a qualitative indication. The effect of changes in particulate characteristics on the accuracy of continuous particulate monitors can be significant. Also, the accuracy of the currently available calibration methods is uncertain at the low concentrations of fine particulate commonly emitted from modern fume abatement systems. No satisfactory methods are available for continuous particulate measurement in the emissions from wet scrubbers, which are still in use in the Metals Industry. However, surrogate methods based on plant variables such as fan motor current, spray pressure, etc, may be adopted to monitor the function of such abatement equipment.

Many of the instruments that are well established for continuously monitoring emissions from Incinerators and Large Combustion Plant are also suitable for application to **combustion processes** in the Metals Industry. However, these instruments have proven less suitable for monitoring the **gases emitted from metals processes**. In particular, instrumentation for monitoring emissions from those smelting operations which are characterised by corrosive emissions associated with hydrogen chloride, sulphur compounds and fluoride, have proven difficult to keep in operation owing to fouling and corrosion of the monitors and their sampling systems.

Continuous monitoring of **metals and other substances in airborne particles** has so far proven impractical, because of apparently insurmountable problems of continuous extractive sampling of particulate in air.

Continuous monitoring of the common parameters associated with liquid effluent, such as **flow, pH, suspended solids and oil-on-water**, is well established in the water treatment industry and relatively straightforward to apply to the Metals Industry. However, the associated sampling arrangements are extensive and have relatively high maintenance demands.

Continuous monitoring of the **metals content** of releases to water has been shown to be practicable, but the instruments are costly (>£50 000), difficult to apply and expensive to maintain.

In some cases it is appropriate to consider **surrogate methods** of monitoring, including where it is impractical to apply direct continuous measurement of a released substance. Surrogate methods are usually based on process measurements. Process data is usually available stored within sophisticated control systems on larger plant in the Metals Industry. Software is available which can assist in the application of surrogate techniques, but the difficulty of keeping instruments in operation and calibrated can often cast doubt on the accuracy and interpretation of the results.

Systems suitable for **logging** monitoring data are widely available. On sites where process control and data acquisition systems are already established, these can provide a convenient means of logging data.

It was evident from the study that it is not practicable to apply continuous monitoring to **releases to land** from Metals Industry sites. However, contaminants in leachate and surface water run-off from material stored on site are amenable to continuous monitoring.

PRESENTATION OF THE REPORT

Section 1 of the report summarises the objectives and scope of this study, together with the sources of data used.

Section 2 is a brief overview of the UK ferrous and non-ferrous Metals Industry potential releases of prescribed substances within each sector; [Tables 2.2 to 2.6 summarise potential releases and the processes are described in Appendix 1].

Section 3 of the document describes the application of continuous monitoring equipment, the sensitivity and cross-sensitivity of current proprietary instruments and European best practice; [See Tables 3.3 to 3.6 for details].

Section 4 summarises the feedback on some of the UK Metal Industry's experience of Continuous Monitoring Systems, the likely costs of monitoring and the typical locations where monitors are currently used within the industry; [See Tables 4.1 and 4.2 for details].

Section 5 and 6 deal with calibration of continuous monitoring instruments and the current development of new continuous monitoring technology.

Section 7 presents the conclusions of the study.

Detailed background information forming part of the study is contained in the following Appendices:

- Appendix 1 - Description of Metals Industry processes and potential releases
- Appendix 2 - Generic principles of continuous monitoring techniques
- Appendix 3 - Detailed data on available continuous monitoring instruments
- Appendix 4 - Summary of the continuous monitoring equipment suppliers contacted during the study, together with their principal products and capabilities.

1. INTRODUCTION

1.1 BACKGROUND

The Environmental Protection Act 1990^{Ref 1} introduced a system of Integrated Pollution Control (IPC) for application to the most potentially polluting and/or technologically complex industrial processes. The processes that are prescribed for IPC are defined in the Environmental Protection (Prescribed Processes and Substances) Regulations 1991^{Ref 2} and subsequent amendments^{Ref 3}. In England and Wales, processes prescribed for IPC are regulated by the Environment Agency ("the Agency").

A key feature of IPC is a requirement for operators to monitor their releases using the best available monitoring techniques. Some guidance on appropriate monitoring techniques is included in the

- Chief Inspector's Process Guidance Notes for the various sectors of industry
- Environment Agency IPC Guidance Notes

However, more detailed information is being provided by the Environment Agency's National Compliance Assessment Service in the form of Technical Reports and Technical Guidance Notes on monitoring.

This Technical Report on the application of continuous monitoring to the Metals Industry forms part of a series providing such additional guidance for all IPC process sectors.

1.2 STUDY OBJECTIVES

McLellan and Partners Ltd were commissioned by the Agency to carry out a study with the following aims:

- To review the application of continuous monitoring techniques to the Metals Industry, in particular the suitability of applying such continuous techniques to metals industry

processes, together with the availability of appropriate techniques and instrumentation.

- To collate details of instrumentation manufacturers, costs, performance characteristics and reliability of techniques and instruments.
- To summarise the present application of these techniques across the Metals Industry.

1.3 SCOPE OF WORK

The Agency's terms of reference listed the following seven tasks:

Task 1 : Review of the suitability of continuous monitoring techniques for Metals Industry processes.

Task 2 : Review of continuous monitoring technique availability.

Task 3 : Review of relevant research and development.

Task 4 : Review of the generic principles of relevant continuous monitoring technologies.

Task 5 : Review of calibration / verification procedures.

Task 6 : Review of manufacturers and techniques/ instrument summary details.

Task 7 : Review of required operator experience and actual operator experience.

It should be noted that the processes covered by this report are limited to those described in the Guidance Notes for the various sections of the Metals Industry (IPR 2/1 to 2/12).

Certain processes associated with the industry are therefore excluded from the report; principally steel coating (coating processes), coke ovens (carbonisation processes) and the manufacture of electrodes for aluminium smelting (tar and bitumen processes).

1.4 ORGANISATION OF THE REPORT

The body of the Report is organised as follows:

- Section 2 summarises the potential releases from the various sectors of the Metals Industry, in the form of Tables of Releases
- Section 3 summarises the infrastructure and impact of legislation on the application of monitors. It then discusses the various pollutant substances in the order in which they have been noted in the Tables of Releases, indicating the applicability and suitability of measurement techniques.
- Section 4 describes the experience of UK metals process plant operators concerning continuous monitoring.
- Section 5 describes the calibration and verification procedures appropriate to continuous monitoring in the Metals Industry.
- Section 6 presents information on relevant developing technology.
- Section 7 summarises the findings of the study.
- A glossary of terms used in the study and a list of references are given in Sections 8 and 9 respectively.
- The principal processes in the Metals Industry are described, and the main sources of potential releases identified, in Appendix 1.
- Generic principles of relevant measurement techniques are presented in Appendix 2.
- Details of proprietary instrumentation available in the UK are tabulated in Appendix 3.

- Data on the various companies supplying continuous monitors are tabulated in Appendix 4.

1.5 INFORMATION SOURCES

The principal sources of information used during the study are described below.

1.5.1 Industry Organisations

- UK Steel Association (formerly the British Iron and Steel Producers' Association).
- British Non Ferrous Metals Federation.
- Aluminium Federation.
- Lead and Zinc Development Associations (LDA and ZDA).
- Minerals Industry Research Organisation (MIRO).
- The Trade Association for the Instrumentation, Control and Automation Industry in the UK (GAMBICA)
- Council of Gas Detection & Environmental Monitoring (COGDEM)

1.5.2 Manufacturers of Instrumentation and Associated Equipment

Questionnaires were issued to 83 manufacturers of equipment for the continuous monitoring of releases to air and water; 36 companies replied with information and a further five were later identified which were able to offer suitable products.

Detailed discussions were subsequently held during visits or by telephone to some twenty manufacturers.

1.5.3 Operating Companies

Visits were made to 16 operating companies and telephone interviews held with a further nine to obtain information on users' experience with continuous monitoring in the following sectors of the UK Metals Industry :

- Iron and Steel
- Aluminium (Primary and Secondary Sectors)

- Copper
- Lead and Zinc

1.5.4 Other Sources

Other sources of information were:

- National Physical Laboratory
- Environment Agency personnel and the Public Registers in their Regional Offices
- Lancaster, Leeds, Luton and De Montfort Universities
- British Standards Institution
- Publications as referenced elsewhere in this report

1.5.5 Acknowledgement

The authors would like to thank all those who contributed information and acknowledge that without the high level of co-operation received, the preparation of this report would not have been possible.

2. POTENTIAL RELEASES FROM METALS INDUSTRY PROCESSES

This Section identifies the various pollutant species released from Metals Industry processes. The releases associated within specific sectors of the industry are summarised in three tables at the end of the Section - emissions to air, discharges to water and solid wastes, respectively. Tables summarising Process Guidance Note recommended achievable levels for Part A processes and emission limits for Part B processes are also given. As an indication of current best-practice requirements elsewhere in Europe for emissions limits, a further table is provided, summarising German regulations.

2.1 INTRODUCTION

The production of metals is usually classified as either:

- Primary production - the extraction of metals from primary sources such as ores, mineral concentrates and mattes or
- Secondary production - the recovery of metals from new and old scrap and other non-primary sources such as drosses and residues.

The UK steel industry was originally developed based on indigenous iron ore deposits. However, owing to the current absence of domestic deposits containing commercially viable contents of iron, the UK production of iron and steel is now based on imported ores, imported concentrates, and scrap predominantly arising in the UK.

Aluminium, lead, nickel and zinc are the only non-ferrous metals produced in significant quantities in the UK from primary sources. There are no commercially viable domestic ore deposits of these metals and the primary production is from imported feed materials.

Despite the absence of domestic ore deposits, the UK Metals Industry is diverse and more than 15 metals are currently produced in its various sectors. The activities of the Metals Industry within the scope of this study are the processes prescribed for IPC, described in the

Chief Inspector's Process Guidance Notes IPR 2/1 to 2/12, which include the production and manufacture of:

Semi-Finished Products: Ingot, slab, bloom, billet and cathode.

Finished Products: Plate, sheet, strip and foil ("flat products").
Rod, bar and sections ("long products").
Castings.

2.2 SIZE AND STRUCTURE

The current total production of the UK Metals Industry is estimated at approximately 17 million tonnes per year. Estimates of the production levels in the main sectors of the industry are shown in Table 2.1.

The iron and steel sector accounts for over 85 % of the total tonnage of metals produced in the UK. The sector is dominated by British Steel plc, which operates the four integrated iron and steel works in the UK. British Steel also manufactures a wide range of flat, tubular and semi-finished steel products, engineering steels and has holdings in UK companies manufacturing stainless steel.

Much of the non-ferrous metals industry is dominated by companies with current, or historical, overseas connections. Examples include RTZ and UK subsidiaries of Alcan Aluminium (Canada) and Alcoa (USA) in the aluminium industry, UK subsidiaries of MIM Holdings (Australia) in the case of lead and zinc, BICC and Delta in the copper sector and UK subsidiaries of INCO (Canada) for nickel and precious metals.

TABLE 2.1
ESTIMATED CURRENT PRODUCTION OF THE UK METALS INDUSTRY
(Tonnes per year)

SECTOR	ANNUAL PRODUCTION	NOTES
ALUMINIUM Primary Secondary	240 000 600 000	
COPPER AND COPPER ALLOYS	500 000	
IRON AND STEEL Integrated Steelworks Ferrous Foundry Processes Electric Arc Steelmaking & Secondary Steelmaking	14 800 000	Includes all sectors
LEAD Primary Secondary	210 000 155 000	
NICKEL	30 000	Includes cobalt
OTHER METALS	5 000	See note
TIN	10 000	Includes bismuth
ZINC Primary Secondary	100 000 240 000	

Note: Other metals include cadmium, gold, mercury, platinum group metals and refractory metals (molybdenum, tungsten and chromium).

The estimated numbers of IPC authorisations in the UK Metals Industry, based on the indexes of Public Registers at March 1996, are shown below:

- Iron and Steel - Section 2.1 (Part A). 38
- Non Ferrous Metals - Section 2.2 (Part A). 106
- Total. 144

2.3 RELEASES

The principal processes used in the UK Metals Industry, and the main releases of prescribed and other substances from the processes, are described in Appendix 1. Further information is available in the HMIP/Agency-commissioned Technical Reports and Process Guidance Notes as referenced in the text of the Appendix.

The prescribed and other principal substances in potential releases to air, water and land from the UK metals industry are summarised in Tables 2.2, 2.3 and 2.4 which follow.

UK emission limits are summarised in Tables 2.5 and 2.6 (Part A and Part B processes respectively). As an indication of practices elsewhere in Europe, the emission limits given in TA Luft ^{Ref 7} are summarised in Table 2.7.

Table 2.2 Principal Releases to Air from Metals Industry Processes

	Integrated Iron & Steel works	Ferrous Foundry Processes	Sec Steelmaking & Special Alloy Processes	Zinc & Zinc Alloy Processes	Lead & Lead Alloy Processes	Refractory Metals Processes	Cadmium & Mercury Processes	Aluminium & Aluminium Alloy Processes	Copper & Copper Alloy Processes	Precious Metals Processes *	Nickel & Cobalt Processes	Tin & Bismuth Processes
Particulate matter	X	X	X	X	X	X	X	X	X	X	X	X
Iron oxide	X	X	X									
Lead and its compounds	X		X	X	X				X	X		X
Zinc and its compounds	X		X	X	X	X			X			
Cadmium and its compounds	X		X	X	X		X					X
Mercury and its compounds				X	X		X					
Copper and its compounds									X			X
Aluminium and its compounds						X		X				
Nickel and its compounds									X		X	
Arsenic, selenium and tellurium				X	X	X				X		X
Antimony and its compounds				X	X							X
Chromium and its compounds						X						
Tungsten, molybdenum compounds						X						
Tin and its compounds									X			X
Oxides of sulphur	X	X	X	X	X	X		X	X	X		
Oxides of nitrogen	X	X	X	X	X			X	X	X	X	
Carbon monoxide	X	X	X	X	X	X		X	X		X	
Hydrogen	X											
Chlorine								X		X		X
Hydrogen chloride	X	X	X	X	X			X	X	X	X	X
Hydrogen fluoride	X		X	X	X			X			X	
Hydrogen sulphide	X											
Ammonia	X	X					X	X			X	X
Amines and amides		X										
Volatile organic compounds	X	X	X	X	X		X	X	X		X	X
Polycyclic aromatic hydrocarbons								X				
Dioxins	X	X	X	X				X	X			
Oil mist	X							X			X	X
Odours	X	X	X	X	X	X	X	X	X	X	X	X

Source: Chief Inspector's Guidance Notes

Table 2.3 Principal Releases to Water from Metals Industry Processes

	Integrated Iron and Steelworks	Ferrous Foundry Processes	Sec Steelmaking & Special Alloy Processes	Zinc and Zinc Alloy Processes	Lead and Lead Alloy Processes	Refractory Metals Processes	Cadmium and Mercury Processes	Aluminium & Aluminium Alloy Processes	Copper and Copper Alloy Processes	Precious Metals Processes	Nickel and Cobalt Processes	Tin and Bismuth Processes
Suspended solids	X	X	X	X	X	X	X	X				X
Metal oxide particulates	X	X	X									
Hydrocarbons	X	X	X	X	X			X	X		X	X
Phenol	X											
Oil and grease	X	X	X					X				
Aluminium								X				
Antimony												X
Arsenic												X
Cadmium	X	X		X	X		X					X
Chromium	X	X										
Copper				X					X			X
Iron	X	X										
Lead	X	X	X	X	X							
Mercury				X	X							
Nickel	X										X	
Platinum group metals										X		
Silver										X		
Tin												X
Zinc	X	X	X	X								
Chlorides										X		X
Cyanides	X											
Fluorides	X										X	
Nitrates												
Phosphates	X	X	X									
Sulphates	X			X	X				X			
Thiosulphates										X		
Ammonia	X									X		X
Acidic waste liquors	X		X						X		X	X
Caustic waste liquors											X	X
Biocides	X	X	X	X	X	X	X	X	X	X	X	X
Coagulents	X	X	X	X	X	X	X	X	X	X	X	X

Source: Chief Inspector's Guidance Notes

Table 2.4 Principal Solid Wastes from Metals Industry Processes

	Integrated Iron and Steelworks	Ferrous Foundry Processes	Sec Steelmaking & Special Alloy Processes	Zinc and Zinc Alloy Processes	Lead and Lead Alloy Processes	Refractory Metals Processes	Cadmium and Mercury Processes	Aluminium & Aluminium Alloy Processes	Copper and Copper Alloy Processes	Precious Metals Processes	Nickel and Cobalt Processes	Tin and Bismuth Processes
Refractories	X	X	X	X	X	X	X	X	X	X	X	X
Slags												
- blast furnace	X											
- steelmaking	X											
- ingot casting	X											
- arc furnace		X	X									
- ladle treatment			X									
- induction furnace			X									
- electroslag remelting			X									
- desulphurisation process		X										
- modularisation process		X										
- ISP (lead, zinc)				X	X							
- soda (lead)					X							
- salt (Al, mer. oxide/chloride/fluoride)								X				
- iron silicate, lime									X			
- miscellaneous						X	X			X	X	X
Drosses												
- zinc recovery process (low Zn)				X								
- Al, mer. oxides/chlorides/fluorides								X				
Sludges												
- gas cleaning - blast furnaces	X											
- gas cleaning - steelmaking	X											
- gas cleaning - (Hg, As, Se, Te)				X	X							
Dusts												
- Fume cleaning - metal oxides	X	X	X									
- Al, metal oxides/chlorides/fluorides								X				
- copper, zinc, lead and tin oxides									X			
Sand - casting/reclamation (silica)		X						X				
Coke fines				X								
Calomel				X	X							
Plastics & rubber, non-recyclable					X							
SPL - carbon, fluorides, cyanides								X				

Source: Chief Inspector's Guidance Notes

Table 2.5 Achievable Releases for New Processes - SI 472 Section 2 Part A Processes

Parameter of Interest	Sinter Plants IPR 2/1	Blast Furnace IPR 2/1	BOS Gas Cleaning Plants IPR 2/1	Rolling and Pickling IPR 2/1, IPR 2/3	EDF and AOD IPR 2/2, IPR 2/3	Ladle treatment IPR 2/2, IPR 2/3	Leaded Steels IPR 2/2, IPR 2/3	St. Steel & Special Alloy IPR 2/2, IPR 2/3	Zinc and Zinc Alloys IPR 2/4	Lead and Lead Alloys IPR 2/5	Refractory Materials IPR 2/6	Cadmium and Mercury Processes IPR 2/7	Aluminium Processes IPR 2/8	Copper and Copper Alloys IPR 2/9	Platinum Group Metals IPR 2/10	Cobalt and Nickel Processes IPR 2/11	Ti and Bismuth Processes IPR 2/12
	mg/m ³																
Total Particulate	60 [^]	10	50	20	20	10	10	10	10	10	10	2	10	10	10	30	10
Lead and its compounds	1	1	1	1	1	1	3	1	2	2	2			2	2		2
Zinc and its compounds																	
Cadmium and its compounds					0.2	0.2	0.2	0.2	0.5 ¹	0.5 ¹		0.1					
Mercury and its compounds									0.5 ¹	0.5 ¹		0.05					
Thallium and its compounds									0.5 ¹	0.5 ¹							
Copper and its compounds									2 ²	2 ²							5 ²
Antimony and its compounds									2 ²	2 ²							5 ²
Tin and its compounds									2 ²	2 ²							5 ²
Aluminium and its compounds																	
Nickel and its compounds	1	1	1	1	1	1	1	2						5			1 ³
Chromium and its compounds	2	2	2	2	2	2	2	4			2						
Molybdenum and its compounds											3						
Tungsten and its compounds																	
Palladium and its compounds															2		
Phosphorus and its compounds														5			
Platinum and its compounds															1		
Rhodium and its compounds															2		
Tellurium and its compounds									1 ³	1 ³							
Arsenic and its compounds									1 ³	1 ³	0.5 ⁴						1 ³
Selenium and its compounds									1 ³	1 ³	0.5 ⁴				1		
Rhenium and its compounds											0.5 ⁴						
Oxides of sulphur (as SO ₂)	250								800	800	800		500	500	500		
Oxides of nitrogen (as NO ₂)				300									400	400	400-100	300	
Carbon monoxide														800			
Hydrogen																	
Chlorine													5		5		10
Chlorides (as HCl)				10					30	30			30	30	30		30
Fluorides (as HF)	5	5	5	5	5	5	5	5	5				5			5	
Hydrogen cyanide																	
Hydrogen sulphide																	
Ammonia											50						15
Amines and amides																	
VOC (as TC)				50 [^]	50	50	50	50	50	50	50		50	50	50		50
Class A																	20
Class B																	80
Partial Oxidation Products																	50
PAHs																	
Dioxins (ITEQ) ng/m ³	1				1	1	1	1	1	1			1	1	1		
Oil Mist				20													

[^] Peak emission limit¹ Combined limit for Cadmium + Mercury + Thallium² Combined limit for Copper + Antimony + Tin³ Combined limit for Tellurium + Arsenic + Selenium⁴ Combined limit Arsenic + Selenium + Rhenium⁵ Combined emission limit for Nickel + Arsenic

Data source: Chief Inspector's Guidance Notes

Table 2.6 Emission Limits - SI 472 Section 2 Part B Processes

Parameter of Interest	Furnaces for the Extraction of non ferrous metal from scrap PG 2/1	Hot Dip Galvanising Processes PG 2/2	Electrical Rotary Furnaces PG 2/3	Iron, Steel and Non-Ferrous Foundry Processes PG 2/4	Hot and Cold Blast Cupolas PG 2/5	Aluminium and Aluminium Alloy Processes PG 2/6	Zinc and Zinc Alloy Processes PG 2/7	Copper and Copper Alloy Processes PG 2/8	Metal Decontamination Processes PG 2/9
	mg/m ³								
Total Particulate	50	15-50	100	50	100	50	50	50	50
Lead and its compounds	5 ¹	2		2			2	2	
Zinc and its compounds									
Cadmium and its compounds	5 ¹			0.2			1		
Mercury and its compounds									
Thallium and its compounds									
Copper and its compounds				20		20		20	
Antimony and its compounds									
Tin and its compounds								10	
Aluminium and its compounds									
Nickel and its compounds			50	50				10	
Chromium and its compounds			20	20					
Molybdenum and its compounds									
Tungsten and its compounds									
Palladium and its compounds									
Phosphorus and its compounds									
Platinum and its compounds									
Rhodium and its compounds									
Tellurium and its compounds									
Arsenic and its compounds									
Selenium and its compounds									
Rhenium and its compounds									
Oxides of sulphur (as SO ₂)						300			
Oxides of nitrogen (as NO ₂)									
Carbon monoxide									
Hydrogen									
Chlorine									
Chlorides as (HCl)	100	30				30	10		100
Fluorides (as HF)						5		5	
Hydrogen cyanide									
Hydrogen sulphide ppm				5					
Ammonia		18		18					
Amines and amides ppm				5					
VOC (as TC)		50		50		50			20
Class A									
Class B									
Partial Oxidation Products									
PAHs									
Dioxins (FTEQ) ng/m ³									
Oil Mist									

¹ Combined emission limit for Lead and Cadmium

Table 2.7. TA Luft Emission Limits - Summary

Parameter of interest	General requirements	Special Requirements										
		Ore Sinter Plants	Pig Iron Production	Non-ferrous unrefined materials	Ferro-alloys	Steel converters, EAFs	Cupolas with lower gas offtake	Electroslag Remelting	Aluminium Smelters	Other non-ferrous smelters	Rolling, heat treatment	Non-ferrous foundries
		mg/m ³										
Particulate matter (general) (lead works)	50			20 10	20	20	50		20	20 10		20
Lead and its compounds	5											
Zinc and its compounds												
Cadmium and its compounds	0.2											
Mercury and its compounds	0.2											
Thallium and its compounds												
Copper and its compounds	5											
Antimony and its compounds	5											
Tin and its compounds	5											
Aluminium and its compounds												
Nickel and its compounds	1											
Chromium and its compounds	5											
Molybdenum and its compounds												
Tungsten and its compounds												
Palladium and its compounds												
Phosphorus and its compounds												
Platinum and its compounds												
Rhodium and its compounds												
Tellurium and its compounds	1 ¹											
Arsenic and its compounds	1 ¹											
Selenium and its compounds	1 ¹											
Rhenium and its compounds												
Oxides of sulphur	500											
Oxides of nitrogen	500	400									500- 1300	
Carbon monoxide						1000	1000					
Hydrogen												
Chlorine	5								3			
Hydrogen chloride	30											
Hydrogen fluoride	5							1				
Hydrogen cyanide	5											
Hydrogen sulphide	5											
Ammonia												
Amines and amides											5	
VOCs (as TC) general									50	50		
organics Class I	20											
Class II	100											
Class III	150											
PAHs as carcinogens Class I	0.1											
Class II	1											
Class III	5											
Dioxins												
Oil mist												

Data source: TA Luft

• Does not apply during shutdowns

1 Combined emission limit for Arsenic, Tellurium and Selenium

3. APPLICATIONS OF CONTINUOUS MONITORING SYSTEMS

3.1 INTRODUCTION AND GENERAL OBSERVATIONS

3.1.1 Introduction

This Section begins with a general commentary on monitoring applications, then examines the polluting species for air, water and land respectively, noting their origin and considering the types of monitor that may be applied and their suitability for the application.

The generic principles of the various techniques of measurement are described in Appendix 2. A general description of applications, with diagrams of means of sampling is given in Technical Guidance Note (Monitoring) M2 "Monitoring Emissions of Pollutants at Source".^{Ref 4}

Although not widely applied in the Metals Industry, continuous monitoring, at least with regard to emissions to air, is well established in other sectors: the Environment Agency publication "An Assessment of Continuous Monitoring Instrumentation for Incineration Processes"^{Ref 5} describes a variety of technologies that would be applicable to Metals Industry processes. The corresponding document for Large Combustion Plants (LCPs),^{Ref 6} also contains relevant information.

3.1.2 Market Influences

In the USA there are strong regulatory pressures to apply CEM and in Germany, the requirements of TA Luft^{Ref 7} are prescriptive and tailored to state-of-the-art of measurement technology. The instrument industry in Germany has been encouraged by the strong market.

The requirements of TA Luft for continuous monitoring are summarised in Table 3.3 at the end of this section.

The main thrust of US and German legislation has been towards combustion plant and incinerators and primarily new plant in other industries. Even in the US and Germany,

continuous monitoring instruments have not tended to be designed for application to Metals Industry processes.

With regard particularly to monitors for the more exotic species in the industry, the costs incurred in development - or adapting laboratory instruments to the rigours of plant operating conditions - when passed on to the few purchasers would result in prohibitively high prices.

Of the UK instrument suppliers contacted in the course of the survey, only the particulate monitor suppliers were enthusiastic about the Metals Industry market. It was seen as too diverse, unfamiliar and "difficult to target", with a small market volume.

3.1.3. General Application Requirements

The working environment for monitors in the Metals Industry is aggressive. The factors include ambient fumes, dust, high temperatures and condensation with potential for mechanical damage. Unfortunately, most plant in the industry was designed before monitoring was considered and in many cases the available locations for the installation of monitors are far from ideal.

Good installation practice is essential for all instrumentation, and may be overlooked when an operator or his consultants are not familiar with requirements. The general best practice for instrument installation in the UK is provided by BS 6739.^{Ref 8} There is no international equivalent. The standard provides guidance on the handling, mounting and housing of instruments, piping and wiring, power supplies, cleaning and purging facilities, and proposes test and commissioning procedures.

3.1.4 Environmental Protection

Protection afforded by the enclosures of instrumentation and control equipment is categorised in Europe by using the "IP" numbering system defined in BS EN 60529^{Ref 9} (formerly IEC 144). It uses two digits, representing the degree of protection from dust and water, respectively. IP54 is generally accepted as the minimum for equipment enclosures in

the Metals Industry. Externally mounted cubicles should be at least IP55. IP65 is usual for field instruments.

In America, the NEMA classification system is used. NEMA3 is appropriate for outdoor installations, and to indoor use in process facilities. In locations such as equipment rooms with filtered air, the classification can be eased to NEMA2 (equivalent of IP32).

The European CE marking scheme, denoting compliance with certain safety and electromagnetic compatibility criteria, is now mandatory for new equipment in industry. This has barred some American analysers from the European market.

3.1.5 Range Selection

The basic criteria for adjusting the measuring range of a monitoring instrument is for the sensitivity to be low enough so that peaks are registered without the instrument going off-scale, while at the same time being sufficiently high for the normal levels to be effectively resolved. TA Luft^{Ref 7} specifies range setting of between three times the permitted peak level and ten times the average level.

3.1.6 Maintenance

Maintenance is absolutely vital. Even for simple monitoring instruments, regular cleaning is essential, as is regular replacement of consumables and periodic visual checking by specialists.

3.2 MONITORING OF EMISSIONS TO AIR

The suitability and applicability of particular continuous monitoring techniques for emissions to air are described below:

3.2.1 General

Products available in the UK for monitoring emissions to air are detailed in Appendix 3.

The tables of data in the Appendix are divided according to species of interest and the order

of presentation is the same as that adopted in this Section. For a summary of available techniques and associated minimum measurement ranges, see Table 3.4.

3.2.2 Particulate Matter and Smoke

3.2.2.1 General

Particulate measurement is the only widespread application of continuous monitoring in the Metals Industry at the present time.

Particulates are generally measured either by optical or triboelectric methods. There are also a few acoustic devices in use. All proprietary monitors currently in use are of the cross-duct / in-situ type. No beta gauges are presently in evidence in the metals industry, the few mentioned by operators having been abandoned owing to maintenance difficulties. See Appendix 2 for descriptions of measurement techniques.

A wide range of proprietary monitors is available - see Appendix 3 Table A3.2.2.

3.2.2.2 Suitability of Techniques

The suitability of measurement techniques is summarised in Table 3.1.

It should be noted that modern fabric filter plants yield release concentrations of approximately 3 mg/m³. At these concentrations, transmissivity methods are not applicable. Indirect (AC) optical measurement methods have sufficient sensitivity, but the technique is not accepted for continuous monitoring duty in the USA. In Germany one such system has TÜV approval. Indirect (AC) optical and triboelectric techniques in general are accepted for alarm duty as "burst bag" detectors.

It is also pertinent to note limitations associated with the currently available Standard Reference Methods for particulates, that are required to calibrate the respective continuous monitors. BS 3405:1983 offers measurement to an accuracy of $\pm 25\%$ and is not really practical for application to concentrations below about 20 mg/m³. BS 6069:Section 4.3:1992 does have a stated scope down to 5 mg/m³ but its accuracy of $\pm 10\%$ is only quoted for concentrations of 50 mg/m³ and over. The European Standards working group CEN/TC264/WG5 has been given the task to draft a Standard Method specifically for low concentrations but it may be some time before publication. For further information on sensitivity and calibration, refer to Table 3.4 - Minimum Measurement Ranges and Section 5.3.1.1 respectively.

Table 3.1 Overview of Particulate Measurement Techniques

Type	Sensitivity	Influences	Problems/Advantages
Transmissivity (Opacity)	Range limited to approx. 100 mg/m ³ . Output is related to concentration not mass emission	Particle size Particle shape Particle colour Ambient light	Dirt on lenses/windows Misalignment of the transmitter and receiver/reflector units owing to thermal expansion of duct
Scattering	Output is related to concentration not mass emission. Not suitable for high-opacity applications such as smoke.	Particle size Particle shape Particle colour Ambient light	Dirt on lenses/windows, although less sensitive to this than is the transmissivity type
Optical Scintillation	AC measurement * Higher sensitivity than transmissivity type Response is related to mass emission ie velocity dependent	Particle size Particle shape Particle emission/reflection effects Dynamic flow conditions	Dirt on lenses/windows, although less sensitive than the transmissivity type. Suitable for small and large diameter ducts
Triboelectric	DC or AC measurement * High sensitivity DC type: Response is related to mass emission (velocity dependent) AC type: response is related to concentration (velocity independent)	Particle size Particle shape Particle electrostatic characteristics Duct electrostatic characteristics Dynamic flow conditions	Not suitable for damp or wet gases Influenced by ionisation and humidity variations Will tolerate superficial contamination (AC type high tolerance) Applicable to small diameter ducts down to 100 mm
Acoustic	Moderate sensitivity Response is related to mass emission Alarm duty only	Particle mechanical characteristics Duct geometry Dynamic flow conditions Ambient noise	Complex and application-dependent

* See Figure 3.1 for an illustration of DC and AC measurement techniques.

If ambient light is present - as in some stack installations - this can influence the operation of optical monitors. All instruments adopt chopped or pulsed light to counter direct influence, but there are second order effects. Infra-red light is adopted by some manufacturers; this minimises ambient interference, but is less sensitive to finer particles, see Figure 3.2.

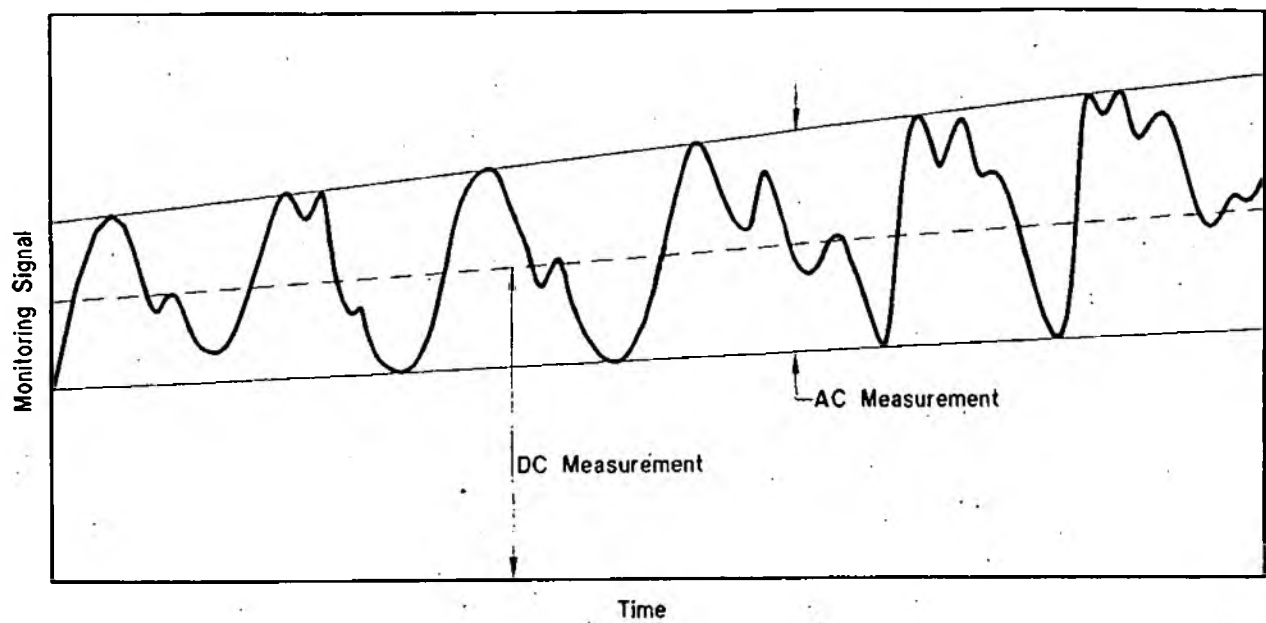


Fig 3.1 DC and AC Methods of Particulate Measurement

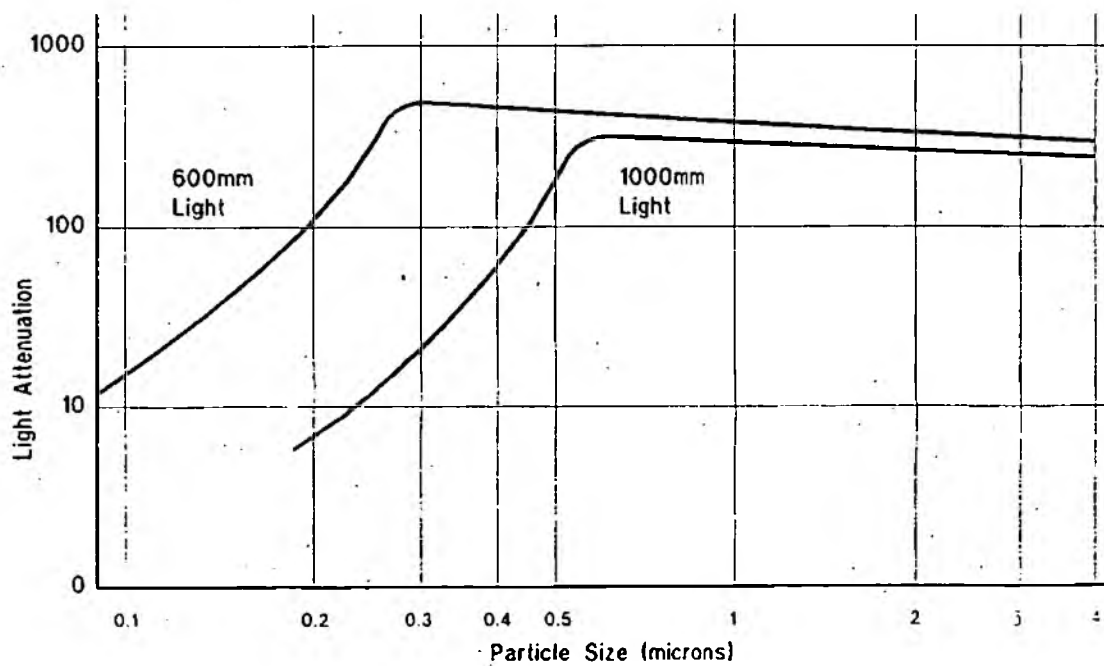


Fig 3.2 Illustrative Effect of Particle Size on Attenuation

3.2.2.3 Application to Bag Filters - Negative Pressure Type

This is the most common field of application of particulate monitoring in the Metals Industry.

Most filter plants are of the negative pressure type, with the extraction fan(s) stationed downstream of the filter units, discharging the flow to atmosphere via a stack. This type of application is ideal for continuous monitoring, with the instrument installed in the stack, usually adjacent to a location for manual measurement and calibration.^{Ref 4}

In addition to fulfilling regulatory monitoring requirements, a recorded trend of particulate concentration is also very useful in tracing faults in the filters. Because these filters are cleaned on a fixed time sequence, the variations of the particulate signal indicate the condition of the individual filters - a periodic drop in particulate signal shows when a leaking group of bags has been taken out of sequence for cleaning. The leaking bags are thus identified. It is possible for the more sophisticated monitors to determine or even locate the faulty bag row because of blocking or tearing, in some cases in advance of gross failure of the bag, thereby reducing the risk of an excessive emission.

To detect the filters blocking, the differential pressure across the filter bank is measured. The differential pressure signal rises as the filter bank blocks. Differential pressure measurements are simple, and also reliable if a good-quality process transmitter is used. It is also possible to identify blocking of individual filters by examining a recording of differential pressure during the cleaning cycle - individual filters that are badly blocked produce little change in the differential pressure across the bank when they are switched out for cleaning (less applicable to filters with on-line pulse jet cleaning).

Low cost versions of triboelectric and scintillation instruments (around £1 000-£2 000) are available specifically for alarm duty.

3.2.2.4 Application to Bag Filters - Positive Pressure Type

Bag filters of the positive pressure type are in use in the steel sector, in melt shop extraction systems. The fan is positioned upstream of the filters and the discharge to atmosphere from

the filters is direct, via the (large) vent spaces above the bags. This arrangement makes measurements difficult. Long-throw opacity meters are the only practicable solution, with the beam crossing the common space above the filter cells. Units of this type are in use, but have poor reliability owing to the instruments being exposed to extremes of dust and heat. The location is difficult to access for maintenance since the plant must remain in operation for long periods.

Manufacturers seem reticent to offer variants with a "throw" (transmitter-to-receiver spacing) longer than about 30m. One problem is the limited strength of light-emitting diodes which comprise the light source of most instruments of this type and another is that misalignment effects increase significantly with path length.

British Steel developed their own long-throw obscuration meter for use in EAF shops, primarily as a control device for extraction systems. It is still in use in this role on several steel plants but the instrument is no longer produced on the grounds of cost. Commercial instruments with path lengths up to 25 m, however, are readily obtainable.

A multi-point extractive system with a single AC triboelectric detector is currently on trial at a UK steelworks.

3.2.2.5 Application to Small-Scale Plant

The metals industry has many combustion installations of relatively small scale such as furnaces, and dust or fume extraction systems. The small diameter flues fitted to these plants present a particular problem for cross-duct optical instrumentation, since the short path length results in a corresponding reduction in the monitor input signal. This effectively reduces the sensitivity of the instrument so increasing the propensity to drift. The light absorbed by a particulate concentration of 10 mg/m^3 will only be of the order of 0.2 % across a 1 m diameter flue. This is close to the limit of sensitivity of transmissivity meters. (cf. the resolution limit of the human eye: approx. 5 %).

DC type optical monitors may thus not be sufficiently sensitive for these applications, but

optical scintillation and triboelectric monitors are produced for installation in ducts down to 100 mm diameter.

3.2.2.6 Application to Fugitive Emissions

For fugitive emissions such as roof ridge vents of buildings with dust or fume-laden atmospheres, monitors of the opacity type are the obvious choice. In practice, however, spot measurements are rarely representative and the concentration is usually too low to be measured by normal cross-duct instruments. Also, long throw instruments are not presently available (see Bag Filters - Positive Pressure Type, above).

Fugitive fumes have been measured by opacity meters, however, in EAF plant where the signals have been used to modulate the power of secondary fans to save energy^{Ref 10}. A high-sensitivity optical device suitable for application to fugitive fume has been reported.

Closed circuit television (CCTV), with cameras stationed to view the buildings at a distance, has been applied successfully but there is no system available that will analyse the scene and identify unusual releases - interpretation of the image is subjective and strongly influenced by varying meteorological conditions. The systems installed depend on daylight.

The TEOM technique (Rupprecht & Patashnick Co Inc) has proved effective for continuous ambient monitoring of fugitive dust and fume at concentrations of 0-1000 microgrammes/m³ (15 min rolling average).

3.2.2.7 Application to Wet Gas

Where the sample gas contains water droplets, eg after wet scrubbers, particulate monitoring is not regarded as practicable, because the water droplets are counted as particulate by optical instruments. Triboelectric monitors are influenced by humidity and the DC type is rendered inoperative by excessive moisture but AC triboelectric monitors with their insulated probes are on trial in these applications.

This raises questions about the direct monitoring of a number of important sources which

utilise wet scrubbers, in particular BOS primary fume extraction systems in steelworks. Where the proportion of particulate is known, for example for P_2O_5 from a phosphor copper plant, indicative monitoring is reported to be practicable using optical techniques.

The alternative to direct monitoring is a surrogate which involves recording the process parameters of the wet scrubber system. The required variables are relatively easy to measure and instruments should in any case be fitted as part of good process control practice. The measurements of interest include:

- Air flow or, if impracticable, fan motor power
- Pump delivery pressures and flows
- pH of sprays
- Air temperature and pressure

Since the processes in question will usually have comprehensive hierarchical process control systems, the parameters may be stored for reporting or inspection by these means.

3.2.2.8 Smoke Measurement Applications

Continuous monitoring of smoke is usually required for furnaces, which are oil fired or dual fired. There is usually a limit of Ringelmann 1 with a higher value for short-term emissions during start-up.

Transmissivity meters, ranged 0-100% opacity (0-5 Ringelmann), are widely used for smoke monitoring. The range of measurement is so large that there is little tendency to drift.

3.2.2.9 Flare Stack Monitoring

Flare stacks burn off waste gases from coke ovens, blast furnaces and BOS plant, usually under abnormal conditions when they cannot be consumed as fuels on site. The requirements for monitoring flare stacks are generally that the operator keeps a written log of the visual appearance of the flare and plume. This is usually done by CCTV, with monitors in the plant control room and managers' offices. The arrangement has been

extended to monitor fugitive fume from the site.

3.2.2.10 Anomalies during Transient Conditions

Most processes in the metals industry are batch processes, but even continuous processes are stopped and started up periodically.

There is often a tendency for particulate monitors to indicate large, anomalous, signals when the flow changes, particularly when it stops, and when it re-starts. The mechanisms are thought to include:

- Trapped/settled dust dislodged from the ductwork;
- Concentration by gravity in the lower areas of the flues and ducts;
- Differences in particle size distribution and composition;
- Differences from the normal concentration distribution across the section being monitored.

3.2.2.11 Requirements for Air Purging

Optical instruments in general, and transmissivity (opacity) types in particular, are sensitive to dirt accumulating on windows and other optical components. Although optical scintillation monitors are reported to tolerate up to 80% obscuration of optics, well designed air purging facilities are essential, and these are generally found to be effective, provided that the quality of the air is good and the air supply maintained without a break.

It is usual to derive purge air either from a low pressure compressor (blower) or from site compressed air services.

The use of blowers for supplying purge air is not recommended by some manufacturers on the grounds that they do not provide the required availability and the delivery pressure is not

sufficient to exclude flue gas under all flow conditions - in practice even a short cessation of air purge results in significant fouling.

"Instrument air" (genuinely oil-free air from a desiccant drier at -40°C dew point, of the type provided on "Petrochemical" plant), used with a simple in-line filter, is excellent but services of this quality are rarely provided on Metals Industry sites. The usual purging arrangement is to connect to the general plant air service via a water separator, a 25°C refrigerant drier and filter(s). Plant compressed air services, however, even with good filtering and separation at source, inevitably contain moisture, oil and scale.

Nitrogen is available at low cost on sites such as steelworks with their own oxygen plant. This dry inert gas provides an excellent purge source.

Air purge is frequently cited as the main reason for the failure of opacity meters. Most incidents indicate the presence of oil contaminating windows, mirrors or other exposed optical components.

Even with good purging, the contamination on the windows must be expected to rise toward the resolution limit of transmissivity monitors, necessitating compensation methods in the design of the instruments.

3.2.3 Metals

3.2.3.1 General

Metals and their components are generally emitted to atmosphere in particulate form. Where it can be established that the metals form a reasonably constant proportion of the total particulate emission, continuous particulate measurement is an effective surrogate for metals monitoring.

In solid particulate form, metals have no useful interaction (absorbance or fluorescence) with infra-red, visible or ultra-violet light that would form a suitable basis for in-situ measurement. AA spectrophotometry and other laboratory analysis techniques are not practicable for on-

line monitoring applications of metals.

3.2.3.2 Application to BOS Fume

X-ray fluorescence spectrometry (XRF) tuned to iron and zinc atomic resonances has been used successfully by British Steel to measure the metals content of fume from BOS plant.^{Ref 11}

Initially used on raw fume, in an exercise to reduce iron losses and improve the efficiency of zinc recovery, the technique is now being applied to emissions to atmosphere after wet scrubbing.

The instrumentation, which requires detectors to be cooled with liquified gas, is not well suited for general use as a proprietary monitor for particulate material but British Steel are installing it on all BOS plant.

3.2.3.3 Mercury and its Compounds

Mercury may be conveniently measured because it does not readily oxidise and is in the vapour form at attainable temperatures.

The element is effectively measured by ultra-violet atomic absorption techniques, since mercury discharge lamps are readily available and these provide UV spectral lines which excite the vapour. The limit of sensitivity of the basic technique is at 9 mg/m³.

The general arrangement for total mercury measurement is to convert mercury compounds to metal vapour by heating the sample stream, which is then taken to a UV absorption spectrophotometry stage.

In a variant of the basic technique, mercury is accumulated by amalgam on gold mesh in the sample stream. The analyser makes periodic sampling phases and measurement phases: in the sampling phase, the mercury accumulates on the mesh; in the measurement phase it evaporates from the mesh over a short period and is fed to the analyser, thus greatly

increasing the effective concentration. The detection limit of 1 picrogramme is achievable in this method.

Examples of proprietary analysers are detailed in Appendix 3, A3.2.3.

3.2.4 Products of Combustion - SO₂, NO_x, CO, CO₂, O₂

3.2.4.1 General

The available methods for measurement of combustion gases and associated minimum measurement ranges can be seen in Table 3.4. For data on proprietary products see Appendix 3, A3.2.4.

The cross-sensitivity of a selection of monitors of various types is given in Table 3.6.

Sources of products of combustion in the Metals Industry can be summarised as:

- Power plant
- Furnaces for re-heating and heat treatment of product
- Metals melting, smelting and refining processes

Power plant is dealt with elsewhere.^{Refs 5,6} The methods given are also applicable to re-heating and heat treatment furnaces. The methods generally used for gas monitoring are either cross-duct or extractive IR or UV techniques. Wet chemical techniques are also applicable but require more servicing and are not normally adopted unless site personnel are well experienced with the use of such analysers.

3.2.4.2 Application to Re-Heating Furnaces

Re-heating furnaces heat slabs or billets before hot rolling operations. They mostly burn natural gas and may also have oil as a stand-by fuel in case of gas supply failure. The thermal rating is typically 50 MW.

Modern furnaces have comprehensive control of fuel flow and air/fuel ratio, utilising distributed control systems (DCSs) or programmable controllers (PLCs). There will usually also be a computer for optimisation of furnace power to suit the product throughput. The scheme is often linked with the mill control system, providing an integrated means of data collection for monitoring purposes.

No applications of gas monitoring to re-heating furnaces were evident during the study, except for the use of oxygen measurement for adjustment of combustion. Zirconia probe oxygen instruments are normally supplied with furnace installations, with the option of closed-loop control of combustion. In practice, users invariably keep the loop open to avoid nuisance disturbance to operations when the instrument malfunctions.

3.2.4.3 Application to Heat Treatment

Heat treatment furnaces are generally batch units with lower thermal rating than re-heating types and somewhat less sophisticated control systems. They are generally not connected with plant-wide control systems. No continuous monitoring of combustion gases emitted from these installations were encountered during the study, but they would be amenable to the same methods of monitoring as used on reheating furnaces.

3.2.4.4 Application to Sinter Plant

Process control of sintering is a relatively sophisticated system and provides a means of surrogate measurement based on combustion conditions. The key parameters are:

- Material feed rate
- Moisture
- Bed thickness
- Gas flow to ignition hood

3.2.4.5 Application to Roasting of Ores and Blast Furnaces

In lead and zinc manufacture (ISP) process gases are used for heating purposes.

As combustion products will vary, continuous monitoring of flue gases is applicable.

Blast furnace gas is monitored before combustion by a combination analyser for CO and CO₂ (using IR methods), and O₂ and H₂ (using the katharometer method). Emissions are also monitored for SO₂ by IR.

In the steel industry, blast furnace control systems are comprehensive and incorporate control equipment with special instrumentation to measure internal conditions such as refractory wear and level of materials in the furnace. Key parameters relating to emissions are:

- Stockline/overburden probes (detect level and slippage)
- Furnace pressure (vent to atmosphere)
- Fuel input

3.2.4.6 Application to EAFs

CO, CO₂ and O₂ have been monitored by means of an IR analyser in EAF fume at a steelworks as part of an innovative project to save energy and improve emissions.^{Ref 12} A high CO signal initiates an increase in the oxygen ratio in the gas mixture to burners which heat the charge above the melt. The installation required inert gas purge facilities for the sample pipework, to keep it clean and avoid flammable exhaust gases creating a safety hazard during maintenance. A solid state CO sensor has since been added, installed in a more convenient location for monitoring purposes and this is dedicated to emissions monitoring.

3.2.5 Hydrogen

Although released from certain Metals Industry processes, hydrogen is not a pollutant gas. It is, however, a safety hazard being explosive in relatively small concentrations in air (~4%) and is also indicative of process conditions. In copper refining (shaft furnaces), CO is measured as a surrogate for hydrogen.

There are two convenient methods of hydrogen detection:

- Thermal catalytic ("Pellistor") method
- Thermal conductivity (katharometry)

Neither method is particularly sensitive or selective (see Table 3.2) but where hydrogen is likely to be the only flammable gas present in the emission, the "Pellistor" method is suitable. The sensor is a relatively low-cost replaceable unit and detectors are available with intrinsically safe or flameproof certification.

Proprietary systems are widely available for monitoring hydrogen as a flammable gas for safety applications or COSHH purposes. They consist of a series of "Pellistor"-based sensors stationed around the plant and common indicator and alarm unit. Appendix 3, A3.2.5 gives examples of proprietary systems with detection by either method of measurement.

3.2.6 Chlorine

Infra-red and ion mobility spectrometry are suitable methods of measurement (see Table 3.2) and proprietary examples are given in Appendix 3, A3.2.6.

Proprietary systems for chlorine monitoring for COSHH purposes similar to those described for hydrogen above but incorporating low-cost electrochemical cells in place of "Pellistor" sensors are available from many companies. This type of equipment is sensitive and may be considered for continuous monitoring of emissions if fugitive releases are of concern, although the limitations indicated in Appendix A2.1.8 should be noted.

3.2.7 Hydrogen Chloride

3.2.7.1 General

The main sources of hydrogen chloride in the metals industry are in the secondary aluminium sector and emissions result from the melting of scrap containing chlorinated oils and plastics. Hydrogen chloride is also formed when chlorine removes hydrogen during aluminium refining.

Continuous monitors have not so far been applied in the Metals Industry in the UK, but suitable monitoring instruments are already established in incinerator applications^{Ref 5}. Versions with 17th BImSchV approval are available.

Hydrogen chloride is a highly reactive gas, dissolving rapidly in condensation to produce an acid solution which attacks sampling systems and analyser components. No effective means are available to separate condensation close to the sampling point, so the sampling pipework, fittings and "wetted" parts of the analyser are heated to 180°C. Alternatively, the sample stream may be diluted with dry air or a reference gas such as nitrogen.

3.2.7.2 Wet Chemistry Methods

Wet chemistry analysers are less convenient than infra-red methods but offer adequate sensitivity. The method consists of bringing the sample gas into contact with a suitable aqueous solution, and then measuring the chloride ion content by use of an ion selective electrode.

3.2.7.3 Infra-Red Methods

NDIR may be used as a means of measurement, but HCl absorbs only weakly in the infra-red region and the technique is barely sensitive enough for CEM use. Significant interference occurs from strongly absorbing compounds, particularly water, thus necessitating the use of gas filter correlation (GFC) or dispersive techniques to improve the sensitivity and selectivity of the method. Special cells with long path lengths are required.

3.2.8 Hydrogen Fluoride

3.2.8.1 General

Fluorides, of which HF is the major constituent, are generated in large quantities in the pot lines (electrolytic extraction cells) of primary aluminium smelters.

Since the emissions can increase when cells in the pot room malfunction, continuous monitoring of the primary extraction system is highly desirable, both to obtain an accurate

estimate of total emissions and also to alert operating staff to the malfunction.

The primary extraction system is effective under normal conditions, but operating problems can lead to the release of raw fumes with high fluoride content into the pot room, resulting in a significant increase in fugitive emissions from the building. Continuous monitoring of fugitive emissions is therefore also desirable, but has yet to be implemented in the UK.

The on-line measurement of hydrogen fluoride involves problems similar to those outlined for hydrogen chloride above, only more extreme because of the higher reactivity of hydrofluoric acid and its propensity to attack glassware. In practice it has not proved possible to implement a satisfactory sampling system with more than a few metres of pipework.

3.2.8.2 Wet Chemistry Method

Early fluoride monitors utilised modified wet-chemistry analysers developed for hydrogen chloride, but corrosion was excessive. Later instruments were specifically designed for the purpose, but the problems with corrosion and fouling of the sampling system persisted.

A method presently in use in the UK utilises extraction, but the sample is contacted with a TISAB (Total Ionic Strength Adjustment Buffer) solution very close to the sampling point and the solution is then pumped to the analyser. A selective ion technique is then used for the measurement. The probe assembly is heated to avoid condensation.

Sensitivity is adequate for the purpose. The instruments carry out automatic calibration checks periodically, against standard solutions.

Maintenance requirements are relatively high, and involve cleaning, checking of operation and changing of reagents. Parts exposed to the fume must be replaced periodically. It is reported that PTFE is the only material resistant to HF in the long term, although other fluorocarbon polymers and monel stainless steel would also seem appropriate.

It is not practicable to apply extractive techniques to measure fugitive emissions because of

the difficulty in obtaining representative samples (the release of excessive fume from a malfunctioning pot is relatively localised and there may be 150 such pots in a building 500m long).

3.2.8.3 Infra-Red Method

The sensitivity required for regulatory monitoring is not achievable by NDIR or conventional dispersive methods, but a new cross-duct laser technique proved successful in trials at a site in the UK and is being installed on a permanent basis. The technique employs a tuned laser to select the wavelength, rather than a prism or diffraction grating.

Maintenance is relatively straightforward. Optical fibres allow the unit to be installed at a distance from the measuring location and multiplexing techniques provide four points of measurement per instrument.

The method is claimed to be applicable to fugitive emissions, with a long-throw version of the instrument installed with its beam running parallel to, and just below, the roof vent. A unit is shortly to be installed for trials in a UK plant.

Factors detrimental to the measurement are likely to include alignment and "heat haze" (c.f. long-throw particulate monitoring).

The necessary permanent access to maintain roof vent installations is a costly item (estimated at £100 000, including ladders and platforms for a 500m pot room).

Calibration of a long-throw monitor presents difficulties, as the simultaneous extraction of samples for analysis at a representative number of points along the beam is obviously impractical. A cell containing a known (high) concentration of the gas in the path of beam is employed.

3.2.9 Hydrogen Cyanide

There are no applications of continuous cyanides monitoring in the Metals Industry. One proprietary NDIR monitor was identified. See Appendix 3, Table A3.2.9.

3.2.10 Hydrogen Sulphide

No applications of continuous hydrogen sulphide monitoring were identified in the study. Proprietary monitors are available, based on electrochemical, UV fluorescence and NDIR. See Appendix 3, A3.2.11. Colorimetric tape systems would appear suitable but were not in evidence.

3.2.11 Ammonia

There were no applications of continuous monitoring of ammonia identified in the study. Ammonia is amenable to IR analysis and a large number of proprietary products are available - see Appendix 3, A3.2.11.

3.2.12 Amines and Amides

No instrumentation for the continuous monitoring of amines or amides was identified during the study.

3.2.13 Volatile Organic Compounds (VOCs)

VOCs are not at present monitored continuously in the Metals Industry, the emissions being determined by manual checks and mass-balance calculations. The limits of resolution are adequately met by FID and PID instruments, on-line GCs and IR monitors, and a wide range is available for continuous applications - see Appendix 3, A3.2.13. Selectivity appears to be the main cause for concern in the application. If a high enough concentration is present in the sample stream, thermal catalytic units offer a straightforward, low-cost solution.

3.2.14 Polycyclic Aromatic Hydrocarbons (PAHs)

It is impractical for continuous monitors to identify the species of interest. As an illustration,

it is reported that FTIR even under field conditions with manual supervision can identify only simple aromatic hydrocarbons.

3.2.15 Dioxins and Furans (PCDD/PCDF)

It is at present impractical to monitor emissions of polychlorinated dioxins and furans continuously. All UK operators that monitor for these species do so manually and generally on an annual basis.

Although the measurement of dioxins cannot be continuous, an automatic sampling system for continuous on-line operation is available. One system, developed by Austrian Energy & Environment Services, utilises an isokinetic sampling head and glass fibre filter media spiked with a recovery standard. Filters are recovered for laboratory analysis. Another system has been developed in Germany and is now undergoing tests for TÜV Approval.

3.2.16 Oil Mist

Oil mist is a significant emission from rolling mills, where oils and greases are dispersed in cooling water sprayed onto hot product. Emission to atmosphere is via extraction systems and/or through roof vents of the mill building by natural convection. The concentrations can be high (20 mg/m³), but no monitoring has been applied. Heated FID systems may be suitable.

If the total quantity of oils emitted to air over a period is known, it should be possible to compute, on-line, a prediction of oil emission concentration based on mill parameters such as running signals, temperatures, product length measurements, cooling rates, all of which will already be actively logged in the process control system.

3.2.17 Flow of Air or Gas

3.2.17.1 Flow in Ducts

Differential pressure devices of the perforated tube type are the traditional solution to flow measurement in ducts. Self-cleaning versions are available.

The time-of-flight correlation technique utilising a pair of scintillation type dust monitors has recently become popular. The accuracy is well within requirements when applied to small and medium sized ducts and flues. It is a low-maintenance technique and does not obstruct the flow.

Both types of flow monitor are widely available: examples of flow monitors are given in Appendix 3, A3.2.17

3.2.17.2 Flow in Large Ducts

Because of the large cross-section of the extraction ductwork in some sectors of the industry, time-of-flight and other techniques which measure flow near to the wall may not be representative. "Annubar" or ultrasonic types, measuring across the total width, offer a more representative measurement.

Ultrasonic techniques are now considered for monitoring applications although, in the past, instruments of this type were subject to accuracy and stability problems. Recent products appear to be operating satisfactorily, especially where there is particulate matter in the stream to provide a target for the ultrasound.

If a plant was designed before monitoring was anticipated, the ductwork may not provide suitable locations for flow metering. It is usually judged to be impractical to modify the ductwork layout to provide the necessary geometry (straight runs with no fittings upstream that would disturb the flow).

In such cases, extensive calibration testing is required at the proposed location, over a range of flow rates, to ensure that the measurements are representative of the total flow. Special care must be taken in the interpretation of results, since calibration measurements would themselves be liable to significant errors.

3.2.17.3 Fugitive Emissions - Roof Vents

Where fugitive emissions are to be measured, difficulties associated with the determination of flow in roof vents (cross-section geometry, cross-winds, thermal effects) are encountered. In addition, the length of buildings makes obtaining a representative measurement particularly difficult. The roof space may be hot, (up to 70°C in steelmaking) and presence of dust can also be a problem.

Multiple instruments of the thermal dispersion type with thermal compensation arranged along the line of the roof vent, probably provide the most suitable arrangement.

3.2.17.4 Fan Motor Power as a Surrogate for Flow

Flow can be estimated from measurements of the power absorbed by the fans. The fan power is obtained from the motor control gear: the transmitter has two sets of inputs - one for voltage, the other for current (a current transformer or transducer).

The measurement of current (I) or voltamperes (VA) is cheaper but a poor substitute for a true power (W) measurement because much of the important information in the phase angle is lost.

Changes in the pipework, blocking of filters etc. which create a change in the pressure/flow characteristic of the system will introduce significant errors in the surrogate measurement.

The power and current measurements tend to fluctuate and require smoothing/filtering.

3.2.17.5 Duct Pressure as a Surrogate for Flow

The flow can be estimated from measurements of suction pressure in a duct, provided that the duct dimensions and valve or damper settings remain unchanged. Although not a satisfactory replacement for flow measurement, it is an effective indicator of disturbances and malfunctions.

3.2.18 Odour

No instruments were identified for the continuous monitoring of odours.

3.3 APPLICATION OF CONTINUOUS MONITORING TO RELEASES TO WATER

3.3.1 Introduction

Techniques for the continuous monitoring of effluent, and the associated minimum measurement ranges are summarised in Table 3.5.

Continuous monitoring of releases to water from Metals Industry sites is generally confined to pH, flow and automatic sampling (see Section 4, Table 4.3), but British Steel has implemented a comprehensive site-wide scheme at Scunthorpe Works for monitoring a variety of species in effluent.^{Ref 13} including conductivity, turbidity, temperature, dissolved oxygen, oil on water, TOC and ammonia as well as pH and flow.

Since the sampling of water is more practicable than that of air, requirements for monitoring of particular pollutants may be met by automatic sampling, followed by off-line analysis in the laboratory.

3.3.2 Sampling

The equipment required for sampling Metals Industry discharges is similar to that for other waste water or natural waters, so a wide range of products is available. Typical examples are given in Appendix 3, A3.3.2.

The primary problems - fouling from oil and the presence of suspended solids - is endemic in Metals Industry discharges. This is less of a problem for sampling systems than for monitors/sensors.

3.3.3 Acidity and Reduction Potential

There is a very large number of manufacturers of pH and REDOX electrodes. In practice, however, it is necessary to apply a complete package including sampling and cleaning facilities.

As for other analyser products, the sensor itself is a relatively low cost item, but the package costs can be significant.

Some examples of packaged equipment for pH monitoring are given in Appendix 3, A3.3.3.

The most significant source of problems in Metals Industry applications is contamination by oil and greases which are often present in effluent streams and, if not continuously present, may well appear from time to time as a result of surges in the water system, shut-down, start-up or as run-off of surface water.

Air sparging is an effective means of automatic cleaning-in-place. Biocide is considered necessary if bacterial slimes develop. Manual cleaning on a periodic basis, however, is always necessary.

pH electrodes with flush membranes are claimed to be less subject to fouling.

Good installation practice, including screened cable to the transmitter and effective earthing, is necessary to avoid electromagnetic interference.

3.3.4 Suspended Solids (Turbidity)

Turbidity (light attenuation or scattering) is universally accepted as the method of monitoring suspended solids. Influences (cf particulates in air) include particle size, distribution, colour and composition.

As for airborne particulate monitors, versions are available for high and low concentrations

of solids, based on light transmission and scattering respectively.

Turbidity instruments may be scaled in terms of nephelometric units [Nephelometric Turbidity Units (NTU) or Formazine Turbidity Units (FTU)], as absorption of light Absorbance Units (AU) or even standard suspensions of natural material Jackson Candle Units (JCU). Alternatively, ranges can be adjusted and units chosen to represent directly ppm or mg/litre concentrations of suspended solids.

Turbidity sensors lowered by automatic winch drives are employed for process monitoring to measure the thickness of settled solids in clarifiers. These may initiate discharge of sludge or warn operators that clarifiers are saturating.

In applications where oils or other substances likely to foul optical surfaces are present, turbidity meters that maintain the sample stream at a distance from the optics are available. In these, the light is transmitted across a steadily falling film or column of sample or through the surface of an open container.

3.3.5 Conductivity

Conductivity is indicative of the concentration of salts present in solution. Unfortunately, its usefulness is limited, as the relationship varies greatly with composition of particular salts in solution. Temperature has also a significant influence and compensation can only be fully effective when the composition is known, as different salts have different temperature sensitivities.

Conductivity is measured downstream of ion-absorption clean-up systems as an indicative monitor of break-through.

The necessary equipment is straightforward and suitable for conditions in the industry. Appendix 2, Table 2.3.5 gives a selection of products.

3.3.6 Dissolved Oxygen

Dissolved oxygen is generally measured where effluent has been de-oxygenated by heat or chemical action. This is not the case for typical Metals Industry discharges. A range of electrochemical monitors is given in Appendix 3, A3.3.6.

3.3.7 Hydrocarbons, Oils and Greases

As noted above in connection with their fouling effects on instruments, oils are often present in Metals Industry discharges. The only satisfactory method of quantitative analysis is solvent extraction followed by IR analysis, although the technique may not extract all the soluble oil in the sample. Solvent extraction is not amenable to on-line application.

Appendix 3 gives data on proprietary monitors using alternative technologies. These methods of measurement are photometric - See Appendix 2, A2.2.5

IR reflection is the basis of oil-on-water measurement. Monitors are provided with the IR source and sensor mounted above the water surface, or installed on a float, which is positioned on a watercourse or open tank. The output is intended for alarm duty only, but in practice the analogue output will provide a rough indication of the thickness of the oil film, below 10 μm . Microwave absorbance and soluble membrane techniques have also been reported.^{Ref 14}

UV fluorescence is the basis for oil-in-water measurement and is well established for monitoring supertanker ballast water discharges but some of the soluble/emulsified oils used in the steel industry are not conducive to measurement by this technique. The equipment, with the necessary continuous sampling arrangements may be easily installed and operated but calibration is a problem - the response is very dependent upon the oil type and particle size distribution and the presence of solid particles. Homogenisation using special pumps has been adopted in an attempt to obtain a consistent oil particle size. Obtaining a representative sample is difficult.

3.3.8 Metals

3.3.8.1 Turbidity and pH as a Surrogate for Metals

Water treatment plants handling effluent from Metals Industry sites prior to release to a sewer or water course are designed to precipitate metals from solution by raising the pH. The resulting sludges are collected in clarifiers for disposal or recycling. By measuring pH and turbidity at the discharge, correct operation of the treatment plant can be monitored. If the turbidity or pH signals fall, it is a sign that metals may be in solution, ie are being released in larger quantities than normal.

Natural run-off from rainfall, mixing with process discharges, will act to confuse the surrogate relationship.

Since metals may form a high proportion of the sludges, carry-over from settling tanks or clarifiers will result in a large increase in discharge of metals from the site. This situation can arise from malfunction of filter flushing controls, flow imbalances, or failure to remove sludges. Turbidity monitoring of the discharge, in these cases registering a high signal, will provide a valuable surrogate warning of the release of metals.

3.3.8.2 Ion Selective Electrodes

A variety of ion-selective electrodes is available on the market - a selection is included in Appendix 3, A3.3.8. Although the equipment is expensive (it must incorporate sampling, cleaning and accurate temperature stabilisation), the basic electrodes are low-cost items.

The technique does not appear to be well suited to the Metals Industry. Potential problems include lack of selectivity and susceptibility to fouling. Manufacturers do not appear enthusiastic about offering them - it seems that ion-selective techniques are considerably more successful for detecting anions than cations such as metals and ammonium.

3.3.8.3 Wet Chemistry Techniques

Volumetric analysers (titration methods) and colorimeters are available for detection of a particular metal. These are selective and suitably sensitive. In Metals Industry applications, however, where analysis is required, it is usually desirable to measure several species simultaneously.

3.3.8.4 Anode Stripping Voltametry (ASV)

This appears to be the most attractive technique and is in use for the simultaneous measurement of several heavy metals in a discharge to an environmentally sensitive area. The cost of the application is in excess of £50 000. The instrument, its reagents and calibration solutions require daily attention, but reliability and suitability have been demonstrated to be satisfactory in the application.

3.3.8.5 Other Methods

UV fluorescence is employed for measurement of mercury in water.

AA spectrophotometry and other laboratory based analysis methods are not available as an on-line instrument for monitoring applications.

Ion Chromatography is available for on-line use but appears far less convenient and more expensive than other techniques.

3.3.9 Cyanide

No monitoring equipment for cyanide was identified in the study.

3.3.10 Chloride

Chlorides, as well as other inorganic anions - fluorides, nitrates and phosphates - are detected easily by ion-selective electrodes. The technique is described in Appendix 2, A2.2.11. The application arrangements and the associated practical problems are generally as for pH, see

Section 3.3.3. Cross-sensitivity may be a problem when more than one species is present. For proprietary monitors, see Appendix 3, A3.3.10.

3.3.11 Fluoride

See chloride, above. Products are listed in Appendix 3, A3.3.11.

3.3.12 Nitrate

See chloride, above. Products are listed in Appendix 3, A3.3.12.

3.3.13 Phosphate and Thiosulphate

(Ortho) phosphate is conveniently monitored using colorimetry. No instruments for continuous monitoring thiophosphates were identified. Products are listed in Appendix 3, A3.3.13.

3.3.14 Sulphate

No monitoring equipment for sulphate was identified in the study.

3.3.15 Ammonia

Ammonia is monitored in the effluent from the coke oven area of a steelworks site. A variety of products is available, see Appendix 2, Table A2.3.15. The gas type of electrode (principles see Appendix 2) is reported to be the most effective but pH must be adjusted to be high enough to ensure that the ammonia is free to cross the membrane.

A device based on a simplified reflection spectrophotometry method has recently been introduced.

3.3.16 Phenol

No continuous monitoring instrumentation for monitoring phenol was identified during the study but there is interest in the Steel Industry in the measurement of phenol in effluent from coke oven areas.

3.3.17 BOD, COD, TOD, and Toxicity

Monitoring of these parameters is not practised at present in the Metals Industry but, for completeness, the principles that may be applied are discussed in Appendix 2, A2.2.15-19. Methods of calibration (Section 5.5.12-13) and developing technology (Section 6.7) also cover this subject and a range of typical products is given in Appendix 3, A3.3.17.

3.3.18 Flow of Water

The final effluent from many larger metals industry sites passes under gravity to a watercourse or sewer, either via an open channel, or a drain pipe which is normally only partly filled with water. In a few cases, the final effluent is pumped (eg out to sea) through pipes normally filled, in which case conventional process flowmeters can be used.

There is a very wide range of flowmeters available, and described in the specialist literature.^{Ref 15, Ref 16} The suitability of selected techniques is summarised in Table 3.2.

Flowmeter signals are generally utilised by sampling control equipment to initiate sampling on a flow-proportional basis. The samples are analysed to fulfil regulatory requirements and as a basis for verification of continuous monitor readings.

Table 3.2 Overview of Selected Water Flow Measurement Techniques

Installation	Advantage	Disadvantages
Flume or weir and ultrasonic level measuring instrument with built-in flow calculation	Accurate Accessible Robust	Large and relatively expensive Obstruction by debris Flooding downstream backing up to the flume will cause large errors Only forward flow measured
Channel with submersible ultrasonic doppler velocity/pressure instrument with built-in flow calculation	Easy to install Accessible for cleaning Will read reverse flow	Velocity measurement affected by deposits Pressure sensor port blockage possible Insensitive at low flows
Channel with submersible electromagnetic velocity/pressure instrument with built-in flow calculation	Easy to install Accessible for cleaning Velocity measurement is unaffected by deposits Sensitive to low flows Reads reverse flow	Pressure sensor port blockage possible
Filled pipe with electromagnetic flow meter	Accurate & linear Low maintenance Does not need excessive upstream straight run Sensitive to low flows Measures reverse flow	Large sizes expensive Installation involves cutting pipe
Filled pipe with electromagnetic insertion flow meter	Installation simple, need not interrupt operations Access easy Measures reverse flow	Measures at one point (straight run needed upstream for representative measurement)

3.3.19 Temperature Pressure and Differential Pressure

Manufacturers' literature on process instruments such as temperature, pressure and differential pressure transmitters was not specially sought for the survey as the requirements for emissions monitoring are well within the capabilities of the standard instruments on the process control market:

Instrument	Typical Accuracy	Approximate Price
Temperature	0.1 °C	£ 200

Pressure	0.5 %	£ 400
Differential pressure	0.1 %	£ 900

Low cost instruments are available, intended for the heating and ventilating (H&V) market. They are not suitable since accuracy, robustness and environmental protection are often found to be lacking in this type of product. They are sometimes encountered, however, supplied with "packaged" plant.

3.3.20 Biocides, Coagulants and Other Additives

Non-oxidising biocides, generally organic compounds, are used in water systems throughout the industry. These chemicals are added to the water automatically, usually on a timed cycle, by dosing pumps. Two different types may be alternated automatically to combat legionella, particularly in open cooling water system applications. The working concentration is typically 20-100 ppm. No means of continuous monitoring was identified (reasons generally as for PAHs). On-line toxicity monitors could be suitable - the usual manual methods involving living cells on test strip employ a similar principle.

Oxidising biocides are applied generally to larger water systems in the industry. They are based on the addition of chlorine, bromine or chlorine dioxide to maintain concentrations of a few ppm in the system. REDOX (ORP) provides a suitable means of monitoring the concentration of such oxidants. The signal from the REDOX instrument may be utilised to modulate the flow of biocide into the system to hold the concentration in the system at a constant value.

Coagulants and flocculants are additives that bind finely divided material in the effluent into a form which is more easily separated for removal from the effluent. The chemicals currently in use for this purpose are relatively innocuous; the use of aluminium compounds has been discontinued. No applications of continuous measurement have been identified.

Corrosion inhibitors are added to cooling water systems and periodically discharged to

drain. Inhibitors are generally phosphorus and/or organic compounds. Zinc compounds are also used. In open (evaporative) systems the addition and discharge are generally automatic. Addition is controlled in proportion to the make-up water flow, the controller receiving pulses from a simple mechanical flowmeter. Conductivity of the cooling water is measured continuously and when the reading exceeds a pre-set value, signifying salts are building up in the system, a valve is opened, bleeding the system to drain. No continuous monitoring of discharges was evident during the study.

3.4 APPLICATION OF CONTINUOUS MONITORING TO RELEASES TO LAND

No continuous monitoring takes place for releases to land on Metals Industry sites in the UK.

3.4.1 Zinc Determination Using LIBS

Voest Alpine in Austria has applied atomic emission spectroscopy to evaluate the zinc content of dust extracted from a BOS plant.^{Ref 17} The aim to selectively withdraw zinc-rich dusts from a cycle in which particulates are collected from the BOS vessel fume, are pelletised and returned to the charge. The instrument's sensor assembly has a lens tube mounted directly over a dust conveyor. A high-energy pulse of light from a laser focused to a point on the surface of the sample vaporises a small quantity of material and the spectrum of the emitted light is analysed.

After successful trials at Linz in 1995, it was proposed to install the equipment (Voest Alpine/Technolas GmbH patent) on a permanent basis as part of a plant upgrade.

Table 3.3 TA Luft Requirements for Continuous Monitoring

Parameter of interest	Limit above which continuous measurement is prescribed		Type of measurement**
	Total kg/h	Conc. mg/m ³	
Particulate matter (as opacity)	2-5		Particulate -opacity
(as mass concentration)	>5		Particulate - mass concentration
Lead in particulates		25	Particulate - mass concentration*
Zinc	not specified		
Cadmium in particulates		1	Particulate - mass concentration*
Mercury in particulates		1	Particulate - mass concentration*
Copper in particulates		25	Particulate - mass concentration*
Aluminium in particulates	not specified		
Nickel,Selenium,Tellurium in particulates (as Class II carcinogens)		5	Particulate - mass concentration*
Arsenic compounds in particulates (as Class II carcinogens)		5	Particulate - mass concentration*
Antimony in particulates		25	Particulate - mass concentration*
Chromium in particulates (as Class II carcinogens)		25 1	Particulate - mass concentration* Particulate - mass concentration*
Tungsten & molybdenum compounds	not specified		
Tin in particulates		25	Particulate - mass concentration*
Beryllium in particulates (as Class I carcinogens)		0.5	Particulate - mass concentration*
Oxides of sulphur (as SO ₂)	50		SO _x
Oxides of nitrogen (as NO ₂)	30		NO _x
Carbon monoxide (for comb. control)	5		CO
(otherwise)	100		CO
Hydrogen	not specified		
Chlorine	1		Cl
Hydrogen chloride	3		HCl
Hydrogen fluoride (fluorides in particulates)	0.5	25	HF Particulate - mass concentration*
Cyanides in particulates (easily soluble)		25	Particulate - mass concentration*
Hydrogen sulphide	1		H ₂ S
Ammonia	not specified		
Amines and amides	not specified		
VOCs (as TC) general	1		TC
general - org.Classes I, II and III	10		TC
org.Class I eg phenol, formaldehyde		100	Particulate - mass concentration*
PAHs	not specified as such		
Dioxins	not specified		
Oil mist	not specified		

* Continuous measurement may be discontinued if daily mean values are found to differ only slightly

** Subject to a suitable instrument being available

Data source: TA Luft

Table 3.4 Methods and Minimum Measuring Ranges - Air

Parameter	Principle of Measurement	Typ. Min. Range *
Particulate matter	transmissivity	20 mg/m ³ **
	scattering	<0.03 mg/m ³ **
	optical scintillation	0.1 mg/m ³ **
	triboelectric	0.1 mg/m ³ **
Mercury	AA spectrometry	0.1 mg/m ³
	AA fluoresc. spectrometry	
Oxides of sulphur	cross-duct NDUV	100 ppm
	cross-duct NDIR	85 ppm
	NDUV	50 ppm
	electrochemical	30 ppm
Oxides of nitrogen (as NO ₂)	cross-duct NDIR	200 ppm
	cross-duct NDUV	100 ppm
	chemiluminescence	4 ppm
Carbon monoxide	electrochemical	100 %
	cross-duct NDIR	20 ppm
Hydrogen	thermal catalytic	4 %
	thermal conductivity	1 %
	electrochemical	2000 ppm
Chlorine	NDIR	500 ppm
	ion mobility spectrometry	100 ppm
	electrochemical	30 ppm
Hydrogen chloride	NDIR	100 ppm
	ion mobility spectrometry	5 ppm
	electrochemical (ion-selective)	<5 ppm
Hydrogen fluoride	tuned laser IR	
	ion mobility spectrometry	5 ppm
	electrochemical (ion-selective)	<5 ppm
Hydrogen sulphide	NDIR	100 ppm
	electrochemical	100 ppm
	UV fluorescence spectrometry	0.1 ppm
Ammonia	thermal conductivity	15 %
	cross-duct NDUV	100 ppm
	conversion & chemiluminescence	20 ppm
	reflection spectrophotometry	16 ppm
	ion mobility spectrometry	5 ppm
Amines and amides		
VOCs (as CH ₄)	thermal catalytic	10 %
	NDIR	500 ppm
	FID	10 ppm
Flow	correlation	1 m/s

* Source: Manufacturers' literature provided in the course of the study

** Lower Limit of Detection for a stack diameter of 1m.

Source: ETIS Project Research: Particle Emission Monitoring (Ref 187) and manufacturers' data.

Table 3.5 Methods and Minimum Measuring Ranges - Water

Parameter	Principle of Measurement	Typ. Min. Range *
pH	ion selective electrode	14 pH
Redox	electrode	1000 mV
Turbidity	transmissivity	400 mg/l
	scattering	50 mg/l
Conductivity	conductimetry	0.05 mS/cm
Dissolved oxygen	electrochemical cell	10 ppm
Oil and grease	differential scattering	2 ppm
Aluminium	colorimetry	0.5 ppm
Cadmium	ion selective electrode	20 ppm
Cadmium	anode stripping voltametry	0.01 ppm
	colorimetry	5 ppm
Chromium	ion selective electrode	0.005 ppm
Copper	ion selective electrode	20 ppm
	colorimetry	5 ppm
Iron	ion selective electrode	0.005 ppm
	colorimetry	1 ppm
Lead	ion selective electrode	20 ppm
	anode stripping voltametry	0.01 ppm
Mercury	AA spectrophotometry	pprox 0.1 ppm
	UV spectrophotometry	ppm
Silver	ion selective electrode	20 ppm
Zinc	anode stripping voltametry	0.01 ppm
Chlorides	ion selective electrode	50 mg/l
Fluorides	ion selective electrode	0.1 mg/l
	ion selective electrode	10 ppm
Nitrates (as N)	ion selective electrode	0.2 mg/l
Phosphates (as P)	ion selective electrode	20 mg/l
Ammonia	ion selective electrode (gas)	1 ppm
	UV spectrophotometry	ppm

Source: Manufacturers' literature provided in the course of the study

Table 3.6 Continuous Emission Monitor Cross-Sensitivities

Type of Monitor		Cross-sensitivity expressed as % *						
		Water vapour	Carbon dioxide	Carbon monoxide	Sulphur dioxide	Nitrogen Oxide	Nitrogen Dioxide	Methane
Oxides of sulphur	NDIR							
	NDIR + GFC							
	NDUV	0.004	0.0005	0.2		0.7	19	0.0002
	Electrochemical							
Oxides of nitrogen	NDIR							
	NDIR + GFC	0.05					50	
	NDUV							
	Chemiluminescence							
	Electrochemical							
Carbon monoxide	NDIR (Luft)	0.04	0.0065					0.0006
	NDIR + GFC	0.0025	0.0005					
	NDIR + GFC	0.005	0.0003		-0.006		3	0.0001
	Electrochemical							
Carbon dioxide	NDIR (Luft)	0.15		0.0025				0.002
	NDIR							0.0001
Oxygen	Paramag.:dumbbell		0.3					
Hydrogen chloride	NDIR + GFC	0.002						0.5

* Instrument response to a 100% concentration of the interfering substance at the input

Source: Manufacturers' literature received during the study

4. OPERATOR EXPERIENCE

This Section is based on interviews with plant operators and discussions with instrument suppliers on the installation of their products. It deals with the impact of regulations, the UK infrastructure for monitoring, corporate strategy of plant operators and the requirements for supporting continuous monitoring applications on metals industry sites. It then considers specific operational experience in monitoring particular species of pollutant.

All operators expect lower limits on releases and increasing requirement to use continuous monitoring. Some users are carrying out trials and evaluations in advance of continuous monitors being required as an authorisation condition.

All operators agreed that there were advantages in having continuous monitoring of pollutants. These advantages were:

- The environmental benefits and associated promotion of public confidence
- Improved knowledge of release levels
- Process control improvements
- Quicker tracing of faults
- Potential operational cost savings
- Actual cost savings, if manual monitoring were reduced (See Table 4.1)
- More realistic limits

Operators can be concerned about one or more of the following:

- Given success of one installation, more continuous monitoring could be expected;
- Inspectors could come to expect more information once it is possible to obtain it. More reporting would be required, entailing time and cost;

- The more continuous data may become available, the more likely it is to fall into the hands of those who might misinterpret it (short peaks, start-ups, erroneous readings);
- Revelations, by continuous monitoring, that emissions were lower than the permitted limits could result in tighter limits being set.

Some operators considered that the limits being set did not provide an appropriate degree of flexibility (short-term incidents, occasional start-up conditions, or testing).

Some large sites have numerous small combustion processes which, when taken together, constitute the equivalent of a large combustion plant. Provision of flue gas monitoring on these, or other multiple small-scale processes, is significantly more expensive than a single large process.

In the absence of legislation or regulations, there was considerable uncertainty surrounding inspectors' requirements. This made planning for the future for capital expenditure and resources difficult.

Some operators were concerned that their Agency inspector would not respond favourably to testing continuous monitors by removing bags to simulate bag failure, or to other steps that would result in an obvious, albeit brief, increase in emissions. Others, however, had instituted regular checking of their monitors by this means with the agreement of their inspector.

4.1 UK INFRASTRUCTURE

Despite the increasing number of instrument applications, there has been significant erosion of the instrument engineering base in the UK. This, in the Metals Industry and elsewhere, has created a weak infrastructure for the implementation of monitoring. Besides de-manning (see later), there are various other mechanisms at work:

- Modern instrumentation is perceived to be very reliable and "maintenance-free". This is true for many simple process instruments, but most analysers including continuous monitors require regular, informed, attention;
- 'Multi-skilling' has diluted the instrumentation knowledge base: mechanics are taught general electrical knowledge but little specifically on instrumentation. Electricians often lack the process knowledge required, despite mechanical training; the old 'instrument tiffys' (specialist instrument artificers) have become rare;
- Use of the word 'skills' misleads recruitment, since it has emphasised ability to use the tools rather than the ability to comprehend the task in hand;
- The adoption of electronics in place of pneumatics for process instrumentation has relieved the work-force of the practice of manual dexterity, care and cleanliness when tending instruments;
- Many instruments are now imported. The expertise of UK distributors is limited. This greatly reduces the available knowledge base in the UK;
- The larger UK metals industry plants have numerous on-line process analysers and so staff are already suitably trained and experienced for dealing with emissions monitoring instruments. This is not usually the case for smaller sites.

4.2 CORPORATE STRATEGY

In the case of British Steel operations, site representatives are backed by a centralised resource with overall responsibility for environmental policy. This co-ordinates monitoring schemes throughout the company's sites, evaluates proprietary monitors, and has a detailed knowledge of Agency inspectors' requirements.

Other large Metals Industry companies are multi-nationals based overseas and do not play

such a large part in implementation of monitoring in the UK. . They co-operate on a company-wide basis for evaluation and also industry-wide, for example in the aluminium industry for evaluating fluoride emission monitors.

The Metals Industry has in any case an established tradition of sharing information between companies (compared to the food or pharmaceuticals industries, which are very guarded).

A number of Metals Industry operators presented written statements of company environmental policy. None of these referred to continuous monitoring.

4.3 STAFFING

4.3.1 Environmental Manager

Each of the operators interviewed had appointed an individual with clearly defined responsibilities, generally:

- Understanding and interpreting the requirements of IPC
- Assembling the appropriate applications
- Instigating trials, installation and calibration of CEMs
- Arranging measurement regimes and preparing reports
- Acting as the focus for communications with environmental organisations
- (In many cases) performing similar functions for safety on site

Most were chemists or metallurgists with considerable process knowledge of the appropriate analytical techniques and a working knowledge of instruments. They were found to be generally open and communicative.

4.3.2 Design and Installation

In larger operations in the Metals Industry, instrument expertise is available from in-house engineering groups. These are not responsible directly to production departments. They design new plant and will manage projects including CEM trials and installations, and will

also provide skilled supervision for the maintenance of complex instruments. Engineering groups will often also be responsible for integrating the logging of environmental data into existing plant process control computer systems.

Engineering groups are expensive to run. Their benefits are long-term and difficult to quantify; as a result, personnel have been drastically reduced over the last 20 years.

Some operators had the policy of calling in contractors to install the instrument as a package but the majority of large operators used in-house staff to specify the work, which was then placed with local mechanical and electrical contractors to carry out under supervision.

Contracts for new plant usually included the requisite CEM installations as part of the package.

Installation (inclusive of logging system, installation, commissioning) is generally more expensive than the purchase price of the monitor itself - see example, Table 4.1.

4.3.3 Commissioning

Commissioning is typically by the instrument manufacturer and usually included hands-on training for site personnel. Sometimes, this work is included in the purchase price of the monitor.

There often seemed to be some delay between the acquisition of an instrument and the completion of the system to the point where data is logged continuously. This was reported to be caused by shortage of cash for (relatively small) capital items such as logging software and computers, or the workload of on-site personnel.

4.3.4 Maintenance and Calibration.

In-house maintenance staff, responsible directly to production, usually carried out the day-to-day maintenance of continuous monitoring systems such as cleaning and replacement of reagents. However, preventive maintenance, of prime importance for CEM operation, can barely be afforded at most sites. In successive cost-cutting exercises, maintenance teams in

the industry have been reduced to levels appropriate to breakdown maintenance on items essential to production.

Maintenance involving breakdown or modification of a monitor is invariably carried out by the supplier, but in some cases he will recommend a local contractor. Figures of the order of 10 days were noted where the instrument had to be returned for repair.

Calibration is usually carried out by specialist independent contractors. This is an expensive aspect of the total cost of ownership. Table 4.1 gives a cost breakdown of a typical (real) installation.

There were no complaints from the operators visited about the quality of maintenance work carried out by suppliers or contractors, but poor calibration work was reported in a few cases.

4.3.5 Support from Suppliers

Operators find suppliers generally willing to assist with the application of standard products. With regard to suppliers' support of an existing installation, however, reports were very variable.

Suppliers were reported to be unwilling to develop special instruments to suit users' needs. It should be noted that there has been a deliberate trend in the instrument industry towards standardisation of product range. Larger production runs result in lower unit production costs and improved, consistent quality. Also, established products have had their "teething troubles" cured. A "special" involves many hours of work, not only in development but also in special installation, commissioning and future servicing.

4.4 EXPERIENCE WITH SPECIFIC MONITORING APPLICATIONS

A summary of continuous monitors in use at a selection of Metals Industry sites is given in Table 4.2.

4.4.1 Particulates and Smoke

Most optical scattering and scintillation types of instrument were found to be satisfactory. Triboelectric types were widely favoured. Only one company (which had selected the AC type after comparative site trials against alternative, optical, types) complained of significant problems, thought to have arisen from moisture. Rain falling down the stack appears a possible source of trouble but, although a cause of concern for most users, it was not reported to have caused problems. One user in Scotland had installed a "Chinese hat" on the stack to keep it dry. Another user, however, reported trials carried out on a triboelectric instrument on the output of a wet scrubber for two weeks (daily checks) with success. One user complained of electrical interference as a problem. Low-cost AC triboelectric units were reported to be affected by burner on-off conditions because of the flame condition affecting the ionization of particulates.

Several users had changed from optical to triboelectric units, usually as a result of fouling problems.

Transmissivity types were found to be the most prone to problems, usually exhibited as variation or drift of the output rather than outright failure.

Most problems had been solved by cleaning the units, and the failure put down to contamination of windows. In some cases, the contamination was observed and reported as oil or oily deposits, almost certainly originating from the compressed air supply.

(Considerable quantities of water with traces of oil from the compressor are often found in plant air supply systems, especially during and after a plant shut-down.)

In cases where integral purge blowers were supplied with monitors, the blowers were reported to operate reliably.

Alignment of transmissivity units was reported to require considerable care in the setting up procedure, but only one stack monitor installation appeared to suffer from long-term alignment problems. A possible cause was rainwater absorbed by the machinable ceramic

insulating collars separating the device from the stack.

Particulate monitors had been applied to closed loop control, to modulate the fans in the secondary extraction system of an EAF plant, ^{Ref 37} but proved unsatisfactory and the monitors were retained for alarm duty only. A similar application is currently being tried, however, by another company.

Particulate monitors had been very effective in detecting filter failure. It was noted by several users that, during testing, the simulated failure of a single bag was registered by the monitor. In one test, the removal of six bags in an array of 1 800 increased the reading from a normal 3 mg/m³ to 15 mg/m³. It was noted, however, that this type of gross local failure was rare. The particulate reading was normally found to increase progressively as a result of minor defects developing in the bags. Particularly bad leaks were traceable by observing the variation in signal as the filter bank went through its cleaning cycle.

Some users did not regularly calibrate particulate monitors for burst-bag duty, owing to the high cost of formal calibration services; it appears that a simple device for in-situ calibration by simulating the effect of particulate matter would be desirable, although none was found during the product survey.

For positive pressure bag filter applications, users reported difficulties in obtaining long-throw units and, where these had been fitted, keeping them operational, given the hot, dirty operating conditions and difficulty of access. Movement of the structure was reported to cause unpredictable drift in instrument readings because of changes in the alignment of the transmitter and receiver units. One operator had devised a technique of accommodating long-term drift by an integration function and using the resulting active zero line as reference for the alarm.

Transmissivity units for smoke monitoring duty were reported to be reliable, except when installed close to the top of a stack where it was thought that the purge blower pressure was not high enough to prevent gusts of wind bringing fume into contact with the windows.

Where smoke monitors had been connected to shut down furnace plant on excessive emissions, the connection had later been removed to avoid "nuisance" tripping.

4.4.2 Combustion Gases

There were few applications of SO_x/NO_x gas monitoring reported in the Metals Industry.

NO_x extractive NDIR monitoring was attempted for extracted fume from acid treatment processes but difficulties arose with corrosion/blockage in the sampling system and the trial units were removed.

Good experience was reported from users of IR SO_2 monitors for combustion gas and process gas measurements on metals extraction processes.

CO was monitored in EAF fume on site, with an IR instrument. Weekly filter changes were found to be essential and three-monthly servicing is carried out by the manufacturers. CO is also being monitored using solid state sensors and these are reported to operate satisfactorily.

4.4.3 Oxygen

Oxygen has long been monitored in the stacks of re-heat furnaces using zirconia in-situ probes. They are used as a basis for manual adjustments to combustion control settings. They were not, however, found to be sufficiently dependable for on-line automatic adjustment of combustion, as failures could cause unacceptable disturbances to production.

4.4.4 Flow of Air

No significant problems were reported with the units in use: "perforated tube" and optical time-of-flight types.

4.4.5 Automatic Sampling of Water

No particular problems were noted, but the majority of users stated a preference for

peristaltic pumps to the air powered type on reliability grounds.

4.4.6 pH and Redox

Manufacturers claimed that the new type of plastic flat-membrane pH electrodes are more easily cleaned. Some of the users interviewed had used this type of electrode, but most were using probes with the conventional bulbous tip. Both groups had problems, caused by contaminants - notably oil. Electrode manufacturers also considered chelated iron to be a problem. No users had run comparative tests on the two types.

Most of the automatic cleaning systems were reported to be of the air sparging type. Some users reported the mechanical brush type to be more effective. Whatever the type of probe or method of cleaning, periodic removal and manual cleaning were found to be necessary. The frequency of manual cleaning varied greatly between users, from daily to two-monthly operations.

There were no complaints about the working life of electrodes.

4.4.7 Conductivity

Occasional malfunctions, resulting in unusual variations in the monitor's output signal, were reported. The problems had been corrected by manual cleaning.

4.4.8 Turbidity

With mechanical cleaning and overall air sparging for the sampling system, turbidity meters were reported to give satisfactory service.

All users reported fluctuations in turbidity signals, accompanied by changes in other parameters, from time to time. The changes were usually associated with the run-off of surface water after rain. Three users had connected a weather stations to the logging system to allow emissions data to be correlated with rainfall and other environmental conditions.

4.4.9 Metals in Water

One application of metals measurement was identified in the study, based on Anode Stripping voltametry (ASV). This was reported to be operating satisfactorily for Pb, Cd and Zn measurement, despite its demanding operational requirements: frequent checking and changing of reagents and calibration solutions. A problem had been experienced with calibration, arising from the element thallium masking the cadmium value, but the plant operator reported tackling this with success.

4.4.10 Oil in/on Water

None of the operators interviewed had requirements in their authorisations to implement oil monitoring but two had experience with oil-on-water monitors of the infrared reflection type. One had favourable results with a free-floating unit, the other unfavourable, the problems generally arising from mooring/locating the unit or it simply sinking. Fixed units were found to perform satisfactorily. The units' analogue outputs were not intended to be proportional to oil thickness but had been found very useful in practice as an indication.

In the Industry in general, oil-in-water monitors are considered prone to significant errors because of variations in droplet particle size distribution, oil type and interaction with solid particulates. Difficulties with detecting and extracting soluble oils for analysis were also experienced.

4.4.11 Flow of Water

For those measuring flow in open channels, there was a general problem of flumes or channels becoming blocked by debris.

One operator had experienced levels downstream backing up to the flume, and failure to register reverse flow. The company had changed from an ultrasonic level measurement/flume system to a submersible ultrasonic Doppler instrument utilising the existing flume. The results were satisfactory. Another user reported good results from a submersible electromagnetic unit.

Most problems relating to submersible probes of the ultrasonic Doppler type stemmed from the deposition of salts; these were difficult to remove. One user wrapped the probe in parcel tape and found this repelled the contamination while not affecting the operation of the unit.

Sites monitoring flow in closed pipes had been well served by electromagnetic flowmeters. On one site where replacement was scheduled, the intention was to install an electromagnetic flowmeter of the alternative immersion type as this could be fitted without the pipe being taken out of use.

4.4.12 Data Transmission

Most effluent water monitoring installations were located at some distance from the main plant, and long cable links and, in some cases radio transmission, were employed. Both types were reported to be very reliable.

In some applications, logging was shared with other site services systems using BMS or SCADA system rather than process control technology; readings took a relatively long time to be communicated. Where this involved sampling a continuous analogue signal, there could be insufficient data to develop a true average. In one particularly bad case with a dialled-up system (with 15 min delay), the scheme was being replaced with a connection to the plant process control system.

4.4.13 Data Processing and Storage

Users have a wide range of systems, including local, self-contained packages or PCs with proprietary software for monitoring, SCADA systems and plant process control systems. At the sites visited during the study, the following arrangements had been adopted for logging:

- 55% DCS or SCADA logging
- 18% Self-contained instrument (download to PC)
- 22% Chart recorder
- 5% BMS

No complaints about the facilities offered by the systems or operational problems were noted with PC-based systems.

There were often minor problems when first setting up in-house systems because of lack of input/output capacity of the existing process control systems or delays in obtaining the services of programmers.

Some users had integrated weather stations into their monitoring systems. The data facilitated the interpretation of such measurements as turbidity, flow of effluent (influenced by rainfall) and ambient fume and gases (influenced by wind speed and direction).

Table 4.1 - Costs of Particulate CEM at an EAF Installation

	Days	Estimated Cost* £1996			Notes
		Rate £/day	Total in First Year	Annual	
Monitor - transmissivity type			3 500		
Logging system PC & printer Central control unit Software			2 500 2 800 2 000		Cost could be shared with other CEM applications on the site Cost could be shared with other CEM applications on the site Cost could be shared with other CEM applications on the site
Design engineering/management	5	100	500		Internal design and project management
Installation			1 000		Includes mechanical fittings and purge air
Gantry & access			0		Access (£10 000) would be required in any case, for manual measurement
Lighting and small power			450		24 hour access required
Cabling, 200m			800		Instrument power and signal
Commissioning	2	200	400		By manufacturer
Commissioning internal admin	1	100	100		In-house
Calibration, 3 conditions	2	2 000	4 000	4 000	CEM calibration, with sampling of dust for metals analysis
Analysis for 6 metals x 3 conditions	1	720	0	0	Metals analysis required in any case, whether CEM or manual monitoring
Saving: 2 manual particulate measurements	-2	2 000	-4 000	-4 000	2/year CEM calibration replaces 4/year manual particulate monitoring
Saving: 2 analyses/year	-2	720	-1 440	-1 440	2/year CEM calibration+analysis replaces 4/year manual particulate + analysis
Calibration admin	1	100	100	100	In-house
Reporting	1	100	100	100	In-house
Maintenance - in house	2	100	200	200	4x3 monthly cleaning and checking
Servicing at site by manufacturer	0	200	0	0	Not normally necessary
First Year Total			13 010		
Subsequent years(/year)				-1 040	

* Prices are ex-VAT, estimated from requirements of an actual installation.

Table 4.2 Continuous Monitors In Use

Company**	Emissions to Air*																	Releases to Water*											
	Moisture	Oxygen	Sampling	Smoke	Particulate	Flow in flue	SO2	NOx	CO2	CO	Cl	DP on filters, scrubbers	UV flame detector	Scrubber water flow etc	pH - scrubber water	Temp dryers & furnaces	Fluorides	pH of effluent	Flow of effluent	Temp of effluent	Auto sampling	Turbidity	Heavy metals	Dissolved oxygen	Ammonia	Conductivity	Oil	TOC	
Alcan Recycling					X						+																		
Alcan S & P, Lynemouth		X			+		X	X	X									X											
Aldec													X	X	X	X													
Anglesey Aluminium Metal				X	X	+												+			X								
ASW, Tremorfa					X																								
ASW, Castle				X																									
Avesta-Sheffield Tins. Pk					X																								
Avimo												X							X										
Battery Rolled Metals					X																								
Bernhard Metals					X							X					X												
BICC Rod Rollers																													
Boliden MKM																													
Brent Smelting Works					X	+											X												
Britannia Alloys & Metals																													
Britannia Recycling					X														X	X		X							
Britannia Zinc				X	X		X		X	X									X	X	X	X		X					
British Steel, Cookley																			X										
British Steel, Llanwern				X	X	X													X	X		X			X	X	X		
British Steel, Port Talbot				X	X					o									X	X									
British Steel, Scunthorpe				X	X														X		X		X		X	X	X	X	X
British Steel, Teesside					X																								
BSES, Aldwarke					X														X	X	X		X						
BSES, Stocksbridge																			X										
Brock Metal		X			+												X												
Brookside Metals					+		+		+			X		X		+													
Calder Aluminium					X																X								
Co-Steel, Sheerness					X					X																			
Cookson Precious Metal					X							X		o					X	X									
Deeside Aluminium					X																								
Delta Enfield Metals					X	X				X										X									
Engelhard					X							X							+	+									
Forgemasters																													
H J Enthoven & Sons	X		X		X									X					X	+									
IMI Refiners					X		+		+										X										
IMI Wolverhampton Metals					X									o															
Inco Alloys					+																								
JBR Recovery		+			X												X												
Midland Lead Manufacturers					+												X												
Rodco										X																			
Thomas Boulton					+														X	X			X						

- X One or more instruments installed
 + To be installed (required by IPC Authorisation)
 o Installed or to be installed (independent of IPC Authorisation)

* Data sources: IPC Authorisations and interviews with operators

** Companies chosen to be representative of the industry - selection verified by Trade Associations

5. CALIBRATION AND VERIFICATION

5.1 INTRODUCTION

It is necessary to calibrate a continuous monitor against an independent measurement method; this calibration should be carried out at the time of installation and commissioning and at set time intervals thereafter dependent upon the known stability or drift characteristics of the analyser.

In the majority of cases covered by the following survey, the reference method is a manual technique, although valid calibrations may be carried out against another continuous monitor, which usually operates on the basis of a different principle of measurement, and provided that the reference monitor has itself been accurately calibrated and is of known stability. For gas monitors, routine calibration using bottled-test gases is convenient and would appear to be straightforward but the handling of low concentration reactive gases requires greater expertise, which may not be available to the user. COGDEM has formed a working group with the aim of publishing guidance on this.

In accordance with requirements of the Environment Agency, analytical methods published by the British Standards Institution and other UK Committees, such as the Standing Committee of Analysts, have been assigned priority in the Sections of this survey which present UK practices and procedures. In the event that no UK standard method has been identified in the literature search, appropriate standards from other countries, in particular those of DIN and VDI in Germany, and United States standards have been highlighted. Separate sections of the survey also provide details of the standards issued by the various organisations in Germany and the United States.

In some instances international standards, in particular those of the International Standards Organisation (ISO), have been identified. There are also some measurements for which few, if any, UK or other national standards are available. In such cases it has been possible to discover which international organisations, such as CEN/CENELEC, have committees and working groups engaged upon monitoring programmes.

Some of these working groups have produced draft documents which are at various stages of the standards procedures. Where possible, these have been identified.

The standards have been identified by use of the library of the British Standards Institution and that of the Environment Agency and by reference to HMIP Technical Guidance Note (Monitoring), M4 and the Environment Agency Consultation document 'The Establishment of a Monitoring Certification Scheme'. Extensive use has been made of the standards catalogues and the original standards have been consulted where necessary.

5.2 REGULATORY REQUIREMENTS

Guidance on standards relevant to IPC (Integrated Pollution Control) monitoring are quoted in HMIP Technical Guidance Note (Monitoring) M4.^{Ref 18}. This Guidance Note provides manual methods of analysis drawn from national or international standards and these methods may be suitable for calibration of Continuous Emission Monitoring instruments. Guidance Note M4 states that preference should be given to analytical methods published by the British Standards Institution (BSI) and other related committees such as the Standing Committee of Analysts (SCA). The SCA is now a committee within the Environment Agency.

In the absence of a British Standard or International Standard method, other national standards may be adopted. Consideration is given to standards such as the following:

- International Standards Organisation (ISO)
- Comité Européen de Normalisation (CEN)
- United States Environmental Protection Agency (US EPA)
- American Society for Testing and Materials (ASTM)
- Deutsches Institut für Normung (DIN)
- Verein Deutscher Ingenieure (VDI)
- Association Française de Normalisation (AFNOR)

For the relevant Technical Committees within BSI, CEN and ISO, reference should be made

to HMIP Technical Guidance Note (Monitoring) M3.^{Ref 19} The Guidance Note M3 also gives brief histories of these organisations and an outline of the interactions between them. Production of standards and the influence on legislation are also reviewed and a survey of the CEC (Commission of the European Communities) Directives, which have an impact on air quality, plant emissions, toxic and dangerous waste, drinking water and ground water, is also provided.

Again with reference to Technical Guidance Note M4,^{Ref 18} there are relatively few British Standard methods for the measurement of releases to air, so, at present, reliance has to be placed on standards from overseas, including for continuous monitoring instrument calibration. The situation is somewhat different in the case of releases to water, a wide range of analytical methods having been published by the Standing Committee of Analysts. As at August 1995, more than 150 analytical methods had been published.

As regards actual legislation, it is clearly stated in BS 0 : Part 2 : 1991 (Guide to BSI Committee Procedures) that 'compliance with a British Standard does not of itself confer immunity from legal obligations.' On the other hand, compliance with a standard can be made mandatory.

Up to now, there has not been a formal certification or type approval scheme within the UK for stack emission monitors. Equally, there has not been a scheme formally acceptable throughout the European Union or internationally.

However, an Environment Agency scheme, MCERTS^{Ref 22} is being launched in April 1998 based on international standards. Under this scheme, official bodies will be established to be formally responsible for implementing and managing a certification service and maintaining performance standards for the instruments. The instruments will be subjected to type tests against these standards. Certification will require both laboratory testing and field testing. Calibration will be against gas mixtures which are traceable to primary gas concentration standards. MCERTS does not explicitly cover calibration at fixed intervals after approval and installation, although the proposals^{Ref 22} have emphasised the recommendation for

periodic on-going performance checks and outlined suggestions for an appropriate methodology.

Germany has a national legal and technical framework for use of continuous monitoring instruments. The requirements for installation and operation of Continuous Emission Monitors are embodied in Regulation 17BIm Sch V^{Ref 20} and an earlier guideline^{Ref 21} covers the subjects of suitability testing and calibration. There is a clear legal requirement for a type approval procedure, and a system for on-site calibration and verification of the monitoring instruments and the data obtained by them; the calibration and verification must be carried out by a registered measurement organisation.

In the USA, there is a somewhat different approach; there is no type approval system, but the performance criteria are well defined and there are requirements for on-site verification, although it seems that there are no regulations to define by which organisations the verification may be carried out, and the work is conducted by the plant operator himself or by private consultancies.

No national schemes covering instrumentation for monitoring effluent discharges or water quality have been identified, but it is intended that MCERTS should be extended later to include monitoring instruments for such applications.

5.3 UK PRACTICES AND PROCEDURES - RELEASES TO AIR

5.3.1 Standards

5.3.1.1 Particulate Matter

The standard UK manual methods for calibration of continuous in-stack monitors are as follows:

- BS 3405 : 1983 (1989). Method for the measurement of particulate emission, including grit and dust (simplified method).^{Ref 23}

- BS.6069 : Part 4 : Section 4.3 : 1992 (ISO 9096 : 1992)
Stationary source emissions. Method for the manual gravimetric determination of concentration and mass flow rate of particulate materials in gas-carrying ducts.^{Ref 24}

It should be noted that the earlier British Standard, BS 893 : 1978 Method for the Measurement of the Concentration of Particulate Material in Ducts Carrying Gases, has been withdrawn.

As a brief survey of the above methods, BS 3405 does not specify any obligatory apparatus but details the method of sampling under isokinetic conditions to an accuracy within $\pm 25\%$. However, certain parameters such as efficiency of filters and cyclones, are specified and an appendix to the Standard provides examples of suitable apparatus. Although this method is the one most commonly used in the UK, the Standard does not state an operable concentration range; most operators claim 20 mg/m^3 as the lower limit for the particulate concentration.

- BS 6069 : Section 4.3 is also silent on sampling equipment but is somewhat more definitive in quotation of the estimated accuracy. The range of application is quoted as 5 to $10\,000 \text{ mg/m}^3$. The accuracy for the concentration range 50 to $10\,000 \text{ mg/m}^3$ is estimated to be $\pm 10\%$ but that for concentrations below 50 mg/m^3 is stated to be poorer.

Working Group 5 of CEN Committee TC264 is working on a manual reference method for total dust measurement at concentrations less than 20 mg/m^3 .

5.3.1.2 Oxides of Sulphur

The standard UK manual methods for measurement of concentrations of oxides of sulphur are listed below. (Note: If an analyser is to be calibrated against sulphur dioxide in a binary mixture, say with nitrogen or simulated air as the complementary gas, the most straightforward method is to construct a calibration curve of instrument response against concentrations of sulphur dioxide in a series of bottled gas mixtures. These are obtainable

with a quoted uncertainty of $\pm 1\%$ of composition. However, the on-site calibration would normally require that the complementary gas should actually be the flue gas itself so that any interference effects resulting from other components of the flue gas are taken into account. This requirement could well preclude the above method. These comments apply also to the other gas concentration measurements covered by this survey.)

Manual methods for measurement of sulphur dioxide concentrations are:

- BS 1756 : Part 1 : 1971
Methods of sampling and analysis of flue gases: Methods of sampling^{Ref 25}
- BS 1756 : Part 4 : 1977
Methods of sampling and analysis of flue gases: Miscellaneous analyses:
Determination of moisture content, sulphuric acid dewpoint, carbon monoxide, oxides of sulphur and oxides of nitrogen^{Ref 26}
- BS 1756 : Part 5 : 1971
Methods of sampling and analysis of flue gases: Semi-routine analyses^{Ref 27}
- BS 6069 : Part 4 : Section 4.1 : 1990 (ISO 7934 : 1989)
Stationary source emissions - Method for the determination of the mass concentration of sulphur dioxide: Hydrogen peroxide/barium perchlorate/thorin method^{Ref 28}

It is relevant to refer also to BS 6069, Part 4, Section 4.4 (ISO 7935). Although the Standard relates to automated measuring methods, it deals with the performance characteristics of instruments for determination of the mass concentration of sulphur dioxide^{Ref 29}

BS 6069 : Part 4 : Section 4.1 : 1990 ((ISO 7934 : 1989)^{Ref 28}) represents a method that has for a long while been used for sulphur dioxide analysis but it has been accepted relatively recently as British Standard (and ISO Standard). It is generally accepted

internationally as the current best practice for measurement of sulphur dioxide concentration by a manual method. It is also equivalent to the VDI Guideline, VDI Richtlinie, 2462, Blatt 8^{Ref 30} and is similar to the US EPA Method 6 Ref³¹ although not identical to it.

At this stage, it is appropriate to comment on the sampling method that is related to the calibration technique. For this, one needs to refer to the German Guideline, VDI Richtlinie 3950, Blatt 1^{Ref 32}. In general, it is not possible to vary plant operating conditions in to change the flue gas composition, since this would interfere with production. However, the VDI Richtlinie allows "artificial" dilution or enrichment of the component of the flue gas that is being measured. Dilution is achieved by introduction of zero gas (for example, simulated air) into the sampling lines/sampling system to mix with the flue gas sample. Similarly span gas, ("pure" sulphur dioxide in this case) may be introduced at various rates so that the required number of points on the analyser span can be checked in turn. The VDI Richtlinie actually calls for "20 measurement pairs", to cover the full range of the Continuous Emissions Monitor under calibration. This is a very detailed calibration procedure.

Draft BS 6069 : Part 4 (new section) : 1992^{Ref 33} calls for five uniformly distributed calibration concentrations to check the entire scale in measuring equipment with a linear calibration function. The recommended concentrations are 20, 40, 60, 80, 90% of full scale. The same Standard calls for an increase in the number of points in the case of a non-linear calibration function but even then, it is stated that 10 points are normally sufficient to establish the response curve. (Note: although Ref 33 refers to oxides of nitrogen, the procedures are equally applicable to sulphur dioxide.)

The point at which the sample is drawn from the sampling line for analysis by the Standard Reference Method (SRM) must be as close as possible to the point from which the sample is drawn to be fed to the continuous emissions monitor (CEM). Ref 38 also allows for calibration against a verified Automated Measuring System (AMS) as an alternative to calibration against a manual reference method. The conditions are that the principle of operation of the AMS must be different from that of the CEM, and that the AMS must have

been independently verified against BS 6069 : Part 4 : (New Section) : 1992 (Draft).

5.3.1.3 Oxides of Nitrogen

The standard UK manual methods for measurement of concentrations of oxides of nitrogen are:

BS 1756 : Part 4 : 1977

Methods of sampling and analysis of flue gases: Miscellaneous analyses: Determination of moisture content, sulphuric acid dewpoint, carbon monoxide, oxides of sulphur and oxides of nitrogen.^{Ref 26}

BS 6069 : Part 4 : New Section : 1992 (Draft) (=ISO DIS 10849.2)^{Ref 33}

Stationary source emissions: Method of determination of the mass concentration of nitrogen oxides - Performance characteristics and calibration of automated measuring systems.

No other British Standard documents relevant to flue gas have been identified (although there is a standard method - BS 1747, Part 8 : 1986 (1991) - for measurement in ambient air). Brief details of calibration against binary gas mixtures are given in Section 5.3.2 above and the same remarks are applicable to nitrogen oxides. Traceable standards of nitric oxide in nitrogen and nitrogen dioxide in nitrogen are available and have a quoted uncertainty of $\pm 1\%$.

Draft BS 6069 : Part 4 (new section) : 1992^{Ref 33} provides for calibration against gas mixtures and also a verified automated measuring system. The latter would appear to be a satisfactory method. The procedure of calibration against binary mixtures is a reliable method and of good accuracy. The complementary gas is, however, normally nitrogen, of necessity in the case of nitric oxide, and may not be representative of the actual flue gas mixture.

If calibration is carried out against a verified automated measuring system, the sampling method of Ref 32 can be applied. This method of calibration would seem to be desirable in

the light of the statement given in HMIP Technical guidance Note M4^{Ref 18} on the subject of manual methods for oxides of nitrogen. The Guidance Note states that generally the measurement of oxides of nitrogen emissions by any of the manual methods is less precise or accurate than the automatic techniques. The chemiluminescence method has the advantage that nitric oxide and nitrogen dioxide concentrations are measured with the same instrument.

Concentrations of nitrogen oxides (NO_x) can be measured by chemiluminescence, non-dispersive infra-red spectroscopy (NDIR), non-dispersive ultraviolet spectroscopy (NDUV) and differential optical absorption spectroscopy (DOAS).

If the verified automated measuring system employed as the standard reference is a chemiluminescence analyser, it must be remembered that the method is subject to interference by ammonia and that carbon dioxide may also interfere, particularly in the presence of water vapour, because of quenching of the chemiluminescence phenomenon. Water vapour may also cause interference in the case of analysis by non-dispersive infra-red methods. The non-dispersive ultraviolet method is also subject to interference by sulphur dioxide and aromatic compounds. If a differential optical absorption spectroscopic method is used, there may be interference from gases for which the absorption bands are in the range of 200 to 2 000 nm^{Ref 22}

In the absence of a UK Standard manual method, it seems that manual analyses are most commonly carried out by the German VDI 2456, Blatt 8, method^{Ref 34}. This is one of three procedures given in VDI 2456. The relevant parts are as follows:

- VDI, Richtline 2456, Messengasförmiger Emissionen
Messen der Summe von Stickstoffmonoxid und Stickstoffdioxid
Blatt 1, Phenoldisulphursäurefahren, 1973^{Ref 35}
Blatt 2, Titrationsfahren, 1973^{Ref 36}
Blatt 8, Natriumsalicylatverfahren, 1986 (Sodium salicylate method^{Ref 34})

The fact that the method requires a period of 24 hours between the sampling procedure and

production of the result would be of no disadvantage for calibration, although the method would be completely unacceptable for process control applications.

HMIP Guidance Note M4^{Ref 18} expresses the view that US EPA Method 7A may be the best Standard Method; the method is based on ion chromatography.

5.3.1.4 Carbon Monoxide

There are many analysers for carbon monoxide on the market, but as recently as August 1995, the time of production of HMIP Technical Guidance Note (Monitoring) M4, there was no satisfactory British Standard method based upon either manual or continuous/ automatic techniques. The only method identified is that given in BS 1756 : Part 1^{Ref 25} which does give a spot reading.

In the absence of UK standard methods, it is opportune to list here the German and United States Standards, although these are detailed in later sections (5.4.1.4 and 5.4.2.4) and are methods for continuous monitoring:

United States Environmental Protection Agency Standard for the Performance of a New Stationary Source: Method 10, Determination of Carbon Monoxide Emissions from Stationary Sources. (Non-continuous, gas chromatography)^{Ref 37}

VDI, Richtlinie 2459, Blatt 6, Messgasförmiger Emissionen, Messen der Kohlenmonoxid-Konzentration, Verfahren der nicht-dispersiven Infrarot-Absorption, 1980^{Ref 38}

There is also an ISO Standard in preparation for automated measurement of carbon monoxide (and also carbon dioxide and oxygen). At the time of writing this study report, this ISO document had reached the CD (Committee Draft) stage ISO C 12039 2. It includes the subject of calibration of automated measuring systems for carbon dioxide, carbon monoxide and oxygen and covers several analyser types, of both extractive and non-extractive systems. The principles of operation of the monitors for carbon monoxide are

non-dispersive infrared spectroscopy (NDIR) and the electrochemical cell.

As indicated above for sulphur dioxide and nitrogen oxides, calibration can be carried out against another automated measuring system which has been previously verified. In the case of carbon monoxide (unlike that of nitrogen oxides), the NDIR method is quite specific for measurement of concentration; the other gases, such as sulphur dioxide, that are likely to be present in stationary source emissions would cause very slight interference.

5.3.1.5 Water Vapour

The measurement of water vapour concentrations in source emissions is important in the context of referencing concentrations of other chemical pollutants to standard conditions. The specified concentration limits are normally quoted on a 'dry gas' basis, whereas the concentrations are often measured in a wet gas. There are considerable problems in sampling because the water vapour content of stack gases is very high; the sampling system must therefore be heated to prevent condensation in the lines.

A "continuous" water vapour monitor may be calibrated by the comparison method against a verified water vapour analyser. This method, accepted in BS 6069 : Part 4 : (new section) 1992 (Draft)^{Ref 33} for oxides of nitrogen, is for general application. To satisfy the requirements indicated in this Standard, one needs to choose a reference instrument that operates on a measuring principle different from that of the instrument under calibration. Care may be needed in the choice of the reference instrument if the actual flue gas is passed to it.

There is one British Standard that covers a manual method of determination:-

- BS 1756 : Part 4 : 1977

Methods of sampling and analysis of flue gases: Miscellaneous analyses: Determination of moisture content, sulphuric acid dewpoint, carbon monoxide, oxides of sulphur and oxides of nitrogen.^{Ref 26}

The recommendation of the Report 'The Establishment of a Monitoring Certification Scheme'^{Ref 22} is that the water vapour calibration mixture used in the measurement range and accuracy tests (in the laboratory performance tests) shall have a concentration accuracy of $\pm 3\%$ relative value (95% confidence level), determined in a manner that is traceable to national humidity standards. In fact, in another part of that report, the requirement is stated even more explicitly that the water vapour calibration mixture must be traceable to the national primary standard.

5.3.1.6 Hydrogen Chloride

The sampling method given in BS 1756 : Part 1^{Ref 25} can be applied.

There is a CEN EN Draft Standard, BS EN 1911 - 1/2/3, prepared by the CEN TC264 (Air Quality) Committee. The Standard is entitled - Air Quality - Stationary source emissions; Manual method of determination of hydrogen chloride.^{Ref 39} This is in three parts:

- Part 1 : Sampling and pre-treatment of gases
- Part 2 : Gaseous compounds absorption
- Part 3 : Absorption solutions analysis and calculation

Three methods of analysis are presented: potentiometric titration, spectrophotometry and ion chromatography. The first two of these methods are similar to those given in VDI 3480, Blatt 1 (Para 1).^{Ref 40}

For purpose of the analysis, the sample is taken from the source, either isokinetically or otherwise, through a high-efficiency filter and is absorbed in water. The methods are subject to interference by other halogenated compounds and halogen gases, which can pass the filter; and by other ionic species. Sampling temperatures must also be high - above 150°C and at least 20°C higher than the acid dewpoint. High sampling rates are necessary and the accuracy of measurement is dependent on the moisture content of the stack gas.

It is possible to measure hydrogen chloride concentration by infrared analysis, but the

absorption is very poor and one needs to use measurement cells of long path length. At the time of writing HMIP Technical Guidance Note M4, there were few standard methods from overseas and none was considered to be satisfactory for flue gas monitoring applications. In the absence of UK Standards, the following, which are detailed later in the survey, may be applied after sampling:

- US EPA Method 26 Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources - Midget Impinger Method (1991)^{Ref 41}
- US EPA Method 26A. Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources - Isokinetic Method (1992)^{Ref 42}

In each case, the actual calibration is carried out against standard chloride solutions.

- AFNOR NF X 43-309 in combination with NFX 44-052, Air Quality - Stationary Source Emission - Determination of Hydrogen Chloride Emissions.^{Ref 43}
- Unichem Method N.607 (1983). Stationary Source Emission Measurements, Conveyed Gas Flows; Determination of Chlorine and Hydrochloric Acid. Colorimetric Method (EM/12).^{Ref 44}

Again, the methods are subject to interference; the EPA methods detect volatile halogen compounds such as ammonium chloride, chlorine dioxide and halogen gases.

5.3.1.7 Hydrogen Cyanide

With reference to the HMIP Technical guidance Note M4, no standards specific to measurement of hydrogen cyanide emissions from combustion processes could be identified.

The present position appears to be the same. The Guidance Note suggests that the sampling procedure of BS 1756 : Part 4^{Ref 26} could be followed with analysis by ion chromatography.

5.3.1.8 Hydrogen Fluoride

There is no British Standard in existence for the determination of hydrogen fluoride. The samples can be obtained by the method described in BS 1756 : Part 1^{Ref 25} and may be analysed by a manual method. These methods could then be used for the purpose of calibration of the continuous emissions monitors for hydrogen fluoride. In the absence of a British Standard the following methods are applicable:

- VDI Richtlinie 2470, Blatt 1. Messen gasförmiger Emissionen.
Messen gasförmiger Fluor-Verbindungen. Absorptions-Verfahren^{Ref 45}
- US EPA Method 13A. Determination of Total Fluoride Emissions from Stationary Sources - SPADNS Zirconium Lake Method^{Ref 46}
- USEPA Method 13B. Determination of Total Fluoride Emissions from Stationary Sources - Specific Ion Electrode Method^{Ref 47}

The VDI Guideline 2470, Part 1 is, in fact, a calibration method for automatic instruments. The hydrogen fluoride is absorbed in sodium hydroxide solution. The fluoride is separated by steam distillation and is estimated by means of an Alizarin complex photometric method. Alternatively, the fluoride in the absorption solution is determined by a potentiometric method by means of a fluoride-sensitive electrode.

5.3.1.9 Hydrogen Sulphide

There are no British Standard methods for measurement of hydrogen sulphide. There are, however, methods in which insoluble sulphides are precipitated by hydrogen sulphide and these may be determined by detector tubes or by spectrophotometric or titrimetric analytical methods. In the absence of any British Standard, other published methods are given in references 48 to 50.

5.3.1.10 Dioxins

British Standards for measurement of dioxins have now been published. The method of analysis requires separation of the species by chromatography, followed by identification by means of mass spectrometry or ion capture. The three standards are listed below. Other published standards are listed in references 51 to 56. These are manual methods, which would be applicable for purpose of calibration of any continuous emissions monitor for dioxins, were such to exist.

- BS EN 1948-1. Dioxins - Determination of the mass concentration of polychlorinated di-benzo-p-dioxins (PCDDs) and di-benzofurans (PCDFs) in stationary source emissions - Sampling
- BS EN 1948-2. Stationary source emissions - Determination of the mass concentration of polychlorinated di-benzo-p-dioxins (PCDDs) and di-benzofurans (PCDFs) - Part 2: Extraction and clean up
- BS EN 1948-3 - Dioxins - Determination of the mass concentration of polychlorinated di-benzo-p-dioxins (PCDDs) and di-benzofurans (PCDFs) in stationary source emissions - Identification and quantification

5.3.1.11 Volatile Organic Compounds

There are two British Standards that are worthy of note:

- BS 6069 : Part 3 : Section 3.3 1991 (= ISO 9486 : 1991)^{Ref 57}
Method for the determination of vaporous chlorinated hydrocarbons by charcoal tube/solvent desorption/gas chromatography.
- BS 6069 : Part 3 : Section 3.4 : 1991 (=ISO 9487 : 1991)^{Ref 58}
Method for the determination of vaporous aromatic hydrocarbons by charcoal tube/solvent desorption/gas chromatography.

Provided that the identities of the particular volatile organic compounds (VOCs) emitted are known, the continuous monitor can be calibrated against reference calibration gas mixtures of those species in a suitable carrier gas.

No British Standards for methods of calibration have been identified. A measure of the level of VOCs can be obtained by measurement of the concentration of total organic carbon. For low concentrations (<20 mg carbon/m³), the FID method proposed by the CEN TC 264, in document CEN/N 150,^{Ref 59} can be calibrated against calibration gas mixtures (for example, propane) in a carrier gas. (The draft CEN Standard (N 150) can also be used as a reference method, as well as for continuous monitoring, and is the preferred method.) For concentrations above 20 mg carbon/m³, the continuous monitoring method proposed by US EPA Method 25A^{Ref 60} can also be calibrated against a range of reference gas mixtures. An FID procedure is also given in US EPA Method 25^{Ref 61} as a manual reference method. Another US EPA Method^{Ref 62} describes an infra-red method.

The German Guideline VDI 3481, Part 3 (1992)^{Ref 63} also presents an FID technique for measurement of TOC at concentrations greater than 20 mg carbon/m³. This is also a continuous monitoring technique which may be calibrated across the range of measurement against calibration gas standards.

VDI 3481, Part 2^{Ref 64} identifies a standard reference method in which a sample of the organic compounds is adsorbed onto a silica gel, is thermally desorbed, and is oxidised to carbon dioxide which is determined coulometrically.

5.3.1.12 Additional Parameters

Gas Flow Measurement

The physical parameter necessary to be measured is flue gas flow, which is essential in the context of measurement of mass emissions of a specific pollutant. It should be noted that measurements of flow rate are influenced by several factors: presence of particulates, turbulence and non-uniformity of flow across the stack, fluctuations in gas composition and

temperature. The calibration can be carried out on-site against a standard reference method.^{Ref 65}

BS 5857 : Part 2 : Section 2.1 : 1980 (1986) (= ISO 4053/1)^{Ref 65} is a General Standard on measurement of gas flow, and Section 2.4 of the same series presents a flow measurement method using radioactive tracers.^{Ref 68}

ISO 10780^{Ref 67} specifies manual methods for determination of velocity and volume flow rate of gas streams by use of Pitot tubes.

US EPA Method 2 also presents a method for measurement of average velocity and volume flow rate by use of a Pitot tube.^{Ref 68}

Finally, another American Standard ASTM - D3154 - 91 provides a method for the same measurements and includes procedures for determination of stack gas composition and moisture content.^{Ref 69} The method of calibration of the Pitot tubes is presented in another Standard prepared by the American Society for Testing and Materials - ASTM D 3796 - 90.^{Ref 70}

5.3.2 Instrument Certification Schemes

Although there has been no formal scheme in the UK for either pattern approval or certification of continuous emission monitoring instruments up until now, the Environment Agency is launching its MCERTS in April 1998 (see section 5.2). Equivalent gas monitors for COSHH applications, rather than stack monitoring, should shortly be able to be performance tested to draft CENELEC Standard prEN 45544 - Workplace atmospheres - Electrical apparatus used for direct detection and direct concentrated measurements of toxic gases and vapours.

5.4 INTERNATIONAL PROCEDURES - RELEASES TO AIR - STANDARDS

5.4.1 Germany

5.4.1.1 Particulate Matter

The German Standard VDI 2066, Measurement of particulate matter, comprises several parts. Parts 2 and 7^{Refs 71 & 72} are isokinetic sampling methods in which the particulate matter is separated from the flue gas by a filter; in the method presented in Part 2, the filter is a thimble filled with quartz "wool", and in that presented in Part 7, it is a flat fibreglass filter. The quantity of particulate matter is then gravimetrically determined. The methods represented by these two parts are the ones recommended in Germany.

Part 1^{Ref 73} also describes the manual method of measurement by extractive gravimetric sampling.

Part 3^{Ref 74} presents the method for determination of dust content in the lower range. A high sampling rate (40 m³/h) is specified for this purpose and the detection limit is then 0.225 mg/m³.

Part 4^{Ref 75} presents a method for continuous measurement by an optical technique and has been included here for the sake of completeness of the VDI 2066 series. The dust content in the flue gas is determined by measurement of transmission of a light beam through the sample and comparison of the intensity of the transmitted beam with that of a reference beam of identical optical path.

Part 6^{Ref 76} has also been included here for sake of completeness. It also presents an optical (continuous) method in which the dust content is determined on the basis of light scattering.

VDI 3950 Part 1^{Ref 32} describes the procedures by which the relationship between the output of the continuous emissions monitor and the particulate content of the flue gas, as determined by VDI 2066 (various parts), is established.

The continuous monitor must be pattern approved, after being tested by a licensed testing organisation, and must be calibrated in situ also by a licensed testing organisation. Re-calibration is necessary after any modifications have been made either to the process itself or to the measuring equipment, and in any case after a maximum of five years after installation. The procedure is controlled by the above-mentioned VDI Standards.

5.4.1.2 Oxides of Sulphur

The manual methods are embodied in the various parts of VDI 2462; eight parts of this Standard were published between 1974 and 1985, the most relevant of which, for purposes of calibration, are Parts 1, 2, 3 and 8^{Refs 77,78,79,30} respectively). Part 1 describes the iodine-thiosulphate method, Part 2 the hydrogen peroxide/titration method and Part 3 the hydrogen peroxide method with gravimetric determination. Part 8 presents the hydrogen peroxide-thorin method and which is generally accepted throughout Europe as the current best practice for measurement of sulphur dioxide concentrations by a manual method. This Standard should be used in conjunction with VDI 3950, Part 1^{Ref 32} for calibration of a continuous monitor against the manual method, Parts 4, 5 and 6 of VDI 2462 describe automatic methods of measurement.

5.4.1.3 Oxides of Nitrogen

The manual methods for measurement of concentrations of oxides of nitrogen are given in the various parts of VDI 2456 as follows: Part 1^{Ref 35} presents the phenol disulphonic acid method, Part 2^{Ref 36} gives a titration method and Part 3^{Ref 34} gives the sodium salicylate method. The remaining parts of VDI 2456 cover automatic methods of measurement of nitrogen oxides concentrations. Part 7, for example, describes the chemiluminescence method.

As for other gases, the standards that describe the manual methods should be taken in conjunction with VDI 3950, Part 1^{Ref 32}

5.4.1.4 Carbon Monoxide

VDI 2459, Part 6^{Ref 38} presents a measurement method for carbon monoxide concentrations, based upon non-dispersive infra-red absorption. This should be read in conjunction with VDI 3950^{Ref 32} if necessary. Strictly, however, the infra-red method is a continuous monitoring technique. Nevertheless, this could be used as a basis for calibration if the output of the continuous monitor under calibration is compared with that of an independently calibrated analyser.

5.4.1.5 Water Vapour

Performance standards for continuous measurement of water vapour have been issued in Germany. The guideline^{Ref 80} relates to the suitability-testing, installation, calibration and maintenance of measuring apparatus for continuous emissions measurement. On the basis of these guidelines, some measuring systems have been type approved. With reference to Clause 5.3.1.5 of this report, measurement of water vapour content is important in interpretation of other results; concentration limits are quoted on a "dry" basis but the actual concentrations are often measured in gases containing water vapour.

5.4.1.6 Hydrogen Chloride

The reference method in Germany for the measurement of hydrogen chloride concentrations is VDI 3480, Part 1^{Ref 40}. In the absence of a British Standard method, the present BS EN 1911-1/2/3 being still at the draft stage, details of the VDI 3480 methods have been summarised earlier in clause 5.3.1.6 of this report as being similar to the BS EN methods.

There are two methods of analysis, similar to two of those given in BS EN 1911-1/2/3, potentiometric titration and spectrophotometry. The methods are also subject to interference by other species, such as halogens, sulphides, sulphates and cyanides, the extent and nature of the interference being dependent on the analytical method selected.

5.4.1.7 Hydrogen Cyanide

No standard methods for the measurement of hydrogen cyanide in gaseous emissions have been identified.

5.4.1.8 Hydrogen Fluoride

The manual method for determination of concentrations of hydrogen fluoride is given in VDI 2470, Part 1.^{Ref 45} This describes gaseous emission measurements on fluorine compounds by an absorption method. A summary of the technique has been provided in clause 5.3.1.8 of this report, in the absence of a British Standard Method.

5.4.1.9 Hydrogen Sulphide

There is a published standard in Germany for the measurement of concentrations of hydrogen sulphide, VDI 3486.^{Ref 48} Two parts of the standard respectively provide two methods of determination - potentiometric titration method (Part 1) and iodometric titration (Part 2). In the first method, the flue gas is passed through a sulphuric acid/hydrogen peroxide solution to combine the available sulphur dioxide; the hydrogen sulphide is then absorbed in caustic soda solution and the sulphide is estimated by potentiometric titration against silver nitrate solution. In the second method, the gas is passed through a cadmium acetate solution; the hydrogen sulphide in the gas is converted quantitatively to cadmium sulphide, which is determined by iodometric titration.

5.4.1.10 Dioxins

There are standards published in Germany for the measurement of concentrations of dioxins and furans.

VDI 3499, Part 1^{Ref 54} presents a method for determination of a range of pollutants, polychlorinated dibenzodioxins and dibenzofurans, in stack emissions by a dilution method. Part 2 of the same standard presents a filter/condenser method and Part 3 gives a "cooled probe method".

These are sampling methods and, with reference to clause 5.3.1.10 of this report, the method of analysis is separation by gas chromatography followed by identification by mass spectroscopy or ion capture.

5.4.1.11 Volatile Organic Compounds

Reference should be made to clause 5.3.1.11 of this report, where the German and US Standards have been presented in the absence of relevant UK Standards.

5.4.2 USA

5.4.2.1 Particulate Matter

The US Environmental Protection Agency has published a standard for manual measurement of particulates emissions from stationary sources. This method, ^{Ref 81} Method 5, utilises a Universal Stack Sampler. Particulate matter is withdrawn isokinetically from the source and is collected on a fibre-glass filter maintained at an elevated temperature ($120 \pm 14^{\circ}\text{C}$, typical). The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after removal of uncombined water.

The stack sampler consists of a series of impingers, vacuum lines which include a vacuum gauge, pump and dry gas meter and thermometers.

5.4.2.2 Oxides of Sulphur

The United States Environmental Protection Agency Method 6^{Ref 31} is similar to BS 6069 : Section 4.1^{Ref 28} and VDI 2462: Part 8^{Ref 30}, being a Standard that presents the hydrogen peroxide/barium perchlorate/thorin method. A gas sample is extracted from a sampling point in the stack. The sulphuric acid mist (which includes sulphur trioxide) is separated from the sulphur dioxide. The sampling system consists of a probe followed by a series of impingers, needle valve, pump, surge tank, flow meter and dry gas meter. The sample is collected in a solution containing isopropanol and hydrogen peroxide and is titrated against barium perchlorate solution with thorin as an end point indicator. (Thorin is 1 - 10 - arsonophenylazo - 2 - naphthol - 3, 6 - disulphonic acid, disodium salt.)

5.4.2.3 Oxides of Nitrogen

The United States Environmental Protection Agency has issued a manual method, Methods 7 and 7A.^{Refs 82, 83} A grab sample is collected in an evacuated flask which contains a mixture of dilute sulphuric acid and hydrogen peroxide. The nitrogen oxides (with the exception of nitrous oxide) are measured spectrophotometrically by the phenoldisulphonic acid procedure. In Method 7A, a grab sample is taken in the same way and is absorbed in a dilute sulphuric acid/hydrogen peroxide mixture. The nitrogen oxides (except nitrous oxide) are oxidised to nitrate, which is measured by ion chromatography.

5.4.2.4 Carbon Monoxide

The United States Environmental Protection Agency has issued two methods for determination of carbon monoxide and which could be used as calibration methods. Method 10^{Ref 84} is an infra-red, continuous monitoring technique. However, it could be used as a basis for calibration if the output of the continuous monitor under calibration is compared with that of an independently calibrated analyser. Method 10B^{Ref 37} describes a non-continuous method by gas chromatography. A gas sample is extracted from the sampling point, is passed through a conditioning system to remove interfering species and is collected in a Tedlar bag. The carbon monoxide is separated from the sample by gas chromatography and is catalytically reduced to methane which is then determined by means of a flame ionisation detector.

5.4.2.5 Water Vapour

No exhaustive survey of the measurement of water vapour concentrations in the United States has been carried out. An ASTM Standard^{Ref 85} has been identified. The Standard relates directly to the measurement of the water vapour content of electrical insulating gases by dewpoint measurement, but the method would be of more general application. Four test methods are provided in the standard.

5.4.2.6 Hydrogen Chloride

In the absence of a British Standard method for calibration of hydrogen chloride analysers,

the United States Environmental Protection Agency methods have already been given in clause 5.3.1.16 of this report.

US EPA Method 26^{Ref 41} describes the "Midget Impinger Method", by which the hydrogen chloride in the sample extracted from the source is passed through a pre-purged, heated probe and filtered into dilute sulphuric acid and dilute sodium hydroxide. These solutions respectively collect hydrogen halides and halogens and the filter collects particulate matter, including halides. The analysis method is ion chromatography and calibration is carried out against standard chloride solutions. The method is subject to interference by volatile compounds such as ammonium chloride, chlorine dioxide and halogen gases.

Method 26A^{Ref 42} describes the "Isokinetic Method", by which the sample is collected via a filter, and an optional cyclone if it is necessary to remove droplets, and via dilute sulphuric acid and dilute sodium hydroxide solutions. Again, the acidic solution collects the hydrogen chloride and the alkaline solution collects the halogens. The principle of analysis is again ion chromatography

5.4.2.7 Hydrogen Cyanide

No standard method for the measurement of concentrations of hydrogen cyanide in stack emissions has been identified. HMIP Guidance Note M4^{Ref 18} suggests that ion chromatography could be employed as the analysis method following a suitable sampling technique but no American Standard has emerged from the literature search.

5.4.2.8 Hydrogen Fluoride

The United States Environmental Protection Agency has issued Standards for analysis by manual methods:

US EPA Method 13A^{Ref 86} describes a method for determination of total fluoride by the SPADNS/Zirconium Lake Technique. Method 13B presents a method for determination of total fluoride by use of a specific ion electrode.^{Ref 87}

In Method A, gaseous and particulate fluorides are withdrawn isokinetically from the source and are collected in water or on a filter. The method of determination is a spectrophotometric technique in which the reagent is an aqueous solution of zirconyl chloride and 'SPADNS' (4,5 dihydroxy - 3 - - (p - sulphophenylazo) - 2, 7 - naphthalene - disulphonic acid trisodium salt.

In Method B, gaseous and particulate fluorides are withdrawn isokinetically from the source and are collected in water or on a filter. The total fluoride content is then determined by means of a fluoride activity sensing electrode and with reference to a single junction, sleeve type, reference electrode.

5.4.2.9 Hydrogen Sulphide

The United States Environmental Protection Agency has issued standards for the measurement of "Total Reduced Sulphur" by manual methods. These are as follows:

USEPA Method 16^{Ref 88} is described as a semi-continuous determination in which a gas sample is extracted from the source and an aliquot is analysed for hydrogen sulphide and organic sulphides (eg mercaptans) by gas chromatographic separation and detection by a flame photometer.

Method 16A^{Ref 89} presents a method by an impinger technique and by which the sample extracted from the stack is passed through a citrate buffer to remove sulphur dioxide; the total reduced sulphur compounds, such as hydrogen sulphide are then thermally oxidised to sulphur dioxide which is then determined by US EPA Method 6^{Ref 54} - the hydrogen peroxide, barium peroxide, thiorin Method 1.

In Method 16B^{Ref 90} the hydrogen sulphide (and organic sulphides) are thermally oxidised to sulphur dioxide which is analysed by gas chromatography with a flame photometric detector.

5.4.2.10 Dioxins

The United States Environmental Protection Agency has issued a Standard method, US EPA Method 23^{Ref 91} for determination of dioxins. A sample is extracted isokinetically from the gas stream and is collected in the sample probe on a fibre-glass filter and on a packed column of absorbent material.

The method is stated to be applicable to polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). These are extracted from the sample, are separated by high resolution gas chromatography and are measured by high resolution mass spectrometry.

5.4.2.11 Volatile Organic Compounds

Reference should be made to clause 5.3.1.11 of this report where the German and US Standards have been presented in the absence of relevant UK Standards.

5.5 UK PRACTICES AND PROCEDURES - RELEASES TO WATER

5.5.1 Standards

In this section of the report, a format different from that of Sections 5.3 (UK Practices and Procedures - Releases to Air) and 5.4 (International Procedures - Releases to Air) has been adopted. The reason for this is the large number of chemical species covered by the literature search, which made it impracticable to consider each separately and in detail; in addition, the same physical chemical principle is employed in the determination of many metals in water. The topics of suspended solids, chemical oxygen demand and other analytical methods peculiar to water quality have been presented under separate headings, but the methods of analysis for heavy metals have been presented under a common heading. The methods described are, in the main, those produced by the Standing Committee of Analysts (SCA). **However, Section 5.5.1.10 (Inorganic ions) should also be read in conjunction with all other Sections 5.5.1.1 to 5.5.1.9.**

5.5.1.1 Suspended Solids and Turbidity

Methods for the measurement of suspended solids are given in two SCA Standards and in a laboratory report.^{Refs 92,93,94} Of particular interest is the SCA method, Colour and Turbidity of Water 1981.^{Ref 94} The part of the Standard devoted to colour describes three methods; "Simple determination of colours", "Visual method for the determination of colour" and "Instrumental measurement of colour by absorbance". The first of these is an assessment by eye and said to be purely qualitative and highly subjective. The second is a visual comparison against inorganic colour standards or calibrated permanent glass standards. The third method is an instrumental measurement of colour by an absorbance method.

The part of the Standard devoted to turbidity describes two methods: The "Secchi Disc" method, by which the limit of visibility is assessed, and the nephelometric method, in which the intensity of light scattered by the sample is compared (instrumentally) with that measured for standard formazin suspensions.

5.5.1.2 Biochemical Oxygen Demand

Methods for measurement of biochemical oxygen demand are provided in three SCA Standards.^{Ref 95,96,97} Two of these state specifically a method for determination of the "Five-day biochemical oxygen demand (BOD 5)" and one^{Ref 95} identifies in the title that the subject is dilution and seeding methods.

5.5.1.3 Chemical Oxygen Demand

Two SCA Standards provide methods for the determination of the chemical oxygen demand (COD) (Dichromate Value) of polluted and waste waters.^{Ref 98,99} Ref 99 gives two methods, one of which is described as tentative.

5.5.1.4 Hydrocarbons

Although not specifically covered by this report, the following SCA Standards are provided for determination of hydrocarbons in water:

The Determination of Six Specific Polynuclear Aromatic Hydrocarbons in Water, with notes on the Determination of Other PAH^{Ref 100}

The Determination of Very Low concentrations of Hydrocarbons and Halogenated Hydrocarbons in Water^{Ref 101}

The Determination of Hydrocarbon Oils in Water by Solvent Extraction, Infrared Absorption and Gravimetry^{Ref 102}

5.5.1.5 Phenols, Oils and Fats

Although not specifically covered by this report, the following SCA Standards have been identified in the literature search and may be of interest in the context of organic releases to water:

Phenols in Waters and Effluents by Gas-Liquid chromatography^{Ref 103}

The Determination of Oils and Fats in Waste Water by Filtration, Solvent Extraction and Gravimetry^{Ref 104}

5.5.1.6 Dissolved Oxygen

Three Standards that provide methods for determination of oxygen dissolved in water have been identified; two of these are British Standards and one an SCA Standard. BS EN 25814 : 1992^{Ref 105} gives a method of measurement by means of an electrochemical probe. It is applicable to both field and laboratory measurements and the principle of operation is an electrochemical cell which is isolated from the water samples by a gas-permeable membrane.

BS EN 25813 : 1993 : 1989^{Ref 106} provides a method based upon iodometry. This is described as a reference method for the determination of oxygen in all types of waters and is applicable to oxygen concentrations greater than 0.2 mg/litre.

The SCA method is presented in the document "Dissolved Oxygen in Natural and Waste Waters, 1979" ^{Ref 107}.

5.5.1.7 Total Organic Carbon

This determination is described in the SCA Standard entitled "The Instrumental Determination of Total Organic Carbon, Total Oxygen Demand and Related Determinands, 1979" ^{Ref 108}.

5.5.1.8 Electrolytic Conductivity and pH

Methods for the measurement of electrolytic conductivity and pH are given in the SCA Standard:

The measurement of Electrical Conductivity and the Laboratory Determination of the pH Value of Natural, Treated and Waste Waters. ^{Ref 109}

Note: The industrial conductivity monitor can be checked/calibrated with reference to the measurements for the same solutions, made by use of a laboratory conductivity meter which has been itself calibrated against standard potassium chloride solutions. The electrolytic conductivity of potassium chloride solutions is well documented. Similarly, the industrial pH meter can be checked against a laboratory pH meter which has itself been calibrated against standard pH buffer solutions. British Standards for pH measurement are:

BS1647 - pH measurement : Part 1 : 1984 (1991), Specification for pH scale, and Amendment AMD 5567 (1987) : Part 2 1984 (1991) Specification for reference value standard solutions and operational reference standard solutions, and amendment AMD 5566 (1987).

5.5.1.9 Heavy Metals

Determinations of heavy metals in water by manual methods are, in the main, carried out by

atomic absorption spectrophotometry (AAS) and methods are provided in the standards of the Standing Committee of Analysts. These methods may be employed as reference techniques against which the continuous monitors are calibrated. In particular cases, methods other than AAS are employed and these are identified in the following summary:

Aluminium in water determination is covered in two SCA Standards - Acid soluble Aluminium in Marine, Raw and Potable Water^{Ref 110} and Acid Soluble Aluminium in Raw and Potable Waters by Spectrophotometry^{Ref 111}

Antimony is determined by the SCA Method, Antimony in Effluents and Raw, Potable and Sea Waters by Spectrophotometry Using Crystal Violet^{Ref 112}

Arsenic is determined by either of two SCA methods:

- Arsenic in Potable Waters by Atomic Absorption Spectrophotometry^{Ref 113}
- Arsenic in Potable and Sea Water by Spectrophotometry - (Arsenomolybdenum Blue Procedure).^{Ref 114} An SCA Method for Arsenic^{Ref 115} also covers determination of selenium

There are three SCA Standard methods for determination of Cadmium:

- Cadmium, Chromium, Copper, Lead, Nickel and Zinc in Sewage Sludges by Atomic Absorption Spectrophotometry following Digestion with Nitric Acid^{Ref 116}
- Cadmium in Potable Waters by Atomic Absorption Spectrophotometry.^{Ref 117} This is given as a tentative method
- Lead and Cadmium in Fresh Waters by Atomic Absorption Spectrophotometry^{Ref 117}

There is also a British Standard^{Ref 118} for the determination of Cadmium by flame atomic absorption spectrometric methods.

Determination of chromium features in two SCA Standards, Ref 116 (above) and in Chromium in Raw and Potable Waters and Sewage Effluents.^{Ref 119}

Copper^{Ref 120} and Iron and Manganese^{Refs 121, 122} are determined by atomic absorption spectrophotometry (SCA Methods).

There are two SCA Standard methods for determination of Lead:

- Lead and Cadmium in Fresh Water by Atomic Absorption Spectrophotometry^{Ref 122}
- Lead in Potable Waters by Atomic Absorption Spectrophotometry^{Ref 123}

There are five standards that describe methods for determination of mercury in water - three British Standards and two SCA Standards.

The method of analysis described in each of the three British Standards is flameless atomic absorption spectrophotometry. BS 6068 : Part 2 : Section 2 : 4 (= ISO 5666 : Part 1) describes a method after digestion with permanganate/ peroxydisulphate^{Ref 125}, BS 6068 : Part 2 : Section 2.5 (= ISO 5666 : Part 2) describes a method after pre-treatment with ultraviolet radiation^{Ref 126} and BS 6068 : Part 2 ; Section 2.6 (= ISO 5666 : Part 3) describes a method after digestion with bromine.^{Ref 127}

All are well characterised but have different applications. Taken in the above order, the first method is applicable to surface waters and to domestic and industrial waste waters and the second is applicable to drinking water and the limit of determination is $0.02/\mu\text{g}$ of mercury in the sample. The third is applicable to soft water, brine, drinking water and waters that have very small organic content.

One of the SCA Standards^{Ref 128} presents two methods for determination of mercury in waters, effluents and sludges; again, the measurement principle is flameless atomic absorption spectrophotometry but two pre-treatment methods are described: A) Digestion with sulphuric acid and reduction with a stannous compound, and B) Digestion with nitric acid/sulphuric acid mixture and reduction with a stannous compound.

The other SCA Standard^{Ref 129} is a later one and which supplements the first. Four distinct methods are presented, two of which, A and C, are applicable to water. Method A applies to raw, potable and saline waters and describes oxidation with acidified bromine and reduction by a stannous compound, and a gold concentration step. Method C is applicable to all waters and again describes the acidified bromine oxidation, stannous tin reduction and gold concentration step.

A method of analysis for nickel is given in an SCA Standard^{Ref 130} and a tentative SCA method is given^{Ref 131} for determination of manganese by spectrophotometry using formaldoxime.

Silver^{Ref 132} and zinc^{Ref 133} are determined by SCA methods, the principle of measurement being atomic absorption spectrophotometry in each case.

Tin is determined by an SCA method.^{Ref 134}

Ref 115 is an SCA method for determination of selenium in sludges, soils and related materials and also covers determination of arsenic.

5.5.1.10 Inorganic Ions (BS 6068)

SCA Standards for the determination of inorganic anions, in particular chloride, cyanide and sulphate, are given in Refs 135 to 140. In addition, an SCA Standard for ammonia in waters is given in Ref 141.

There is a very large number of British Standard Methods for determination of inorganic ions

in water. In the case of heavy metals for which SCA methods are enumerated above, there are also British Standard methods. There are also British Standard methods for determination of inorganic anions. In view of the very large number of inorganic ions covered by the standard, no attempt has been made in this report to make reference to each method individually. Reference should be made to BS 6068 ^{Ref 142}. The Standard consists of seven parts as follows:

- Part 0 Introduction
- Part 1 Glossary
- Part 2 Physical, chemical and biochemical methods
- Part 3 Radiological methods
- Part 4 Microbiological methods
- Part 5 Biological methods
- Part 6 Sampling

This entire list has been given here for the sake of completeness but the part of interest relative to calibration of continuous monitors is Part 2, Physical, chemical and biochemical methods. This in itself consists of 50 sections, each devoted to a specific analysis method and covers, in the main, inorganic cations and anions and other specific determinations, for example, Turbidity : Section 2.13, pH : Section 2.50; electrical conductivity : Section 2.35. (A few organic species such as determination of phenol index, Section 2.12, and non-ionic surfactants; Section 2.24 are also covered by the standard which is otherwise exclusively devoted to inorganic species.) A complete list of the titles of all parts and sections of BS 6068 is presented in the Introduction, Part 0.

With the exception of Part 0 : Introduction, the Standards are dual-numbered as BS and ISO Standards.

5.5.2 Accreditation Bodies and Instrument Certification Schemes

There is at present no formal certification scheme. It is intended that the Environment Agency's Monitoring Certification Scheme for continuous stack emission monitoring

MCERTS^{Ref 22}, should be extended later to instruments for monitoring effluent discharges and water quality.

5.6 INTERNATIONAL PROCEDURES - RELEASES TO WATER - STANDARDS

5.6.1 Germany

The standard test procedures considered suitable as reference methods for calibration are given in DIN Standards 38402 to 38415 inclusive, German methods for the examination of water, waste water and sludge.^{Ref 143} The complete series of standards is extremely comprehensive and for this reason, a summary only is given in this report. Of particular interest in the present context are standards DIN38402, 38404, 38405, 38406 and 38408 and 38409.

DIN 38402

Twenty parts of the Standard were identified in the literature search although the highest numbered part is Part 71. These cover the subjects of sampling (many parts), pre-treatment procedures, interlaboratory tests, calibration of analytical methods, evaluation of analytical results and linear calibration functions and verification of the equivalence of analytical methods.

DIN 38404

Thirteen parts of this Standard were identified although the highest numbered part is Part 21. These cover the subjects of physical and physicochemical parameters such as determination of colour, ultraviolet absorption, determination of temperature, pH values, oxidation-reduction (redox) potentials and radiological measurements.

DIN 38405

This Standard, 19 parts of which were identified (although the highest numbered part is Part 29), covers a wide range of different anions and methods. It is entitled "Anions (Group D)"

and covers chloride, fluoride, sulphate, nitrate, nitrite, phosphorus compounds, arsenic (anionic), cyanides, borates, selenium, chromium (anionic) and sulphides.

DIN 38406

Twenty-eight parts of the Standard were identified and these cover a wide range of elements and methods. It is entitled "Cations (Group E)" and covers metals such as manganese, iron, aluminium, mercury and cadmium. The highest numbered part is Part 28.

DIN 38407

Fourteen parts of this Standard were identified in the literature search. The Standard is entitled "Substance group analysis (Group F)" and covers compounds such as low-volatility halogenated hydrocarbons, volatile halogenated hydrocarbons, benzene, phenols and polycyclic aromatic hydrocarbons. The highest numbered part is Part 19,

DIN 38408

Seven parts of this Standard were identified, although the highest numbered part is Part 24. The Standard is entitled "Gaseous components (Group G)" and covers solutes such as dissolved ozone and dissolved oxygen.

DIN 38409

Twenty-seven parts of this Standard were identified, although the highest numbered part is Part 52. The Standard is entitled "Parameters characterising effects and substances (Group H)" and covers subjects such as total organic carbon, polycyclic aromatic hydrocarbons, total bound nitrogen and biological oxygen demand.

DIN 38410 to DIN 38415

The remaining standards in this series are outside the scope of this survey but are summarised here for sake of completeness:

DIN 38410 covers biological and ecological analysis of water (Group M), DIN38411 covers microbiological methods and DIN38412 covers test methods using water organisms (Group L)

DIN38413 includes several parts, devoted to specific determinations, for example Part 1 - Hydrazine, Part 2 - Vinylchloride, Part 4 - Carbon disulphide

DIN38414 covers sludges and sediments (Group S) and includes methods for determination of chemical oxygen demand, pH, polychlorinated byphenyls.

DN38415, the final standard in the series (sub-annual testing, (Group T) is of no interest in the present context.

Many of the standards are dual-numbered as DIN and ISO documents.

5.6.2 USA

The list of inorganic test procedures approved by the United States Environmental Protection Agency is very comprehensive and comprises 75 parameters, for many of which several methods of analysis are given. For this reason, in this report coverage of reference methods of calibration has been restricted to those chemical species enumerated in the earlier sections (5.5.1, United Kingdom).

These test procedures approved by the US EPA are, for the most part, derived from four major sources, with the addition of particular methods from some other sources. All methods are presented in the Code of Federal Regulations, in particular Volume 40^{Ref 142} which also provides a summary in tabular format. This tabular format has been adopted in this report as the most clear and concise method of presentation.

The major sources of the approved procedures are the following (the complete titles are presented in the References Section of this report):

(1) EPA

Methods for Chemical Analysis of Water and Wastes. US Environmental Protection Agency^{Ref 144}

(2) Standard Methods 18th Edition

Standard Methods for the Examination of Water and Waste Water

APHA, AWWA, WEF; 18th Edition^{Ref 145}

(3) ASTM

Annual Book of ASTM (American Society for Testing and Materials), Water and

Environmental Technology^{Ref 146}

(4) USGS

M J Fishman et al. Methods for Analysis of Inorganic Substances in Water and Fluvial

Sediments, US Department of the Interior, Techniques of Water - Resource

Investigations of the US Geological Survey^{Ref 147}

In addition to these, some other methods from particular sources are approved.

(5) Others

Nine other sources are listed in the following notes to the table of standard methods of measurement. The entries in the seventh column of the table identify the sources of the methods, with reference to these notes, for the methods listed in column six. Some of the sources are American Standards and some are commercial, being documents provided by instrument or chemical companies.

The notes have been entered at this part of the report because they relate directly to the table of US standard methods of measurement which follows, and the documents that are the subjects of Notes 5.1 to 5.10 have not been included in the "References" Section.

For standard methods of analysis for other inorganic species, reference should be made directly to the Code of Federal Regulations, Protection of Environment, 40, Part 136.3.^{Ref 144}

Note 5.1 Official Methods of Analysis of the Association of Official Analytical Chemists. Methods Manual, 15th Edition (1990).

Note 5.2 American National Standard on Photographic Processing Effluents, April 2 (1975). (Available from ANSI, 1430, Broadway, New York, NY 10018).

Note 5.3 Standard Methods for the Examination of Water and Waste Water, 14th Edition; Method 510A for distillation, Method 510B for the manual colorimetric procedure, or Method 510C for the manual photometric procedure.

Note 5.4 Direct Current Plasma (DCP) Optical Emission Spectrometric Method for Trace Elemental analysis of Water and Wastes. Method AES0029, 1986 - Revised 1991, Fison Instruments Inc., 32 Commerce Center, Cherry Hill Drive, Denver, MA 01923.

Note 5.5 Hydrogen Ion (pH), Automated Electrode Method, Industrial Method Number 378-75 WA, October 1976, Bran and Luebbe (Technicon) Autoanalyser II, Bran and Luebbe Analysing Technologies Inc., Elmsford, NY 10523.

Note 5.6 Iron; 1,10 Phenanthroline Method, Method 8008, 1980; Hach Chemical Company, PO Box 389, Loveland, CO 80537.

Note 5.7 Copper, Bicinchoninate Method, Method 8506, Hach Handbook of Water Analysis, 1979, Hach Chemical Company, PO Box 389, Loveland, CO 80537.

Note 5.8 Manganese; Periodate Oxidation Method, Method 8034, Hach Handbook of Waste Water Analysis 1979, pages 2-113 and 2-117, Hach Chemical Company, PO Box 389, Loveland, CO 80537.

Note 5.9 Zinc; Zincon Method, Method 8009, Hach Handbook of Water Analysis, 1979, pages 2-231 and 2-333. Hach Chemical Company, Loveland, CO 80537.

Note 5.10 Warshaw, R L et al - Methods of Analysis of Organic Substances in Water. Techniques of Water - Resources Investigation of the US Geological Survey, Book 5, Chapter A3, (1972, Revised 1987, p14).

Summary of Table 5.1 US Standard Methods of Measurement

The analysis methods for most cations are similar; atomic absorption spectroscopy (AA), inductively coupled plasma/atomic emission spectrometry (ICP/AES), direct current plasma (DCP) and specialised colorimetric methods. The colorimetric methods are specific, for example dithizone method for cadmium and the heptoxime method for nickel. There are specialised methods for measurement of mercury and for parameters such as electrolytic conductivity, pH and dissolved oxygen. For dissolved oxygen, the Code of Federal Regulations draws attention to a particular volume of ^{Ref 147}. This is quoted as Book 5, Chapter A1 (1989) of the Methods of Analysis of Inorganic Substances in Water and Fluvial Sediments.

TABLE 5.1

5/40

US STANDARD METHODS OF MEASUREMENT

Parameter, Units and Method	EPA Methods	STD Methods 18th Edition	ASTM	USGS	Others	Note *
Turbidity; NTU; Nephelometric	180.1	2130B	D1889-88(A)	1-3860-85	-	-
Biochemical oxygen demand (BOD ₅); mg/l. (Dissolved oxygen depletion)	405.1	5210B	-	1-1578-78	973.44, page 17	5.1 5.2
Chemical oxygen demand; mg/l; Titrimetric	410.1	5220C	D1252-88(A)	1-3560-85	973.46, page 17	5.1 5.2
Spectrophometric, manual or automated	410.2	-	-	1-3562-85	-	-
	410.3	-	-	-	-	-
	410.4	5220D	D1252-88(B)	1-3561-85	-	-
Polynuclear aromatic hydrocarbons	-	6410B, 6440B	D4657-92	-	-	-
Phenols; mg/l; Manual distillation	420.1	-	-	-	510A	5.3
followed by: Colorimetric (4AAP) manual or automated	420.1 420.2	-	-	-	510B & C	5.3
Dissolved oxygen; mg/l; Winkler (azide modification) Electrode	360.2 360.1	4500-OC 4500-OG	D888-92(A) D888-92(B)	1-1575-78 1-1576-78	973.45B	5.1
Total organic carbon (TOC); mg/l Combustion or oxidation	415.1	5310 B,C or D	D2579-93 (ANB)	-	973.47 p 14	5.1 5.10
Electrolytic conductivity (Specific conductance); $\mu\Omega^{-1}/\text{cm}$ at 25°C Wheatstone fridge	120.1	2510B	D1125-91(A)	1-1780-85	973.40	5.1
Hydrogen ion (pH); pH units Electrometric measurement or automated electrode	150.1	4500-H'B	D1293-84(90) (A or B)	1-1586-85	973.41 378-75WA	5.1 5.5
Aluminium - Total; mg/l; Digestion followed by: AA direct aspiration (atomic absorption) AA furnace (atomic absorption) Inductively coupled plasma/atomic emission spectrometry (ICP/AES) Direct current plasma (DCP) Colorimetric (Eriochrome cyanine R)	202.1 202.2 200.7	3111D 3113B 3120B	- - - D4190-82(88)	1-3051-85 - - -	- - - AES0029	- - - 5.4
Antimony - Total; mg/l; Digestion followed by: AA direct aspiration AA furnace ICP/AES	204.1 204.2 200.7	3111B 3113B 3120B	- - -	- - -	- - -	- - -

Parameter, Units and Method	EPA Methods	STD Methods 18th Edition	ASTM	USGS	Others	Note *
Arsenic - Total; mg/L; Digestion followed by:	206.5					
AA gaseous hydride	206.3	3114B 4.d	D2972-93(B)	1-3062-85	-	-
AA furnace	206.2	3113B	D2972-93(C)	-	-	-
ICP/AES	200.7	3120B	-	-	-	-
Colorimetric (SDDC)	206.4	3500-AsC	D2972-93(A)	1-3060-85	-	-
Cadmium - Total; mg/L; Digestion followed by:						
AA direct aspiration	213.1	3111B or C	D3557-90(A or B)	1-3135-85 or 1-3136-85	974.27 p 37	5.1 5.2
AA furnace	213.2	3113B	D3557-90(D)	-	-	-
ICP/AES	200.7	3120B	-	1-1472-85	-	-
DCP	-	-	D4190-82(88)	-	AES0029	5.4
Voltametry	-	-	D3557-90(C)	-	-	-
Colorimetric (dithizone)	-	3500 - CdD	-	-	-	-
Chromium - Total; mg/L; Digestion followed by:						
AA direct aspiration	218.1	3111B	D1687-92(B)	1-3236-85	974.27	5.1
AA chelation-extraction	218.3	3111C	-	-	-	-
AA furnace	218.2	3113B	D1687-92(C)	-	-	-
ICP/AES	200.7	3120B	-	-	-	-
DCP	-	-	D4190-82(88)	-	AES0029	5.4
Colorimetric (diphenyl carbazide)	-	3500CrD	-	-	-	-
Copper - Total; mg/L; Digestion followed by:						
AA direct aspiration	220.1	3111B or C	D1688-90(A or B)	1-3270-85 or 1- 3271-85	974.27 p.37	5.1 5.2
AA furnace	220.2	3113B	D1688-90(C)	-	-	-
ICP/AES	200.7	3120B	-	-	-	-
DCP	-	-	D4190-82(88)	-	AES0029	5.4
Colorimetric (Neocuproine)	-	3500 - CuD	-	-	-	-
Colorimetric (Bicinchoninate)	-	3500 - CuE	-	-	8506	5.7
Iron - Total; mg/L; Digestion followed by:						
AA direct aspiration	236.1	3111B or C	D1068-90(A or B)	1-3381-85	974.27	5.1
AA furnace	236.2	3113B	D1688-90(C)	-	-	-
ICP/AES	200.7	3120B	-	-	-	-
DCP	-	-	D4190-82(88)	-	AES0029	5.4
Colorimetric (Phenanthroline)	-	3500-FeD	D1068-90(D)	-	8008	5.6
Lead - Total; mg/L; Digestion followed by:						
AA direct aspiration	239.1	3111B or C	D3559-90(A or B)	1-3399-85	974.27	5.1
AA furnace	239.2	3113B	D3559-90D	-	-	-
ICP/AES	200.7	3120B	-	-	-	-
DCP	-	-	D4190-82(88)	-	AES0029	5.4
Voltametry	-	-	D3559-90(C)	-	-	-
Colorimetric (dithizone)	-	3500PbD	-	-	-	-
Mercury - Total; mg/L;						
Cold vapour, manual	245.1	3112B	D3223-91	1-3462-85	977.22	5.1
Cold vapour, automated	245.2	-	-	-	-	-

Parameter, Units and Method	EPA Methods	STD Methods 18th Edition	ASTM	USGS	Others	Note *
Manganese - total; mg/l; Digestion followed by:						
AA direct aspiration	243.1	3111B	D858-90(A or B)	1-3454-85	974.27	5.1
AA furnace	243.2	3113B	D858-90(C)	-	-	-
ICP/AES	200.7	3120B	-	-	-	-
DCP	-	-	D4190-82(88)	-	AES0029	5.4
Colorimetric (persulphate)	-	3500-MnD	-	-	920.203	5.1
Colorimetric (periodate)	-	-	-	-	8034	5.8
Nickel - total; mg/l; Digestion followed by:						
AA direct aspiration	249.1	3111B or C	D1886-90(A or B)	1-3499-85	-	-
AA furnace	249.2	3113B	D1886-90(C)	-	-	-
ICP/AES	200.7	3120B	-	-	-	-
DCP	-	-	D4190-82(88)	-	AES0029	5.4
Colorimetric (heptoxime)	-	3500-NiD	-	-	-	-
Selenium - Total; mg/l; Digestion followed by:						
AA furnace	270.2	3113B	D3859-93(B)	-	-	-
ICP/AES	200.7	3120B	-	-	-	-
AA gaseous hydride	-	3114B	D3859-93(A)	1-3667-85	-	-
Silver - Total; mg/l; digestion followed by:						
AA direct aspiration	272.1	3111B or C	-	1-3720-85	074.27 p 37	5.1 5.2
AA furnace	272.2	3113B	-	-	-	-
ICP/AES	200.7	3120B	-	-	-	-
DCP	-	-	-	-	AES0029	5.4
Zinc - Total; mg/l; Digestion followed by:						
AA direct aspiration	289.1	3111B or C	D1691-90(A or B)	1-3900-85	974.27; p 37	5.1 5.2
AA furnace	289.2	-	-	-	-	-
ICP/AES	200.7	3120B	-	-	-	-
DCP	-	-	D4190-82(88)	-	AES0029	5.4
Colorimetric (dithizone)	-	3500-ZnE	-	-	-	-
Colorimetric (zincon)	-	3500-ZnF	-	-	8009	5.9

* Explanatory notes are provided in Section 5.6.2

Sources of data are identified in the notes.

5.7 ASSESSMENT AND APPLICABILITY OF AVAILABLE PROCEDURES

Reference methods available for calibration of continuous monitors used in the metals industry are summarised in this Section. Methods for measurement of releases to air and releases to water have been covered. Priority has been given to identification of methods published by UK standards organisations, in particular the British Standards Institution and the Standing Committee of Analysts. However, there are no published UK standards for measurement of some of the chemical species, and in these instances the standards published in other countries have been included under the heading "UK Practices and Procedures". Separate parts of the survey have also been devoted to practices in Germany and the USA.

The methods are normally well documented procedures involving manual sampling followed by laboratory analysis, although provision is made for calibration of a continuous monitor against another pre-calibrated, continuous analyser in some instances.

When all standards published in the UK, in Germany and in USA are taken into consideration, there are suitable methods available for calibration of most of the continuous monitors used for measurement of releases to air and releases to water, and which are covered in other parts of this report.

In the case of stationary source emissions, no national or international standard methods suitable for measurement of concentrations of hydrogen cyanide have been identified.

The range of standards within the UK, Germany and USA for measurement of concentrations of pollutants in water is very extensive and for this reason the format in which the information has been presented is different from that for concentrations in stationary source emissions.

The UK Standards have been presented in 5.5.1 in more detail than have the German and US Standards in 5.6.1 and 5.6.2 respectively. The US Standards have been presented in tabular

form, as being a manner in which the US EPA approved methods, from a large number of sources, could be concisely summarised.

The documents published by the Standing Committee of Analysts provided methods for measurement of all of the parameters, covered in the other parts of this report, related to releases to water, and these - together with the DIN Standards (Germany) and the US EPA approved methods - provide a very comprehensive range of techniques, suitable for the calibration of continuous analysers.

6. DEVELOPING TECHNOLOGY

6.1 PARTICULATE MONITORING

Manufacturers of continuous particulate monitors without a time-of-flight (see A2.1.22) flow monitor in their product range will be adding one (it is a simple correlation exercise for an on-board computer).

In view of the potential market for long-throw particulate monitors, it is surprising that relatively straightforward instruments are not being developed using low-cost lasers of the types used in bar-code readers at supermarket check-out desks. The wavelengths are similar to those used in existing monitors.

Using pattern recognition in conjunction with CCTV, it should be possible to detect concentrated areas of fume or dust emissions - to raise an alarm if not provide a traceable measurement. The technique might be applied to the wind-blown dust from stockpiles or fugitive fume from scrap cutting or de-skulling operations.

It should also be possible to monitor ambient fume or dust using a CCTV camera: dust will act to blur the background detail, reducing the bandwidth of the video signal - it should be possible to detect changes in dust concentration with very little processing.

A comparative evaluation of five different types of particulate monitor has been carried out by the AEA "Burner Club" at a Metals Industry site in the Midlands.

The National Measurement System Policy Unit of the DTI has a programme on particle measurements, which is setting up task forces on subjects including environmental monitoring.

6.2 SPECTROPHOTOMETERS

Currently, ultraviolet monitors use a fixed array of photodiodes in conjunction with a fixed prism or grating for the identification of a specific peak or peaks of the species of interest.

This principle is likely to be extended to obtain a complete spectrum using an integrated array of some thousand sensors. Such arrays operating on the charge coupled device (CCD) principle are obtainable at relatively low cost and the computing hardware needed to analyse the resulting spectrum by fourier transform or pattern recognition techniques is also readily available. The resulting instruments should be capable of monitoring many species and be site programmable for selection of the various species of interest to the user.

Low-cost electrochemical cells, well established for COSHH monitoring schemes and vehicle exhaust testing, may be applicable to continuous monitoring of a wide range of gases under certain conditions of use - see Appendix 2, A2.1.8. The first system is already on the market - see Appendix 2, A2.2.4.

The BOC Group has developed a low-fume cupola process in which oxygen is injected in the coke bed. This effectively raises the temperature to combust CO and unburnt hydrocarbons in the emerging gases. In their report,^{Ref 146} BOC note that "permanent monitoring of waste gas temperature, CO and perhaps free O₂, would prove beneficial...." Correct process operation ("clear stack conditions") would be inferred from monitor readings of O₂ 5-10%, waste gas temperature >500°C and CO <500 ppm.

6.3 SOLID STATE SENSORS AND ELECTRONIC NOSES

Solid state sensors and electronic noses have been developed to detect some of the common pollutant gases. They have the potential for the quantitative determination of odours and other dilute, complex airborne pollutants.

There are several generic techniques, featuring the use of compounds having receptor sites akin to enzymes or catalysts deposited on microcircuits. Like electrochemical sensors, they suffer from potential interferences, historical effects and poisoning.

The first conference on electronic noses was held in 1991. UMIST is understood to be a major centre for development of the devices.

Work on the subject in the Department of Engineering at the University of Warwick has concentrated on the discrimination of specific chemicals, using an array of different sensors and pattern recognition techniques to combine the outputs and tune the response of the system to the species of interest. A prototype system has been tuned to alcohol.^{Ref 149}

6.4 HEAVY METALS, PLUS PH AND REDOX

The University of Luton Sensor Research Group has developed a small flat combination probe using thick-film deposition techniques. It incorporates conductivity electrodes and temperature sensors. No electrolytes need be added as these are deposited into the assembly during manufacture. The units are disposable. The work is carried out as part of the DTI CENSAR programme. The work is being funded by the Environment Agency and WRC Medmenham. Trials are currently in progress with a pharmaceutical company.

New developments by manufacturers include an adoption of a capillary connection with the sample rather than a porous plug. The arrangement is claimed to be less easily blocked by deposits.

UMIST Department of Instrumentation and Analytical Science is developing a chemiluminescent technique for trace metals detection^{Ref 150} and preconcentration methods for Pb, Cd and As determination by AAS.

6.5 HIGH TEMPERATURE SOLID-STATE SENSORS FOR METALS

The Minerals Industry Research Organisation (MIRO) is co-ordinating a three-year EU funded project on sensors for on-line control of high temperature metallurgical processes with the following aims:

- To improve process control in the zinc, copper and electronics industries through the use of high-temperature solid sensors;
- To identify and create new solid electrolyte sensors for the determination of aluminium in zinc for specialist galvanizing;

- To improve the lifetime of solid state sensors in high temperature melts.

The technique may have relevance to the metals content of solid wastes.

6.6 HEAVY METALS ANALYSIS BY DGT (DIFFUSIVE GRADIENTS IN THIN-FILM)

Although currently being developed as a technique for manual field sampling, DGT can, in principle, provide a basis for automatic sampling of effluent and may have potential for on-line analysis in the future.

The Lancaster University Institute of Environmental and Biological Science is developing the new technique of diffusive gradients in thin-film for measuring metals in water and effluents^{Refs 151,152,153}. DGT quantitatively accumulates metal ions on a chelating resin after they have diffused through a layer of gel. It is the diffusion through a well defined path that enables the collection of metal to be fully quantitative. The metal is continuously accumulated during deployment. It is subsequently eluted with dilute acid and measured by AAS or ICP-MS. DGT offers the following features:

- In situ accumulation and fractionation of up to 10 metals simultaneously
- Provides time-averaged mean concentration during deployment
- Automatically pre-concentrates in situ avoiding contamination problem
- No calibration is necessary as concentrations can be calculated quantitatively
- DGT, similar to anodic stripping voltametry, measures labile metal
- Deployment times can be from 1 hour to several weeks
- It operates in the pH range 5-9 (possibly 10, but not yet tested)
- It is a simple, cheap, plastics device
- The measurement is independent of flow, above the low threshold flow rate
- The measurement is independent of ionic strength ($10^8 + 10^0 M$)

DGT is patented and commercial production of DGT devices with a back-up analytical service is being actively pursued. A project to investigate the feasibility of DGT for

measuring Hg, Cd and radionuclides, funded by the Agency, is just coming to an end.

6.7 TOXICITY AND BOD

Several toxicity-monitoring initiatives are under way.

The Microbic Corporation has developed its MICROTOX toxicity measurement system into an on-line system. The method monitors the health of marine phosphorescent bacteria by measuring changes in light emitted when they are exposed to the sample. The measurement is not continuous but cyclic, but considerably faster and more convenient than manual laboratory methods.

The University of Luton Sensor Research Group is developing biosensor systems incorporating living microbial cells for BOD estimation and rapid toxicity assessment. The sponsor group does not include Metals Industry operators but it is considered that the sensors may have application to the detection of cutting oils as well as organic and inorganic toxins and heavy metals.

6.8 DATA PROCESSING

Most manufacturers are enhancing their instruments by adding additional functionality to on-board computers.

Logging systems are being enhanced and moved from the Microsoft DOS operating system to the Microsoft Windows environment. The use of Microsoft Windows NT is becoming established as a reliable operating system as a basis for SCADA Systems.

Modern analysers and particulate monitors have the facility for direct modem connection to a telephone line. This feature will be implemented more widely in products of this type and has already been of use in many applications for remote trouble shooting of an instrument on site by the manufacturer from his own premises.

6.9 SURROGATE MEASUREMENT OF EMISSIONS BY NEURAL NETS

Neural nets (functionally parallel computing networks which are taught rather than programmed for a given application) have been tested as a means of calculating emissions of pollutant substances based on measurements of process variables, these being available within the existing process control systems of a plant.

Such systems depend totally on accurate measurements since errors can affect both operational control and monitoring functions. Techniques for identifying and accommodating the lack of a signal or absence of a significant measurement are required.

The degree of reliance on any particular measurement and its significance to the calculation is not known in advance, so it is necessary to carry out an audit that will establish these dependencies, the implications of breakdown of the process instruments utilised (in their various failure modes), and the probability of these events, as well as the actual accuracy expected under a range of operating conditions. Other types of adaptive system may also be applicable.

An example of such a system based on neural nets is the Callidus PEMS Predictive Emissions Monitoring System, a number of applications of which are reported^{Ref 154} and demonstrate that good correlation can be achieved in predicting products of combustion emitted from power generating plant and an ethylene furnace.

As a basis for the model, data is collected over a period of operation via the plant's DCS or Level 2 computer systems and from temporary emission monitors. The neural net model is then fed with the recorded data, adapts to provide a usable model, and is evaluated before being applied on-line.

7. CONCLUSIONS

7.1 BACKGROUND

In the USA and Germany, where continuous monitors have been actively encouraged by the environmental regulations, there is a strong home market for such instruments. In the UK, the capability of indigenous suppliers of continuous monitoring instrumentation is limited and most analytical instruments are imported.

The UK Metals Industry is not targeted for sales of continuous monitors by equipment suppliers in general, as it is very diverse and the demand for specialist instruments is perceived to be small. However, particulate monitors, combustion gas analysers, some of the more common water quality monitors and standard process transmitters are widely used.

There are clear advantages in applying continuous monitors, including environmental benefits, promotion of public confidence and process control improvements.

The cost of operating continuous monitoring facilities is relatively high, particularly in the context of the smaller operators. The purchase prices of continuous monitors range from £2 000 for a bag burst detector, £4 000-8 000 for a particulate or water quality monitor, £10-20 000 for a gas analyser, to £50 000-70 000 for specialist analysers.

To the purchase price must be added the cost of installation (say £5 000-10 000 inclusive of a data logging system), maintenance costs (possibly £3 000 per year) and perhaps as much as £6 000 per year for calibration.

Considerable savings in the cost of calibration are possible by utilising in-house personnel, although calibration usually requires specialist equipment not normally available on site, unless it can be carried out against bottled test gases. There is a serious shortage of instrumentation expertise and staff for maintenance of continuous monitors within the Metals Industry.

Continuous monitoring instruments are demanding to maintain. Many process operators

within the metals industry, particularly the smaller operations, do not at present have the resources or expertise to maintain continuous monitoring instruments satisfactorily. Consequently, such operators would need to rely on third parties to maintain and calibrate continuous monitors or, alternatively, train existing staff to perform such tasks.

Plant operators acknowledge that continuous monitoring can provide useful process information and potentially help optimise the operation of the plant. However, they are concerned that CEM will precipitate increasingly restrictive emission limits, involve them in more work, incur higher external costs and load their human resources, which are already stretched. No formal policies on continuous monitoring were elicited from process operators during the study.

With the exception of a limited number of continuous processes, such as sinterplant and to a lesser extent primary aluminium potlines and electrolytic copper refineries, the vast majority of processes encountered in the metals industry are either batch processes or involve operating cycles that give rise to variations in emission rates. Consequently, care is needed in interpreting the readings of continuous emission monitors in the Metals Industry and satisfactory regulatory protocols will need to be established if such measurements are to be used as the basis of demonstrating compliance with process authorisations.

7.2 SUMMARY OF APPLICATIONS

Particulate matter is the only species for which continuous monitoring is widespread in the UK Metals Industry. There is a large number of devices on the market. Low-cost versions are available as "burst bag" detectors. Smoke monitors are relatively simple variants, which may be calibrated without special equipment.

Opacity and scattering techniques are relatively direct types of measurement, (similar to turbidity as a method of measuring suspended solids in water). Scintillation and triboelectric types of monitoring instrument depend on properties that are less closely related to the measurand and less (perhaps even not) amenable to theoretical justification. An alternative acoustic technique is already in use for burst bag detection.

The use of AC rather than DC techniques in scintillation and triboelectric devices makes the measurement less direct, although ostensibly still valid and widely used.

The generic principles most applicable to continuous measurement of fine particles emitted to atmosphere via bag filters on modern dust extraction systems are scattering and triboelectric types of instrument. The finest particles released from bag filters are below the theoretical limit of detection of optical devices. All particulate monitors in use in the metals industry are of the cross-duct or other in situ types; extractive systems do not appear to be maintainable in the long term.

Surprisingly, for such a well-established range of products, there has been no general study under controlled laboratory conditions of the effects of changes in major variables, such as particle size distribution and flow rate, on the performance of particulate monitors. Lack of this primary information on the performance of continuous particulate monitors, in conjunction with the limitations of the corresponding calibration methods - probably 25% uncertainty - result in relatively poor traceability of measurement. There are continuing debates concerning the merits of the various techniques of particulate measurement; these will not be resolved until the characteristics of the instruments are established on a firm basis. (Note: a DTI task force may emerge to address this topic. There has also recently been a field evaluation by the "AEA Burner Club" of five types of instrument at a Metals Industry site).

Particulate monitors are relatively cheap to purchase, but the installation and running costs, particularly for calibration, are significant. There is a temptation for users to avoid calibration of bag-burst detectors. There is a need for a technique to simulate particulate matter, to allow calibration checks to be made with reasonable accuracy at low cost, and so allow the formal calibration interval to be lengthened.

Maintenance of particulate monitors is straightforward; most problems arise from oil in the purge air supply contaminating the optics, or build-up of excessive dirt or moisture on triboelectric probes.

Particulate monitors have proven difficult to apply to bag filters of the positive pressure type.

They have not been successful for closed-loop control of fume extraction systems. Apart from one report of a successful trial, they cannot be applied to wet gas - hence surrogate monitoring is likely to be applicable in this situation. The measurement of fugitive emissions is difficult, owing to the limited path lengths of the available devices, but CCTV monitoring is used effectively.

Metals in air are generally emitted in particulate form; this may be monitored using a combination of continuous particulate measurement, with periodic manual analysis to confirm that the proportion of metal species is consistent.

“On-line” measurement of metals emissions, except for mercury that can be accumulated in sufficient quantities for measurement, is not regarded as economically practicable. X-ray spectrometry has been used successfully for “on-line” measurement of iron, zinc and other species but the equipment is not yet in a marketable form.

Products of combustion, including SO₂, NO_x, CO, CO₂ and O₂ are emitted from many sources in the Metals Industry. There is a large number of proprietary continuous monitors of both the extractive and cross-duct type on the market, but very few installations are at present in evidence in the Metals Industry, apart from O₂.

Larger, relatively modern combustion plants in the metal industry have process control systems that already gather comprehensive data and this could form a basis for surrogate monitoring of emissions.

Smaller heating processes may be numerous on some Metals Industry sites. In such a situation, the cost of installing a monitor on each flue would be very high. Small flues on such process systems and also on extraction systems for certain acid pickling processes eg (NO_x) do not adapt to cross-duct monitoring because of the short optical path length. This necessitates extractive systems, which are more expensive to install and maintain, especially under the site conditions prevailing in the Metals Industry.

There are relatively few CEM applications on combustion plant in the Metals Industry, the exception being oxygen, where in-situ zirconia probes are often fitted to the flues of large heating plant. The measurement is commonly used as a basis for manual (open-loop) air/fuel ratio trimming. Closed-loop control is sometimes available, but usually not utilised; (it is a nuisance if the instrument malfunctions).

Sinter plants, smelters and blast furnaces do not generally have CEM equipment but there is a variety of process measurements available in the plant process control systems, which could allow surrogate monitoring of pollutants. Measurement is made difficult where, as is often the case, wet scrubbers are used.

Hydrogen, although not a pollutant gas, is included in the report in view of the potential risk of explosion hazards. It may be measured easily in the concentrations of interest by thermal catalytic or thermal conductivity methods.

Chlorine may be measured by infra-red methods and ion mobility spectroscopy. The latter is a new innovative technique. There are several monitors available but only one Metals Industry application was identified during the course of the study (still to be installed).

Hydrogen chloride is not very amenable to infra-red analysis, although several instruments based on the selective GFC variant are available. Ion mobility and wet chemistry methods based on ion-selective electrodes are applicable. No Metals Industry applications were found during the study.

Hydrogen fluoride is a major pollutant emitted from primary aluminium processes. It will attack the components of analysers and sampling systems. Several methods have been applied, the earliest being a wet chemistry technique similar to that for hydrogen chloride. A new technique, pioneered in Canada for this application and tried in the UK, utilises a tuned laser. It can be arranged to measure in several ducts virtually simultaneously by multiplexing the light through optical fibres. It is proposed to measure fugitive emissions

with the same equipment. There is also the potential for monitoring other species, including particulate matter, but the equipment is expensive.

Hydrogen cyanide is not monitored and only one proprietary CEM instrument for this species was identified during the study.

Hydrogen sulphide is emitted from blast furnace slag processing at steelworks but together with saturated steam, which renders continuous monitoring impractical. Various types of monitor are available for H_2S , including ultra-violet fluorescence and infra-red analysers.

Ammonia is not continuously monitored in the Metals Industry, although there are processes in several sectors of the industry that emit it. Ammonia is well suited to infra-red analysis techniques and a large number of monitoring instruments are available.

Significant releases of **amines and amides** arise from chemically bonded sand moulds in ferrous and non-ferrous foundry processes. No suitable continuous monitoring instruments were identified during the study for these species.

Volatile organic compounds (VOCs) are emitted from plant in most sectors of the Metals Industry. FID measurement is practicable and PID measurement may be suitable, depending on the compounds present. However, neither of these techniques will usefully discriminate between the numerous species of VOC.

Polycyclic aromatic hydrocarbon compounds (PAHs) are evolved during the curing of anodes containing pitch, which are used in primary aluminium smelters, from coke ovens in steelworks and to a much lesser extent from other activities. There are no proprietary continuous monitoring techniques which even approach the selectivity required to distinguish between the many species of PAHs present.

Dioxins and furans (PCDD/PCDF) are such specific compounds, and are of concern in such small quantities, that they cannot be continuously measured on-line. There are permanent sampling techniques, however, in use in Austria and Germany.

Oil mist, which is evolved mainly from cold rolling mills, is not presently monitored continuously. No instruments marketed specifically for this application were identified during the study but optical opacity techniques and heated PIDs, as well as surrogates, may be applicable.

Monitoring the flow of air is a common requirement to determine mass flow or to correct the output of other instruments for flow velocity. It is measured satisfactorily by a wide variety of well established differential pressure techniques, and the new time-of-flight methods, which may conveniently be integrated into particulate monitoring schemes.

Automatic sampling and monitoring of water is well established, and there is a wide choice of proprietary equipment. It is practised at several sites in the Metals Industry. The main operational difficulties are connected with fouling and pump reliability.

Acidity and reduction potential (pH and REDOX) are straightforward measurements, but, as for all water monitoring applications, the main costs and failings lie in the provision of the necessary sampling and conditioning systems. pH measurement is established at many Metals Industry sites and a large range of proprietary equipment is available for this purpose.

Automatic cleaning by air sparging is usually included in the monitoring package, but in spite of this, manual cleaning of electrodes is the main maintenance requirement. The frequency of cleaning varies widely from application to application, from days to months. The usual contaminant is tramp oil.

Suspended solids (as turbidity), conductivity and dissolved oxygen are monitored continuously at several sites in the Metals Industry. The instruments are readily available and no special problems are reported, except for the necessity of regular cleaning.

Hydrocarbons, oils and greases in water are likely to be present in many Metals Industry discharges, but the availability of suitable instrumentation is significantly affected by the type of oil, film consistency and particle size. Nevertheless, instruments are installed for alarm

duty and their analogue outputs are found to be useful as a rough indication of the level of pollutant present.

Metals in water discharged from Metals Industry sites are a significant concern.

Ion selective electrodes to monitor such species are available at low cost but do not appear to be satisfactory. Anode stripping voltametry is very effective but expensive and requires considerable maintenance. The study only identified one system installed at a Metals Industry site, which is situated in an environmentally sensitive area. AA spectrophotometry, the reference method for metals measurement, is not available as an on-line technique. Ion chromatography is suitable but extremely expensive. Sensors based on diffusion through thin films and chemiluminescence are long-term possibilities for monitoring metals in water.

In practice, the usual basis for monitoring metals is a surrogate. By monitoring pH and turbidity, disturbances in the operation of the site's water treatment plant can be identified. For example, low pH increases the risk of metals escaping in solution and high turbidity might indicate a risk of metals escaping in particulate form. In situations where rainfall run-off from material stockpiles, roofs and other areas mixes with process effluent before monitoring, interpretation of the results can be difficult.

Cyanide and sulphate are present in some Metals Industry discharges but no continuous monitoring instruments for these species were identified during the study.

Chloride, fluoride, nitrate and phosphates, which are released in water from particular processes in several sectors of the industry, are amenable to detection by ion-selective electrode techniques. There are several instruments available to monitor such species but none appear to be in use in the Metals Industry.

Ammonia in water is readily monitored by gas type ion selective electrodes. The only application evident in the Metals Industry was at integrated steel plant, on the waste-water discharge from the coke ovens area of the site.

Phenols monitoring is also of interest at coke ovens. No suitable continuous monitors have so far been identified by the study.

BOD, COD, TOD are not continuously monitored in the Metals Industry, but a number of surrogate methods, based on ultra-violet and solid-state sensors are available.

On-line measurement of **toxicity** is now possible by monitoring the metabolism of small organisms exposed to the sample stream through measurement of their phosphorescence, or by sensors that utilise living cells deposited directly on electrodes that monitor their activity.

Monitoring the flow of water is a straightforward measurement and there is a large selection of well established methods. The ultrasonic level measurement technique, with a weir or flume, is widely used. Where access is difficult (e.g. a sewer with no room for a flume) or if reverse flow can occur, ultrasonic or electromagnetic submersible instruments have been successfully employed. The main problems reported are blockage of the flume or channels by debris or deposits building up on submersible instruments.

Temperature, pressure and differential pressure monitoring instruments are available at low cost and are generally both reliable and accurate.

No instances of **continuous monitoring of releases to land** could be found in the UK Metals Industry during the course of the study. The one application identified (in Austria) utilises a pulsed laser technique to perform emission spectrometry in-situ on gas-cleaning dust from a BOS plant, to determine its zinc content.

The acquisition, storage and analysis of data was also covered by the study. There is a large range of products available for such purposes and more products under development.

Conventional chart recorders are still in use but they run out of paper (which is also an inherent weakness of beta gauges and colorimetric tape analysers) and most users are changing to "intelligent" recorders or computer-based systems.

Monitors that store their own data are attractive, but there is a tendency for the user to eliminate the tedious periodic manual downloading of data at some stage by connecting several monitors on-line to a common computer-based logging system.

Since large metals industry sites have integrated process control systems, which log process variables for production control and quality purposes, they can be - indeed, already are being - extended to accommodate logging of emissions data. Process logs are available for inspection on numerous processes within the metals industry.

Systems based on neural nets have been developed and have been demonstrated to predict emissions from combustion processes accurately, based on routine process data available in the plant control system. This type of system will tolerate certain types of instrument malfunction but it is likely that drift and changes in the process would affect the surrogate readings in unpredictable ways.

8. GLOSSARY OF TERMS

Instrument industry terms are given informal definitions unless a specific standard is quoted. Metals Industry technical terms used in the report are also included in the glossary; definitions are from industry general usage and extracted from metallurgical textbooks. Where possible, they are harmonised with Chief Inspector's Guidance Notes for the appropriate industry sectors.

AAS	Atomic Absorption Spectrophotometry.
AC	Alternating Current.
APT	Ammonium paratungstate.
ASV	Anode Stripping Voltametry.
AU	Absorbance Units $A = \log_{10} (I_0/I) = a.b.c$ where a = molar absorption or extinction co-efficient. where b = sample path length. where c = concentration in sample.
Absolute pressure	Pressure measured (unusually) with respect to vacuum, eg 100 kPaA (cf Gauge pressure).
Accuracy	The closeness of the agreement between the result of a measurement and the (conventional) true value of the measurand.
Additions	Alloys and other materials, introduced during metal refining to achieve the required metallurgical properties.
Analogue	Output from an instrument in the form of a dc current or voltage (normally 4-20 mA).
Availability	The ability of an item (under combined aspects of reliability, maintainability and maintenance support) to perform its required function at a stated instant of time or over a stated period of time (BS 5760).
Average error	The arithmetic mean of the errors at each point of measurement, for rising and falling inputs.
BAT	Best Available Technology.
BATNEEC	Best Available Technology Not Entailing Excessive Cost.
BMS	Building Management System.
BOD	Biochemical Oxygen Demand.
BOS	Basic Oxygen Steelmaking (converter plant).

BS	British Standard or as indicated by the context British Steel plc.
Ball mill	Rotating cylinder containing stone or iron balls for grinding materials into a fine powder.
Bar	Metal product with circular square or hexagonal cross section, formed in long lengths in a rolling mill (bar mill).
Billet	A semi-finished product of up to 130 mm rectangular section for hot rolling into rods, bars, or sections (steel industry) or circular section of any size for extrusion (aluminium industry).
Black copper	The product obtained by smelting copper ores in a blast furnace.
Blast furnace	A vertical smelting furnace, usually fuelled by coke added to the charge, through which a blast of air is driven to aid combustion.
Bloom	A steel semi-finished product with a cross section larger than a billet, for hot rolling into heavy bars or sections.
Briquetting	Pressure moulding of granular materials or swarf, to reduce oxidation in storage and for ease of handling.
Bullion	Gold or silver in bulk form.
Buffer solution	Solution with a defined pH value containing acid or alkali and a salt, the latter having the effect of keeping the pH constant.
CCTV	Closed Circuit Television.
CEM	Continuous Emission Monitoring (Monitor).
COD	Chemical Oxygen Demand.
COGDEM	Council of Gas Detection & Environmental Monitoring.
COSHH	Control of Substances Hazardous to Health Regulations 1988.
CRT	Cathode Ray Tube.
Calcining	Calcination. Heating in the absence of air to expel moisture, carbon dioxide or sulphur.
Calomel	Mercurous chloride Hg_2Cl_2 .
Casting	The pouring of molten metal into moulds and its solidification.
Cathode copper	Electrolytically refined copper.
Channel furnace	Induction furnace in which the melt flows (via the "channel") around the core of the induction heating coil.
Centronics	Parallel data interface.
Charge	The materials loaded into a furnace.

Chopper	A rotating shutter used to interrupt a light beam. The (chopped) resulting light, when it reaches a detector, will produce a singular alternating signal (easier to amplify and identify from interference).
Configuration (configurable) (configured)	A method of setting up or adjusting a programmable instrument or system. The user selects from a series of options which are presented in a logical sequence. Easier and less error-prone than traditional computer programming methods.
Converter	Steelmaking vessel charged with liquid iron or steel, though which gases are blown to carry out the conversion of iron to steel and to refine the product.
Cryolite	Sodium aluminium fluoride $\text{AlF}_3 \cdot 3\text{NaF}$.
Cupellation	Refining of silver by alloying it with lead and then removing the lead by oxidation.
Cupola	A coke-fired shaft furnace for melting, rather than smelting, metals.
Cuvette	Transparent cell for photometry.
Cyclone	Device in an extraction system in which a vortex is created to separate particulate material from the air stream.
DC	Direct Current.
DC casting	Direct Chill casting.
DCS	Distributed Control System.
DGT	Diffusive Gradients in Thin-film.
DO	Dissolved Oxygen.
DOAS	Differential Optical Absorption Spectrophotometry
DP	Differential Pressure.
Decarburising	The removal of carbon from heated steel, generally by the action of oxygen.
Depolarisation	Formation of a non-conducting layer of gas on an electrode.
Desulphurisation	The removal of sulphur, for example by the reaction of sodium carbonate with sulphur in molten iron to form sodium sulphide.
Determinand	Substance to be determined.
Direct chill casting	Continuous vertical casting (in the aluminium industry)
Discrimination	The property that characterises the ability of a measuring instrument to respond to small changes in the quantity measured (BS 5233).
Drift	The change in indications of an instrument for a given input over a stated period of time, under reference conditions that remain constant and without any adjustments being made to the instrument by external means.

Dross	Metallic oxides on the surface of molten metal removed by skimming.
EA	Environment Agency.
EAF	Electric Arc Furnace.
Electrowinning	Recovery of metal from ores by electrolysis.
Eluent	Fluid medium carrying the sample in chromatography.
Error of measurement	The discrepancy between the result of a measurement and the true value of the quantity measured (BS 5233). Generally, error = measured value - conventional true value.
Ethernet	See IEEE 802.3.
fsd	Full scale deflection = span
FIR	Far Infra-Red - wavelengths approximately 28-280 μ m
FTIR	Fourier Transform Infra-Red.
FTU	Formazine Turbidity Units.
Ferro master alloy	Iron rich alloy containing a sufficient quantity of one or more other elements to be useful as an agent for introducing these elements into molten iron or steel.
Fettling	The cleaning and excision of unwanted material from castings after their removal from the mould.
Fieldbus (FIP)	A set of hardware specifications and protocols for a LAN to connect field instruments, backed by an international group of manufacturers. Comprehensive specifications but slow to be adopted.
Flux	Substance added during smelting or refining to removal of oxides, lower the fusion point and/or lower the viscosity of the melt.
Foundry	Workshop for casting processes.
Foundry returns	Scrap castings and cleaned runners, of known composition, for returning to the melting process.
Foundry sand	Sand, used mainly for moulds, in casting operations.
GAMBICA	The Trade Association for the Instrumentation, Control and Automation Industry in the UK.
GC	Gas chromatograph
Galvaniser's ashes	Residues from processes of coating steel with zinc, including metallic zinc, zinc oxide, zinc chloride and ammonium chloride.
Gauge pressure	Pressure measured (as is usually the case) with respect to atmospheric pressure.
Granulation	The conversion of slag to particulate form by contact with water.

Green sand	A mixture of ground sand and coke dust for moulds in casting operations.
HART	A hardware specification and protocol for a serial link to connect field instruments (Trademark of HART communication Foundation).
Heavy Metals	Antimony, bismuth, cadmium, lead, mercury, thallium and tin, also often taken to include other metals - for example copper, tungsten and iron.
Holding furnace	A furnace used for holding liquid metal awaiting processing and where temperature and metallurgical adjustments may be made.
Hysteresis	That part of the instrumental error which results from error hysteresis (BS 5233). Generally hysteresis = the algebraic difference between the average errors at corresponding points of measurement approached from opposite directions ie rising and falling.
ICP	Inductively Coupled Plasma (a source for mass spectrometry).
IEEE 802.3	Hardware and protocol developed by the Digital Equipment Corp, Intel and Xerox as the "Ethernet", standardised and now the most widely used LAN
IP	The environmental protection category. ^{Ref 9}
IPC	Integrated Pollution Control.
ISO	International Standards Organisation.
ISP	Imperial Smelting Process (for lead and zinc).
IR Infra-red light	Electromagnetic radiation, wavelength 750 nm to 280 μ m
Impulse pipework	Pipe or tubing connecting an instrument to the process.
Inclusions	Impurities trapped in a metal during solidification - may be slag, alumina, or gases.
Induction furnace	Electrical heating without contact with the melt, utilising magnetic induction, either from a coil wrapped around the furnace ("core-less furnace") or with a core passing through the furnace body ("channel furnace").
Ingot	Metal cast into a mould with a shape suitable for subsequent mechanical forming operations - typically hot rolling.
Integrated iron and steel works	A works having iron and steel production on the same site, with iron being taken to the steelmaking facility in a molten state ("hot metal").
Intensor	Proprietary digital link scheme similar to HART, by Endress & Hauser.
Investment casting	Casting using a fired ceramic mould, prepared using a lost wax process.
JCU water.	Jackson Candle Unit. The turbidity of a preparation of 1 ppm Fullers Earth in water.

Kettle	An open-top vessel used in refining low melting-point metals.
LAN	Local Area Network. Means of linking computers usually by a serial digital link with protocol.
LCD data.	Liquid Crystal Device; usually for the display of numerical or alphanumerical data.
LED	Light Emitting Diode; used as an indicator, or in groups for the display of numerical or alphanumerical data.
Labile (metal)	Unstable, liable to change.
Ladle	A refractory lined vessel used to hold and transport molten metal.
Ladle furnace	An arc furnace installation which is placed over a ladle of liquid steel en route from the steelmaking process. The facility provides a means of increasing the temperature and adjusting the metallurgical composition of the steel before casting.
Lance steelmaking.	A tube, usually water-cooled, for introducing oxygen into the melt during
Leachate	Aqueous solution draining out of bulk solids, bearing dissolved compounds arising from the solid material.
Level 1 System	Basic automation and instrumentation systems (PLCs, DCSs).
Level 2 System	Supervisory computers for product tracking, data acquisition and storage.
Litharge	Fused lead oxide of a reddish-yellow colour.
Lump iron ore	Iron ore particles above the minimum size acceptable to a smelting or reducing furnace.
MIR	Mid Infra-Red - wavelengths approximately 1600 nm to 28 000 nm.
MIRO	Minerals Industry Research Organisation.
MMI	Man-Machine Interface; usually based on a cathode ray tube or flat-screen LCD display and an embedded computer which is configured by the user. Provides indication, control and alarm annunciation facilities.
MODBUS	A serial link protocol developed by Modicon for their PLCs and now widely adopted for links between equipment from different manufacturers.
Mackareth electrode	Fuel cell for the measurement of dissolved oxygen in water.
Master alloy	Alloy used for introducing a desired element into the melt.
Matrix	Cocktail of substances accompanying the species of interest in a sample.
Mattes and zinc.	Impure metallic sulphides resulting from smelting sulphide ores of copper, nickel

Measurand	The variable to be measured.
Melt	The molten metal being melted or smelted.
Melt(ing) shop	The building in a steelworks housing the steelmaking process.
Mill scale	Oxides, generally in the form of fine and coarse flakes, that form on the surface of steel and are removed during rolling operations.
Modem	Connection device between a computer and a telephone line, usually handling call control and dialling as well as providing the basic interface circuitry.
NAMAS	The UK accreditation service for laboratories offering calibration services. The service is now provided by UKAS which retains the logo NAMAS for this work.
NEMA	(US) National Electrical Manufacturers Association.
NDIR	Non-dispersive Infra-Red.
NIR	Near Infra-Red - wavelengths 750 to 1600 nm.
Nephelometry	Turbidity measured with reference to samples precipitates in water, prepared using standard chemical techniques.
Nodulisation	The transformation of the structure of the graphite in cast iron from flakes into spheroidal form.
Non-linearity	That part of the instrumental error whereby a change of error indication, or response, departs from proportionality to the corresponding change of value of the measured quantity (BS 5233). Generally non-linearity = departure from the "best fit" straight line by "least-squares" for the available data.
NTU	Nephelometric Turbidity Units.
ORP	See REDOX
Off-gas (furnace)	Partially oxidised gas evolved from a smelting or other reducing process.
PAH	Poly-aromatic hydrocarbon.
PC	Personal Computer. In the USA it can also mean PLC.
PGM	Platinum Group Metal.
PLC	Programmable Controller. The L in PLC once denoted "Logic" but is retained in the acronym to distinguish it from Personal Computer.
PROFIBUS	A hardware specification and protocol for a LAN to connect instruments and systems, backed by a number of manufacturers, mostly European, including Siemens, AEG and Danfoss.
pH	A measure of acidity/alkalinity.
ppb	Parts per billion (10^9); by volume unless otherwise stated.

ppm	Parts per million: by volume unless otherwise stated.
PT100	Standard RTD of the commonly used platinum type: of 100 ohms nominal resistance.
Pellets	A compressed ores limestone and other materials, convenient for transportation and storage before smelting.
Peltier cooler	Device producing cooling effect when a current is passed through semiconductor junctions - no moving parts.
Pickling	The chemical removal of oxides from the surface of a metal, usually involving acids.
Pig iron	Iron from a blast furnace, gravity cast into open moulds.
Pot	Aluminium electrolytic extraction cell.
Potroom	Building enclosing aluminium extraction cells.
Prills	Metals in finely divided form.
Protocol	A definition of the physical link, data structures and logical state transitions involved in sending data over a link or network.
Pulpit	Manned control room overlooking a (steel industry) process.
REDOX	A measure of oxygen-reduction potential (=ORP in the USA). Generally measured directly in millivolts as received from the electrode assembly.
rms	Root Mean-Square - the square root of the sum of the squares of a series of readings.
RS232(C) RS285, RS422	Specifications for electrical circuits of serial links.
RTD	Resistance Temperature Detector (resistance thermometer).
Range	The difference between the upper and lower limits of the measured variable that an instrument can be adjusted to measure.
Remelt	Scrap of known composition arising from finishing operations, returned to the melting process.
Repeatability error	The reading that results from the dispersion of the indications (responses) of a measuring instrument under stated conditions of use (BS 5233). Generally, repeatability = the rms deviation of the errors from the average error at each point of measurement, for rising and falling inputs separately.
Report to ...	Metallurgical term equivalent to "migrate to and are collected in ..."
Resolution	The change in input corresponding to the smallest perceptible change in output of an instrument.

Reverberatory	A hearth furnace in which products of combustion, but not the fuel, come in contact with the furnace charge.
Ringelmann Number	A measure of the opacity of smoke on a scale of 0-5 in steps of 20% opacity.
Roasting	Heating of material in air, for example to oxidise sulphide ores.
Rod	A rolled drawn or extruded product, usually of circular cross-section, diameter approx. 3-100 mm (smaller than bar and larger than wire).
Rough copper	The product obtained when copper bearing material is smelted to yield a metal containing approximately 96% copper.
SCADA	Supervisory Control And Data Acquisition system.
SPL	Spent Pot Lining.
Scarfig	Removal of surface defects by oxy/gas cutting.
Screening	Sorting by size using metal sieves.
Scrubbing	Gas cleaning by contact with falling liquids or powders.
Section	Metal product with a special cross-section such as "angle-iron" or "channel", formed in long lengths in a rolling mill (section mill), or extruded.
Semi finished Products	Materials such as slabs, blooms and billets which will be subject to further processing.
Serial link	Means for data communication where the data is transmitted sequentially as a series of pulses.
Settling time	The time taken for the output to reach 99 % and remain within 1 % of the final value of the output change resulting from a step input.
Shell sand	Sand bonded by resin, shaped and cured as mould for casting.
Shot blasting	The cleaning and removal of scale by metal particles in a high-velocity air jet.
Shrouding	The exclusion of air by inert gas or mechanical device to guard liquid metal.
Sintering	The conglomeration of fine materials for before charging to a blast furnace.
Slab	Continuously cast or rolled block of metal or rectangular section, for subsequent rolling into plate or strip.
Slag	A vitreous material formed from minerals, refractory materials and fluxes which floats on the melt in metallurgical processes. It removes impurities, excludes air and provides a means of adjusting the process.
Smelting	The fusion of an ore or concentrate to obtain crude metal or a matte.
Soda ash	Sodium carbonate.

Span	The algebraic difference between the upper and lower values specified as limiting the range of operation of a measuring instrument (BS 5233).
Sparging	Cleaning by injection of high pressure air or nitrogen.
Specification Alloys	Alloys produced to comply with a specific requirement such as a British Standard.
Stainless steel nickel.	Corrosion resistant steel with a minimum of 12% chromium, generally with nickel.
Steel	Iron with 0.1 to 1.9% carbon.
Stoves	A process for pre-heating air - for example before introduction to a blast furnace.
Strand	Continuously cast metal section from which slabs, blooms or billets are cut.
Strip	Flat metal product, typically less than 3 mm in thickness.
Super alloys	Iron/chromium/cobalt/manganese or nickel alloys having a good stability in the 600-1000°C range.
Swarf	Waste material produced by cutting and lathe turning operations.
Sweeps	Sweepings from floors or benches, gathered for the recovery of precious metals.
TEOM	Tapered Element Oscillating Microbalance (Rupprecht & Patashnick Co Inc patent).
T/C	Thermocouple.
THC	Total Hydrocarbon.
TISAB	Total Ionic Strength Adjustment Buffer; typically includes compounds for controlling pH and ionic strength.
TOD	Total Oxygen Demand = COD + BOD.
Tapping	Outflow liquid metal from a process, usually by unplugging a hole in the bottom of the vessel.
Time constant	The time taken for the output to reach 63% of the final value of the output change resulting from a step input.
Top gas	Gas from the upper part of a blast furnace.
Tower furnace	Vertical shaft furnace into which metals are charged through an opening in the upper part and air and gas or oil are introduced into the lower part.
Tramp materials	Materials (eg iron) containing impurities.
Transmitter	Instrument that transforms a measured variable into a signal (eg 4-20 mA) strong enough to be sent some distance without attenuation or interference.

Turbidity	A measure of suspended solids in water. May be measured in ppm, NTU, FTU or JCU.
Tuyeres	Water-cooled nozzle introducing air into a blast furnace or cupola.
Two-wire	Connection scheme whereby the instrument output circuit also provides the power to operate the instrument.
UKAS	United Kingdom Accreditation Service. UKAS still issues accreditations under the NAMAS logo.
Ultra-violet	Electromagnetic radiation, wavelength 30 to 400 nm. The deep ultra-violet (below 300 nm) light has an ionizing effect.
Uncertainty of measurement	An estimate characterising the range of values within which the true value of the measurand lies (BS 5233). Example: a voltmeter of calibration uncertainty $\pm 0.1\%$, has a 95% probability of giving a reading within $\pm 0.1\%$ of the International Standard Volt.
V24	= RS232.
VOC	Volatile Organic Compound.
Visible light	Electromagnetic radiation, wavelength 400-750 nm.
WG	Water Gauge: pressure expressed as the height of a column of water.
WRc	Water Research Centre.
Wave number	The reciprocal of wavelength measured in centimetres.
Wire rod	Rod specially prepared for reduction to wire.
XRF	X-Ray Fluorescence.
Zircon	Zirconium silicate $ZrSiO_4$.

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APPENDIX 1

DESCRIPTION OF METALS INDUSTRY PROCESSES AND POTENTIAL RELEASES

A1.1 INTEGRATED IRON AND STEEL WORKS (IPR 2/1)

A1.1.1 Principal Processes^{Ref 155}

Integrated iron and steel works convert iron ores into finished steel products in a series of processes which are briefly described below. The manufacture of coke, used in blast furnaces, is excluded from this report while the processes used for treating molten steel before it is cast into the required shape are covered under Section A1.3

Iron ores are stored in individual open stockpiles and blended with recycled materials such as small-size coke, flue dust, mill scale and flux (e.g. limestone and lime) fines to ensure a consistent quality of feedstock to the process. As large quantities of fines in the charge to the blast furnace would restrict the gas flow through the furnace, the blended materials may be agglomerated by sintering on a moving grate. In this process, the surface of the bed of blended materials is heated to ignite the coke content, which burns to form a sintered bond between the particles. The sintered material is discharged from the grate, broken and screened to produce lumps of suitable size for feeding to the blast furnace.

The blast furnace charge can consist of various combinations of lump iron ores, sinter, pellets, limestone and coke. Air, for combustion of the coke, is preheated in stoves fired with cleaned recycled furnace top gas and is blown into the lower portion of the furnace. The iron oxides in the charge are reduced to molten iron by carbon monoxide from the burning coke while the limestone reacts with impurities in the ore and coke to form a liquid slag. The slag

is tapped from the furnace at regular intervals and is usually granulated by contact with water. Iron is tapped continuously from the base of the furnace into ladles and is desulphurised using reagents such as soda ash, magnesium and calcium carbide. The bulk of the sulphur is removed in the slag before the molten iron is transferred to the steelmaking process.

Steelmaking is carried out in a converter which contains the molten iron together with cold scrap steel and fluxes. High-pressure oxygen, fed to the vessel via a water cooled lance, agitates the bath and oxidises the carbon in the iron to carbon monoxide and carbon dioxide. Silicon, manganese and other elements are also oxidised and report to the slag. The steel is then tapped into a ladle and deoxidants and alloying elements are added to achieve the desired composition.

Steel is usually cast into a continuous strand of billet, bloom, or slab, using water-cooled copper moulds. Shroud tubes or inert gas may be used to limit the contact between the metal stream and air. The strand is continuously withdrawn and further cooled using direct water sprays before it is cut to length using automatic oxy-gas cutters. Steel is also cast into ingots in open top cast iron moulds.

Surface rectification of blooms, billets and slabs is carried out by grinding (manually or by machine). Cracks, scale inclusions or seams are removed by scarfing, which uses an oxy-fuel flame to remove a thin layer of the surface by localised melting. Scale is then removed by water jets.

Primary hot rolling mills are used to roll cast ingots and continuously cast blooms and slabs. Secondary hot mills roll semi-finished blooms, slabs or billets from primary mills into smaller unfinished products. The final product is rolled in hot finishing mills where the material obtains its final shape and physical dimensions. Some hot finished products are further processed by cold strip rolling, cold drawing, pickling and heat treatment processes. Sulphuric and hydrochloric acids are normally used to pickle carbon and low alloy steels, while nitric and hydrofluoric acids are used for stainless steels.

A1.1.2 Potential Releases of Prescribed Substances^{Ref 156}

Although the releases of principal concern from integrated iron and steel works are airborne in nature, significant quantities of liquid effluents and solid wastes are also produced.

(a) Particulate Emissions

Particulate emissions from integrated iron and steel works processes arise:

- As fugitive emissions during the transportation, unloading, storage and mechanical handling of raw materials and solid wastes such as slag;
- As fugitive emissions and releases from sintering, blast furnaces, steelmaking, casting and scarfing processes.

The particulates are likely to contain coke dust, iron, zinc, lead, and cadmium.

(b) Gaseous Substances

The principal gaseous substances released from integrated iron and steel works are:

- Oxides of sulphur mainly from sintering, blast furnace smelting, desulphurisation and steelmaking processes. Also from oil-fired reheat and heat treatment furnaces;
- Carbon monoxide (and hydrogen) from the sintering process, blast furnace and steelmaking process;
- Oxides of nitrogen from sintering, blast furnace smelting and acid pickling. Also from reheat furnaces;
- Hydrogen chloride and hydrogen fluoride from the sintering process and hydrogen chloride from pickling operations;

- Dioxins, volatile organic compounds and PAHs from sintering, blast furnace smelting and steelmaking processes. VOCs are also released from rolling processes.

Other gaseous releases include hydrogen sulphide, primarily from slag processing, ammonia and hydrogen cyanide.

(c) Liquid Effluents

The main sources of effluents from integrated iron and steel works arise from:

- Blast furnace primary gas cleaning, slag processing and steelmaking
- Continuous casting, scarfing, rolling and pickling operations
- Surface water run-off

The main pollutants in the effluents are suspended iron oxide and other metal oxides, dissolved metals such as lead and zinc, oils and greases and hydrochloric acid.

(d) Solid Wastes

The principal solid wastes from integrated iron and steel works are :

- Slags from blast furnace, steelmaking and ingot casting processes
- Sludges from gas cleaning systems associated with blast furnaces and steelmaking
- Refractories

A1.2 FERROUS FOUNDRY PROCESSES (IPR 2/2 AND PART B PROCESSES)

A1.2.1 Principal Processes Ref 157,158

Ferrous foundry processes include the melting of metals and subsequent processes leading to the production of castings to final, or near final, shape.

Electric Arc Furnaces (EAFs) are used for melting iron or steel for the production of large castings. Cupolas are used for melting iron. Induction furnaces of various types are used for melting of most metals, both ferrous and non-ferrous.

(a) Electric Arc Furnaces

The charge materials to the electric furnaces are scrap and limestone flux; in some plants, the scrap may be preheated by the furnace off-gases. Oxy-fuel burners are often used to assist in the early stages of melting. Oxygen is injected into the molten bath to remove sulphur, silicon and phosphorus. Oxygen lancing oxidises iron in the bath, which reports to the slag, and carbon may be either added to the scrap charge before charging, or be injected into the slag to reduce the oxide back to metallic iron. Alloying and other additions are often made into the ladle before or while the molten metal is tapped from the electric furnace. Slag is tapped from the furnace into pots or onto the ground below the furnace. In the latter case, the slag is removed while hot, using excavators, and transferred to open areas for further natural cooling in the open air or by water sprays.

(b) Cupolas

A cupola is a vertical shaft furnace to which iron or steel, limestone or other fluxing materials and coke are charged through an opening in the upper part of the shaft. Air is supplied through tuyeres near the base of the shaft and molten iron is tapped from the base of the furnace.

The limestone calcines and combines with acidic impurities in the feedstock to form a slag, which is tapped off either periodically or continuously.

Feedstocks typically include pig iron, steel scrap, foundry returns and cast iron scrap. Scrap may be contaminated with undesirable materials such as paint, plastics, oil, zinc and other heavy metals.

Combustion conditions within the cupola are controlled to minimise generation of iron oxide.

Particulate emissions from the shaft contain mainly silica, iron oxides, calcium oxide and aluminium oxide. However, contaminants in the scrap feedstock may contribute zinc, lead and other heavy metal oxides to the fume emissions.

Organics and low-melting-point metals in the feedstock will be volatilised as they descend the shaft.

(c) Induction Furnaces

Various types of induction furnace, such as coreless and channel furnaces, are used to melt metal for casting. In the size range of up to 10 tonnes capacity, coreless crucible furnaces are operated at medium frequencies, typically between 250 and 1000 Hz. Furnaces of larger capacity are often operated at mains frequency. Operation may be batch or semi-continuous. In the latter case, each batch of feed is charged into a molten bath. Induction channel furnaces are used mainly for holding and pouring.

Whilst induction furnaces have hardly any refining capability and require a reasonably clean feed, alloys can be made by adding other pure metals, or master alloys containing a high proportion of the required element.

Gaseous and particulate emissions are small where the feed is clean and, consequently, fume collection equipment is often not provided. Where the feedstock contains zinc, or some contamination is expected, fixed or moveable exhaust hoods are normally used to capture fume, which is then collected in a fabric or cartridge type filter.

(d) Desulphurisation and Nodularisation

Molten iron can be desulphurised with magnesium or calcium carbide, which reacts with the

sulphur to produce a slag, batchwise in a barrel-shaped ladle or continuously in a divided ladle.

Molten grey iron can be converted into ductile iron (nodular or spheroidal graphite iron) by treatment with magnesium and rare earth elements.

(e) Casting Practices

The binder systems available for the manufacture of moulds from foundry sand include green sand (with a clay binder), shell sand (for which phenol and formaldehyde are used as binder) and several cold setting techniques which rely on the chemical reaction between resins, such as phenolic urethane, and hardeners, such as a sulphonic acid.

Casting is carried out in static sand moulds, on automatic moulding lines, or in a rapidly rotating horizontal mould for the manufacture of pipe. Roll casting can be carried out centrifugally in a vertical mould, which is spun at a high speed, or in static moulds. The cooled castings are then finished by processes such as shotblasting and fettling. Sand can be reclaimed from used moulds by mechanical means such as crushing and screening. Sands with organic binders are reclaimed thermally by burning off the organics at a temperature of around 750°C in a fluidised bed.

Investment casting uses an expendable pattern, usually of wax, around which a ceramic mould is formed by coating with a refractory slurry and "stuccoing" with refractory grains of calcined china clay or zircon. The ethyl silicate binder is subsequently set using ammonia. The mould is then dried, dewaxed and fixed to prepare it for casting.

The "lost foam" process utilises an expendable polystyrene pattern around which dry sand is poured. The polystyrene is vapourised as the molten metal enters the mould and the resulting volatile gases are evacuated through the dry sand. The process facilitates sand reclamation.

A1.2.2 Potential Releases of Prescribed Substances^{Ref 159}

Although the releases of principal concern from ferrous foundry processes are airborne in nature, significant quantities of liquid effluents and solid wastes are also produced.

(a) Particulate Emissions

Particulate emissions from ferrous foundry processes arise:

- As fugitive emissions during the transportation, unloading, storage and mechanical handling of raw materials and solid wastes such as slag;
- As fugitive emissions and releases from electric arc furnaces, desulphurisation, nodulisation, casting and sand reclamation processes.

The particulates are likely to contain metals, metal oxides, fluxes and carbon.

(b) Gaseous Substances

The principal gaseous substances released from foundry processes are:

- Oxides of sulphur from melting, desulphurisation, mould preparation and casting processes
- Carbon monoxide primarily from electric arc furnaces and cupolas
- Hydrogen sulphide and ammonia from mould preparation and casting processes
- Dioxins from melting furnaces
- VOCs from melting furnaces, mould preparation and casting

(c) Liquid Effluents

The main sources of effluents from foundry processes arise from:

- Slag or dross processing
- Fettling and finishing of castings
- Surface water run-off

The main pollutants in the effluents are suspended iron oxide and other metal oxides, and dissolved metals such as cadmium, lead and zinc, oils and greases.

(d) Solid Wastes

The principal solid wastes from foundry processes are:

- Slag or dross from melting arc furnaces, desulphurisation and nodularisation processes
- Sand from mould preparation and sand reclamation processes

A1.3 ELECTRIC ARC STEELMAKING, SECONDARY STEELMAKING AND SPECIAL ALLOYS (IPR 2/3)

A1.3.1 Principal Processes^{Ref 157, Ref 158}

The electric arc furnace (EAF) steelmaking process has been described in Section A1.2.1. Secondary steelmaking covers the treatment of molten steel after it has been tapped from the steelmaking furnace up to the point of casting. The principal processes, which are briefly described below, are typically carried out at ladle treatment stations using an overhead crane or transfer car to move the ladle between stations.

A wide range of alloying and micro-alloying agents is used in secondary steelmaking and these are introduced as ferro-alloys or in elemental form. Pneumatic injection systems, often

employing argon as the carrier gas, are used for specific refining duties - for example, lime and lime/fluorspar for the removal of sulphur and the injection of lead to improve the machinability of the steel.

Dissolved hydrogen and nitrogen can be removed by degassing under vacuum while dissolved oxygen is removed under vacuum, using solid deoxidants.

Low-carbon stainless steel and nickel alloys are produced by injecting a mixture of argon and oxygen into a converter; refined steel and slag are tapped by rotating the vessel. Carbon can also be removed by injecting oxygen into the molten steel in a vacuum vessel.

Vacuum arc remelting, in which a steel ingot electrode is continuously melted under vacuum by a DC arc passing between the base plate of a water cooled copper mould and the ingot, is used to produce higher purity steels. An alternative refining process is electroslag remelting, in which ingots are melted by AC or DC resistance heating of a liquid slag (typically a mixture of fluorspar, lime and alumina) held between an electrode and the surface of the ingot to be melted. As the ingot melts, droplets fall through the slag and are collected in the bottom of a water-cooled copper mould.

Induction melting under vacuum is used for the manufacture of complex super alloys and nickel-based alloys which can be subsequently refined by vacuum arc or electroslag remelting.

Induction melting in air is used to produce a wide range of alloys from recycled scrap, ingots, alloying additions and fluxes.

Ferrous alloy powders are produced melting raw materials in air or vacuum induction furnaces. The molten metal is then atomised either with high-pressure water or by supersonic jets of nitrogen or argon to produce powder, which is settled from the aqueous slurry in the case of water atomisation or is separated from the gas by cyclone.

Ferro-boron master alloy is produced by reducing boric oxide with carbon in an open top DC electric arc furnace followed by the addition of ferrous material. The product is cast into small ingots. Ferro-titanium is manufactured by melting ferrous and titanium scrap in an air induction furnace.

Associated processes such as continuous casting, ingot casting, scarfing, rolling and pickling have been described in Section A.1.1.

A1.3.2 Potential Releases of Prescribed Substances^{Ref 160}

The releases of principal concern from EAF, secondary steelmaking and special alloy processes are airborne in nature but significant quantities of solid wastes are also produced.

(a) Particulate Emissions

Particulate emissions from the processes arise:

- As fugitive emissions during the transportation, unloading, storage and mechanical handling of raw materials and solid wastes such as slag;
- As fugitive emissions and releases from electric arc furnaces, induction furnaces, ladle treatments and decarburisation processes.

The particulates are likely to contain iron, iron oxide, zinc, lead, cadmium and their oxides, limestone and fluorspar and, in the case of high-alloy steel production, hexavalent chrome. Boron and titanium may also be present, although these are not prescribed substances.

(b) Gaseous Substances

The principal gaseous substances released from the processes are:

- Oxides of sulphur from electric arc furnace melting, decarburisation and induction melting processes;

- Carbon monoxide, primarily from electric arc furnaces and decarburisation processes;
- Hydrogen fluoride from electric arc furnace melting, ladle treatments and electroslag remelting;
- Dioxins from electric arc furnace melting;
- VOCs from electric arc furnaces.

(c) Liquid Effluents

The main sources of effluents from ferrous foundry processes arise from slag processing and surface water run-off.

The main pollutants in the effluents are suspended iron oxide and other metal oxides, dissolved metals such as cadmium, lead and zinc, and in the case of high-alloy steel production hexavalent chrome, as well as oils and greases.

(d) Solid Wastes

The principal solid wastes from EAF, secondary steelmaking and special alloy processes are slag from electric arc furnaces, ladle treatments, induction furnaces and electroslag remelting, as well as particulate matter from fume extraction plant.

A1.4 LEAD AND ZINC AND THEIR ALLOYS (IPR 2/4 & 2/5)

A1.4.1 Principal Processes

(a) Primary Lead^{Ref 161} and Primary Zinc^{Ref 162}

Primary lead and zinc are produced in the UK from imported sulphide concentrates using the Imperial Smelting Process (ISP). Blended and pelletised concentrates are desulphurised and agglomerated by sintering. Sulphur is oxidised to sulphur dioxide in a reaction that generates enough heat to fuse the pellets. The gases from the sinter machine are wet

scrubbed before the sulphur dioxide is recovered in the form of sulphuric acid. Cadmium and mercury are also recovered in gas cleaning systems upstream of the acid plant.

Crushed and screened sinter is charged to the ISP blast furnace, together with metallurgical coke and briquetted secondary materials such as oxides, galvanisers ashes and drosses. Air, injected through tuyeres, reacts with the coke to produce carbon monoxide, which reduces the metal oxides in the charge to lead and zinc.

Zinc is volatile at the furnace operating temperature and passes out of the furnace in the gases, which also contain some cadmium and lead. The gases are quench cooled in a splash condenser by a shower of molten lead which absorbs the metals. (The residual gases containing carbon monoxide and hydrogen are cleaned in a washing tower before being burned to preheat the tuyere air and coke). Zinc floats to the surface of the cooled alloy and is separated from the lead and is transferred to the zinc refinery. Impurities such as cadmium, lead, copper, arsenic and iron are removed by a two-stage distillation process in externally heated columns to produce 99.99% pure zinc.

Cadmium is recovered via two separate routes in the ISP. Some cadmium follows the zinc and is recovered from the second distillation stage. The balance is volatilised during sintering and reports to the liquors in the gas cleaning systems. Cadmium is recovered as a carbonate filter cake by ion exchange and precipitation. Pure cadmium is produced from the cake by a process involving redissolution, precipitation of cadmium sponge, melting and distillation.

Slag and molten lead are tapped from the bottom of the ISP furnace. The slag is granulated using water while the lead, which may contain copper, silver, bismuth, tin, or antimony, is sent to the UK's primary lead refinery at Gravesend. Lead bullion is treated in a series of kettles, which are indirectly heated with oil or gas. Chemical additives such as sulphur and caustic soda are used to remove the impurities at successively lower temperatures. The 99.97% pure lead is cast into ingots or blocks or converted into "specification alloys".

(b) Secondary Lead^{Ref 163} and Secondary Zinc^{Ref 164}

Secondary lead is produced from scrap lead batteries and metallic lead scrap.

Scrap batteries are separated into various fractions by crushing, followed by screens, wet classifiers and filters to obtain separate fractions containing metallics, lead oxide-sulphate paste, plastics, rubber and dilute sulphuric acid. The metallics and paste are commonly smelted with sodium carbonate flux and coke as a reductant in oil or gas-fired rotary furnaces. The off gases are cooled and cleaned in fabric bag filters before being discharged to atmosphere. Slag is tapped and crude lead is cast into blocks or transferred into kettles for refining, using techniques similar to those for primary lead production. The purified lead is cast into ingots and alloying elements may be added to produce alloys.

Metallic lead scrap, which may be alloyed with other elements, is melted in kettles indirectly heated by oil or gas. Dross or tramp materials are skimmed from the surface of the molten lead which may be alloyed or refined as described above.

Zinc is recovered from secondary sources such as filter dust from the manufacture of copper alloy products, galvanisers ashes, residue from the shredding of steel scrap, drosses etc. The process used depends on the form and percentage of contained zinc.

Galvanisers ashes (a mixture of zinc metal, zinc oxide, zinc chloride and ammonium chloride) are ball milled to liberate the materials for subsequent physical separation into a coarse metallics and a fine non-metallic fraction. The metallics are melted and cast into ingots while the non-metallics may be processed by smelting.

Zinc is recovered from drosses containing zinc metal and zinc oxide by melting with a flux followed by casting into ingots.

Shredder residue, the product of shredding of cars after separation of ferrous metals, is melted in two stages in gas-fired reverberatory furnaces. The lead melts first and is cast into ingots and the temperature is then raised to melt the zinc, which is also cast into ingots.

A1.4.2 Potential Releases of Prescribed Substances Ref 165, Ref 166

Although the releases of principal concern from the lead and zinc industry are airborne in nature, significant quantities of liquid effluents and solid wastes are also produced.

(a) Particulate Emissions

Particulate emissions from lead and zinc processes arise:

- As fugitive emissions during the transportation, unloading, storage and mechanical handling of raw materials and solid wastes such as drosses, filter dusts and slag;
- As fugitive emissions and releases from smelting, melting and refining processes.

The particulates are likely to contain coke dust, zinc, lead, cadmium, copper and arsenic as well as chlorides arising from the use of fluxes.

(b) Gaseous Substances

The principal gaseous substances released from the lead and zinc sector are:

- Oxides of sulphur, mainly from the sulphur content of lead and zinc concentrate;
- Carbon monoxide (and hydrogen) from the coke used as reductant in the ISP blast furnace and secondary lead-smelting furnaces;
- Mercury in the gases from the sintering stage of the ISP.

Other emissions include hydrogen chloride, hydrogen fluoride and ammonia arising from the use of fluxes and oxides of nitrogen, volatile organic compounds, PAHs and dioxins.

(c) Liquid Effluents

The main effluents from lead and zinc processes are:

- Contaminated water from wet scrubbing systems
- Acidic wash water from battery-breaking operations
- Surface water run-off

The main pollutants in the effluents are suspended solids, dissolved metals such as cadmium, mercury, copper, lead and zinc, sulphates and hydrocarbons.

(d) Solid Wastes

The principal solid wastes from the lead and zinc industry are:

- ISP slag containing lead and zinc in a calcium-iron-silicate matrix
- Mercury, arsenic, selenium and tellurium in sludges from gas-cleaning systems
- Calomel (mercurous chloride) from mercury removal upstream of the acid plant
- Coke fines
- Soda slag containing lead from secondary lead-smelting operations
- Non-recyclable plastics (PVC and Bakelite) and rubber from battery-breaking
- Low-zinc-content drosses from secondary zinc recovery processes

A1.5 ALUMINIUM AND ALUMINIUM ALLOYS (IPR 2/8)

A1.5.1 Principal Processes

(a) Primary Aluminium^{Ref 167}

All the UK primary aluminium smelters use the Hall-Heroult process, which produces

aluminium by the electrolytic reduction of alumina in a molten bath of cryolite (sodium aluminium fluoride) at 960°C.

The electrolysis cells comprise a carbon cathode, inside a rectangular steel shell insulated with refractory bricks, and carbon anodes, which are continuously consumed during the process. One UK smelter uses anodes produced in situ from a paste of calcined petroleum coke and coal tar pitch, which is baked by the heat arising from the molten bath. The other smelters use prebaked anodes manufactured from a mixture of petroleum coke and coal tar pitch, which is formed into a block and baked. The manufacture of prebaked anodes is classed as a tar and bitumen process under the Environmental Protection (Prescribed Processes and Substances) Regulations^{Ref 2,3} and is excluded from further consideration in this study). The cathode is not consumed in the process but the carbon blocks absorb electrolyte and have to be replaced every 6-8 years because of swelling and cracking, which can result in penetration of molten electrolyte and aluminium into the shell. The waste material is known as spent pot lining (SPL).

Crucibles of molten aluminium are transferred to fuel-fired furnaces where the aluminium may be refined to remove sodium, calcium, magnesium and hydrogen by the injection of chlorine, or chlorine mixed with argon or nitrogen.

Primary aluminium is produced mainly in the form of slab, billet and remelt ingot containing 99.7 % aluminium. Slabs and billets are cast in vertical, direct chill casting machines consisting of a fixed water-cooled metal mould and a water-cooled metal stool which is lowered as the aluminium is being cast.

Remelt ingots are produced by pouring molten aluminium into steel moulds mounted on an inclined chain conveyor. Large ingots are cast in static moulds.

(b) Secondary Aluminium ^{Ref 168}

The main activities of the secondary aluminium industry are secondary smelting (the manufacture of slab, billet and remelt ingot from scrap materials), the manufacture of rolled,

extruded and drawn semi-finished products and the production of castings.

Scrap materials may be prepared by sorting, size reduction, magnetic separation, differential melting, drying/de-oiling, decoating and compaction before being blended to suit the required product composition.

The purity, size and batch weight of the feed materials influence the choice of melting furnace. Oil or gas-fired rotary furnaces are commonly used to melt low-grade materials under a layer of molten flux, typically sodium or potassium chloride with some fluoride, which reduces oxidation of the aluminium and promotes wetting of the charge. Slag is periodically tapped into metal containers where it cools and solidifies.

Reverberatory furnaces can accept larger material, use less flux compared with rotary furnaces and can be used for alloying and refining the molten aluminium. Dross is skimmed through a door into cast iron containers.

Crucible furnaces with oil or gas-fired heated jackets are typically used to manufacture smaller quantities of aluminium alloys.

Electric furnaces avoid the emissions associated with fossil fuels and can be blanketed with an inert gas to prevent oxidation of the molten metal. Induction furnaces are used widely in aluminium foundries and for melting high-grade scrap and alloying elements.

Gas-fired tower furnaces are used in repetition foundries. Because both the feedstock and fuel are "clean", there is usually no requirement for fume abatement.

The molten aluminium is refined and/or degassed. Alloying elements are added as molten metal, ingots or rod before the product is cast into remelt ingots, slabs or billets.

Dross consists mainly of aluminium metal alloy and aluminium oxide. Large pieces of metal are manually separated before the dross is fed to a mill where the more friable oxide is

preferentially ground. The fine metallics are separated from the oxides and are recycled, together with larger metallic material, to secondary smelters.

The most widely used casting processes in aluminium foundries are casting in natural or resin bonded sand moulds and gravity/low/high pressure die casting.

A1.5.2 Potential Releases of Prescribed Substances^{Ref 169}

In the aluminium sector, airborne releases are of most concern. Significant quantities of solid wastes are also produced, while releases to water are of less significance.

(a) Particulate Emissions

Particulate emissions from the primary and secondary aluminium industry arise:

- As fugitive emissions during the transportation, unloading, storage and mechanical handling of raw materials and solid wastes such as filter dusts, SPL, slag and dross;
- As fugitive emissions during size reduction, swarf drying, decoating, melting and refining furnace operations;
- From the electrolytic reduction process, both as fugitive emissions and in the exhaust from cell fume cleaning plant;
- From dross-processing operations.

The particulate emissions are mainly composed of alumina, petroleum coke, carbon dust, cryolite and other metal fluorides and chlorides.

(b) Gaseous Substances

The principal gaseous substances released from aluminium industry processes are :

- Hydrogen fluoride, arising mainly from the electrolytic reduction process and from

melting furnaces using fluxes containing fluorides;

- Sulphur dioxide, principally from the sulphur contained in petroleum coke and coal tar pitch but also from liquid fuels used for melting and heating operations;
- Carbon monoxide, released during the electrolytic reduction process;
- Tar fumes containing polycyclic aromatic hydrocarbons (PAHs) are released during the storage of molten pitch and during the electrolytic reduction process;
- Hydrogen chloride from swarf drying, decoating, melting and refining furnaces;
- Chlorine gas from refining operations;
- Volatile organic compounds and dioxins arising from oil contamination and plastics and paint coatings on scrap materials.

Carbon fluorine compounds such as CF_4 and C_2F_6 may be released during operational disturbances in the operation of electrolytic reduction cells. Ammonia and acetylene can arise from the reaction between hot dross and moisture. Other gaseous emissions include oxides of carbon and oxides of nitrogen from the combustion of fuel used in melting and heating operations.

The releases from aluminium processes that require special monitoring techniques are fugitive releases from the roof vents of pot rooms housing electrolytic cells; PAHs ; CF_4 and C_2F_6 (released during upsets in the electrolytic reduction process) and dioxins.

(c) Liquid Effluents

The principal potential releases of prescribed and other substances to water from aluminium industry processes are:

- Cyanides, chlorides and fluorides arising from the leaching of SPL;
- Hydrocarbons from swarf contaminated with cutting oils and lubricants used in casting operations;
- Metal oxides, chlorides and fluorides in effluents from wet scrubbers and leachate from solids wastes such as salt slag and drosses stored in the open.

(d) Solid Wastes

The substances contained in the principal solid wastes from the aluminium sector are :

- Carbon, fluorides and cyanides in SPL;
- Aluminium metal, metal oxides, metal chlorides and fluorides in salt slag and drosses;
- Metal oxides, chlorides and fluorides in dusts collected by cyclones and bag filters.

A1.6 COPPER AND COPPER ALLOYS (IPR 2/9)

A1.6.1 Principal Processes^{Ref 170}

There is no primary copper production in the UK. The main activities of the UK copper industry are the production of cathode copper from scrap and other secondary sources, the production of copper alloy ingots and billets from scrap materials and the manufacture of semi finished products, including castings.

(a) Production of Cathode Copper

Low-grade materials are smelted with coke, limestone and sand fluxes in a blast furnace to produce black copper, which is upgraded to anode copper in two stages. Medium-grade scrap is smelted in oil-fired reverberatory furnaces producing rough copper, which is upgraded to anode copper. Anode copper contains approximately 98% copper and is continuously cast into strip, which is cut into lengths suitable for suspension in electrolytic

refining cells with stainless steel cathode blanks and acidified copper sulphate solution as electrolyte. Copper ions dissolved from the anodes migrate to the blanks and are deposited as cathode copper containing 99.95% copper.

(b) Production of Copper Alloy Ingots

Scrap is prepared by sorting, magnetic separation, baling and drying/de-oiling.

Batches of mixed alloy scrap, swarf and drosses are generally melted with silica and borax fluxes and alloying elements in oil-fired rotary and reverberatory furnaces. Higher-quality materials are melted in gas-fired reverberatory or electric induction furnaces. Ingots are cast in static cast iron moulds or in moulds on an inclined chain conveyor. Billets are cast using semi continuous and continuous vertical and horizontal systems.

(c) Manufacture of Semi Finished Products

Copper wire rod is manufactured by melting cathode copper in a gas-fired shaft furnace and continuously casting the molten copper into bar or strip for subsequent hot rolling.

Most copper foundry castings are produced using induction furnaces and consumable sand moulds. Die casting is the only other significant casting process used for copper products.

A1.6.2 Potential Releases of Prescribed Substances^{Ref 171}

The releases of prescribed substances of principal concern from the copper sector are airborne in nature. Liquid effluents and solid wastes are also produced but are of less significance than the releases to air.

(a) Particulate Emissions

Particulate emissions from the copper industry arise mainly:

- As fugitive emissions during the transportation, unloading, storage and mechanical handling of raw materials and solid wastes such as filter dusts;
- During feed preparation, smelting, melting and alloying operations;

- The emissions contain copper fines and oxides of copper, lead, zinc and tin. Also, from special alloys, cadmium, arsenic and beryllium.

(b) Gaseous Emissions

The principal gaseous substances released from copper processes are:

- Metallic fumes of copper, lead and zinc;
- Sulphur dioxide arising from the sulphur contained in metallurgical coke and fuel oil;
- Hydrogen chloride from swarf drying and the melting of materials contaminated with plastics and rubber coatings;
- Volatile organic compounds from the melting of materials contaminated with oil and lubricants. VOCs are also released from the hot rolling and alcohol pickling stages in the manufacture of wire rod and in foundry operations.

Other emissions include carbon monoxide from blast furnace and shaft furnace operations, dioxins, and oxides of nitrogen from the combustion of fuels.

(c) Liquid Effluents

The most significant effluents arise from pickling operations during the manufacture of semi finished extruded, drawn and rolled products. These effluents are generally acidic and contain copper and other heavy metals. The other potential releases to water are oil and heavy metals from the action of rain on raw materials in open storage areas.

(d) Solid Wastes

The substances contained in the main solid wastes from copper processes are:

- Iron silicate and lime in the slags from smelting and melting operations
- Oxides of copper, zinc, lead and tin in bag filter dusts

- Silica in the waste sand from foundries.

The releases from copper processes that require special monitoring techniques are fugitive releases from roof vents and dioxins.

A1.7 OTHER METALS

A1.7.1 Principal Processes

(a) Cadmium and Mercury Ref 172, Ref 173

The only primary production of cadmium in the UK is as a by-product of primary zinc manufacture, which has been described in Section A1.4.

Low-melting-point fusible alloys containing bismuth, tin, lead and 5 - 10% cadmium are produced by melting pure metals or master alloys in gas or electrically heated cast iron pots and casting the alloy into ingots, billets or bars in water-cooled moulds.

Gold and silver alloys containing cadmium are manufactured by melting the ingredients in an electric induction furnace under a charcoal cover. The molten alloys are cast into ingots, rod or bars or are granulated in a water quench tank to produce granular prills.

There is no primary mercury production in the UK. High-purity (99.999% +) mercury is manufactured by vacuum distillation of imported virgin mercury or recovered material. After filtration and washing with dilute nitric acid, batches of mercury are transferred to electrically heated glass and steel retorts. The distilled mercury vapour passes to a water-cooled condenser and is collected in containers. The residual impurities, mainly lead and zinc, are removed from the retorts on a regular basis.

Mercury is recovered from wastes such as unused dental amalgam, spent mercury and silver oxide batteries and chemical industry residues. Weighed, sorted waste is loaded into gas-fired retorts which are heated to 700 - 800°C. Mercury vapour flows from the retort into a water-cooled condenser and is collected in receivers. The non-condensable vapour is drawn

off by a vacuum pump and released to atmosphere. At the end of the cycle, the mercury-free residue in the retort is processed to recover valuable fractions such as precious metals.

(b) Nickel and Cobalt and their Alloys ^{Ref 174, Ref 175}

The nickel carbonyl process is used in the UK for the primary production of nickel from imported nickel oxide. In this large-scale continuous process, nickel oxide is reduced in an unfired rotary kiln by pre-heated hydrogen at about 425°C to produce impure nickel. The nickel is fed to another kiln where it is volatilised into nickel carbonyl gas by reaction with carbon monoxide at 50-60°C. After filtration, the gas is fed into "decomposer" vessels, where the carbonyl is decomposed at 200°C onto pre-heated nickel seeds which grow to form high-purity nickel pellets. Carbon monoxide from the decomposers is recycled to the volatilisation kiln while hydrogen is recovered from the reduction kiln and recycled.

Scrap or virgin cobalt and nickel alloys are melted in induction or electric arc furnaces. After the removal of slag, the molten alloy is cast into ingots or billets. Vacuum induction melting is used for the production of more complex alloys, with further refining by the electroslag and/or vacuum arc refining processes (see Section A1.3.1). Nickel and cobalt castings are manufactured by the investment casting process which uses wax patterns coated with a ceramic slurry. Castings are acid etched, pickled and degreased.

(c) Precious Metals and Platinum Group Metals ^{Ref 176, Ref 177}

Silver is recovered from industrial wastes, mainly from the photographic industry. Films, papers and sludges are incinerated in batches in single-hearth furnaces, or continuously in rotary kilns, to produce a silver-rich ash which is blended with sweeps and other residues and is smelted in a variety of furnaces. Lead is used as a collector for the silver; coke, gas or oil are used as fuel and to generate a reducing atmosphere. The metal is transferred to a cupellation furnace where the lead is oxidised to litharge (lead oxide) using air or oxygen. The litharge is recycled to the smelting furnace and the silver is cast into anodes.

The anodes are electrolytically refined in cells with titanium or stainless steel cathodes in an acidified silver nitrate electrolyte. The silver crystals deposited on the cathodes are scraped off, washed and melted before being cast into ingots, slab or billets.

Silver produced by smelting and high-grade silver residues can be refined by dissolution in nitric acid, followed by recrystallisation as silver nitrate or electrolysis to fine silver. Silver is also recovered from waste film, by leaching using a thiosulphate solution and electrowinning from the leach liquor, and from waste solutions by chemical precipitation as a powder.

Gold is recovered from industrial, jewellery and dental scrap. In the Miller process, the feed materials are melted in an indirectly heated crucible or electric induction furnace. Chlorine is injected into the melt and reacts with all the metals present, except for gold, forming molten or gaseous chlorides. The molten gold is cast into bullion bars or into anodes, which are electrolytically refined in cells containing gold foil or titanium cathodes in acidified gold chloride electrolyte. The deposit on the cathodes contains 99.99% gold.

Gold is also recovered and refined by dissolving the feed materials in aqua regia or in hydrochloric acid/chlorine followed by precipitation as powder. In some cases, solvent extraction is used to remove impurities before the precipitation stage.

The principal materials used for the recovery and refining of platinum group metals (PGMs) are concentrates, mattes and slimes from nickel operations, and secondary materials such as spent chemical and automobile exhaust catalysts along with electronic scrap. The feed materials may have to be incinerated, crushed, blended or melted before the dissolution of the PGMs in aqua regia or hydrochloric acid/chlorine.

Chemical and solvent extraction techniques are used to purify and separate the PGMs, which are then precipitated as salts or oxides. The metals are produced by reduction and distillation processes.

(d) Refractory Metals^{Ref 178, Ref 179}

Chromium metal is manufactured in the UK by the reduction of chromic oxide with aluminium. A mixture of aluminium powder, chromic oxide and oxidants such as potassium perchlorate is ignited in a slag-lined crucible. The reaction is sufficiently exothermic to melt the metal and slag. After cooling, the metal and slag are separated and the chromium metal is cleaned, crushed and screened. A proportion of the slag may be crushed and reused to line the crucible.

Molybdic oxide is produced by roasting molybdenum sulphide concentrates in multiple hearth furnaces. The process is almost self-supporting and requires only limited amounts of auxiliary fuel.

Tungsten is manufactured by calcining ammonium paratungstate (APT) at about 750°C in indirectly heated rotary furnaces to form tungsten oxide. The oxide is then reduced to tungsten metal powder by hydrogen at around 1000°C in similar furnaces.

Molten zinc is used to recover tungsten carbide from scrap. The zinc forms an amalgam with the cobalt matrix which disintegrates the structure of the carbide and permits separation of the cobalt and carbide. The zinc is removed by distillation, condensed and recycled.

(e) Tin and Bismuth^{Ref 180, Ref 181}

There is no primary production of tin and bismuth in the UK.

Tin-solder alloys are recovered from metallic scrap and high-metal-content drosses by melting in kettles indirectly heated by fuel or electricity. Lower-metal-content materials are melted in directly-fired rotary or sloping hearth reverberatory furnaces. The crude molten alloy is refined either pyrometallurgically or by an electrolytic process.

The pyrometallurgical process involves the staged addition of chemicals to remove iron, copper, zinc and other impurities. The alloy is then cast into ingots, billets, bars and sticks. The electrolytic process uses anodes of crude alloy and thin sheets of refined solder as cathodes in cells with hydrofluorosilicic acid or hydrofluoroboric acid as the electrolyte. Tin

and lead are deposited on the cathodes, which are periodically removed, washed and melted and the processes are followed by casting refined solder into ingots.

Scrap tinplate is detinned using either a chemical or electrochemical process. In the chemical process, the scrap is shredded and non ferrous materials are removed by a magnetic separator. Tin is leached from the scrap using hot solutions of sodium hydroxide and sodium nitrite. After filtration, tin is recovered from the sodium stannate solution in electrowinning cells where the tin is deposited on steel cathodes. The cathodes are removed periodically and dipped into a bath of molten tin to melt the deposited tin, which is cast into ingots. Depleted solution from the cells is recycled to the leaching process, but a bleed is withdrawn to prevent the build-up of impurities.

In the electrochemical detinning process, shredded scrap is cleaned by magnetic and air separation techniques before residual aluminium is removed by leaching in dilute sodium hydroxide solution. The tinplate is then placed in steel baskets forming the anodes of electrorefining cells containing hot sodium hydroxide solution as electrolyte. The tin loosely deposited on the steel cathodes is scraped off and pressed into nuggets.

Hot-dip tinning processes involve pickling of items such as steel plate in a bath of warm dilute hydrochloric or nitric acid to remove any dirt and oxide layer, and passage of the clean item through a bath of flux (typically based on zinc chloride) before it is coated in a bath of molten tin or tin alloy. The item may be cooled by passage through an oil bath to prevent oxidation before the coated item is degreased.

Bismuth and bismuth alloys are recovered from scrap bismuth alloys, from aero engine components and from waste bismuth salts. Scrap alloys are melted in indirectly fired kettles. After the removal of dross, the molten alloy is refined by use of chemicals to remove impurities before it is cast into ingots. Waste bismuth salts from the pharmaceutical industry are smelted in oil-fired kettles by use of sodium hydroxide as flux and charcoal as a reductant. After slag has been removed, the molten bismuth is cast into ingots. The production of low-melting-point alloys of bismuth is described in (a) above under cadmium.

A1.7.2 Potential Releases of Prescribed Substances

The principal potential releases of prescribed substances from the processes described in Section A1.7.1 are summarised below:

(a) Particulate Emissions

Particulate emissions arise from most of the processes used for the extraction and recovery of the metals and alloys covered by Section 2.8 and as fugitive emissions during the transportation, unloading, storage and mechanical handling of raw materials and solid wastes such as filter dust, drosses and slag.

(b) Gaseous Substances

The main releases of gaseous substances from the processes under Section 2.8 are:

- Oxides of sulphur, arsenic and selenium from the roasting of molybdenum sulphide concentrates;
- Carbon monoxide from the nickel carbonyl process and the calcination of APT;
- Ammonia from the chemical detinning of scrap tinplate, the calcination of APT and the production of PGMs;
- Mercury during the vacuum retorting of mercury;
- Hydrogen chloride from incineration and smelting processes used for the production of silver, gold and PGMs and from the hot-dip tinning process;
- Chlorine from processes used for the production of gold and PGMs;

- Volatile organic compounds are released from incineration and solvent extraction processes used for the production of precious metals and PGMs, the hot-dip tinning processes and investment casting of nickel and cobalt.

Other gaseous emissions include oxides of nitrogen from the combustion of fuels, fluorides from electroslag remelting and hydrofluoric acid pickling of nickel and cobalt.

(c) Liquid Effluents

The principal potential releases of prescribed and other substances to water are :

- Suspended solids
- Metals including cadmium, chromium, lead, tin, copper, antimony and PGMs
- Ammonia
- Hydrochloric and nitric acids
- Fluorides and chlorides
- Oil and organic compounds

(d) Solid Wastes

The principal potential releases of solid wastes from the processes in Section A1.7 are slags from smelting and melting operations and waste sand from foundry processes.

APPENDIX 2

GENERIC PRINCIPLES OF MONITORING TECHNIQUES

This Section briefly outlines the main principles of measurement appropriate to continuous monitoring of pollutants in the metals industries. The field is very large, so for a more detailed treatment, manuals of instrument technology should be consulted.^{Refs 182,183}

For completeness, techniques are described which are recognised as being applicable to, but not necessarily in use for, continuous pollution monitoring.

Sampling is dealt within this report only as it is related to specific measurement techniques. The field is extensive and the subject of specialised literature.^{Refs 4,184,185}

General functions are not described for specific instruments, since modern process and analytical instruments have on-board computers and therefore may reasonably be expected to provide the following functions:

- Automatic control and sequencing of instrument operations
- A comprehensive operator interface for commissioning and maintenance
- Digital range selections and adjustment
- Linearisation calculations
- Correction for temperature and other easily-measured local influences
- Maintenance of continuous output signals from sampled readings
- Averaging and filtering

- A choice of analogue output signal range (4-20 mA, 0-20 mA, 1-5V etc)
- Contacts to signal "fault" and "high" alarms
- Digital serial output(s) for connection to an external recording/logging system

Additionally, the following functions may be available:

- Predictive failure detection and alarm
- Self-documentation of the instrument's settings and parameters
- Remote telephone access by the manufacturer for fault diagnosis

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A2.1 RELEASES TO AIR

A2.1.1 Particulate Sampling

The primary method of quantifying particulate matter in air is to collect a sample from the duct, classically by means of a sharp-edged pipe facing upstream, with the extraction rate adjusted to be equal to the velocity in the duct (isokinetic sampling). The sample stream may need to be heated to prevent condensation. The measurement must be made at a grid of locations across the duct cross-section to yield a representative figure.

The method is well established.^{Ref 186} It has not been automated for continuous monitoring, otherwise than for beta gauging (see below). The accuracy is generally accepted to be no better than $\pm 25\%$ at below 20 mg/m^3 . Below 10 mg/m^3 there are concerns about the applicability of the technique.

A2.1.2 Photometry

These techniques are generally of the cross-duct type. Optical components are protected by air purging with instrument air at approximately $3 \text{ Nm}^3/\text{h}$.

a) Transmissivity (Opacity)

Light is transmitted across a duct carrying the process stream and the amount of light reaching the detector is measured. Automatic calibration can be achieved by use of mirrors or scanning devices which return the beam to source location and/or switch it periodically through a reference sample. From the ratio of the transmitted and received signals, the instrument computes the extinction and hence estimates the quantity of the particulate across the duct.

Instruments for conventional particulate measurement employ visible light (generally 640 nm red LEDS - more reliable than incandescent or discharge lamps). The signal is modulated to avoid interference from ambient light.

The measurement is strongly affected by the density, size distribution, and also shape and colour of the particles, so much so that there is not *a-priori* setting - the instrument must be set up against a manual sampling method during commissioning.

b) Scattered Light

Light is transmitted across the duct scattered back to a detector by the dust measured. The detector may be periodically switched off from back-scatter measurement to the transmitter via a reference cell to provide an automatic calibration check.

The technique is intrinsically more sensitive than the transmissivity method.

The measurement is affected by influences similar to those described for opacity, above.

c) Scintillation

The scintillation detector estimates the particle content of the gas stream by measuring the modulation of the light from passing "gusts" of particles. This technique is not affected by ambient light. Although dependent on the type of particulate, the instrument will nevertheless perform reproducibly in a given application once calibrated against dust sampling. It will operate at lower mass flow applications (ie smaller ducts) than opacity systems.

A2.1.3 Triboelectric

Particles collide with, or pass close to, a metal rod installed across the duct, each event generating a small electric charge which may then be measured by a sensitive amplifier. The characteristic is linear with respect to the number of events per unit time. Variations in gas velocity may therefore affect the measurement and concentration reading.

Instruments require calibration in-situ as there is no tractable theory from which a setting can be derived. The readings are, in principle, affected by changes in dust characteristics and moisture, but in practice readings of the DC type and AC version (TriboACE: PCME

patent) ^{Ref 187} are found to be repeatable in a given application. The technique is now widely used. Installation is straightforward.

As individual particle impacts are detected, the technique is claimed to be well suited to low particulate concentrations.

Insulation resistance must be maintained at a high value and the assembly is affected by condensation.

A2.1.4 Collection with Weighing or Beta Ray Absorption

a) Collection and Weighing

Particulate from the sample is collected, either by deposition on a suitable surface or on a filter, and weighed using a microbalance. In the TEOM technique (Rupprecht and Pataschnick patent), the filter is mounted on the extremity of a thin quartz tube through which the sample is drawn at a controlled rate. The assembly is vibrated at its natural frequency, which falls as the filter mass increases. From accurate frequency measurement the mass collected is calculated continuously and a rolling average output signal corresponding directly to dust concentration is produced.

b) Beta Ray Absorption

A sample is extracted isokinetically from the duct and is passed through the filter. After a pre-set period, the filter is transferred to a beta gauge consisting of a beta ray source and detector. The attenuation of beta radiation is a measure of the quantity of particulate material retained in the filter.

The technique is particularly sensitive to metals. The measurement is affected by variations in sample flow rate and changes in the nature and composition of particulate materials.

A2.1.5 Infra-Red Techniques

a) Non Dispersive Infra-Red Analysis (NDIR)

SO₂, CO, CO₂ and other pollutant gases absorb light strongly at particular wavelengths in the infra-red region. By selecting filters and infra-red sources to include the appropriate wavelengths and exclude others, the concentration of a particular pollutant may be measured by its absorption with minimal cross sensitivity to other species.

Dual beam NDIR analysers (Luft type) use a chopper (rotating shutter) system to route the IR beam alternately through each of two cells, one containing the gas sample, the other containing a reference medium, generally nitrogen gas.

Single beam NDIR analysers incorporate filters on a rotating wheel to pass two different wavelengths through the sample chamber, one wavelength selected to be absorbed by the species of interest, the other not attenuated. By storing the signals and dividing one by the other, the instrument computes the species concentration. The principle is that any contamination will attenuate both wavelengths equally and so have minimal effect on the final measurement.

The Gas Filter Correlation (GFC) technique uses the single-beam principle as above except that the rotating filters include a cell containing the species of interest so that the wavelengths are chosen automatically. Instruments with several filters are available which measure more than one determinand.

In the crossflow modulation method, the sample gas and a reference gas containing a known concentration of the species of interest are introduced in an alternating sequence to a single measurement cell and the difference in output measured.

Extractive and cross-duct versions of NDIR instruments are available.

Water vapour absorbs IR light strongly at many wavelengths, so if moisture is present the sample may need to be extracted by Peltier refrigeration or permeation drying before analysis.

b) Dispersive Infra-Red Techniques (Spectrometry, Spectrophotometry)

In conventional infra-red spectrophotometry the sample is subject to a beam of wide-band infra-red light and the emerging beam is split by a prism or diffraction grating which is rotated, scanning the resulting spectrum across a wide-band detector.

Discrete infra-red spectrophotometry (FTIR) takes the spectrum obtained from conventional spectrophotometry and applies the Fourier transform techniques and correlates the spectrum with (stored) spectra of the species of interest, to yield discrete outputs.

In Differential Optical Absorption Spectroscopy (DOAS) two specific wavelengths are compared. The wavelengths are selected such that one acts as a reference, unaffected by the species present; the other corresponds to an absorption peak of the species of interest.

Tuned Laser Spectrophotometry - a tuned laser is used in place of the conventional prism or grating as the method of wavelength selection. This has the advantage of channelling the full power of the source into the measurement. The resulting spectrum may be subjected to fourier transform analysis discrete wavelengths chosen for DOAS, or a single very precise wavelength selected.

In Photo Acoustic Spectrometry, the sample gas itself forms part of the detector. The sample is irradiated by intense pulses of monochromatic infra-red light. At each pulse, any molecules in the sample that are resonant at the radiation frequency become strongly heated and the sample gas expands rapidly causing an audible "pop" which is detected by a sensitive microphone. The instrument varies the wavelength of the infra-red source and stores the response from the microphone. The stored data is subjected to Fourier transform analysis as in conventional FTIR.

A2.1.6 Ultra-Violet and Visible Light Techniques

a) Ultra-Violet Absorption

The dispersive and non-dispersive techniques described above for infra-red are also applicable to ultra-violet and visible light.

b) Ultra Violet Fluorescence

UV radiation causes the species of interest to fluoresce, emitting light at longer wavelengths.

The discharge lamp and detector generally have filters to restrict the sensitivity to the required wavelengths. Both ND and dispersive techniques may be used. The various gases in the sample stream can interact in a complex way with both the excitation and emitted radiation affecting the measurement (quench effect), so that each application requires calibration with samples of the local matrix.

A2.1.7 Conductometric Analysis

The sample gas stream is contacted with an aqueous solution and compounds of interest dissolve. The solution is treated with a reagent specific to the species of interest and the reaction produces ions, which increase the conductivity of the solution. The instrument computes the quantity of the species of interest from measurements of the conductivity of the liquid before and after reaction.

A2.1.8 Electrochemical Cells

a) Polarographic Cells

The plates of simple electrochemical cells (for example Cu/Zn in H_2SO_4) quickly become depolarised by an insulating layer of gas (H_2), which forms on the electrodes. Molecules such as chlorine, diffusing into the cell from the sample, will react with the gas, depleting the depolarising film, so allowing the cell to generate current.

The technique is not intrinsically selective, but species may be selectively admitted to the cell by choice of appropriate membrane and electrolytes.

Cells of this type were first established in portable instruments, but are now beginning to be used in continuous monitors owing to recent improvements in selectivity, temperature correction, reproducibility and ease of set-up. One needs to rest the cells periodically using fresh air or zero sample gas and to avert any exposure to high concentration to avoid permanent damage. Cells may be used in groups alternately - in use and resting - with periodic automatic calibration checks on standard gases to detect excessive loss of sensitivity.

Because the electrodes are consumed, cells must be replaced periodically. Life in air is specified as two years for a typical cell, but service life is reported to be from 15 months to two years, up to three years in certain cases.

b) Fuel Cells

Dissolved oxygen can be detected by its ability to oxidise an electrode, creating an electric current. A typical cell contains a lead anode and a gold plated porous cathode in an alkaline electrolyte. Oxygen permeates through a protective membrane, enters the cell via the cathode and oxidises the anode, generating a potential proportional to the oxygen partial pressure.

Water is not consumed by the reaction, but where the cell membrane is permeable to water, it may be necessary to humidify the sample gas stream to prevent the cell from drying out.

The *Hersch Cell* has a third electrode to reduce consumption of the cadmium anode. It introduces a non-linearity in the response which is corrected by signal processing.

A2.1.9 Colorimetry

Colorimetry is essentially visible light spectrophotometry, at a selected wavelength or in a band of wavelengths.

Compounds are extracted from the sample gas stream in a bubbler and mixed with reagent. Reaction with the species of interest forms a strongly coloured compound.

The concentration of the compound is then measured using a visible light source and detector. The optics operate at a wavelength at which the compound absorbs most strongly.

To select the required wavelength, the instrument may employ a diffraction grating and lens system (a monochromator) or - at a considerably lower cost - a set of filters.

If the species is present in particulate form, solids are dissolved in acid (hydrolyser stage).

In an alternative method, the colour chemistry reagents are pre-applied to a tape which is moved through the sample stream, then to a light source and photocell for analysis (cf beta ray absorption for particulates (see Section A2.1.4).

A2.1.10 Chemiluminescence

The reaction of ozone with nitric oxide releases visible and infra-red light. A photomultiplier filtered to the 600-900 nm band detects emissions.

The technique is a standard method for NO analysis. Ozone, the only reagent required, is generated from ambient air using radiation from a UV lamp. Any NO₂ in the sample is first converted to NO by being heated in the presence of a catalyst before measurement, and this yields a total NO_x figure. By storing readings while the converter is switched in and out, separate figures for NO, NO₂ and total oxides can be calculated by the instrument.

A2.1.11 Ion Selective Electrodes

See Section A1.2.11.

A2.1.12 FID, PID and Gas Chromatography

a) Flame Ionisation Detector (FID)

Molecules are irradiated by injecting a sample into a flame. Hydrocarbon bonds in the sample are ionised and the resulting charge is collected on an electrode and amplified.

A hydrogen flame is a useful means of ionisation because it contains high-energy atoms but few ions. The presence of as little as 10 picogrammes of a hydrocarbon in a FID will ionise to produce a detectable current.

The current is proportional to the mass of carbon in the sample. To measure concentration, the sample flow must be held constant and the species of interest must be known. In addition to carbon, chlorine and sulphur ions have a (small) effect. Inorganic gases and water have no effect.

b) Photo Ionisation Detector (PID)

In PID, ionisation is by ultra-violet light from a discharge lamp. The cell and detector electrode assembly is different from the FID, but the principle is the same.

Unlike the FID, the PID responds to ionisation potential rather than carbon mass. The sensitivity bears little relationship to the normal classes of chemical compounds but includes amines, halogenated hydrocarbons and large organic molecules. Some selectivity to species of interest can be achieved by choice of UV lamp wavelength. There is no response to N_2 , CH_4 , CN , CO or CO_2 in the sample but inorganic substances such as H_2S can interfere.

c) Gas Chromatography (GC)

The sample gas is diluted and injected into a column filled with a porous solid. As the gas molecules progress through the column the species separate, the larger and more reactive molecules travelling slower than lighter, less reactive, species. At the end of the column, the emerging gas is detected by a FID, PID, katharometer or electron capture device.

When the output is plotted against time, a peak occurs as each species arrives at the detector. The position of the peak identifies the species and the height of the peak indicates the concentration.

Modern instruments measure the position and area under the peaks to obtain a direct output of the concentration of the several species of interest. Sensitivity is high, and response can be optimised by choice of appropriate column and detector and by programming changes to the sequence of operation of the unit.

A2.1.13 Paramagnetic Analysers

When subject to a magnetic field, paramagnetic substances experience a force at right angles to the field (unlike ferromagnetic substance for which the force is parallel).

Oxygen and nitric oxide (NO) are paramagnetic gases. There are three types of oxygen analyser based on the principle:

- a) Magnetic wind type:* the flow of the gas impelled by a strong magnetic field is measured via its thermal effects. Changes in the specific heat and viscosity of sample gas mixture are significant sources of error.
- b) Magnetopneumatic type (Quincke cell):* two pipes are arranged to discharge nitrogen into a sample gas stream. A strong magnetic field across one of the discharge points restrains any oxygen in the sample, impeding the flow from the adjacent pipe. The resulting flow imbalance is detected by differential pressure or thermally as for the thermal wind detector, but because the latter measurement is in pure nitrogen, it is not affected by sample gas properties. A nitrogen source is required.
- c) Magnetodynamic type:* the sample gas stream passes around a sealed dumbbell-shaped armature containing nitrogen suspended in strong magnetic fields. The torque exerted on the dumbbell is proportional to oxygen content. The technique is linear, sensitive and accurate.

A2.1.14 Zirconium Oxide Analysers

A hollow probe of zirconia, heated above 600°C, develops a potential proportional to the difference in oxygen partial pressure between the inside and outside surfaces.

A typical probe assembly for flue gas oxygen measurement has a zirconia tube heated to 850°C, with instrument air fed to the centre to act as a reference gas (23%O₂). The probe is inserted directly in the flue. The potential developed across the zirconia is picked up by electrodes on the inside and outside surfaces of the probe. The response is rapid. Typical accuracy is quoted as 10% in a 100 ppm span.

A2.1.15 Psychrometry

Solid state detectors are the most convenient means of humidity measurement. Moisture is adsorbed by a film (e.g. a porous layer of aluminium oxide) between the plates of a capacitor and the resulting increase in permittivity increases the capacitance of the assembly, which is in turn measured using an ac bridge circuit. Polymer films and salts can also be used in this way. Most detectors are affected in the long term by contamination, so frequent calibration is essential. Change in resistance has also been used as the basis of the measurement.

Dew point may be measured directly by controlling the temperature of a mirror in a sample cell until a film of dew is detected by an optical system. Once confined to the standards laboratory, the technique is now the basis of on-line monitors. These are available at reasonable cost, utilising computer control, low-cost optics and Peltier cooling (no moving parts).

The use of wet-and-dry thermometers for humidity measurement is limited to higher humidity owing to practical problems - chiefly the tendency for the wet bulb wick to dry up and accumulate dirt. The need for pure water is inconvenient.

A2.1.16 X-ray Spectrophotometry

X-rays excite the inner orbitals of electrons in the atom, so may be used as a means of identifying elements in the sample. A beam is passed through the sample (usually in-situ) and wavelengths are separated by using the regular molecular structure of a crystal such as quartz as a diffraction grating. Detection is by the principle of scintillation (fluorescence at optical wavelengths and detection with a photomultiplier). The means of scanning and

analysing the spectrum are similar in principle to those for optical or infra-red spectrophotometry.

X-ray fluorescence spectrophotometry is a highly selective and sensitive variant, in principle well suited to detection of heavy metal atoms. Equipment is available for use off-line for Fe, Cu, Zn, Pb and As, with lower detection limits of 300, 110, 90, 30 and 20 ppm (by weight), respectively.

A2.1.17 Ion Mobility Spectrometry

This is an atmospheric pressure "time-of-flight" spectrometer technique (patented Environmental Technologies Group) applicable to Cl_2 , ClO_2 , HF, HCl, NH_3 . See also Section A.2.2.4.

Sensitivity is claimed to be down to 'ppb levels'.

A2.1.18 Solid State Detectors

The current through certain semiconductors increased when gases adsorbed on their surface. The detector is heated to encourage adsorption and release of the gas. Selectivity is intrinsically poor but may be improved by choice of materials. The response must be linearised.

A2.1.19 Thermal Catalytic Detectors ("Pellistors")

The sample gas stream is passed over a detector consisting of two heated beads, identical, with the exception that one is coated with a catalyst. The catalyst causes combustible compounds in the sample to oxidise, preferentially heating the coated bead. The temperature difference is detected by a bridge circuit, providing a measure of the concentration of the combustible compounds in the sample. A measure of selectivity can be provided by choice of catalysts and coatings.

A2.1.20 Thermal Conductivity (Katharometry)

Certain gases, notably hydrogen, have a thermal conductivity significantly higher than that of air. Their presence can therefore be detected by means of their cooling effect. In its simplest form, a katharometer consists of an assembly heated by a stabilised electrical source, through which the sample stream passes at constant flow and pressure. Resistance thermometers measure the resulting temperature of the device and - as a reference - the temperature of the gas stream.

A2.1.21 Acoustic Measurements

Acoustic transducers mounted externally on ductwork, sensitive to a suitable band of high frequency acoustic noise, may be used to detect the impact of dust particles.

A2.1.22 Gas Flow Measurement

A large range of different types of flow meter applicable to gas flow in a duct or flue is available. The descriptions given below are limited to those types of flow meter most often employed for gas flow measurements in ducts. For more detail, the reader should consult the Shell Flow Measurement Handbook^{Ref 15} or the more recent and more detailed publication BS 7405 (1991).^{Ref 16}

a) Differential Pressure Devices

Differential pressure flow meters operate by obstructing the flow and measuring the resulting differential pressure (DP) developed across the obstruction. The DP increases as the square of the flow. This characteristic makes the readings inaccurate at low flow and the signal is usually "noisy". Whatever technique is used to obstruct the flow, there is always the tendency for dirt to block orifices and impulse piping.

The classical restriction device is the venturi, in which the whole duct is smoothly constricted over a considerable length. This ductwork is expensive to fabricate (and virtually impossible to retro-fit). The advantage is that usefully high pressure drops can be generated and the drop "recovers" downstream so there is no loss of energy.

A Pitot tube is a small open-ended tube facing upstream, inserted in the duct. The differential pressure between this tube and a static tapping point in the duct is measured. Devices of this type are easily blocked by particulate. The measurement is valid only at one point in the cross-section, which may not be representative of total flow.

Devices with multiple ports, usually in the form of a perforated tube extending across the cross-section of the duct - for example the "Annubar" (KDG Mobrey) - obtain an average-differential pressure more representative of total flow, produce a smoother signal and are not so easily blocked.

b) Thermal Dispersion

A probe in the flow stream is heated and its temperature is measured. Heat loss is a function of flow. The fluid temperature is also monitored by the probe and used in the calculation. A steady reading is obtained. The device is fairly resistant to fouling and cleaning is straightforward. The measurement is somewhat dependent on gas characteristics and valid at only one point in the duct cross-section.

c) Time of Flight Method

Flow of gases containing particulate matter can be measured by correlating the output signals from two particulate monitors, one located at a distance downstream of the other. The arrangement effectively measures the time delay between the arrival of random patterns of dust, as they pass first one sensor then the other. There are no moving parts. Dust may be excluded from the lenses by air purge.

A2.1.23 Gas Temperature Measurement

See Section A2.2.21

A2.2 RELEASES TO WATER

A2.2.1 Water Sampling

The basic principle is to extract the sample using enough flow to ensure there is no separation of species, and to provide a means of preserving the sample free from degradation or contamination.

The basic requirements for sampling are set out in ISO5667-10.^{Ref 185} The principal requirements are:

a) Sample Extraction

- the point of extraction must be located such that the inflow is representative of the whole discharge
- The inlet must be designed to prevent blocking or fouling
- Sample stream velocity must be high enough to prevent the separation of suspended solids
- Suction pressure must not be sufficient to draw gases out of solution
- The system must meter the required quantity of sample.

b) Sample Stabilisation

- Sample containers must be protected from contamination before and after filling
- Degradation of the sample must be minimised, if necessary by cooling, and pH adjustment.

c) Pumps

There are two methods of pumping - air pressure method and electrically driven peristaltic

pump. In the former method, air is used to empty a container on a timed cycle and a valve is closed and air propels the sample into a measuring chamber.

Designs of peristaltic pump vary only in the size with flexible tubing arranged in a semi-circle, pressed on by a series of rollers on a circular armature rotated by a motor.

The pump is usually designed with the mechanism open so that it can be checked for proper operation and easily accessed for replacing the tubing.

A2.2.2 Atomic Absorption (AA) Spectrophotometry

A small sample (10 ml) is nebulized into a flame, through which a beam of light is transmitted. A monochromator is arranged to filter the spectral lines of interest and the emerging radiation is measured by a detector. The technique is highly sensitive and selective, down to 0.1 ppm. The instruments are generally automated, scanning the monochromator and analysing the resulting spectra using correlation methods to obtain outputs corresponding directly to species content.

Mercury vapour can be detected in very low concentration by collecting it as an amalgam on gold mesh for periods long enough to accumulate samples in sufficient quantity for AA analysis.

A2.2.3 Atomic Fluorescence Spectrophotometry

This technique is similar to atomic absorption spectrophotometry except that the detector is at right angles to the beam to sense light re-transmitted by atoms in the sample. The method is more sensitive than absorption. Instruments may utilise various modes of re-transmission as follows:

Resonance fluorescence: radiation is re-transmitted at the same frequency as absorption.

Direct line fluorescence: re-transmission occurs at a longer wavelength than the primary transmission. For example, thallium absorbs at 535 nm and re-transmits at 377.6 nm.

Step-wise fluorescence: atoms fall to a state lower than that from which they were raised by the radiation, so emitting at a higher frequency.

Sensitised fluorescence: atoms of interest are energised by interaction with another species. The second species may be introduced into the sample for this purpose.

A2.2.4 Mass Spectrophotometry

The sample is introduced into an evacuated vessel where it is ionised and the ions accelerated to form a beam. The beam is focused via an electrostatic lens and is passed through a magnetic field where it spreads, individual ions being deflected according to their charge/mass ratio. In the classical instrument, a photographic plate records the spectrum but for continuous measurement the magnetic field is varied, scanning the spectrum across a detector.

An alternative arrangement, "time-of-flight" accelerates the ions in a series of fields. The smaller ions travel faster, reaching the detector first. The resulting series of peaks with time generated by the arrival of ions is stored and is amenable to similar means of analysis such as spectrophotometry.

A2.2.5 Photometry

a) Opacity - Turbidity Measurement

A beam of light is projected through the sample to a detector and the attenuation is a direct function of particulate, according to the Lambert-Beer Law.

If an incandescent light source is used, its brightness is monitored by a separate detector and a feedback control system adjusts the lamp supply to hold the emitted power constant.

Contamination of the cell windows is the main problem in practice, necessitating frequent cleaning.

The system is shrouded from ambient light; by pulsing the source or chopping the beam, the effects of stray ambient light are minimised.

b) Scattered Light - Turbidity Measurement

An alternative to the transmission method of determining turbidity is to measure the light scattered by the particulate matter, using a detector positioned at an angle, usually 90° , from the path of the light beam in the sample. The technique is suitable for low levels of suspended solids.

By arranging the light source and detector above an open tank, focused downwards, the measurement may be made without contact with optical windows, eliminating the problem of cell window contamination.

c) IR Reflection - Oil-on-Water Detection

Water absorbs light in the near infra-red region, but an oil film is reflective. The principle is applied to detect an oil film on the surface of water, with an NIR LED source and photodetector installed in a flow assembly. Films as thin as $0.1\mu\text{m}$ are detectable. The output is indicative of oil presence rather than a proportional measurement.

d) UV Fluorescence - Oil-in-Water Detection

Oil droplets fluoresce when irradiated by ultra-violet light. A relatively simple arrangement using a minimum of optical components consisting of a cell with a UV lamp and visible light detector mounted to view a sample through windows set 90° apart.

The response of the instrument is affected significantly by the properties of the oil, the size distribution of the droplets, emulsification effects and turbidity.

e) UV Opacity - Organic Carbon Detection

Ultra-violet light is absorbed by organic molecules. Light of approximately 250 nm is used, chopped with visible light (derived via filters from the same lamp to act as a reference). This

is transmitted through a sample cell and the emerging light is measured by photocells. By selection of filters and sources, the instrument can be arranged to estimate BOD, COD or TOC. The sample cell dimensions must be chosen for sufficient absorbance but not excessive because the characteristics become non-linear above 2AU.

A2.2.6 Infra-Red Spectrophotometry

See section A2.1.5

A2.2.7 Ultra-Violet Spectrophotometry

See section A2.1.6

A2.2.8 Titrimetry

This is the wet chemistry technique in which reagent is added to a pre-treated sample until an end point, such as neutral pH, is detected and the quantity of reagent added is then related to the quantity of determinand in the sample.

A2.2.9 Colorimetry

See Section A2.1.9.

A2.2.10 Conductivity

Inert - precious metal or graphite - electrodes in a stable insulating assembly form the basis of the probe. A constant voltage is applied to the electrodes and the resulting current is measured. The current is linearly related to conductivity. The unit of conductivity is Siemens/cm (formerly mho/cm).

Measurement circuits utilise alternating current to avoid polarisation of the electrodes. The probe will normally incorporate a temperature sensor and the transmitter corrects the conductivity reading to the equivalent at a standard temperature, generally 25°C. The effect of temperature is significant and markedly dependent upon the type of salts in solution.

The electrode-less form of conductivity probe consists of a sealed toroidal coil immersed in the sample. The sample acts as a transformer secondary winding, and current flows in proportion to conductivity. The effect is reflected in the primary winding as a measurable current. The technique is suitable for higher conductivity media in which contamination or corrosion would be a problem for exposed electrodes.

A2.2.11 Voltametry - Selective Ion, pH, Redox

a) Ion-Selective Electrodes

Ion-selective electrodes generate a voltage related to the activity of specific ions in the sample. The characteristic is given by the Nernst equation - voltage increasing logarithmically with ion activity and linearly with temperature. Temperature effects are countered by bringing the sample to a constant temperature, or automatically compensated by the instrument by a temperature sensor included in the electrode assembly.

A typical continuous monitoring arrangement would include several electrodes with a common reference electrode (see below), a sampling system, a temperature-controlled bath and automatic calibration scheme using standard reagents and buffers. Pre-treatment would include filtration to remove particulate. Biocide may be necessary if bacterial growth is a problem.

Activity depends on the form in which the ion is present in the sample, so for the measurement to represent concentration of the species in the sample, the compounds present in the sample must be known.

Ranges in the low ppm region are practicable.

Control systems based on the ion-selective electrode measurements - notably the addition of alkali to control the final pH in waste water - are notoriously difficult to design and set up. This stems from the non-linearity of the Nernst characteristic, making the control action sluggish/ineffective towards the ends of the scale and overactive/unstable near the neutral

point. Modern adaptive controllers with "robust" (unconditionally stable) control algorithms are claimed to have solved this problem.

There are four basic types of ion-selective electrode:

Glass electrodes have a membrane of ion sensitive glass, responding to pH (see "solid state electrodes" below).

Solid state electrodes utilise a crystalline membrane, pressed from a salt containing the element to be measured. Electrodes of this type can be constructed to detect the halogens, cyanide, lead, copper and cadmium.

Liquid-ion exchange electrodes have a membrane of porous hydrophobic material, saturated with an organic ion-exchange material dissolved in an organic solvent. The reservoir had periodically (~monthly) to be recharged with ion-exchange solution. Versions are produced to detect calcium and various divalent ions.

Gas electrodes in which a gas such as ammonia leaves the sample in which it is dissolved and permeates a membrane into a cell, where it is measured by a conventional ion-selective mechanism.

b) pH Electrodes

pH is the most commonly used ion-selective electrode. The assembly consists of a probe containing a buffer solution, at the tip of which is a thin membrane of glass sensitive to hydrogen ions. Connection is by a fine platinum wire to the buffer solution.

The glass membrane is traditionally in the form of a bulb at the end of a plain glass tube but more recently, it has become available in the flush form, installed in the tip of a plastic probe.

Automatic cleaning is usually required - by ultrasound, physical brushing, water jets or air sparging.

The glass membrane is damaged by fluorides if the medium becomes too acidic.

The low potential and very high resistance of the membrane calls for special high-resistance connections and well screened cabling to avoid interference.

An alternative electrode based on antimony is no longer a preferred option. Antimony is environmentally undesirable and has become expensive and difficult to obtain.

c) Redox (ORP) Electrodes

Redox or ORP, the reduction/oxidation potential of a solution, may be measured using an electrode containing a mixture of ferric and ferrous salts. Reducing agents in the solution permeate into the electrode where they convert ferric salts (Fe^{3+}) to ferrous salts (Fe^{2+}). Electrons are released and are picked up by a platinum wire. Oxidising agents in the solution have the reverse reaction, causing the electrode to become positive. As for pH, the characteristic is logarithmic and temperature influences the reading, but the impedance is lower so the signal is handled more easily.

The circuit is completed by a reference electrode (see below). Combined pH and Redox instruments are available with three electrodes - the reference electrode is shared by the two measurement circuits. Provisions for automatic cleaning apply as for pH electrodes, above.

d) Reference Electrodes

All ion-selective electrode systems require a second electrode to make potential-free contact with the sample. Connection to the sample is made via a KCl solution and a porous plug. The traditional arrangement of continually supplying KCl solution to the electrode which is lost by diffusion through the plug, is still used in some application but has been largely superseded by the non-loss version with a high density plug, where the diffusion rate is so low that the electrode is essentially a "consumable". Reference electrodes using calomel have largely been superseded on environmental grounds.

A2.2.12 Voltammetry

a) Fuel Cells (Dissolved Oxygen)

Oxygen in water may be detected by its ability to oxidise a metal. The usual arrangement is the Mackereth electrode, in which the gas diffuses through a silicone rubber membrane into a silver/lead cell with K_2CO_3 as electrolyte. The lead anode is sacrificially oxidised, generating a current in the cell. The membrane is impermeable to water and many interfering ions, so that the electrolyte is not lost or contaminated. Range of use is from 1 mg/litre up to 200% saturation. Temperature correction is essential (the coefficient can be up to $6\%^\circ C$).

b) Voltammetry - Anode Stripping Potentiometry

This is a two-step electroanalytical technique. In the first step-pre-electrolysis-oxidised metal ions are reduced and concentrated in, or on, a hanging mercury droplet electrode or thin mercury film electrode. In the second step, anode stripping, the metal is stripped rapidly from the electrode at an oxidising potential. The resulting current flow is proportional to metal concentration.

The technique is sensitive since metal ions can be accumulated over a period of time before the measurement step.

A2.2.13 Ion Chromatography

A small quantity of the sample is injected into an eluent (a salt solution) which is continuously pumped through a column containing very fine beads of ion-exchange resin. The ions are separated - delayed according to their charge - and are detected as they emerge from the column by a miniature conductivity sensor.

As the conductivity of the eluent is high, the peaks of interest are difficult to resolve. The background conductivity can, however, be greatly reduced by mopping up the eluent salts in a second column (suppressor column) with resin of opposite polarity to that of the separation resin (eg cation, if the separator was anion).

The technique is very sensitive - resolves down to 1 ppb.

A2.2.14 Gas and Liquid Chromatography

a) Gas Chromatography (GC)

See Section A2.1.12.

b) Liquid Chromatography (LC) and High Performance LC (HPLC)

The HPLC variant is the basis of most modern automatic instruments. It is a faster and more reproducible technique than conventional LC. It is suitable for detection of substances in small quantities, although LC is generally not as sensitive as GC.

In LC, the separation medium, the stationary phase is a liquid that coats the surface of finely divided beads packed into an analytical column. The sample in the eluent stream is pumped at high pressure into the system via a pre-column; this saturates the eluent with the stationary phases liquid to avoid stripping the latter from the beads in the analytical column.

Detection of the separated species as they emerge is by UV absorption or, if this does not suit the media, changes in refractive index. The latter requires temperature correction.

A large range of effluents, stationary phase chemicals and eluent materials is available.

A2.2.15 Biochemical Oxygen Demand (BOD)

There are several techniques for BOD determination. All involve the introduction of a seed for a bacterial culture and measurement the oxygen taken up as the bacteria consume the carbohydrates in the sample. Nitrates can affect the measurement. Bacteria vary, the tests take days and are highly dependent upon skilled manual involvement; continuous monitoring is not practicable.

A2.2.16 Chemical Oxygen Demand (COD)

A variant of the reference methods (all skilled manual procedures) is termed CO_2D . In this technique, the sample is injected in a dry CO_2D carrier gas and combusted in the presence of a catalyst where pollutants are oxidised to CO and H_2O . The resulting CO is measured by an NDIR detector.

A2.2.17 Total Oxygen Demand (TOD)

The sample is injected into a nitrogen stream into which a small amount of oxygen is introduced by permeation. The stream is then heated, the water is removed and the stream is then heated again in the presence of a catalyst, when the pollutants are oxidised. After scrubbing, the gas is taken through an oxygen detector of the fuel cell type. The reduction in the trace oxygen level, which occurs after introduction of the sample, is a measure of TOD.

Interference results from the oxygen released when nitrates and sulphuric acid in the sample decompose and the catalyst is impaired by heavy metals ions in the sample.

A2.2.18 Total Organic Carbon (TOC)

Combustion method with NDIR

The sample stream is passed over a catalyst in a heated chamber where the total carbon, inorganic plus organic carbon ($\text{TC}=\text{IC}+\text{TOC}$), is converted to CO_2 . The water vapour is extracted and the gas is taken to an NDIR chamber where TC is determined by measurement at a characteristic CO_2 absorbance wavelength.

The NDIR chamber is then switched to measure a second stream of the sample; this has been routed through a lower temperature vessel containing phosphoric acid, in which only the IC has been converted to CO_2 . TOC is then computed as the difference between the TC and IC readings. Ranges down to 1 ppm are possible.

A2.2.19 Toxicity

Toxicity is estimated by measuring the effect of the sample on the activity of living organisms such as algae, bacteria, daphnia or small fish. A method recently adapted for use on-line (Microbics Corporation) utilises a strain of marine phosphorescent bacteria. A freeze-dried capsule of the bacteria is hydrated and the light emitted is measured before and after introducing the sample. Reduction in light output is taken as a measure of the impairment of the bacteria's metabolism, hence toxicity.

A2.2.20 Liquid Flow Measurement

There are many techniques for flow measurement in water in closed pipes^{Ref 15, 16} and open channels^{Ref 188} so the devices considered here are limited to those considered most convenient and reliable. Electromagnetic and vortex instruments have linear characteristics, stable output and are suitable for use over a large range of flow 5%-100% (20:1 turn-down), compared with traditional DP devices such as orifice plates 33%-100% (3:1 turn-down).

a) Electromagnetic flow meters

A magnetic field is set up across the flow, and the liquid acts as a generator, creating an emf at right angles to the field. The emf is picked up by a pair of electrodes. The magnetic field is set up by coils carrying an alternating or pulsed current; this avoids electrical interference and polarisation of the electrodes. Maintenance is minimal. The pipe must be full. Temperature and conductivity have no significant effect. Insertion type units are available.

b) Vortex flow meters

A trail of vortices is set up by a bluff body in the flow stream. As the flow increases, so does the rate with which the vortices are shed. As each vortex is shed, the disturbance it creates is detected by the instrument. Little maintenance is required. The pipe must be full.

c) Flow Metering Open Channels using a Weir or Flume and Ultrasonic Level Measurement

In a weir or flume the level varies with flow according to well established formulae (BS 3680). Since modern ultrasonic level instruments have comprehensive processing on board to interpret the echoes and calculate level, it is a simple matter for the manufacturer to add the automatic calculation of flow, based on parameters of the weir or flume entered by the user. Maintenance is low and the instrument is clear of the water and easily accessible.

d) Flow metering in Open Channels using a Submersible Flow Sensor

Total flow can be measured by setting a probe at the bottom of the channel; it contains a velocity transducer (ultrasonic Doppler or electromagnetic) and a depth transducer (static pressure sensor). Knowing the shape of the channel, the two measurements are computed to obtain a volume flow reading.

A2.2.21 Temperature Measurement

a) Platinum resistance thermometers (TDSs or Pt100 sensors)

RTDs are accurate. The change of resistance of platinum with temperature is large and linear enough to be corrected accurately by simple means. Accuracy $\sim 0.05^{\circ}\text{C}$.

b) Thermocouples

Thermocouples are generally adopted at temperatures over 200°C ; they are cheaper than RTDs and of sufficient accuracy for most applications at lower temperatures. They require compensation for the temperature of the cold junction and also a linearisation, both of which are relatively straightforward. Accuracy $\sim 0.1^{\circ}\text{C}$.

c) Semiconductor temperature sensors

Accurate semiconductor temperature sensors are now becoming available, after having been regarded for some time with some suspicion as being subject to long-term drift.

Thermocouples and RTDs are supplied installed in standard probe assemblies with the element protected by a stainless steel sheath. The probe is inserted in a thermowell, permanently fixed in the duct or pipe. A "hockey-puck" style 4-20 mA transmitter is often

included in the sensor head junction box to boost the signal, thereby reducing susceptibility to electrical noise.

A2.3 Data Transmission, Processing and Recording Techniques

Whatever type of instrument is chosen for a particular measurement, the options of transmitting, processing and recording the signal are similar. All measurement mechanisms ultimately produce an electrical signal and once in this form, a wide range of products is available for transmitting, monitoring and recording the data.

A2.3.1 Data Transmission

Analogue instruments in the process industries have 4-20 mA analogue outputs to allow signals to be transmitted over a distance without interference (hence the term “transmitters”).

The use of an offset, (the scale beginning at 4 mA rather than zero) allows a broken wire or faults to be detected by the receiving instrument. The use of a current signal rather than a voltage provides much improved immunity to electrical and magnetic interference. It also allows the instrument to be powered from the same pair of wires is used to connect it to the signal (a “2-wire” system). The 4-20 mA option has become the standard in industry in general, although instruments can often also be setup for 0-20 or 1-10 mA, or 1-5V output. Nowadays, instruments will also convert the output signal to digital form and send it by serial link. In many cases, and especially in analytical instruments, the signals already originate in digital format, in which case their conversion to analogue form would only degrade the accuracy of the system. Popular means of digital transmission include:

RS422 and RS485	Serial	Electrically robust proven on plant using differential (bipolar) circuitry. Fast.
RS232(C)	Serial	Conversion to RS422 or RS485 or optical fibre required before running any distance on plant. Moderate speed.

Centronics	Parallel	Intended for short links to printers: not robust enough for field connection plant
HPBus (IEEE488)	Parallel	Intended for laboratory instruments: not robust enough for use on plant.

Optical fibres may be used for transmission especially over long distances, although modern equipment with robust serial connections using good quality screened cable is rarely found to suffer from interference.

There are now serial links specifically suitable for field instrumentation in which both the hardware and the protocol are to an agreed specification. Examples include:

MODBUS	Long-established protocol developed by Modicon (now AEG) for the PLCs, now a popular practical "standard" most companies are able to implement.
Fieldbus	Developed over a long period by an international group of manufacturers. Many potential backers but not many products as yet.
PROFIBUS	A number of mainland European companies, notably Siemens, AEG, Danfoss. Becoming well established.
HART (HART Communications Foundation)	Well established scheme for linking small groups of instruments to allow remote set-up and fault diagnosis using the same connection as the 4-20 mA output. Rosemount and other petrochem-based instrument companies.
Ethernet (IEEE 802.3)	The full spec Ethernet is widely used for PLC networks and is already in use linking instruments with computers in rolling mills.
CAN	Developed for vehicles (Mercedes S-class cars are fly-by-wire using CAN). Has been applied to industrial products but not widely.

DeviceNet

Development of CAN for industrial applications - already a large number of products and much interest in US and Europe. Allen Bradley (now Rockwell), Crouzet and many others. Cable will power the instruments as well as handle communications.

It is now cost-effective for an instrument manufacturers to utilise an established link/protocol, even for a single point-to-point digital link, rather than "re-invent the wheel".

Instruments or systems can be accessed by modem and normal telephone connections allowing remote diagnosis by the manufacturer from his own premises. Remote access to equipment status and data records by regulatory authorities should also be feasible.

A2.3.2 Signal Processing

Custom microprocessor-based circuits as a basis for "intelligent" industrial instrumentation have improved tremendously in terms of reliability, maintainability and general quality in recent years. The incorporation of proprietary products produced in volume helps to improve reliability and eases maintenance.

Although much equipment especially designed for environmental monitoring is available, general purpose data loggers and intelligent variants of chart recorder may be "configured" for the necessary data acquisition, storage, calculation and recording. Basic automation (Level 1) and supervisory (Level 2) systems on sites used for logging may include:

PLCs	Programmable Controllers. A modular computer system adapted specifically for Level 1 industrial control with electrically robust input and output circuitry, simplified programming languages and proven system software.
DCSs	Distributed Control systems. Level 1 systems somewhat similar to PLC systems but handle numerical data and proportional control more easily. Less well suited to sequence control. Expensive. Excellent MMI and configuration facilities.

BMSs	Building Management System for supervising buildings and services. Originally slow but faster, more comprehensive versions have emerged.
SCADA Systems	Supervisory Control and Data Acquisition Systems. Level 2 systems providing comprehensive facilities for all kinds of data acquisition and manipulation, analysis and storage. Also for the preparation of set points and "recipes" for downloading to Level 1. Advanced display facilities but usually too slow to be a satisfactory MMI for shop floor production purposes. Often runs on PC with MS windows. Many on the market but the quality is very variable.
Level 2 Computers	Used for supervision, tracking of items through production, optimisation and maintaining comprehensive records. Generally based on "bespoke" (1-off) software. DEC VAX and more recently DEC ALPHA computers are widely used for this task in the steel industry. Will generally be connected to Level 1 for data acquisition using a network, but may also have their own field data capture units (RTUs).

Where the site process control system is used for data collection, analysis and storage of environmental monitoring data, there is considerable potential for acquiring extensive process information in addition to environmental data.

A2.3.3 Data Storage

For recording data, standard PC cards and 3.5 inch MS_DOS formatted diskettes have become the norm for advanced instrumentation, as has the adoption of PC standard file data formats such as ".DAT" (numerical), ".CSV" comma separated value text) or ".DIF" (data interchange format). These files may be imported directly into spreadsheets or other PC application software for analysis. The media are easily available and cheap.

APPENDIX 3

PRODUCTS FOR MONITORING EMISSIONS

A3.1 GENERAL

The data in this Appendix is arranged as follows:

- A3.2 Products for Monitoring - Emissions to Air
- A3.3 Products for Monitoring - Releases to Water
- A3.4 Products for Monitoring - Loggers and Recorders

All products are characterised by species, in subsections numbered according to the scheme adopted in the Applications section of the report.

A3.2 Products for Monitoring Emissions to Air

A3.2.2 Products for Monitoring Emissions to Air - Particulate Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
BHA International	CPM 500 (Optical scintillation)	Particulate		0.01 mg/m ³ 0-3000 mg/m ³		LED bar-graph	Alarms				Low cost unit specifically for bag leak detection.	
Cassella	APM950 (IR forward scattering)	Particulate (Designed for ambient monitoring)	12	0.01-20 mg/m ³ 0.1-200 mg/m ³ 1-2000 mg/m ³	1 % / °C span 1.5 µg/m ³ zero	LCD	0-2 V	Built-in data logger (PCMCIA card)	Yes, for Grant Squirrel data logger and PCs	Intrinsically safe version	Gravimetric filter available	
Codel	I01D3 (Cross-duct transmissivity)	Particulate	3	0-100 % 0-5 Ringelmann	0.2 % opacity	LCD % Extinction	4-20 mA, Serial data (own protocol) Alarm, Status	IEM Via package	Yes - comprehensive: Codel IEM Integrated Emission Monitoring System	Will be participating in EMCERTS	Rolling average. Diagnostics. Purge air req'd.	
Codel	200 (Cross-duct transmissivity)	Particulate	6	0-0.2 extinction 0-999 mg/m ³	0.2 % opacity	Ringelmann mg/m ³ mg/Nm ³	4-20 mA, Serial data (own protocol) Alarm, Status	IEM Via package	Yes - Codel IEM	Will be participating in EMCERTS	Auto calibration. Purge air req'd.	
Codel	StakGard (DC Triboelectric)	Particulate	0.6	0.1-1000 mg/m ³	Indicative only	None (via Reporter)	4-20 mA via repeater unit	None (separate recorder is available)	Yes - Codel IEM	Low cost unit specifically for bag filter leak detection	New product - aimed at small Metals Industry plant	
Dynoptic	SM-200 (Transmissivity)	Particulate		0-100 %opacity 0-1 Transmiss. 0-3 Log extinct. 0-5 Ringelmann	± 2 %	LCD	4-20 mA RS 232 RS 485					
Dynoptic	DSL-2000 (Scintillation)	Particulate		0.001 mg/m ³ - 9999 mg/m ³			4-20 mA RS 232 RS 485					
Dynoptic	DSL-5000 (Scintillation)	Particulate 8 channel		0.001 mg/m ³ - 9999 mg/m ³			4-20 mA RS 232 RS 485					
Enviro-nics Cerebus	Cerebus P-Watch (Scintillation)	Indicative dust monitor (bag failure alarm)			Indicative only	None	2 relays RS485	None	Not applicable		Upgradable to type PMEM. 2 x light source	
Enviro-nics Cerebus	Cerebus P-MEM (Opacity plus scintillation)	Particulate mass emission meter		0-3000 mg/m ³ 0-100% opacity		Multi-line alpha-numeric	4-20 mA 3 relays RS485 for network	Data logger built in	Yes, comprehensive		Can be connected in network. 2 x light source	

A3.2.2 Products for Monitoring Emissions to Air - Particulate Monitors (Continued)

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Erwin Sick Optic Electronic Ltd	Filter Watch FW 56-D/T Dust Monitor (Cross-duct transmissivity - reflected beam)	Particulate	3.12	0-100 % absolute transmission, 0-100 % dynamic transmission	± 5 % absolute, ± 0.2 % dynamic (resolution)	None	4-20 mA RS232 Alarm and Status			TÜV type approval for bag filter monitoring	Insensitive to contamination of optics in dynamic mode. Portable version available.	Recent product (1995) intended for Foundries, Bag Plants, Galvanisers
Erwin Sick Optic Electronic Ltd	Filter Watch FW 56-I Dust monitor (Cross-duct transmissivity - reflected beam)	Particulate	4	0-100 % trans or opacity, 0-100 % delta transmission, 0.3-2.0 extinct, 0-100 g/m ³	± 2 % absolute, ± 0.2 % differential transmission	LCD	4-20 mA RS232 Alarm and Status, RS485/422 option.	Self contained logger	Up to 5000 measured values and 500 events with time & date	TÜV - 17BlmSchG	Easy to install. Low maint. Insensitive to contamination of optics in differential mode.	Recent product (1995) intended for Foundries, Bag Plants, Galvanisers.
Erwin Sick Optic Electronic Ltd	RM 200 Dust monitor (Cross-duct - scattering)	Particulate	7.6 - but no longer a current model	0-0.1 mg/m ³ to 0-20 mg/m ³		None	2 x 4-20 mA, 4 x relay, RS232, RS422			TÜV	Multiple range operation. Purge blower.	Superseded - but still in use in industry.
Erwin Sick Optic Electronic Ltd	RM 210 Dust monitor (Cross-duct - scattering)	Particulate	8.2	0-0.5 mg/m ³ to 0-200 mg/m ³	± 2 % fsd	None	2 x 4-20 mA, 4 x relay, RS232, RS422			TÜV - TA Luft, 13BlmSchV, 17BlmSchV	Multiple range operation. Purge blower. Options: Remote control, purge air fail shutter.	Recent product (1995) intended for lead and heavy metals plant, after bag filters.
Erwin Sick Optic Electronic Ltd	RM 41 Dust monitor (Cross-duct transmissivity - reflected beam)	Particulate								TÜV		Superseded - but still in use in industry.
Erwin Sick Optic Electronic Ltd	OMD 41 Dust monitor (Cross-duct transmissivity - reflected beam)	Particulate	7.5	0-100 % or 0-50 % opacity, 0-0.3, 0-2 extinction	± 2 % fsd	LCD	4-20 mA, 2 x relay, RS232, RS422			Version 2: US EPA	Version 2 includes zero correction.	Recent product (1995) - for sinter plant, electrostatic precip. monitoring
ETI Group Ltd	Emission SA BETA 5M (Beta gauge ¹⁴ C)	Particulate	20	7 ranges: 0-100 mg/l to 0-10 mg/l		Fluorescent						
ETI Group Ltd	Rupprecht & Pataschnick TEOM 1400A (Filter on microbalance)	Total particulate (Designed for ambient monitoring)	20	very wide range typ 0-1 mg/m ³ for 15 min rolling average		Multi-line LCD	4-20 mA (multiple), RS232, Alarms Status	Data storage built in			Pump, air conditioning, periodic filter change	3 in steel

A3.2.2 Products for Monitoring Emissions to Air - Particulate Monitors (Continued)

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
ETR Ltd	Sigma Quantitative Probe Assembly (DC Triboelectric)	Total particulate	Indic. 2.5 Probe 0.7	0-1000 mg/m ³	± 0.04 mg/m ³ accuracy ± 0.04 mg/m ³ repeatability	Up to 4 channel - large display	4-20 mA (up to four)	Data logger built in	Yes, comprehensive	Will be participating in EMCERTS	Multi-probe Full instal + service support	New product - offered for all applications except multi-velocity stacks
ETR Ltd	Omicron Dust Monitoring System (DC Triboelectric)	Total particulates	Indic. 0.6 Probes 0.6 Chart rec 0.6	0-1000 mg/m ³	Indicative only	Bar-graph	4-20 mA	Chart rec. of Data logger	Yes, comprehensive	Will be participating in EMCERTS	Multi-probe Full instal + service support	Mb - 1 Al - 15 Steel - 4 Iron - 30
ETR Ltd	Alpha (Scintillation) (Note: Omega model no longer produced)	Total particulate	Probes 1.0 Indic. 2.5	0-1000 mg/m ³	± 0.04 mg/m ³ accuracy ± 0.04 mg/m ³ repeatability	Up to 4 channel - large display	4-20 mA (up to four)	Data logger built in	Yes, comprehensive	Will be participating in EMCERTS	Unaffected by fouling. Low maintenance	Al - 15 Steel - 4 Iron - 304
Milltronics	Senaco Plus and CU02 relay unit (Acoustic)	48 Unit	0.48 Unit 0.2 Relay		Indicative only	None	0-10 V Alarms				Easily fitted to exterior of duct/flue	
PCME	Dustalert 80 (AC Triboelectric)	Baghouse Performance	2	0.02 - 1000 mg/m ³	Process Dependent	Digital & Graphic	4-20 mA Alarms RS-232	EPA memory: 600 day x 1h 24h x 30sec	Yes: 'EPA Reporter'		4 channels	New
PCME	Dustalert 25 (AC Triboelectric)	Baghouse Failure	1	0.02 - 1000 mg/m ³	Process Dependent	LED bargraph	Alarm	None			12 channels	New
PCME	DT-770 (AC Triboelectric)	Particulate	3.5	0.02 - 1000 mg/m ³	Process dependent	LCD Digital & Graphic	4-20 mA Alarms RS-232	EPA memory: 600 day x 1h 24h x 30sec	Yes: 'EPA Reporter'	TA Luft CE	4 channels	300+
PCME	SC-600 (Optical scintillation)	Particulate	3.5	2.5 - 10 000 mg/m ³	Process Dependent	Digital & Graphic	4-20 mA Alarms RS-232	EPA memory: 600 day x 1h 24h x 30sec	Yes: 'EPA Reporter'	TA Luft CE	4 channels	10+
PCME	200 i (Optical scintillation)	Particulate	4	2.5 - 10 000 mg/m ³	Process Dependent	Digital & Graphic	4-20 mA Alarms RS-232	EPA memory: 600 day x 1h 24h x 30sec	Yes: 'EPA Reporter'	Ex (CENELEC)		
Rosow Technical	Sigrist KTN "R" (Extractive)	Particulate (toxic metals emission)	45 to 55	0.1-500 mg/m ³	± 2 % of top span	Analog meter	4-20 mA serial		No		Can be used on wet samples ow detection range.	
Skil Controls	Emission Monitor - Opacity (Transmissivity)	- Smoke	1.7 incl. air purge	0-100 %	< 1 %	Digital	4-20 mA Relays RS422 RS485		No	"Complies with BS2811 & BS2740." Intrinsically Safe.	Stack temp 0-950 °C	Scrap Al furnaces Scrap Fe furnaces Steel plants
Skil Controls	Emission Monitor - Particulates (Transmissivity)	Particulate	1.8 incl. air purge	0-999 mg/m ³	< 1% of kinetic sample	Digital	4-20 mA Relays RS422 RS485		No	"Complies with BS2811 & BS2740. US EPA - PG2/4(9) PG2/1(91)" Intrinsic safe	Stack temp up to 950 °C. Stack/duct diameter 6-7 m [sic]	Scrap Al furnaces Scrap Fe furnaces Steel plants

A3.2.2 Products for Monitoring Emissions to Air - Particulate Monitors (Continued)

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Senseco	Sentinel Filter Fail (IR scintillation)	Particulate/dust	0.2 incl. mounting kit	0-1000 mg/m ³	Indicative only	Audible alarm	4-20 mA				24 Vdc powered	UK Iron and Steel: 6

A3.2.3 Products for Monitoring Emissions to Air - Metals Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Perkin Elmer	MERCEM (AA spectrophotometry)	Hg		0-100 µm ³	2 %/month	LCD alphanumeric multi-line	4-20 mA Status				Can share sampling system with MCS100HW multicomponent analyser. Needs air or N ₂ and reagent: 10 l/month	
PS Analytical	PSA 10.525 'Sir Galahad' (Gold collection and UV fluorescence)	Hg		1 picogramme typ 1000 ng/m ³								
Windsor Scientific	Seefolder Messtechnik Hg-Mat 2 (AA Spectrophotometry)	Hg		0-50 µm ³ to 0-1200 µm ³	1 µm ³	CRT	4-20 mA Relays				Auto-zero without relays	

A3.2.4 Products for Monitoring Emissions to Air - Monitors for Combustion Products: CO, CO₂, O₂, NO_x, SO_x

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Anatrol Ltd	M&C PMA-25 (Paramagnetic)	O ₂	4	0-3 % to 0-100% in 4 ranges	1 % f.s.d	Analog Meter or Digital	4-20 mA		No	TÜV	Requires sample system	All industries - numerous applications
Anatrol Ltd	Rosemount Analytical Model 951A (Chemiluminescent)	NO/NO _x		0-10 ppm to 0-10 000 ppm in 7 ranges	~1.5 % f.s.d	Analog Meter	0-5 V		No		Response 1.5s	
Anatrol Ltd	Rosemount BINOS 100 (2-channel NDIR)	CO CO ₂ Hydrocarbons (C ₄ H ₁₀ equiv)		CO and CO ₂ : 0-300 ppm to 0-100 % C ₄ H ₁₀ equiv : 0-500 ppm to 0-100 %	~1.5 % f.s.d	LED	4-20 mA		No			
Blakell Europlacer Ltd	TO 89 Flammable and Toxic Gas Monitor (Electrochemical)	CO H ₂ S SO ₂		0-100 0-1000 ppm	1%/month 0.5 %/°C	LCD		PC Logger Interface to user	Yes			
Bruel & Kjaer	1301 (IR / visible spectrometry)	?	25	Any range 1 ppm	1 %/6 month		4-20 mA RS232 RS485	Diskette	Yes			Total for types 1301 and 1302: Al (freons): 6 Steel (CO): 30
Bruel & Kjaer	1302 (IR / visible spectrometry)	?	12-18	Any range 1 ppm	1 %/6 month		4-20 mA RS232 RS485		Yes	TÜV		See type 1301
Codel	3000 series (Cross-duct NDIR)	CO NO _x SO ₂ HCl Unburnt HCs Ammonia CO ₂ H ₂ O	11	CO, NO _x , SO ₂ and Ammonia: 0-100 ppm to 0-1000 ppm. HCl & unburnts: 0-10 ppm to 0-1000 ppm. CO ₂ and H ₂ O: 0-99 %	± 0.5 %	LCD: ppm, % mg/m ³ mg/Nm ³	4-20 mA, Serial data (own protocol) Alarms, Status	IEM Via package	Yes - comprehensive: Codel IEM Integrated Emission Monitoring System	Will be participating in EMCERTS	Rolling average. Diagnostics. Up to five gases in one unit. Purge air req'd.	
Erwin Sick Optic Electronic Ltd	GM 910 Gas analyser (In-duct NDIR with GFC)	CO	10	0-300 to 0-5000 ppm	± 2 % f.s.d	None	4-20 mA 3 x relay RS232 RS422			TÜV	Purge blower required	Recent product (1993) intended for steelworks power plant

A3.2.4 Products for Monitoring Emissions to Air - Monitors for Combustion Products: CO, CO₂, O₂, NO_x, SO_x (Continued)

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Erwin Sick Optic Electronic Ltd	GM 31 Gas analyser (In-duct NDUV)	SO ₂ NO NO ₂ NH ₃	19 to 37	SO ₂ : 0-100 to 0-30000 mg/m ³ NO : 0-150 to 0-4000 mg/m ³ NO ₂ : 0-100 to 0-4000 mg/m ³ NH ₃ : 0-30 to 0-4000 mg/m ³	± 2 % f.s.d	LCD	4 x 4-20 mA 4 x relay RS232 RS422			TÜV Version: US EPA	Purge blower required	Recent product (1995) intended for power plant associated with metal plants
ETI	Environment SA CO 11M (NDIR)	CO		4 ranges: 0-10 ppm to 0-100 ppm	~1 %	Fluor- escent	4-20 mA RS232	printer			Affected by H ₂ O (5ppm) CO ₂ (15ppm)	
ETI	Environment SA AC 31M (Chemiluminescence)	NO NO _x NO ₂		5 ranges: 0-0.1 ppm to 0-10 ppm	~2 %	Fluor- escent	4-20 mA RS232	printer			Dual version AC20M available	
ETI	Environment SA AF 21M (UV fluorescence)	SO ₂ H ₂ S		5 ranges: 0-0.1 ppm to 0-10 ppm	~1.5 %	Fluor- escent	4-20 mA RS232	printer				
ETI	Environment SA MIR 9000 Multigas (GFC NDIR)	Up to 6 gases: HCl SO ₂ NO/NO _x CO CO ₂ HC		Respectively: 0-60 ppm 0-170 ppm 0-150 ppm 0-30 ppm 0-10 ppm 0-25 ppm as CH ₄	Various	Fluor- escent	4-20 mA RS232C					
ETI	Environment SA MTC 9000 (GFC NDIR)	as MIR 9000 but cross-duct version		Various	Various		4-20 mA RS232C					
Foxboro GB	Maihak MULTOR 610 (Lufi NDIR)	CO SO ₂ NO (many others)		0-200 ppm 0-85 ppm 0-190 ppm (other ranges on request)	~1.5%	LCD + bar chart	4-20 mA RS232C				Controls for automatic zero & test gases & pump	

A3.2.4 Products for Monitoring Emissions to Air - Monitors for Combustion Products: CO, CO₂, O₂, NO_x, SO_x (Continued)

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Foxboro GB	Maihak UNOR 610 (NDIR)	CO SO ₂ NO (many others)		0-20 ppm 0-85 ppm 0-75 ppm (other ranges on request)	~ 1.5%	LCD + bargraph	4-20 mA RS232C - AK protocol			TUV 17.BImSchV (for CO, SO ₂ , NO)	Built in gas sample pump	
Foxboro BG	Maihak UNOR 600 (NDIR)	CO SO ₂ NO (many others)		0-20ppm 0-85ppm 0-75ppm (other ranges on request)	~ 1.5%	meter	4-20 mA			TUV 17.BImSchV (for CO, SO ₂ , NO)	Simple analogue design	
Hartmann & Braun	URAS 4 2 components (NDIR)	CO SO ₂ NO NH ₃ CN H ₂ O	6	ppm: 0-100 CO 0-100 SO ₂ 0-500 NO 0-500 NH ₃ 0-500 CN 0-3 % H ₂ O		LCD	4-20 mA & others RS232C RS422	Any		17.BImSchV (0-75 mg/m ³ CO & SO ₂)	Automatic self-calibration by internal gas filter cell or test gas	
Hartmann & Braun	Optichrom Advance FMR (FT Infrared)		50						"Interdec"		Automatic self-calibration, Remote control	
Hartmann & Braun	URAS 10 up to 4 components (NDIR)	URAS 4 plus O ₂	to 9	10-25 % v/v	~ 3%*		0-20mA & others RS232	Any				
Hartmann & Braun	Magnos 6 (Paramagnetic)	O ₂	5		~ 1.5%*	LCD	4-20mA & others RS232C					
Hartmann & Braun	Magnos 7 (Paramagnetic)	O ₂	4		~ 3%*	LCD	4-20mA & others RS232			TA Luft	NO, NO ₂ interferences	
Hartmann & Braun	Radas 2 (NDIR absorption)	up to 3 components: NO NO ₂ SO ₂ Cl ₂ H ₂ S	9	ppm: 0-75 NO 0-500 NO ₂ 0-100 SO ₂ 0-500 Cl ₂ 0-100 H ₂ S	~ 3%*	LCD	4-20 mA & others RS232C RS 422	Any		17.BImSchV 13.BIm (NO) TA Luft	Automatic self-calibration by internal gas filter cell or test gas	

A3.2.4 Products for Monitoring Emissions to Air - Monitors for Combustion Products: CO, CO₂, O₂, NO_x, SO_x (Continued)

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Hartmann & Braun	URAS 10 (NDIR)	up to 4 components: CO CO ₂ CFCs CH ₄ , C ₂ H ₆ NO	4-9	ppm: 200 CO 100 CO ₂ 100 CFCs 500 CH ₄ , C ₂ H ₆ 1000 NO		LCD	4-20mA & others RS232	Any				
Horiba Instruments	ENDA-1150 (NDIR)	CO		0-25 ppm to 0-5000 ppm		Digital						1 (Japan)
Horiba Instruments	ENDA-1250 (NDIR & Quincke)	CO and O ₂		as ENDA-1150 and -1160		Digital						3 (Japan)
Horiba Instruments	ENDA-1120 (NDIR)	NO _x		0-25 ppm to 0-5000 ppm		Digital						1 (Japan)
Horiba Instruments	ENDA-1220 (NDIR & Quincke)	NO _x and O ₂		as ENDA-1120 and -1160		Digital						3 (Japan)
Horiba Instruments	ENDA-1160 (Paramagnetic - sim. - Quincke)	O ₂		0 or 5-10 % 0 or 10-15 % 0 or 5-25 %		Digital						2 (Japan)
Horiba Instruments	ENDA-1130 (NDIR)	SO ₂		0-100 ppm to 0-5000 ppm		Digital						10 (Japan)
Orbital Gas Systems	Siemens Ultramat 5E	NO SO ₂ CO CO ₂ Ammonia H ₂ O	6 - 16	0 - 100 % Too many to list	1 % full scale	Digital	4-20 mA and digital			EPA TÜV	Low maintenance. High durability. Extreme corrosion resistance.	5 - Steel UK 1 - Al UK 3 - Steel (US/Europe) [SIC]
Orbital Gas Systems	Siemens Oxyamat 5E	O ₂	4 - 14	0 - 100 % Too many to list	1 % full scale	Digital	4-20 mA and digital			EPA TÜV	Low maintenance. High durability. Extreme corrosion resistance.	5 - Steel UK 1 - Al UK 3 - Steel (US/Europe)

A3.2.4. Products for Monitoring Emissions to Air - Monitors for Combustion Products: CO, CO₂, O₂, NO_x, SO_x (Continued)

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Procal Analytics	P200LR (NDIR with GFC)	SO ₂ NO NO _x CO CO ₂ Aramonia H ₂ O	13.6		± 2 % f.s.d		4-20 mA serial (Modbus)			USEPA	Multi-point sampling option	1 Alum. UK 2 Alum US/Europe 1 Alum + 1 Steel Elsewhere
Rotork Analysis	Emirak (extractive with NDIR, Chemiluminescence, FID, zirconia as required)	SO ₂ NO _x THC CO CO ₂ O ₂ H ₂ O	45 (combined analyser -all species)	SO ₂ : 0-100/500 NO _x : 0-100/1000 THC: 0-100ppm and greater CO: 0-100/500 CO ₂ : 0-500/1000 O ₂ : 0-12 %	2 %/day							
SAMC UK	XENDOS 2500 (NDIR, single beam with GFC)	CO CO ₂ NO HCl		0-50 ppm 0-50 ppm 0-200 ppm 0-100 ppm		Digital alphanumeric		Solid state				
Servomex Plc	XENDOS 2510 (Extractive IR with GFC)	CO NO HCl CO ₂		CO: 0-50 ppm & up NO: 0-200 ppm & up HCl 0-100 ppm & up CO ₂ : 0-50 ppm & up	~ 1.5 % < ± 1 %/week	Vacuum fluorescence	4-20 mA 3 x relay Printer				Sampling systems and auto-cal available.	
Servomex Plc	1491 (Chemiluminescent)	NO NO _x optional	5.9	NO: 0-100 ppm 0-1000 ppm 0-2000 ppm others: min 5 ppm up to 0-3000 ppm	1 % f.s.d precision, < 2 %/week	LED	0-5 V 4-20 mA option.			USEPA	Sampling systems and auto-cal available.	

A3.2.4 Products for Monitoring Emissions to Air - Monitors for Combustion Products: CO, CO₂, O₂, NO_x, SO_x (Continued)

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Servomex Plc	700 EX (in-situ zirconia and thermal catalytic)	O ₂ Combustibles		O ₂ : 0-21 % Combustibles: 0-10 % (resoln.0.01%)	~ 0.1 % fsd < 2.5 % rdg ± 5 %	Vacuum fluorosc. 12-char.	2 x 4-20 mA Option: RS232 or RS423				Sampling systems and auto-cal available.	
Servomex Plc	XENTRA 4900 CEM Analyser (IR with GFC & paramagnetic - extractive)	O ₂ CO		O ₂ : 0-25 % CO: 0-200 ppm or 0-3000 ppm	< 500 ppm 500ppm/week 1 % or 2 ppm < 2 %/week	LCD graphic	2 x 4-20 mA 3 x relay RS232				Sampling systems and auto-cal available.	
Signal Instrument Co	2000 M (NDUV - Luft type)	CO	5.3 to 5.9	15 ranges: 0-100 ppm to 0-100 %	~ 1.5 % 1.5 %/day	LED 4-digit & bar-graph	4-20 mA 3 x relay RS232 (rem control)		Yes		Dual-range version available	
Signal Instrument Co	4000 VM (Chemiluminescent)	NO _x	11.5	8 ranges: 0-4 ppm to 0-10 000 ppm	< 1 % or ± 0.2 ppm	LCD multiline alpha-numeric	4-20 mA 3 x relay		Yes		NO ₂ measurement option.	
Signal Instrument Co	8000 M (Dumbbell type paramagnetic)	O ₂	4.1	0-5 % 0-19 % 0-25 %	Linearity < 0.1 % O ₂	LCD multiline alpha-numeric						
Signal Instrument Co	1100 M (Dual beam NDUV - coated Hg lamp)	SO ₂	12.6	0-100 ppm to 0-1000 ppm with sensitivity x1 or x5	~ 1.5 % 2 %/day	LED 4-digit	4-20 mA 3 x relay RS232 (rem control)		Yes		Auto-cal - one span gas reqd. Sampling sys's available.	
Skil Controls	Oxygen Monitor	O ₂	2.2	0.5 - 20.9 %	at 5 %: ≤ ± 0.15 % at > 10 %: ≤ ± 0.3 %	Digital	4-20 mA Alarm relays		No		Up to 550 °C	A number in iron and steel applications
Sysco Analytica Ltd	Bovar Model 920 Compliance Monitor (NDUV - extractive)	SO ₂ NO _x O ₂	55		± 1 %	Digital	4-20 mA RS232 RS485 (Modbus protocol)		No	US EPA Title 40	Hot/wet basis analysis. Hazardous area cert. Integral sampling sys.	
Sysco Analytica Ltd	Bovar Model 922 (NDUV - extractive)	SO ₂ NO NO _x O ₂	16		± 0.5 % typ. 1 % lin & drift	Digital	4 x 4-20 mA RS232 RS485 (Modbus protocol)		No		Requires dry sample	LCP installations and cement plant

A3.2.4 Products for Monitoring Emissions to Air - Monitors for Combustion Products: CO, CO₂, O₂, NO_x, SO_x (Continued)

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Sysco Analytics Ltd	Bovar Models 924 and 925 (NDUV - extractive)	SO ₂ H ₂ S		0-50 ppm to 0-0.5 % (both species)	< 2 % f.s.d	Digital	4-20 mA RS232 RS485 (Modbus protocol)				924: dry-basis 925: wet-basis. Total sulphur option.	
Sysco Analytics Ltd	Bovar Model 910 Mass Emission Monitor (NDUV - extractive)	SO _x NO _x	60	SO _x : 0-300 ppm to 0-1000 ppm NO _x : 0-500 ppm to 0-1000 ppm	± 1 %	Digital	4-20 mA RS232 RS485 (Modbus protocol)		No		Dry analysis & mass flow calculation. Hazard. area cert. Integral sampling sys.	Sulphur recovery and refineries
TQ Environmental	Stackmaster Series (electrochemical cells)	CO O ₂ HCl	13 incl. logging & auto-cal.		2 % range with autocal	VDU, or LCD version	4-20 mA Alarms and Status	Diskette	Included		Calibration gas required 2 cyl/ year	3 woodburning power 1 maritime

A3.2.5 Products for Monitoring Emissions to Air - Hydrogen Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Crowcon	Gas Monitor Gas Master (Pellistor)	H ₂ and other flammable gases				LED	4-20 mA					
Foxboro GB	Maihak THERMOR 615 (Thermal conductivity)	H ₂ NH ₃		0-1% 0-15% (other ranges on request)	~ 1.5%	LFD + bargraph	4-20 mA RS232C - AK protocol					
Hartmann & Braun	Caldos 5 (Thermal conductivity)	H ₂ CO ₂ SO ₂	5	0-3 % H ₂ 0-5 % CO ₂ 0-1.5 % SO ₂	~ 2%*	LCD	RS232C					

A3.2.6 Products for Monitoring Emissions to Air - Chlorine Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Hartmann & Braun	Radas 2 (NDIR absorption)	up to 3 components: Cl ₂ and NO, NO ₂ , SO ₂ , H ₂ S	9	0-500 ppm Cl ₂	~ 3%*	LCD	4-20 mA & others RS232C RS 422	Any		17.BImSchV 13.BIm (NO) TA Luft	Automatic self-calibration by internal gas filter cell or test gas	
Quantitech	ETG StackMaster-IMS (Ion Mobility Spectroscopy)	Cl ₂ in air (also two-channel Cl / ClO ₂ version)		0-100 ppb to 0-200 ppm	Zero: 0.5%/w < 2 %/month Span: 1 %/wk < 5 %/month	Digital	4-20 mA and Alarms				Included: Dilution probe Autocal option. Needs dry inst. air or N ₂	Applications quoted in pulp & paper processes - (Cl ₂ and ClO ₂ versions)

A3.2.7 Products for Monitoring Emissions to Air - Hydrogen Chloride Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Bran + Lubbe	Ecometer HCl, Sensimeter HCl (Ion-selective)	HCl		0-100 mg/m ³	< 5% fsd	Digital, numeric	4-20 mA Option: RS422A			German approval	Requires TSAB and calibration solutions	
CodeL	3000 series (Cross-duct NDIR)	HCl CO NO _x SO ₂ CO ₂ , H ₂ O Unburnt HCs Ammonia	11	HCl & unburnts: 0-10 ppm to 0-1000 ppm.	± 0.5 %	LCD: ppm, % mg/m ³ mg/Nm ³	4-20 mA, Serial data (own protocol) Alarms, Status	IEM Via package	Yes, comprehensive: CodeL IEM Int. Emission Monitoring System	Will be participating in EMCERTS	Rolling average. Diagnostics. Up to 5 gases (1 unit). Purge air req'd	
ETI	Environment SA MIR 9000 Multigas (GFC NDIR)	Up to 6 gases: HCl plus SO ₂ NO/NO _x CO CO ₂ HC CH ₄		Various	Various	Fluorescent	4-20 mA RS232C					
ETI	Environment SA MTC 9000 (GFC NDIR)	as MIR 9000 but cross-duct version		Various	Various		4-20 mA RS232C					
Quantitech	ETG StackMaster-IMS (Ion Mobility Spectroscopy)	HCl and HF in air		0-5 ppm to 0-200 ppm	Zero: 0.5 %/week < 1.5 %/month Span: 2 %/week < 4 %/month	Digital	4-20 mA and Alarms				Dilution probe Options: Autocal. Sample pre-treatment. Needs dry air or N ₂	Applications quoted in pulp & paper processes - (Cl ₂ and ClO ₂ versions)

A3.2.7 Products for Monitoring Emissions to Air - Hydrogen Chloride Monitors (Continued)

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Servomex Plc	XENDOS 2510 (Extractive IR with GFC)	HCl CO NO CO ₂		HCl 0-100 ppm & up	~ 1.5 % < ± 1 %/week	Vacuum fluorescence	4-20 mA 3 x relay Printer				Sampling systems and auto-cal available.	
SAMAC UK	XENDOS 2500 (NDIR single beam with GFC)	HCl plus CO CO ₂ NO		HCl 0-100 ppm		Digital alphanumeric		Solid state				
TQ Environmental	Stackmaster Series (electrochemical)	HCl plus CO O ₂ and others	13 incl. logging & auto-cal.		2 % range with autocal	VDU, or LCD version	4-20 mA Alarms and Status	Diskette	Included		Calibration gas required 2 cyl./year	3 woodburning power 1 maritime

A3.2.8 Products for Monitoring Emissions to Air - Hydrogen Fluoride Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Thermo Electron	Thermo Environmental Insts./Lasair (Tuned laser IR)	HF										One in UK others in Canada
Bran + Lubbe	SensimeterG-HF, Ecometer HF (Ion Selective Electrode)	HF		0-5 mg/m ³	< 5 % f.s.d.	Digital numeric	4-20 mA 2 Relays Option: RS 422A				Requires TSAB and one calibration solution	
Quantitech	ETG StackMaster-IMS (Ion Mobility Spectroscopy)	HCl and HF		0-5 ppm to 0-200 ppm	Zero: 0.5 %/week < 1.5 %/month Span: 2 %/week < 4 %/month	Digital	4-20 mA and Alarms				Included: Dilution probe Options: Autoc-cal Sample pre-treatment. Needs dry instrument air or N ₂	Applications quoted in pulp & paper processes - (CL ₁ and CLO ₂ versions):
Severn Science (Instruments) Ltd	HF Analyser	HF	Probe 1.5 Analyser 17	0-1000 mg/m ³ resolution: 0.5 mg/m ³	± 5 %	Vacuum fluoresc. digital	2 x 4-20 mA RS232 option.	Chart	No			2 in Aluminium

A3.2.9 Products for Monitoring Emissions to Air - Hydrogen Cyanide Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Hartmann & Braun	URAS 4 2 components (NDIR)	CN plus CO SO ₂ NO NH ₃ H ₂ O	6	CN: 0-500 ppm		LCD	4-20 mA & others RS232C RS422	Any		17.BImSchV (0-75 mg/m ³ CO & SO ₂)	Automatic self-calibration by internal gas filter cell or test gas	

A3.2.10 Products for Monitoring Emissions to Air - Hydrogen Sulphide Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Blakell Europlacer Ltd	TO 89 Flammable and Toxic Gas Monitor (Electrochemical)	CO H ₂ S SO ₂		0-100 0-1000 ppm	1% /month 0.5 %°C	LCD		PC Logger Interface to user	Yes			
ETI	Environment SA AF 21M (UV fluorescence)	SO ₂ H ₂ S		5 ranges: 0-0.1 ppm to 0-10 ppm	~ 1.5 %	Fluorescent	4-20 mA RS232	printer				
Hartmann & Braun	Radas 2 (NDIR absorption)	up to 3 components: NO NO ₂ SO ₂ Cl ₂ H ₂ S	9	ppm: 0-75 NO 0-500 NO ₂ 0-100 SO ₂ 0-500 Cl ₂ 0-100 H ₂ S	~ 3%*	LCD	4-20 mA & others RS232C RS 422	Any		17.BImSchV 13.BIm (NO) TA Luft	Automatic self-calibration by internal gas filter cell or test gas	

A3.2.11 Products for Monitoring Emissions to Air - Ammonia Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Erwin Sick Optic Electronic Ltd	GM 31 Gas analyser (In-duct NDUV)	NH ₃ plus SO ₂ NO NO ₂	19 to 37	NH ₃ : 0-30 to 0-4000 mg/m ³	± 2 % f.s.d	LCD	4 x 4-20 mA 4 x relay RS232 RS422			TÜV Version: US EPA	Purge blower required	Recent product (1995) intended for power plant associated with metal plants
Horiba Instruments	ENHA-C900(&1) (conversion to NO then chemi-luminescence)	Ammonia (& optional NO _x)		3 ranges: 0-20 ppm to 0-100 ppm	zero: 1 %/week span: 2 %/week	Digital	4-20 mA and status contacts	Recorder optional			Optional auto-cal, 1-29 days	
Foxboro GB	Maibak THERMOR 615 (Thermal conductivity)	NH ₃		0-1% 0-15% (other ranges on request)	~ 1.5%	LFD + bargraph	4-20 mA RS232C - AK protocol					
Hartmann & Braun	URAS 4 2 components (NDIR)	NH ₃ plus CN H ₂ O CO SO ₂ NO	6	NH ₃ 0-500 ppm		LCD	4-20 mA & others RS232C RS422	Any		17.BlmSch V (0-75 mg/m ³ CO & SO ₂)	Automatic self-calibration by internal gas filter cell or test gas	
Orbital Gas Systems	Siemens Ultramat 5E	Ammonia plus NO SO ₂ CO CO ₂ H ₂ O	6 - 16	0 - 100 % Too many to list	1 % full scale	Digital	4-20 mA and digital			EPA TÜV	Low maintenance. High durability. Extreme corrosion resistance.	5 - Steel UK 1 - Al UK 3 - Steel (US/Europe) [SIC]
Procal Analytics	P200LR (NDIR with GFC)	Ammonia plus CO CO ₂ H ₂ O SO ₂ NO NO _x	13.6		± 2 % f.s.d		4-20 mA serial (Modbus)			USEPA	Multi-point sampling option	1 Alum. UK 2 Alum US/Europe 1 Alum + 1 Steel Elsewhere
Quantitech	ETG StackMaster-IMS (Ion Mobility Spectroscopy)	Ammonia in air		0-5 ppm to 0-20 ppm	Zero: 0.5 %/week <1 %/month Span: 1 %/week < 5 %/month	Digital	4-20 mA and Alarms				Dilution probe. Options: Auto-cal Sample pre-treatment. Needs dry instrument air or N ₂	Applications quoted in pulp & paper processes - (CL ₂ and ClO ₂ versions):

A3.2.12 Products for Monitoring Emissions to Air - Amine and Amide Monitors

No continuous monitoring instruments suitable for the measurement of amines or amides were identified in the survey.

A3.2.13 Products for Monitoring Emissions to Air - VOC Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Applicon UK	ISCO 3500 (Gas Chromatograph)	TC TOC	14	0-50 ppm to 0-10000 ppm	1.5 or 3% typical	LCD	4-20mA RS232C	Logger PC Chart rec.	On request		Sampling (oil, grease and high salt levels must be removed) Carrier gas Filter Skilled install. Housing	Not known
Codel	3000 series (Cross-duct NDIR)	CO NO _x SO ₂ HCl Unburnt HCs Ammonia CO ₂ H ₂ O	11	HCl & unburnts: 0-10 ppm to 0-1000 ppm.	± 0.5 %	LCD: ppm, % mg/m ³ mg/Nm ³	4-20 mA, Serial data (own protocol) Alarms, Status	IEM Via package	Yes - comprehensive: Codel IEM Integrated Emission Monitoring System	Will be participating in EMCERTS	Rolling average. Diagnostics. Up to five gases in one unit. Purge air req'd.	
Crowcon	LGM 29 (Electrochemical)	Landfill Gas Monitor CH ₄ , CO, O ₂		0-20 % CO, CH ₄ 0-25 % O ₂			None		Yes (windows)			
ETI	Environment SA HC 51M (FID)	Total Hydrocarbon		5 ranges: 0-10 ppm* to 0-1000 ppm* *CH ₄ equiv.	~1%	Fluorescent	4-20 mA RS232	printer				
ETI	Environment SA MIR 9000 Multigas (GFC NDIR)	Up to 6 gases: HCl SO ₂ NO/NO _x CO CO ₂ HC CH ₄		Various	Various	Fluorescent	4-20 mA RS232C					

A3.2.13 Products for Monitoring Emissions to Air - VOC Monitors (Continued)

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
ETI	Environment SA MTC 9000 (GFC NDIR)	as MIR 9000 but cross-duct version		Various	Various		4-20 mA RS232C					
Hartmann & Braun	URAS 10 (NDIR)	up to 4 components: CO CO ₂ NO CFCs CH ₄ C ₂ H ₆	4-9	ppm: 100 CFCs 500 CH ₄ C ₂ H ₆		LCD	4-20mA & others RS232	Any				
Foxboro GB	Maihak FIDOR 610 (FID)	THC		0-10 ppm to 0-10% v/v (ref C ₂ H ₆)	~2% of 0-10 ppm	LCD + bargraph	4-20 mA RS232 - isolated - AK protocol				Compreh. fault diagnosis Control of sample line heating.	
Foxboro GB	Maihak TOCOR 200 (Thermal catalytic oxidation)	TOC (POC)		0-3mg/l to 0-10g/l	~2.5%	LCD + bargraph	4-20 mA RS232C				Two concentration-independent ranges. Acidification & sparging	
GLI International	OPAL (PID, 121 nm)	VOCs		Qualitative (alarm)			4-20 mA	Logger or recorder				
Hartmann & Braun	Optichrom Advance (GC)	Many (thermal, FID, PID, flame photometer detectors)	20									
Hartmann & Braun	Compur FID (FID)	TOC	11	0-1 mg/m ³ to 0-100 g/m ³	~3%*	LCD	4-20mA & others		Programmed in "Basic"	TA Luft	NO, NO ₂ interferences	
Horiba Instruments	ENDA-F1000 (FID)	THC		8 ranges: 0-10 ppm to 0-30 000 ppm	1 %/day	LED digital		Recorder optional			Needs hydrogen. Optional auto-cal, 1-9 days	
Pollution & Process Monitoring	JUM3-300 (FID)	HC	10	5 ranges: 0-10 ppm to 0-10 000 ppm or 0-100% LEL	1 - 5 %	LED digital	4-20mA		Yes	TÜV on specific models	Needs hydrogen	1 - Steel

A3.2.13 Products for Monitoring Emissions to Air - VOC Monitors (Continued)

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Rotork Analysis	Emirak (extractive with NDIR, Chemiluminescence, FID, zirconia as required)	SO ₂ NO _x THC CO CO ₂ O ₂ H ₂ O	45 (combined analyser - all species)	THC: 0-100ppm and greater	2 %/day							
Signal Instrument Co	3000 M (FID)	THC	8.6 to 11.3	8 ranges: 0-4 ppm to 0-10 000 ppm	~ 1.5 % 1.5 %/day	LED 4-digit & bar-graph	4-20 mA 3 x relay RS232 (rem control)		Yes		Needs H ₂ or H ₂ /He 60 ml/min	
Servomex Plc	700 EX (in-situ zirconia and thermal catalytic)	O ₂ Combustibles		O ₂ : 0-21 % Combustibles: 0-10 % (resoln.0.01%)	~ 0.1 % fsd < 2.5 % rdg ± 5 %	Vacuum fluorosc. 12-char.	2 x 4-20 mA Option: RS232 or RS423				Sampling systems and auto-cal available.	
Zellweger Analytics	Model 1950 (Oxydation then NDIR)	TC or THC		0-10 ppm up to 0-10000 ppm using optional dilution system	2 % < 2 %/60 days	LED	4-20 mA 3 x alarms RS232 and RS485 option.				Low cost 2 reagents required.	

A3.2.14 Products for Monitoring Emissions to Air - PAH Monitors

No continuous monitoring instruments specific to poly-aromatic hydrocarbon species were identified in the survey.

A3.2.15 Products for Monitoring Emissions to Air - Dioxin Monitors

No continuous monitoring instruments sufficiently sensitive for dioxin or furan measurement were identified in the survey. Automatic sampling systems are available in the UK from Austrian Energy Systems.

A3.2.16 Products for Monitoring Emissions to Air - Oil Mist Monitors

No continuous monitoring instruments for oil mist measurement were identified in the survey.

A3.2.17 Products for Monitoring Emissions to Air - Flow Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Allison Engineering	FCI MT91	Flow of air										
Codel	500 (Passive IR correlation)	Flow (gas in duct)	8	0-1 to 0-50 m/s	±2 % of measurement	LCD: m/s m/s imperial	4-20 mA Serial data (own protocol) Alarm, Status	IEM Vis package	Comprehensive: IEM Integrated Emission Monitoring System	Will be participating in EMCERTS	Rolling average. Diagnostics. Purge air req'd.	
Erwin Sick Optic Electronic Ltd	FLAWSIC 101 (Cross-duct doppler)	Flow of gas	7	up to 0-40 m/s	± 0.4 m/s typ.	LCD - 2-line	4-20 mA 4 x relay RS232 RS422			TÜV		
Erwin Sick Optic Electronic Ltd	VELOS 500 (Cross-duct doppler)	Flow of gas, Temperature	13.8	0-20 m/s to 0-60 m/s	Flow: ± 2 % fsd typ. Temperature: ± 3 °C	LCD - 2 x 20 alpha-numeric	4 x 4-20 mA 4 x relay RS232			TÜV US EPA		
Flowline Manufacturing Ltd	Eldridge Model 8831-CER (Thermal dispersion)	Flow of air	1	0-8 m/s to 0-80 m/s	± 1.5 % rdg. ± 0.5 % fsd	LCD optional	4-20 mA (RS232 on alternative version)			used in US EPA applications. CENELEC (EEExd)	Anti-contamination shield available	UK; approx. 20. USA; many. Others; many - including Germany
KDG Mobrey	Annubar Stackbar	Flow	3.1 incl. DP and temp.	0.1 m/s upwards	1 %	Digital	4-20 mA & HART		Event Min / max	EPA	Ease of installation Auto cleaning option	2 - 5 UK 100+ US 100+ others
KDG Mobrey Ltd	Annubar, Stackbar	Flow of air	4.1	0.1 m/s upwards	1 %	Digital	4-20 mA HART		Event Min & max	EPA	Easy installation Automatic cleaning option	5 in UK 100+ in USA
SAMAC UK	Flowmeter (Thermal dispersion)	Flow of air (Mass flow) and temperature		0.15 to 0-100 m/s	1 % reading					USEPA		

A3.2.18 Products for Monitoring Emissions to Air - Temperature Monitors

Most monitoring products for temperature measurement suit both air and water applications. Examples are listed in Section A2.3.19.

A3.3 Products for Monitoring Releases to Water

A3.3.1 General

These tables are arranged with sub-section numbers to correspond to those of Section 3 - Applications

A3.3.2 Products for Monitoring Releases to Water - Samplers

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Aquamatic	Aqua 10K with Aqua 12x1 (Liquid sampler)	Sampler	2.7	12 glass bottles or 24 plastic bottles							Valve-free design. Sampling on event, time or flow basis. Refrigerated sample storage option	
Pollution & Process Monitoring	Liqui-box AD (Liquid sample - vacuum pressure grab type)	Sampling	1.7 to 3.5 (all options)	Carousel with 30-350 ml bottles		LCD multi-line	RS232	Date & time recording			Backpressure purge. 12/110/240 V selectable. Refig /carousel options. Only weighs 6kg.	
Endress & Hauser	Liqui-box AD (Sampling systems)	Wide range of waste water sampling systems		Composite sample containers up to 24 x 1 litre or 2.5 litre samples				Date & time recording				

A3.3.3 Products for Monitoring Releases to Water - Acidity and Reduction Potential (pH and REDOX) Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
ABB Kent-Taylor	EIL 7976 Series (pH electrode)	pH		Programmable 0-14 pH	± 0.02 pH	LCD	4-20 mA, RS422 (option), Alarms				Multi-component + sampling, auto cleaning with biocide	
Endress & Hauser	CPM 440 + Type A probe (Voltametry)	pH		0 - 14 pH							of probes	
Endress & Hauser	CPM440 (Voltametry)	Redox									and accessories	
Foxboro GB	870ITPH + 871A pH electrode (Voltametry)	pH		0-14	± 0.009 pH	LCD	4-20 mA digital option (own protocol)		Comprehensive in conjunction with Foxboro "I/A" DCS		Comprehensive fault diagnosis. Remote config from PC. Large range of probes and accessories.	
Foxboro GB	870ITPH + 871PH (pH, REDOX, ion-selective electrodes)	pH Redox/ORP Fluoride		0-14 ± 500mV	± 0.009 pH ± 0.5 mV	LCD	4-20 mA digital option own protocol				Comprehensive fault diagnosis. Remote config from PC. Large range of probes and accessories.	
GLI International	pHOX 710 Series	pH	0.55	0-14 pH 2-12 pH	0.5 % (Indicator)	LCD digital or analog	4-20 mA	Separate data logger or chart recorder	Yes			
GLI International	EE720 (Voltametry)	pH		0-14 pH		LCD	4-20 mA	Logger or recorder				
GLI International	pHOX 710 Series	Redox	0.55	0-1000 mV	0.5 % (Indicator)	LCD digital or analog	4-20 mA	Separate data logger or chart recorder	Yes			
GLI International	EE720 (Voltametry)	Redox		±700 mV		LCD	4-20 mA	Logger or recorder				

A3.3.4 Products for Monitoring Releases to Water - Turbidity Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
ABB Kent-Taylor	EIL 7976 Series (optical)	Turbidity		5 ranges: 0-2 NTU to 0-100 NTU		LCD	4-20 mA, RS422 (option), Alarms				Multi-component + sampling, auto cleaning with biocide	
Horiba Instruments	OPSA-120 (UV absorption)	TOC and Turbidity		0-1 AU 0-0.5 AU	± 2 % ± 3 %/day	LCD Digital	4-20 mA & others				COD by inference from industry-specific curve	
GLI International	pHOX 720 (Optical)	Turbidity	1.3, or 2.4 with cleaning	0-1000 FTU	± 5 %	LCD	4-20 mA	Meter				
GLI International	EE720 (Optical)	Turbidity		7 ranges 0-1 mg/l to 0-100 mg/l		LCD	4-20 mA (two)	Logger or recorder				
Partech Instruments	Turbitech 10i & 7100 controller (IR transmissivity)	Turbidity	0.8 excl cleaning	0-400 mg/l to 0-20 000 mg/l (alternatives: g/l, %SS, NTU, FTU, ppm)	± 5 % f/sd	LCD alphanumeric	4-20 mA Alarms				Self-cleaning options	Several in UK steel & non-ferrous plant
Partech Instruments	Turbitech 20i & 7100 controller (IR scattering)	Turbidity	0.8 excl cleaning	0-50 mg/l to 0-500 mg/l (alternatives: g/l, %SS, NTU, FTU, ppm)	± 5 % f/sd	LCD alphanumeric	4-20 mA Alarms				Self-cleaning options	Several in UK steel & non-ferrous plant
Pollution & Process Monitoring	HF Scientific Micro 200 BW (nephelometric light scattering)	Turbidity	2	0-10 NTU to 0-1000 NTU configurable	0-1 : 1% 0-40: 2% 40-100: 5 %	LCD trend graphics	4-20 mA Alarms RS232	Local (1 or 24 h trend only)	Yes	US EPA approved stds	Backpress to remove entrained air. De-humidifier unit prevents condensation in cell. Self cleaning by vortex in cell.	

A3.3.5 Products for Monitoring Releases to Water - Conductivity Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
ABB Kent-Taylor	EIL 7976 Series (conventional electrode conductivity)	Conductivity		Programmable 0 ... 10 mS	± 1 % f.s.d	LCD	4-20 mA, RS422 (option), Alarms				Multi-component + sampling, auto cleaning with biocide	
Endress & Hauser	CLM 121 or CLM 151 (CD) + CL 521 (Conductivity)	Conductivity		0-10 mS/cm 0-20 mS/cm			4-20 mA (2 wire)				large range	
Foxboro	870ITEC 871EC+LB (Electrode-less conductivity)	Conductivity		17 ranges: 0-50 mS/cm to 0-2000 mS/cm	±0.3 %	LCD	4-20 mA digital option own protocol				Comprehen. fault diagnosis. Remote config from PC. Large range of probes and accessories.	
GLI International	PHOX 710 Series	Conductivity	0.45	5 ranges: 0-1 ms to 0-100 ms	0.5 % (indicator)	LCD digital or analog	4-20 mA	Separate data logger or chart recorder	Yes			
GLI International	EE720 (Conductivity)	Conductivity		0-10 000 mS		LCD	4-20 mA	Logger or recorder				

A3.3.6 Products for Monitoring Releases to Water - Dissolved Oxygen Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
ABB Kent-Taylor	EIL 7976 Series (electrochemical cell)	Dissolved oxygen		0-10 ppm 0-20 ppm 0-100 % sat. 0-200 % sat		LCD	4-20 mA, RS422 (option), Alarms				Multi-component + sampling, auto cleaning with biocide	
Endress & Hauser	COM 121 or COM 151 + COS 3 (Electrochem.)	Dissolved oxygen		0-5mg/l			4-20 mA RS485 RS232				Alternative indications for pH control	
GLI International	pHOX 710 Series	Dissolved oxygen	0.9	0-20 mg/l 0-200 %	0.5 % (Indicator)	LCD digital or analog.	4-20 mA	Separate data logger or chart recorder	Yes			
Pollution & Process Monitoring	Contronic MOW11-L2 (Mackareth type)	Dissolved oxygen	1.8	0-200 %sat 0-40 mg/l	0.1 mg/l	LCD multi-line	4-20 mA Contacts including alarm on cell (membrane) failure.		Yes		PTFE membrane. Buffered carbonate electrolyte. Cell can be dismantled on site	

A3.3.7 Products for Monitoring Releases to Water - Hydrocarbon and Oil Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
GLI International	pHOX 500 Oil on water detector (IR reflection)	Oil-on-water	3.25	0.1 mm film	not applicable	LCD digital LED bar-graph	4-20 mA	Meter				
GLI International	pHOX 500 OPAL (PID: 121nm)	Organic solvents	OPAL 12 Pump 1	0-1000 ppb V.O.A.	±10 % or 10 ppb of reading	LCD	4-20 mA & others RS232 RS485	Meter			Calib. with Toluene, uses 100 ml/month	
Ionics	Slikwatch (IR reflective)	Oil-on-water	8	0.1 mm film	not applicable	none	2 Relays (4-20 mA)			CSA explosion-proof	NEMA 4. No contact with sample. Zero maint.	5-6 in UK Metals, ~20 overseas Metals, others in LCPs
Pollution & Process Monitoring	Protoc (Chem oxidation, UV and heat accelerated)	TOC	13 - 15	0-100 ppb to 0-50 000 ppm selectable	2-5 % depending on analyser and application	LCD single- or multi-line	4-20 mA RS232 Contacts	Printer for status and data	Yes	WRC approved	Self clean and auto-cal. Option: forced acid/alk clean. Intelligent adaptive multiplexing up to 6 streams.	
Pollution & Process Monitoring	Protoc 200 (Chem oxidation, UV and heat accelerated)	TOC	8 - 9	0-4000 ppm	5 %	LCD trend graphics	4-20 mA RS232 Contacts		Yes		Low cost version of Protoc with only 2 streams.	New
Pollution & Process Monitoring	Protoc 100 (Chem oxidation, UV and heat accelerated)	TOC	6.5	0-4000 ppm	5 %	LCD trend graphics	4-20 mA RS232 Contacts		Yes		Manual clean and manual cal version. Single stream.	
Pollution & Process Monitoring	DKK ODL-12 (laser visible)	Oil-on-water - also petroleum and kerosene	7 - 10	1 micron film detected - (range depends on oil type)		LCD multi-line	4-20 mA Contacts (hi/lo alarm)				Non-contact Low maintenance. Winch option if level varies > 2m	
Pollution & Process Monitoring	Bristol-Babcock OPM-4 (IR scattering)	Oil-in-water	4 - 5	0-2 ppm 0-40 ppm	5 %	LCD single-line	4-20 mA Contacts		Yes			Designed for marine bilge water applications.
Sysco Analytics Ltd	VAF Oilcon (differential scattering)	Oil-in-water		0-2 ppm to 0-120 ppm	Application and range dependent		4-20 mA Alarms					

A3.3.8 Products for Monitoring Releases to Water - Monitors for Metals

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Applicon UK	AOI 2011 AOI 2011 HD (Titrators)	Acids Metals	10-14	ppm to 100 %	1 %	LCD	4-20mA RS232C	Printer Logger PC Chart Rec.	On request		Water supply Sampling sys. Housing Installation	Used for monitoring, plating/pickling in UK and USA.
Applicon UK	AOI 2013 (Ion selective electrodes)	Cu Cd Pb Ag	10	0-20 ppm to 0-100 ppm	2 %	LCD	4-20 mA or RS232C	Printer Logger PC Chart Rec.	On request		Water supply Sampling sys. (grease and oil must be removed) Housing Installation	
Applicon UK	AOI 2014 (Colorimetry)	Cu Al Fe Cr	11-12	0-5 ppm typical	2-3 %	LED /LCD	4-20mA RS232C	Printer Logger PC Chart Rec.	On request		As above	
Applicon UK	AOI 2015 (Colorimetry)	Cu Al Fe Cr	18-22	0-5 ppm typical	2-3 %	LED /LCD	4-20mA RS232C	Printer Logger PC Chart Rec.	On request		As above	
Dionex	Series 8200 (Ion Chromatography)	Anions Cations Metals Organic compounds	80 - 280			LED	Yes	Industry standard databases Disk	No	US EPA SEMI		None in UK Many in USA
GLI International	pHOX 100 (Colorimetry)	Aluminium Iron Mn PO ₄	Unit 8 Pump 1	0-0.5 mg/l Al 0-1 mg/l Fe others available	±7 % or 0.01 mg/l		4-20 mA (two) RS232 RS485	Meter			Auto calibrates at 6, 12 or 24h intervals. Reagents last ~3 weeks	
Process Measurement and Analysis	Tytronics FPA800 (Ion selective)	Fe Cr and other metals in solution	13	0-5 ppb to 0-100 ppm (depending on type)	2 % of reading	Digital	4-20 mA RS232C	On-board memory	No	USEPA	Complete with sampling systems. Tolerates up to 200 ppm suspended solids without filtration.	(Various industries): 6 - Copper in UK 20 - Fe/Acid in US 2 - Al. in US 2 - Al. Elsewhere

A3.3.8 Products for Monitoring Releases to Water - Monitors for Metals (Continued)

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
PS Analytical	PSA 10.223 (UV fluorescence)	Hg	20	low ppb to ppm region	$\pm 5\%$	Computer printout			Yes 'Touchstone'			(Chemical processing): 3 - UK and Europe
Sartec Ltd	Chemtronics OVA3000 (Anode stripping voltammetry using mercury film)	Sb, Cu, Th, Ag, As, Au, Zn, Bi, Pb, Fe, Cd, Hg, Cr		depends on sample volume: lower det. limit: 10 ppb typ.	reproducibility $\pm 5\%$ of 100 ppb	Vacuum fluoresc. alpha-numeric	4-20 mA Alarms RS232	Diskette			Programmable multicomponent. Needs cal solutions, acids etc. Many avail. accessories	1 UK in Metals 2 UK in other industries
Windsor Scientific Ltd	Analysis BV MM 90 (Anode or cathode stripping voltammetry using mercury droplet*)	Cu, Cd, Pb, Zn (also for As, Co, Cr, Fe, Mn, Mo, Ni, Sn, Ti)		depends on dilution, sensitivity, electrolyte composition: 1 to 10 ppb typ.	Reproducibility: $< \pm 5\%$ linearity: $< \pm 0.5\%$	LCD full screen alpha-numeric and graphics	4 x 4-20 mA Alarms RS232 Optional: RS422/485/Modem	On-board - download by serial link			Programmable multicomponent. Needs cal solutions, acids etc. Many accessories	Used in the Dutch surface-water network since 1983.
Windsor Scientific Ltd	Seefelder Messtechnik Hg-Mat 1 (AA spectrophotometry)	Hg		0-10 µg/l to 0.5 mg/l		Digital	4-20 mA				Requires SnCl ₂ solution	Version for Hg in scrubber water

*Uses CSA and DIN38406 Part 16 standard method of analysis

A3.3.9 Products for Monitoring Releases to Water - Cyanide Monitors

No continuous monitoring instruments suitable for the measurement of cyanides in water were identified in the survey.

A3.3.10 Products for Monitoring Releases to Water - Chloride Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
GLI International	pHOX 600 (ion-selective electrode)	Chlorides	Unit 7.75 Filter 2.25 Pump 1	0-50 mg/l 0-100 mg/l 0-1000 mg/l	$\pm 10\%$ or 0.1 mg/l	Fluorescent digital	4-20 mA	Separate data logger or chart recorder			Auto calibrates at 6, 12 or 24h intervals. Reagents last ~3 weeks	

A3.3.11 Products for Monitoring Releases to Water - Fluoride Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
ABB Kent-Taylor	EIL 8230 Series (Ion-selective electrode)	Fluorides		0-0.1 mg/l to 0-1000 mg/l	$\leq \pm 5\%$	Large fluorescent	4-20 mA, RS422 (option), Alarm and Status				Auto 2-point calibration. 2 reagents required	Numerous as on-line process analysers in chem industry
Foxboro	870ITPH + 871PH (pH, REDOX, ion-selective electrodes)	Fluorides pH Redox/ORP		0-14 ± 500 mV	± 0.009 pH ± 0.5 mV	LCD	4-20 mA digital option own protocol				Compreh. fault diagnosis. Remote config from PC. Large range of probes and accessories.	
GLI International	pHOX 600 (Ion-selective electrode)	Fluorides	Unit 7.75 Filter 2.25 Pump 1	0-2 mg/l	$\pm 10\%$ or 0.1mg/l	Fluorescent digital	4-20 mA	Separate data logger or chart recorder			Auto cal at 6, 12 or 24h intervals. Reagents last ~3 weeks	
Horiba Instruments	FLIA-101 (Ion-selective electrode)	Fluorides		0.1-10 ppm				Recorder optional				

A3.3.12 Products for Monitoring Releases to Water - Nitrate Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
ABB Kent-Taylor	EIL 8230 Series (Ion-selective electrode)	Nitrates		As N : 0-0.2 mg/l to 0-1000 mg/l As -NO ₃ : 0-1 mg/l to 0-5000 mg/l	$\leq \pm 5\%$	Large fluorescent	4-20 mA, RS422 (option), Alarm and Status				Auto 2-point calibration. 2 reagents required	Numerous as on-line process analysers in chem industry
Bran+Lubbe	DiaMon (Ion-selective electrode)	NO ₃ NO ₂		NO ₃ 0-20 mg/l NO ₃ 0-100 mg/l	$< 2\%$ fsd $< 0.1\%$ /day	LCD monitor	0-20 mA 4-20 mA RS232/485	24 h trend display	Yes- AACE, SESAME, InfraNet		Remote control and diagnostics	New product to UK, introduced 1996
GLI International	pHOX 600 (Ion-selective electrode)	Nitrates	Unit 7.75 Filter 2.25 Pump 1	0-50 mg/l 0-100	$\pm 10\%$ or 0.1 mg/litre	Fluorescent digital	4-20 mA	Separate data logger or chart recorder			Auto calibrates at 6, 12 or 24h intervals. Reagents last ~3 weeks	(landfill leachates)

A3.3.13 Products for Monitoring Releases to Water - Phosphate and Thiophosphate Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
ABB Kent-Taylor	EIL 8242 (Colorimeter)	Phosphate		As P : 0-20 mg/l As -PO ₃ : 0-60 mg/l	<± 5 % <± 5 %/month	LCD graphic	4-20 mA, RS485 (option), Alarm and Status				Multi-stream version avail. Reagent required (10 litre/month)	Numerous as on-line process analysers in chem industry
Bran+Lubbe	DiaMon (Ion-selective electrode)	PO ₄		0-6 mg/l	<2 % fsd <0.1 %/day	LCD monitor	0-20 mA 4-20 mA RS232/485	24 h trend display	Yes- AACE, SESAME, InfraNet		Remote control and diagnostics	New product to UK, introduced 1996
GLI International	pHOX 100 (Colorimetry)	PO ₄ plus Al Fe Mn	Unit 8 Pump 1	0-0.5 mg/l Al 0-1 mg/l Fe others available	±7 % or 0.01 mg/l		4-20 mA (two) RS232 RS485	Meter			Auto calibrates 6, 12 or 24h. Reagents last ~3 weeks	

A3.3.14 Products for Monitoring Releases to Water - Sulphate Monitors

No continuous monitoring instruments suitable for the measurement of sulphates were identified in the survey.

A3.3.15 Products for Monitoring Releases to Water - Ammonia Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
ABB Kent-Taylor	EIL 8230 Series (Ion-selective electrode, gas type)	Ammonia		0-0.05 mg/l to 0-1000 mg/l	<± 5 %	Large fluorescent	4-20 mA, RS422 (option), Alarm and Status				Auto 2-point calibration. 2 reagents required	Numerous as on-line process analysers in chem industry
Bran+Lubbe	DiaMon (Ion-selective electrode)	Ammonia		0-20 mg/l	<2 % fsd <0.1 %/day	LCD monitor	0-20 mA 4-20 mA RS232/485	24 h trend display	Yes- AACE, SESAME, InfraNet		Remote control and diagnostics	New product to UK, introduced 1996
GLI International	pHOX 600 (Ion-selective electrode)	Ammonia	Unit 7.75 Filter 2.25 Pump 1	0-5 mg/l 0-10 0-25 0-50 0-100 mg/l	±10 % or 0.1mg/litre	Fluorescent digital	4-20 mA	Separate data logger or chart recorder			Auto calibrates at 6, 12 or 24h intervals. Reagents last ~3 weeks	
Horiba Instruments	AMNA-101 (Ion-selective electrode)	Ammonium compounds		0.01-1 ppm 10-1000 ppm		Analog meter		Recorder optional				
Orbisphere Laboratories	3670 (Reflection spectrometry)	Ammonia		0-16 ppm to 0-60 ppm	50 ppm or 5 % span	LCD	4-20 mA RS485				Needs reagent: 3.5 l monthly	New product August 1996

A3.3.15 Products for Monitoring Releases to Water - Ammonia Monitors (Continued)

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Pollution & Process Monitoring	Contronic AutoAmmonia	Ammonia in water	8	0-0.5 ppm to 0-1000 ppm	2 % of measurement	LCD multi-line	4-20 mA Contacts		Yes - PC and interface card based products for logging		Auto 2-point calibration. <200 mg/l needs no filtration. Compensates sensor temp.	

A3.3.16 Products for Monitoring Releases to Water - Phenol Monitors

No continuous monitoring instruments suitable for the measurement of phenols were identified in the survey.

A3.3.17 Products for Monitoring Releases to Water - Monitors for BOD, COD, TOD and Toxicity

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Bran+Lubbe	DiaMon (UV absorption, 254 nm)	SAC (estimate of oxygen demand)		0-200 mg/l		LCD monitor	0-20 mA 4-20 mA RS232/485	24 h trend display	Yes- AACE, SESAME, InfraNet		Remote control and diagnostics	New product to UK, introduced 1996
GLI International	OPM	BOD		0-2 AU 0-28 mg/l 0-70 mg/l 0-215 mg/l	5 % or 10 % >1.5 AU			Recorder or meter				
GLI International	OPM	COD		0-2AU 0-120 mg/l 0-238 mg/l 0-475 mg/l	5 % or 10% >1.5AU			Recorder or meter				
GLI International	OPM (UV absorption, 254nm)	TOC in water		0-2 AU 0-50 mg/l 0-60 mg/l 0-120 mg/l	5 % (10 % >1.5 AU)			Logger or recorder				
Horiba Instruments	OPSA-120 (UV absorption)	TOC and Turbidity		0-1 AU 0-0.5 AU	± 2 % ± 3 %/day	LCD Digital	4-20 mA & others				COD by inference from industry-specific curve	

A3.3.18 Products for Monitoring Releases to Water - Flow Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
Endress & Hauser	Magphat Flow Monitor (Electromagnetic insertion type)	Water flow in pipes 50 - 300 mm diameter	5.6	0.5 m/s upwards	2 %	None	4-20 mA alarm relay	Via separate PC based SCADA system	Yes comprehensive		Easily retro-fitted	New to market.
Flowline Manufacturing Ltd	Marsh-McBirney Flosystem 253 (Electromagnetic & pressure)	Flow in open channel - additional level output optional	6.5 - 7	0-0.35 m/s to 0-3.5 m/s and reverse: -1.5 m/s	volume flow: ± 3 to 5 % level: ± 1 mm	LCD	4-20 mA RS232 Relay Pulse		Yes		Compensates flow for any shape of channel	New to UK USA : 100+ Others : 100+
Milltronics	OCM III (Ultrasonic level & flow)	Flow of liquid (open channel)		Any (depends on flume or weir)	0.02 % (level)	LCD 3-line alphanumeric	4-20 mA 3 alarms Serial				Remote access via modem Hazardous area cert.	

A3.3.19 Products for Monitoring Releases to Water - Temperature Monitors

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
ABB Kent-Taylor	EIL 7976 Series (RTD)	Temperature		-5 to 40 °C	± 0.5 °C	LCD	4-20 mA, RS422 (option), Alarms				Multi-component + sampling, auto cleaning with biocide	

A3.4 Products for Monitoring - Loggers and Recorders

Company	Instrument Type or Model	Parameter or Substance Measured	Budget Price £ k	Operating Range	Accuracy and Precision	Local Display	Output	Recording Medium	Data Logging Software Availability	Approvals	Special Features or Requirements	Metals Industry Applications
ADC	Advocate (data acquisition system)	RS 232 or RS 485 option for own instruments. Version with 16 analogue inputs.				PC screen	Analogue version: 2 analogue 4 digital	Diskette in CSV format. Live spreadsheet. Printed reports.	Included		Microsoft Windows environment. Requires PC printer.	
Eurotherm Recorders Ltd	Cheasel Model 345 (chart recorder with CEM logging software)	3 channels user configurable: V, mV, t/c, RTD (mA with optional shunt)	2.1	User configurable	0.1% span	100mm chart	4 alarms per channel	Paper (continuous trace)	Included - for reports to satisfy HMIP requirements		Annotation, trace history, range magnify facilities	
Eurotherm Recorders Ltd	Cheasel Model 346 (chart recorder with CEM logging software)	6 channels user configurable: V, mV, t/c, RTD (mA with optional shunt)	1.7	User configurable	0.1% span	100mm chart & vacuum fluoresc. digital		Paper (dotted trace)	Included - for reports to satisfy HMIP requirements		Annotation, trace history, range magnify facilities	
Penny and Giles	Minitrend (chart recorder style intelligent data logger)	2 & 4 channel versions: mA mV t/c Pt100 RTD	2 chan: 1.5 4 chan: 1.8	Very wide range - configurable by user		140 mm back-lit LCD, or CRT. 230 mm option	Serial (Modbus + own protocol download to PC)	Electronic - replay to chart, or serial link	Range of built-in functions including averaging and trending		Plant mounting version. Up to 32 units communicate on multi-drop bus.	Used in numerous IPC monitoring applications
Penny and Giles	Multitrend 628 (chart recorder style intelligent data logger)	6 & 8 channel versions: mA mV t/c Pt100 RTD	6 chan 2.3 8 chan 2.6	Very wide range - configurable by user		150 mm back-lit colour LCD. 230 mm option	Serial (Modbus + own protocol download to PC)	Electronic - replay to chart, or serial link	Range of built-in functions including averaging and trending		Up to 32 units communicate on multi-drop bus.	Used in numerous IPC monitoring applications

APPENDIX 4

COMPANY DATA

Information in this Appendix is arranged as follows:

Table A4.1	Suppliers contacted
Table A4.2	Company data on suppliers
Table A4.3	Suppliers' capabilities for monitoring emissions to air
Table A4.4	Suppliers' capabilities for monitoring releases to water
Table A4.5	Suppliers' techniques for monitoring emissions to air
Table A4.6	Suppliers' techniques for monitoring releases to water

Table A4.1 - Suppliers Contacted

ABB Kent Taylor Ltd	ABB Process Analytics Ltd
Allison Engineering Ltd	Anachem Ltd
Analytical Development Co Ltd	Anatrol Ltd
Applikon Analyzers (UK) Ltd	Aquamatic Ltd
Aztec Environmental Control Ltd	BHA International GmbH
Blakell Europlacer Ltd Gas Det. Div.	Bran & Luebbe (GB) Ltd
Bristol Industrial Research Associates Ltd (BIRAL)	Brueel & Kjaer (UK) Ltd
Ceram Research	City Technology Ltd
Codel International Ltd	Crowcon Detection Instruments Ltd
Dionex (UK) Ltd	Drager Ltd
DynOptic Systems Ltd	Endress & Hauser Ltd
Emission Technology Instrumentation (ETI) Ltd	Enviro Systems Ltd
Enviro Technology Services plc	Envirocon Cerebus Ltd
ETR Ltd	Erwin Sick Optic-Electronic Ltd
Eurotherm Chessel Recorders Ltd	Field Electronics Ltd
Fisher-Rosemount Ltd	Flowline Manufacturing Ltd
Fluid Data Ltd	Foxboro GB Ltd
GLI International Ltd	Graseby Andersen Ltd
Green World Instruments Ltd	Hartmann & Braun (UK) Ltd
HNU Systems Ltd	Hobre Instruments (UK) Ltd
Horiba Instruments Ltd	Ionics UK Ltd
Jenway Ltd	KC Controls Ltd
KDG Mobrey Ltd	Land Combustion
Leeds & Northrup Ltd	M Squared Instrumentation Ltd
Microbics (UK) Ltd	Milltronics
Neotronics Ltd	Octopus Instruments Ltd
Orbisphere (UK) Ltd	Orbital Gas Systems Ltd
Partech Instruments Ltd	PCME Ltd
Penny & Giles Instrumentation Ltd	Perkin-Elmer Ltd
Pollution and Process Monitoring Ltd	Pollution Monitors Ltd
Procal Analytics Ltd	Process Measurement & Analysis Ltd
PS Analytical Ltd	Quantitech Ltd
Rosow Technical Ltd (Sigrist)	Rotork Analysis Ltd
Samac Ltd	Senseco Ltd
Semat Technical (UK) Ltd	Sartec Ltd (Chemtronics)
Severn Science Instruments Ltd	Servomex plc
Skil Controls Ltd	Signal Instrument Co Ltd
Sysco Analytics Ltd	Stepstech Instrument Services Ltd
Thermo Electron Ltd	Teledyne Analytical Instruments
VG (now Fisons) Gas Analysis Systems	TQ Environmental Ltd
Windsor Scientific Ltd	YSI Ltd
Zellweiger Analytics Ltd	

Table A4.2 Company Data

Company Contacts	Principal Activities	Principal Products	Agencies	Test Facils.	Service	QA Cert.	Notes
ABB Kent Taylor Ltd Oldends Lane, Stonehouse, Gloucestershire GL10 3TA <i>Mike C Hall</i> 01453-826-661 01453-826-358	Combine a leading edge product range with more than 100 years experience in water analysis. World leaders in the design and manufacture of instrumentation solutions for industrial process control, gas analysis, flow measurement & environmental applications.	Analytical instrumentation for conductivity, pH, dissolved oxygen, ammonia; fluoride, nitrate, phosphates, silica, sodium; gas analysers for oxygen & binary gas mixtures. Process recorders & controllers, electronic transmitters for pressure & level. Advanced control.	No	Full internal testing facilities including NAMAS accredited flow calibration plant.	Yes, through a network of strategically positioned customer 'assist' centres.	ISO 9001 1987, BS5750 Part 1:1987 and EN 29001 1967. Certificate No.Q5907	Also make systems and packages; also magnetic, turbine & mass flow meters.
ABB Process Analytics Ltd Howard Road, Eaton Socon, St Neots Cambridgeshire PE19 3EU <i>Glen Lancaster</i> 01480-404-440 01480-405-775	Instrument manufacture for the Hydrocarbon Processing Industry (HPI).	Analysers - gas chromatographs, IR and UV spectrophotometers, mass spectrometers.	None	Full equipment at manufacturing site (in USA). Verification checks in UK.	Four service engineers in UK for Europe and E Hemisphere, also busy applications package design group.	ISO9000 in USA ISO9000 applied for in UK.	Parent company is in Louisburg W Virginia.
Allison Engineering Ltd Allison House, Capricorn Centre, Cranes Farm Road, Basildon, Essex SS14 3JA <i>Simon Harwood</i> 01268-523-616 01268-533-144	Instrument manufacture and service.	Manufacturers of thermal dispersion flow meters, infrared gas detectors, flame detection systems, gas monitoring, liquid level and interface controllers, and bursting discs					
Analytical Development Co Ltd Pindar Road, Hoddesdon Herts EN11 0AQ <i>Dr Jim Rutherford</i> 01992-469-638 01992-444-567	Specialises in the design and manufacture of gas analysers and associated equipment for a wide variety of measurements and markets.	Gas analysers, particulate monitors					
Anatrol Ltd Unit 1A, Hampton Heath Ind Estate Hampton Heath Cheshire SY14 8BB <i>IM Muten</i> 01948-820-271 01948-820-282.	Design, fabrication & supply of all types of process analytical systems including stack emissions & furnace gas analysis.	Flue-gas sample system components: Complete flue-gas sample systems, including the analysers: Ultra-Trace gas analysis: High pressure gas reduction sample system.	Anatrol Ltd, AMS GmbH, Bieler & Lang, Collins Products, IN-USA Inc, Madur GmbH - Austria, M&C Instruments BV, M&C Products GmbH, Nippon Sanso, PBI-Dansensor, Trace Analytical, Rosemount Analytical, SKI GmbH	Normal pressure, electrical & analytical testing, oxygen & ozone calibration service.	Yes. Full maintenance of emissions systems.	Proceeding towards EN-ISO 9001.	

A4.4

Company Contacts	Principal Activities	Principal Products	Agencies	Test Facils.	Service	QA Cert.	Notes
Applikon Analyzers (UK) Ltd Farnborough Business Centre, Eelmoor Rd, Farnborough, Hants GU14 7QN Tony Chester 01252-372-303 01252-372-628	Supply & installation/servicing of a range of on-line analysers for the measurement of process & effluent liquids. Also suppliers of laboratory instrumentation.	On-line:- titrators, ion selective electrodes, colorimeters, total organic carbon. Laboratory:- sulphur/halogen analysers.	Euroglas BV - Holland: ISCO - USA	Electrical /mechanical /chemical	Yes, tailored to customer requirements.	Applikon BV submitting for ISO 9001.	
Aquamatic Ltd 12 Greenleach Lane, Worsley, Manchester M28 2RU Peter Smith 0161-790-7468 0161-790-7468	Manufacturers of wastewater sampling systems for industry.	Samplers, collection vessels, ancillaries and consumables					
BHA International GmbH Filtrastrasse 5-7, 59227 Ahlen, Germany Peter Lund 0800-964-984 00-49-2528-30100	Air pollution control products and services.	Continuous particulate monitors by US BHA Group Inc.					
Blakell Europlacer Ltd Gas Detection Div Blandford Heights, Blandford Forum, Dorset DT11 7TE Brian Goddard 01258-451-353 01258-480-183	Design and manufacturer of gas detection equipment.	Own full range of monitors - low cost, up to full rack mounted turn-key systems plus own approved comprehensive sensor range - toxic, flammable plus oxygen	No	QA to ISO 9002 - 1994 (E). Testing to meet SIRA and BASEFA approvals.	Yes. Calibration plus full servicing (Installation also if required).	ISO 9002 - 1994 (E).	
Bruel & Kjaer (UK) Ltd Harrow Weald Lodge, 92 Uxbridge Road, Harrow Middlesex HA3 6BZ Dr T Hoban 0181-954-2366 0181-954-9504	UK company is sales & marketing arm of the Spectris Division of AGIV distributing the Bruel & Kjaer MBM BTG brands.	Gas and liquid chemical monitoring systems. Sound and vibration monitoring. Condition monitoring.	No, however some 3rd party items used in systems	NAMAS Lab at Harrow. Full laboratory facilities in UK & Denmark. Some toxics eg nerve agents are calibrated in Denmark.	Yes. Field service available throughout UK.	ISO in all manufacturing plant.	
Ceram Research Queens Road, Penkhull Stoke on Trent, ST4 7LQ S McQuade 01782-454-431 01782-412-331	R&D in materials based industries. Environmental unit provides emissions monitoring services on a contract basis.	Service sector.	No	Full NAMAS Labs XRF, ICP, XRD, AA.	N/A	NAMAS No. 0013.	
Codel International Ltd Station Building, Station Road, Bakewell Derbyshire DE45 1GE R Horne 01629-814-351 01629-814-619	Manufacture of analysers and systems for continuously monitoring gaseous emissions to atmosphere from a point source.	Continuous flue gas analysis. Continuous measurement of particulate in gas. Data logging and reporting of emissions to atmosphere. Continuous exhaust gas flow measurement. Acoustic pyrometry.	No	Gas laboratory.	Fully trained service engineer for service contracts, & remote diagnostics via MODEM	Quality system being constructed to meet BS EN ISO 9001.	

Companies listed here are those whose products are detailed in the report and who returned the company data questionnaire. Details shown are verbatim as given in the questionnaire returns.

Crowcon Detection Instruments Ltd 2 Blackland Way Abingdon Industrial Estate, Abingdon, Oxon OX14 1DY <i>T J Bird</i> 01235-553-057 01235-553-062	Design, manufacture and sale of toxic and flammable gas detection equipment.	Fixed & portable, toxic & flammable gas detection equipment. Programmable sampling systems for gas monitoring. Combined fire, gas & extinguishant control safety systems.	No	Gas handling facilities to produce gas in air concentrations for calibration purposes.	Yes. Service Manager can provide service contracts for regular routine servicing on equipment.	BS EN ISO 9001-1994 BSI. Design, manufacture, commissioning & servicing of equipment.	
Dionex (UK) Ltd 4 Albany Court, Camberley, Surrey GU15 2PL <i>Roger George</i> 01276-691-722 01276-691-837	Sales, service and training for our products within the UK and Ireland.	Ion chromatography, HPLC and CE systems.	No	N/A	Yes. See customer satisfaction products leaflet.	ISO 9002 SGS 94/3094	
DynOptic Systems Ltd Furlong House, Crowfield, Nr Brackley Northants NN13 5TW <i>John Jones</i> 01280-850-521 01280-850-434		Manufacturers of optical particulate monitors.					
Emission Technology Instrumentation (ETI) Ltd Units 9 CDE, Alstone Lane Industrial Estate, Cheltenham Gloucester GL51 8HF <i>P R Jones</i> 01242-233-330 01242-242-353	Ambient air monitoring, emission monitoring, calibration, portable gas analysis, particulate monitoring & sampling.	Provision of advanced technology products of intrinsically reliable design. Great importance placed on interchangeability of instruments & components to provide most appropriate system for any given purpose.	BIOS International; Enviroincs Inc Environment SA Emission SA PE Photovac Rupprecht & Patashnick Co. Inc.		Maintenance & management contracts	Working towards ISO 9001	
Endress & Hauser Ltd Floats Road Manchester M23 9NF <i>J Salisbury</i> 0161-998-0321 0161-998-1841	Manufacture, supply, application, commissioning and service of industrial instrumentation.	Flowmeters, level equipment, temperature, pressure, water analysis, gas analysis, recorders, samplers, controllers.	Generally not.	Accredited calibration facilities.	Yes, via Service Department at above address	World wide group operates to ISO 9000 QA standards.	
Enviroincs Cerebus Ltd <i>G Tabor</i> 0161-62-2000							
ETR Ltd Unit 15 Apex Business Centre Boscombe Road, Dunstable Beds LU5 4SB <i>P Greening</i> 01582-477-277 01582-477-344	Manufacture of on-line dust meters & monitors. Emissions sampling services. Data acquisition systems.	"Sigma" Dust Meter. "Alpha" Dust Meter. "Omicron" Dust Monitor. "Datalink" - Data Acquisition System. BW Technologies gas detection products. Graseby Anderson probes.	No	All instruments conform to CE Requirements (Heavy Industry) & QA procedures are documented and checked regularly.	Yes. Other services include service contracts, training courses, extended warranties.	The company is working towards BS 5750.	

Erwin Sick Optic-Electronic Ltd Waldkirch House 39 Hedley Road, St Albans Herts AL1 5BN M Taylor 01727-831-121							
Eurotherm Chessel Recorders Ltd Worthing Bill Lamb 01903-205-222	Design, manufacturing, supply, installation and servicing of chart recorders and data acquisition equipment.	Recording and data acquisition equipment including products expressly designed for use in CEM which have been offered for approximately 18 months.	None	NAMAS certified test facilities	Factory and on-site service facilities	BS5750 Part 2.	
Fisher-Rosemount Ltd Heath Place, Bognor Regis West Sussex PO22 9SH G Flischer 01243-863-121							
Flowline Manufacturing Ltd 50 Shenley Road, Borhamwood, Herts WD6 1DS Mark Davies 0181-207-6565 0181-207-3082		Process instrumentation, flow measurement, level control, interface detection.					
Forboro GB Ltd Manor Royal, Crawley, West Sussex RH10 2SJ J Whiting 01293-526-000 01293-541-312	Process control systems.	Electrochemical - pH, conductivity, dissolved O ₂ . Gas chromatography. Gas and liquid emissions.	Yes. Maihak of Hamburg.	Service workshop.	Yes. On demand and maintenance contracts.	ISO 9001.	
GLI International Ltd Eastman Way Hemel Hempstead Herts HP2 7HB Peter Dorling 01442-218-355 01442-229-311	Manufacture, sale & service of (a) civil engineering laboratory equipment. (b) water quality monitoring instrumentation & systems.	b) Analytical instruments & systems.	No, but many items sold are manufactured by others.	Routine post manufacturing testing followed by QA check.	Yes. 5 full time engineers doing routine & emergency maintenance, also service contracts.	BS5750.	Formerly pHox Systems (ELE International Ltd)
Hartmann & Braun (UK) Ltd Moulton Park Northampton NN3 6TF P Batty 01604-646-311 01604-491-027	Analysers and analyser systems.	Infrared, ultra-violet, paramagnetic, thermomagnetic, thermal conductivity, FID analysers; gas chromatographs, FTIR analysers, analyser systems.	No	Test laboratory for H&B analysers /systems.	Yes. We provide service & maintenance contracts to end users.	ISO 9001. Authority = BSI. CertNo. = FM14910.	
Horiba Instruments Ltd Summerhouse Road Moulton Park Northampton NN3 1FL M Best 01604-671-166 01604-671-080	Design and manufacture of analysers, systems and laboratory instrumentation.	Vehicle exhaust emission systems. CEMS. Air quality analysers and stations. Process gas analysers. Particle size distribution.	Rupprecht & Patashnick. Automotive Particulates. STEC: Mass Flow controllers meters, flow monitors	Yes.	Yes. Service contracts for preventative and breakdown. Installation, commissioning, operator training.	ISO 9001.	

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KC Controls Ltd 17 Bell Centre Newton Road, Crawley West Sussex RH10 2UQ Roger Glass 01293-538-940 01293-538-833	Sales and service for the process measurement, control and analysis industries.	On-line / in-line analysis equipment for gases and liquids, process and environmental. Also particulates. Valves, transmitters for pressure, temperature, flow, conductivity, DO etc. Gauges, switches, camera systems, s/ware	Procal A&R Designs Optek PCME PPM Foxboro.	NAMAS calibration facilities available at sister company.	Full maintenance support for all products. 2 full time service engineers and specialists.	ISO 9002.	
KDG Mobrey Ltd 190/196 Bath Road Slough, Bucks SL1 4DN A Norris 01753-534-646 01753-823-589	Instrumentation and controls.	Flow, level and pressure, mechanical & electronic	Yes, Dieteach Standard, USA	Flow rig, pressure testing, pressure transmitter calibration.	Yes, Bestobell Service - Sister Company		
Militronics Karl Bambynek 01905-784-404							
Orbital Gas Systems Ltd Maer Lane Industrial Estate Market Drayton TF9 1QS P Clews 01630-658-123 01630-655-735	Gas analysis systems for emissions and process control. Examples: (1) Sub burden CO/CO ₂ /H ₂ in blast furnace. (2) Post combustion in arc furnaces.	Gas analysers, probes, heated lines, coolers/conditioners, pumps, filters, pipework & electrical systems.	Yes - Siemens, Eco Physics, Bovar, IBSAT, Helisheim, Chandler, Groger and OBST, Victor.	Calibration, repair, testing/evaluation.	Yes. Full product support.	BS EN ISO 9001.	
PCME Ltd Stonehill, Stukeley Meadows Industrial Estate, Huntingdon Cambs PE18 6EL S Werrell 01480-455-611 01480-413-500	Manufacture & supply of continuous particulate emission monitors.	DT770, DT270, DA25, DA80, SC600 particulate monitors.	No	Wind tunnel test loop; in house QA test facilities.	Yes. Dependent on individual contracts	BS5750 applied for.	
Penny & Giles Instrumentation Ltd 4 Airfield Way, Christchurch Dorset BH23 3TS Brian Cole 01202-476-621	Design, manufacture, marketing and servicing of instrumentation products.	Paper-less recorders, pressure transmitters and transducers, point-to-point telemetry systems, bar-graph indicators.	No	NAMAS pressure electronics, humidity, altitude, temp, EMC.	Yes	ISO9000-2.	
Pollution and Process Monitoring Ltd Bourne Enterprise Centre, Borough Green, Nr Severnoaks, Kent TN15 8DG Steven D Tuck 01732-882-044 01732-780-190	Design, manufacture and installation of process instrumentation for the water and wastewater industry, specialising in TOC measurement. Design and supply complete packages including sample acquisition, filtration, data processing and data retrieval.	TOC, Oil-on-water, Oil-in-water, turbidity, ammonia, nitrates, DO (auto-clean, auto-calibrate), pH/Redox, conductivity (5-ring electrode), U/sonic level & flow. Auto sampling, FID for emissions monitoring.	Represent as a UK distributor Contronic, Dev ab, HF Scientific, JUM, DKK, Turo	Use external laboratories as necessary. Own wet chemistry facility.	Yes- team of 5 service engineers and representation in Scotland & N. Ireland & Eire	QA manual but not ISO9000-1 certification. Contronic and HF Scientific have ISO9000.	

Quantitech Ltd Unit 3, Old Wolverton Road Milton Keynes Bucks MK12 5NP Keith Goulding 01908-227-722 01908-227-733	Distributor of environmental and workplace monitoring equipment.	Portable & installed IR gas analysers. Portable & installed FID & dual FID/P11 gas detectors. VOC emission monitors. Ion mobility spectrometers. UV fluorescence UV absorption. IR gas filter correlation, chemiluminescence analyser, laser light scattering.	Foxboro Co, USA. Sensidyne-Gilian, USA. ETG Inc. Pasibi Environmental, USA. Industrial Scientific Corp, USA. EPM, Holland. Umsearch, Canada. Grimm Laboritechmk, Germany. Bermath Atomic, Germany. Rion of Japan.		Yes. We provide a range of tailored maintenance schemes from once a year preventative to comprehensive insurance.	ISO 9002.	
Rosow Technical Ltd (Sigrist) 1 Pembroke Avenue Waterbeach Cambridge CB5 9QR J Kupczak 01223-860-595 01223-861-819	Supplier of on-line photometers /continuous monitors for process control /environmental & policing purposes. All monitors use modern 2 beam chopped design eliminating zero & stray light errors, etc.	KTN'R' extractive system for monitoring 'wet' stacks for particulates. Turbidity, colour, ozone, dissolved organics, nitrate and visibility monitors.	Dyo optics. Range of cross-duct particulate monitors		Yes, via Cambridge based service technicians.	Sigrist Photometer AG are undergoing this exercise at present. Rosow Technical are also considering it.	
Sartec Ltd (Chemtronics) Bourne Enterprise Centre, Borough Green, Sevenoaks Kent TN15 8DG Norman Willis 01732-884-815							
Signal Instrument Co Ltd Standards House 1 Doman Road, Camberley Surrey GU15 3DF J Nicholls 01276-682-841 01276-691-302	Manufacture of gas analysis equipment for combustion research, air pollution compliance monitoring & automotive certification & development.	Model 1100M UV SO2 analyser. Model 2000M series infra-red CO, CO2 analysers. Model 3000 series FID hydrocarbon/VOC analysers, Model 4000 series chemiluminescent NOx analysers, sample conditioning systems.	No.	Calibration and service facility.	Yes. Range of service contracts available including emergency cover.	ISO 9001.	
Skil Controls Ltd Greenhey Place, Skelmersdale Lancs WN8 9SB L Taft 01695-723-671 01695 728-044	Emergency shutdown systems, control valve actuators, emission monitoring equipment, precision engineering, service/repair.		No	Full inspection facilities, incl. pressure, EMC to ISO 9001.	Yes, engineers throughout UK offering service/repair & contracts.	BS EN 9001 : 1994.	
Senseco Ltd Mike Stahand 0171-785-0500 0171-785-0505	Design, manufacture and sales of low-cost environmental monitors.	Sentinel Filter Fail dust monitor.	No				
Sysco Analytics Ltd Broadway Market Lavington, Devizes Wiltshire SN10 5RQ Miss Sue Blattner 01380-818-411 01380-812-733	Engineering, design & manufacture of analyser systems, ranging from a single simple sample system to multiple fitted-out purpose built analyser houses.	Sample systems, analyser houses, sample conditioning components, agents for range of analysers.	Bovar GmbH (Western Research) VAF Inst.	Pressure-containment, wiring cont. /earth bonding /Megger, functional test, others as required.	Yes, as required.	Registered as meeting ISO9000 /EN29001 /BS5750 by SGS Yarsley Int. Certification Services Ltd.	

Companies listed here are those whose products are detailed in the report and who returned the company data questionnaire. Details shown are verbatim as given in the questionnaire returns.

Thermo Electron Ltd 910 Birchwood Boulevard Birchwood, Warrington Cheshire WA3 7QN <i>Colin Craggs</i> 01223-374-234			Agents for Canadian Laser FTIR equipment.				
TQ Environmental Ltd Flanshaw Way, Wakefield West Yorkshire, WF2 9LP <i>P Luen</i> 01924-380-700 01924-361-700	Design, manufacturing, supply installation and servicing of gas monitoring systems.	RPB600E range of continuous emissions monitoring systems. RPB120/122 range of flameproof toxic & flammable gas sensors. RPB4000/800 range of control equipment. RPB sequential sampling systems.	Yes, Compur Monitors (Germany) range of intrinsically safe gas sensors. GD100MkII Simrad Optronics (Norway) - infra-red hydrocarbon sensor.	Research and development department.	Yes, we have a team of highly qualified service engineers. The service function is encompassed in our ISO 9001 accreditation.	ISO 9001 - 1994 certified by ABS Quality Evaluations Ltd.	
VG (now Fisons) Gas Analysis Systems Aston Way, Holmes Chapel Rd Middlewich Cheshire CW10 0HT <i>Mrs K Hines</i> 01606-834-731							
Windsor Scientific Ltd 854 Plymouth Road Slough Trading Estate Slough, Berkshire SL1 4PL <i>Dr Keith Dawes</i> 01753-696-139 01753-696-208							

Table A4.3 Manufacturers' Capabilities For Continuous Monitoring of Emissions to Air

	Particulate matter	Metallic fumes	Mercury vapour	Water vapour	Oxygen	Carbon monoxide	Oxides of sulphur	Oxides of nitrogen	Hydrogen chloride	Hydrogen cyanide	Hydrogen fluoride	Hydrogen sulphide	Hydrogen	Chlorine	Ammonia	Amines and amides	Total Hydrocarbons	VOCs	Dioxins	PAHs	Flow rate	Temperature
ABB Kent Taylor Ltd					X																	
ABB Process Analytics Ltd						X	X	X	X			X		X	X		X					
Acal Auriema Ltd				X	X	X	X	X	X	X	X	X	X	X	X		X	X		X	X	
Allison Engineering Ltd																					X	X
Anatrol Ltd	X				X	X	X	X	X	X	X	X	X	X	X		X				X	X
BHA International GmbH (PCM)	X																					
Blakell Europlacer, Gas Det.Div					X	X	X	X	X	X	X	X	X	X	X		X					X
Bruel & Kjaer (UK) Ltd	X			X		X	X		X	X		X				X	X	X	X	X		X
Codel International Ltd	X	X			X	X	X	X	X							X					X	X
Crowcon Detection Insts. Ltd					X	X	X	X	X	X		X	X				X					
Dionex (UK) Ltd							X	X	X	X	X	X				X	X		X	X		
DynOptic Systems Ltd	X																					
Emission Tech.Inst'n (ETI) Ltd	X			X	X	X	X	X	X	X		X		X	X		X	X		X	X	X
Endress & Hauser Ltd					X			X	X	X	X			X	X						X	X
Environmental Tech. Research Ltd	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Fluid Data Ltd	X					X	X	X				X					X	X				
Foxboro GB Ltd	X			X	X	X	X	X				X	X				X	X		X		X
GLI International Ltd							X					X	X				X	X				
Hartmann & Braun (UK) Ltd				X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X		
Horiba Instruments Ltd					X	X	X	X				X			X		X	X				
KC Controls	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X	X
KDG Mobrey Ltd																					X	X
Octopus	X			X	X	X	X	X	X			X		X	X		X	X			X	X
Orbital Gas Systems Ltd	X			X	X	X	X	X	X	X	X	X	X		X		X	X		X		X
PCME Ltd	X				X																	
Procal Analytics Ltd			X	X		X	X	X	X		X	X		X	X			X				X
Process Meas. & Analysis Ltd							X	X				X		X								
PS Analytical Ltd			X																			
Quantitech Ltd	X		X			X	X	X	X	X	X	X		X	X	X	X	X		X		
Rotork Analysis Ltd	X			X	X	X	X	X	X		X				X		X	X		X		
Samac Ltd		X			X	X		X	X	X	X	X	X		X	X	X		X	X	X	X
Semat Technical (UK) Ltd																						
Senseco Ltd	X																					
Servomex plc				X	X	X	X	X	X	X				X	X	X	X	X				
Severn Science Instruments Ltd							X	X	X		X				X							
Signal Instrument Co Ltd					X	X	X	X							X		X	X				
Sigrist Photometer (LancerUK) Ltd	X						X															
Skil Controls Ltd	X				X																	X
Sysco Analytics Ltd					X		X	X				X									X	X
Testo Ltd					X	X	X	X													X	X
Thermo Electron Ltd																						
TQ Environmental Ltd	X			X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X

Source: Manufacturers' responses to survey questionnaire

Table A4.4 Manufacturers' Capabilities For Continuous Monitoring of Releases to Water

	Sampling	Suspended solids	Turbidity	Dissolved oxygen	Biological oxygen demand	Chemical oxygen demand	Total Organic Carbon	Oil and hydrocarbons	Conductivity	pH	Aluminium	Cadmium	Mercury	Iron	Copper	Chromium	Other heavy metals	Ammonia	Chlorides	Cyanides	Dioxins	Fluorides	Nitrates	Phenol	Sulphates and thiosulphates	Water treatment chemicals	Flow rate	Level	Temperature
ABB Kent Taylor Ltd			X	X					X	X								X	X			X	X				X		X
ABB Process Analytics Ltd							X																						
Acal Auriema Ltd		X	X	X				X	X	X																	X		
Allison Engineering Ltd																											X		X
Anatrol Ltd				X			X	X	X	X																			
Applikon Analyzers (UK) Ltd							X				X	X		X	X	X	X	X	X	X		X	X	X	X	X			
Aquamatic Ltd	X																												
Brüel & Kjær (UK) Ltd							X																	X					X
Dionex (UK) Ltd									X			X	X	X	X	X	X	X	X	X		X	X	X	X				
Endress & Hauser Ltd		X	X	X					X	X																	X		X
Fluid Data Ltd							X	X		X																			
Foxboro GB Ltd				X			X		X	X								X					X				X		X
GLI International Ltd			X	X	X	X	X	X	X	X	X						X	X	X			X	X						X
Horiba Instruments Ltd			X	X				X	X	X																			
KC Controls Ltd		X	X	X		X	X	X	X	X			X	X				X	X	X		X	X	X	X		X		X
KDG Mobrey Ltd		X																									X		X
Octopus		X	X	X	X	X	X	X	X	X																	X		X
Partech Instruments Ltd		X	X																										
Procal Analytics Ltd													X																
Process Meas. & Analysis Ltd		X	X	X				X	X	X	X	X			X	X	X	X	X	X		X	X	X	X				
PS Analytical Ltd													X																
Quantitech Ltd							X				X			X	X	X													
Samac Ltd																		X	X		X		X		X		X		X
Sigrist Photometer (LancasterUK)		X	X				X									X													
Skil Controls Ltd																													
Sysco Analytics Ltd							X																						
Testo Ltd									X	X	X					X	X	X	X				X						X

Source: Manufacturers' responses to survey questionnaire

Table A4.5 Suppliers' Techniques For Continuous Monitoring of Emissions to Air

	Sampling / Conditioning	Opt. transmissivity	Triboelectric	Beta gauging	Opt. scintillation	ND IR	GFC IR	Cross-duct IR	Dispersive IR	FTIR	UV fluorescence	Cross-duct UV / visible	Chemiluminescence	Sevective ion	Colorimetry	Gas Chromatography	FID	PID	IC/HPLC	Ion mobility spectrometry	Zirconia probe	Paramagnetic	Electrochemical cells	Katharometer	Catalytic ("Pellistor")
ABB Kent Taylor Ltd																									
ABB Process Analytics Ltd																									
Acal Auriema Ltd																									
Anatrol Ltd																									
BHA International GmbH (PCM)																									
Blakell Europlacer Ltd, Gas Det.Div																									
Bruel & Kjaer (UK) Ltd																									
Codel International Ltd																									
Crowcon Detection Instruments Ltd																									
Dionex (UK) Ltd																									
DynOptic Systems Ltd																									
Emission Tech. Instr. (ETI) Ltd																									
Environmental Tech. Research Ltd																									
Erwin Sick Optic-Electronic Ltd																									
Fluid Data Ltd																									
Foxboro GB Ltd																									
GLI International Ltd																									
Hartmann & Braun (UK) Ltd																									
Horiba Instruments Ltd																									
KC Controls Ltd																									
KDG Mobrey Ltd																									
Octopus																									
Orbital Gas Systems Ltd																									
PCME Ltd																									
Procal Analytics Ltd																									
Process Measurement & Analysis Ltd																									
PS Analytical Ltd																									
Quantitech Ltd																									
Rotork Analysis Ltd																									
Senseco Ltd																									
Servomex plc																									
Severn Science Instruments Ltd																									
Signal Instrument Co Ltd																									
Sigrist Photometer (LancasterUK) Ltd																									
Skil Controls Ltd																									
Sysco Analytics Ltd																									
TQ Environmental Ltd																									

Source: Manufacturers' responses to survey questionnaire

Table A4.6 Suppliers' Techniques For Continuous Monitoring of Releases to Water

	Atomic Absorption	Atomic Fluorescence	Atomic Emission	Mass Spectrometry	IR Spectrophotometry	X-Ray Fluorescence	UV Spectrophotometry	Polarography	Ion Chromatography	Gas Chromatography	Liquid Chromatography	Titrimetry	Ion-Selective Electrodes	Voltammetry	Colorimetry	Gravimetry	Amperometry	Other
ABB Kent Taylor Ltd																		
ABB Process Analytics Ltd																		
Applikon Analyzers (UK) Ltd																		
Aquamatic Ltd																		
Bruel & Kjaer (UK) Ltd																		
Dionex (UK) Ltd																		
Fluid Data Ltd																		
Foxboro GB Ltd																		
GLI International Ltd																		
Hartmann & Braun (UK) Ltd																		
KC Controls Ltd																		
KDG Mobrey Ltd																		
Octopus																		
Procal Analytics Ltd																		
Process Meas. & Analysis Ltd																		
PS Analytical Ltd																		
Quantitech Ltd																		
Sigrist Photometer (LancerUK) Ltd																		

Source: Manufacturers' responses to survey questionnaire

MANAGEMENT AND CONTACTS:

The Environment Agency delivers a service to its customers, with the emphasis on authority and accountability at the most local level possible. It aims to be cost-effective and efficient and to offer the best service and value for money.

Head Office is responsible for overall policy and relationships with national bodies including Government.

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For general enquiries please call your local Environment Agency office. If you are unsure who to contact, or which is your local office, please call our general enquiry line.

ENVIRONMENT AGENCY GENERAL ENQUIRY LINE

0645 333 111

The 24-hour emergency hotline number for reporting all environmental incidents relating to air, land and water.

ENVIRONMENT AGENCY EMERGENCY HOTLINE

0800 80 70 60



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