Interim Report R&D Project 427

Equipment for Monitoring Alternatives to Biochemical Oxygen Demand and Suspended Solids

WRc plc
December 1992
R&D 427/1/HO

EQUIPMENT FOR MONITORING ALTERNATIVES TO BIOCHEMICAL OXYGEN DEMAND AND SUSPENDED SOLIDS

E Hatton

Research Contractor:
WRc plc
Henley Rd Medmenham
PO Box 16 Marlow
SL7 2HD

National Rivers Authority
Rivers House Waterside Drive
Almondsbury Bristol BS12 4UD

NRA Interim Report 427/1/HO

National Rivers Authority
Rivers House Waterside Drive
Almondsbury Bristol BS12 4UD
Tel: 0454 624400
Fax: 0454 624409

This report is the result of work jointly funded by the National Rivers Authority and the Scotland and Northern Ireland Forum for Environmental Research

Dissemination status
Internal: Restricted
External: Restricted

Research contractor
This document was produced under R&D Contract 427 by:
WRc plc
Henley Rd Medmenham
PO Box 16 Marlow
SL7 2HD
Tel: 0491 571531
Fax: 0491 579094

WRc Report Nº NR 3261/7058

NRA Project Leader
The NRA's Project Leader for R&D Contract 427:
Terry Long - Headquarters Region

Additional copies
Further copies of this document may be obtained from Regional R&D Co-ordinators or the R&D Section of NRA Head Office.

CONTENTS

		Page
LIST OF TABLES		ii
EXECUTIVE SUMMARY		1
KEY WORDS		1
1.	INTRODUCTION	3
2.	BOD MEASUREMENT	5
2.1	Alternative parameters	5
2.2	Surrogates for BOD	15
3.	SUSPENDED SOLID MEASUREMENT	19
3.1	Turbidity	19
4.	CONCLUSIONS	27
5.	RECOMMENDATIONS	29
REFERENCES		31
BIBLIOGRAPHY		33
APPENDIX A - LIST OF MANUFACTURERS AND SUPPLIERS		35

LIST OF TABLES

Page

2.1 On-line TOC equipment 7

2.2 Laboratory injection TOC equipment 9

2.3 On-line COD equipment 10

2.4 COD test kits 11

2.5 On-line TOD equipment 13

2.6 Laboratory TOD equipment 13

2.7 On-line DOC equipment 14

2.8 On-line respirometers 16

2.9 Portable respirometers 16

3.1 On-line turbidity equipment 21

3.2 Laboratory turbidity equipment 24

3.3 Portable turbidity equipment 25

EXECUTIVE SUMMARY

Traditionally Biochemical Oxygen Demand and suspended solids have been measured for consent purposes for effluent discharge. However, conventional measurement techniques have limitations and are not amenable to continuous monitoring. Consequently, it has been recommended in the Discharge Consent and Compliance Policy that alternatives be sought, evaluated and included into consent policy.

The report provides information regarding on-line, laboratory and portable equipment that is available for the parameters identified by Project No. 402, as alternatives to BOD_5 and suspended solid measurement.

The conclusions of the review, is that there is a wide selection of instruments commercially available utilizing a variety of different methods for analysis of the parameters identified.

The recommendation of the review is that an evaluation of the parameters and the methods used for analysis should commence. The evaluation will be carried out using field operating conditions with different sample types. Following the study, replacements for the BOD_5 and suspended solids test will be selected.

KEY WORDS

Bioprobes, chemiluminescence, organic carbon, oxygen demand, respirometry, turbidity.

1. INTRODUCTION

Currently the five day Biochemical Oxygen Demand (BOD_5) and suspended solid measurement are used in assessing the impact of effluent discharge and long term water quality. The BOD measures the amount of biodegradable organic compounds in waste water through the determination of the quantity of dissolved oxygen that is consumed by micro-organisms during oxidation of the material under aerobic conditions. While suspended solid measurement quantifies the nonfilterable residue in water or wastewater. Despite being useful pollution control determinands, both have limitations and consequently alternatives are required which are less time consuming tests and amenable to continuous monitoring.

The Kinnersley Report (Discharge Consent and Compliance Policy: A Blueprint for the Future - July 1990) recommends key changes in the discharge consent system concerned with the monitoring of numeric parameters. It recommends that a detailed assessment of the capability of alternative parameters to BOD_5 and suspended solids be made due to their limitations. Amongst the alternative parameters to be investigated are Total Organic Carbon (TOC) and turbidity for BOD_5 and suspended solids respectively with the emphasis for on-line continuous monitoring as stated by recommendations 15 and 24 in the Kinnersley Report.

A review (Parr 1992) was carried out under Project No. 402 which identified suitable alternatives/surrogates for BOD_5 and suspended solid measurement. This report gives information on commercially available equipment for the alternatives/surrogates and will provide the basis of the selection of instruments for the evaluation programme which will subsequently follow.

2. BOD_5 MEASUREMENT

Definition of BOD_5

The BOD_5 measurement is defined as "the amount of oxygen consumed by aerobic microbial action in a sample under defined conditions over a specified period - normally 5 days at 20 °C " (SCA 1979).

Method of Analysis

The method of analysis used for BOD_5 measurement is detailed by SCA (1981, 1988).

As stated by Parr (1992) and Bealing (1988) BOD_5 measurement is subject to a number of major drawbacks including the expense and time of test, plus technical and interpretational difficulties. The NRA are interested in a surrogate/alternative for the test, due to its limitations and suitable parameters have been identified (Parr 1992), which could replace BOD_5 in terms of practicability and usefulness. The following sub-sections describe these parameters, summarising methods of analysis and details currently available instrumentation.

2.1 Alternative parameters

Alternative parameters include any method which measures a chemical parameter as a replacement for BOD_5 (e.g. chemical oxidizability, carbon content etc.). A number of parameters have been identified by Parr (1992) and are listed below with a description in the following sub-sections.

- Total Organic Carbon (TOC)
- Chemical Oxygen Demand (COD)
- Total Oxygen Demand (TOD)
- Dissolved Organic Carbon (DOC).

2.1.1 Total Organic Carbon

Definition of TOC

The TOC measurement is defined as "the amount of carbon present in all organic forms and is the difference between the total carbon and the total inorganic carbon" (SCA 1979).

Method of Analysis

There are five methods of oxidizing organic carbon used in commercially available TOC equipment. The methods are detailed by SCA (1979) with a list given below.

1. Persulphate-ultraviolet oxidation
2. High temperature combustion
3. Elevated temperature/persulphate oxidation (wet oxidation)
4. Ultraviolet
5. Ozone

Available instrumentation

There are numerous examples of on-line and laboratory analysers commercially available which use all of the methods previously described and Tables 2.1 and 2.2 give instrument specification details.

2.1.2 Chemical Oxygen Demand

Definition of COD

The COD measurement is the expression of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant.

Methods of Analysis

There are four methods used to oxidize organic matter in commercially available COD equipment and these have been listed below together with references for more details.

1. Dichromate oxidation (SCA 1986)
2. Permanganate oxidation (SCA 1983)
3. Ultraviolet
4. Ozone oxidation (Anon 1991)

Available Instrumentation

There are numerous examples of on-line analysers and test kits commercially available which use all of the methods previously described and Tables 2.3 and 2.4 give instrument specification details.

Table 2.1 On-line TOC equipment

Manufacturer	Model	Method	Range mg l⁻¹ C	Accuracy	Analysis time	Ambient temp.	Flow rate	Output signal	Power requirired	Options	Max. particle size	Price £
Hartmann and Braun	TOCAS	High temp (750 °C) NDIR-CO2 detector	0-10 0-1000	N/S	4-8 mins	5-40 °C	20 ml min^{-1}	0-20 mA 4-20 mA RS232	115/230V 48/52 Hz	TN TC	50 μM	25K
Ionics	6800	High temp (900 °C) NDIR-CO_2 detector	0-2 0-30,000	± 2%	6 mins	-18/38 °C	50-1000 ml min^{-1}	0-10V 4-20 mA	115/220V 50/60 Hz 10A	TC	200 μM	12K
Maihak	TOCOR 2	High temp (850 °C) NDIR-CO2 detector	0-3 0-10 g l^{-1}	± 1%	2 mins	0-30 °C	20-60 ml h^{-1}	0-4 mA 4-20 mA	220V 50 Hz 2000VA	TC TIC VOC	500 μM	30K
Shimadzu	TOC-5000	High temp. (680 °C) NDIR-CO2 detector	0-200 0-1000	± 2%	6 mins	5-35 °C	100-200 ml min^{-1}	N/S	100V 50/60 Hz 5A	TC IC NPOC	N/S	18K
TORAY	TOC-610	High temp. (650 °C) NDIR-CO_2 detector	0-250 0-2500	± 2%	4 mins	0-40 °C	500 ml min^{-1}	4-20 mA	100V 50/60 Hz 500VA	None	150 μM	25K
Astro	1800	Acid sparge Persulphate/UV NDIR-CO2 detector	0-5 0-10,000	± 2%	2 mins	0-49 °C	28 ml min^{-1}	4-20 mA, 0-10 VDC RS232	120/240V 50/60HZ 600/660W	None	300 μM	14K
Astro	1900	Acid sparge Persulphate/UV NDIR-CO_2 detector	0-5 0-10,000	± 2%	2 mins	0-49 °C	28 ml min^{-1}	4-20 mA, 0-10 VDC RS232	120/240V 50/60Hz 600/660W	None	300 μM	19K
Maihak	TOCOR 4	Acid sparge Persulphate/UV NDIR-CO2 detector	0-3 0-30	± 2%	4 mins	0-30 °C	10 ml hr^{-1}	0-4 mA 4-20 mA 500VA	220V 50 Hz	DOC TC	50 μM	28K
O.I Co.	700	Acid sparge Persulphate/UV NDIR-CO2 detector	4-10,000	± 2%	7 mins	0-30 °C	N/S	0-1V RS232	115/240V 50/60 Hz 800W	TIC	500 μM	15K
P.P.M	PROTOC	Acid sparge Persulphate/UV NDIR-CO2 detector	0-10,000 0-50,000	± 2%	3-6 mins	2-50 °C	100-1000 ml min^{-1}	0-1V 4-20 mA RS232	115/240V 50/60 Hz	TC	100 μM	12K
P.P.M	PROTOC 100	Acid sparge Persulphate/UV NDIR-CO2 detector	0-10 0-50,000	± 2%	2-3 mins	2-50 °C	100/1000 ml min^{-1}	4-20 mA	115/240V 50/60 Hz	TC	100 μM	6K
Rosemount	2100	Acid sparge Persulphate/UV NDIR-CO2 detector	0-2 0-5,000	± 2%	5 mins	2-50 °C	50-200 ml min^{-1}	0-1V 0-10 mV 4-20 mA	120/240V 50/60 Hz 350W	None	100 μM	N/S

Table 2.1 continued

Manufacturer	Model	Method	Range $mg\ l^{-1}\ C$	Accuracy	Analysis time	Ambient temp.	Flow rate	Output signal	Power requirired	Options	Max. particle size	Price £
Seres	TOC 2000	Acid sparge Persulphate/UV NDIR-CO2 detector	0-10 0-10,000	± 3%	9 mins	5-40 °C	$30\ l\ h^{-1}$	0-20 mA 4-20 mA RS232	220V 50/60 Hz 500W	None	100 µM	N/S
MIT	Organic Pollution Monitor	UV	0-100	N/S	20 secs	-10/50 °C	$5\ l\ min^{-1}$	0-4 mA 0-20 mA RS232	90-130V 180-240V 50/60 Hz	BOD,COD pH,colour temp,cond. NH_3,s.s turbidity	N/S	23K
Poll. Control Systems	BioTector TOC	Ozone CO_2 detector	10-30,000	± 5%	N/S	5-35 °C	30 ml sample	4-20 mA	220V 50/60 Hz 400W	TC IC	2 mm	25K

N/S - Not stated

Table 2.2 Laboratory injection TOC equipment

Manufacturer	Model	Method	Range mg l⁻¹ C	Accuracy	Analysis time	Ambient temp.	Output signal	Power requirired	Options	Max. particle size	Price £
Carlo Erba Instruments	TCM 480	High temp (1000 °C) flame ionization detection	0.1-1000	±5%	5 mins	0-25 °C	0-1 mV 0-10 mV	115/240V 50/60Hz 1000VA	TC	300 pM	25K
Dohrmann	DC-190	High temp. (900 °C) NDIR-CO2 detector	0-50000	± 2%	3 mins	0-25 °C	RS232 Analogue	120/230V 50/60 Hz	TC IC NPOC POC	500 µM	N/S
Ionics	1505	High temp (750-900 °C) NDIR-CO2 detector	0-2 0-2000	± 2%	6 mins	-18/38 °C	0-10V	115/220V 50/60 Hz 10A	TC	200 µM	14K
Ionics	1555	High temp. (875 °C) NDIR-CO_2 detector	0-2 0-2000	± 2%	90 secs	-18/38 °C	0-10V RS232	115/220V 50/60 Hz 10A	TC	200 µM	10K
Shimadzu	TOC-500	High temp. (680 °C) NDIR-CO2 detector	1-3000	± 3%	2 mins	5-35 °C	N/S	100/240 50/60 Hz	VTC IC VOC	N/S	14K
Shimadzu	TOC-5050	High temp. (680 °C) NDIR-CO2 detector	0-4000	± 2%	2 mins	5-35 °C	N/S	100/240 50/60 Hz	VTC IC VOC	N/S	17K
UIC	130	High temp (950 °C) titration, colour detection	1-10000	±1%	3-5 mins	0-25 °C	0-20 mA RS232	240V 60 Hz	TC TIC	N/S	18K
Astro	2001	High temp, UV, persulphate NDIR-CO_2 detector	0-10000	±4%	3-4 mins	0-25 °C	RS232	115/240V 50/60 Hz 500W	None	500 µM	17K

N/S - Not stated

Table 2.3 On-line COD equipment

Manufacturer	Model	Method mg l^{-1} C	Range	Accuracy	Analysis time	Ambient temp.	Flow rate	Output signal	Power required	Options	Max. particle size	Price £
Applikon	COD	Oxidation of dichromate Colorimetric detection	0-5000	±8%	12 mins	0-25 °C	10 ml sample	0-20 mA	110/120V 220/240V 50/60 Hz	None	N/S	35-40K
Arkon	K.CSB.ST.88	Oxidation using hydrogen peroxide under UV radiation	0-250	±10%	5 mins	N/S	N/S	0-4 mA 60 Hz	220V	None	N/S	32K
Ionics	304	Oxidation of dichromate (150 °C) Colorimetric detection	0-100 0-5000	±8%	10 mins to 5 hr	0-40 °C	N/S	0-1 VDC 2-20 mA RS232	115/220V 50/60 Hz 3A	None	200µM	13K
MIT	Organic Pollution Monitor	UV	0-100	N/S	20 secs	-10/50 °C	5 l min^{-1}	0-4 mA 0-20 mA RS232	90-130V 180-240V 50/60 Hz	TOC, BOD pH,colour Temp, cond. NH3, s.s	N/S	23K
STIP	PHOENIX	Oxidation of ozone Ozone probes	5-1000 5-10000	±2%	3 mins	N/S	500ml min^{-1}	0-20 mA 4-20 mA	220/240V 380/415V 50 Hz 16A	None	500 µM	33K
Horiba	CODA 111	Sulphuric acid based potassium permanganate	0-500	N/S	1 hr	N/S	0.5-3 l min^{-1}	0-16 mA 4-20 mA	10V 50/60Hz	None	N/S	N/S
Horiba	CODA 112	Alkali based potassium permanganate	0-500	N/S	1 hr	N/S	0.5-3 l min^{-1}	0-16 mA 4-20 mA	10V 50/60 Hz	None	N/S	N/S

N/S - Not stated

Table 2.4 COD test kits

Manufacturer	Model	Method	Range mg l^{-1} C	Accuracy	Analysis time	Ambient temp.	Output signal	Power required
DR Lange	LCK 014, 114, 314, 414	Chromosulphuric	2-10,000	N/S	2 hrs	0-25°	None	220/240V 50/60 Hz
Hach	21258/9 24158/9	Dichromate	0-15,000	N/S	2 hrs	0-25 °C	None	220/240V 50/60 Hz
WPA	HC6151	Dichromate	10-160	N/S	2 hrs	0-25 °C	None	220/240V 50 Hz
WPA	HC6151	Dichromate	100-1500	N/S	2 hrs	0-25 °C	None	220/240V 50 Hz

N/S - Not stated

There is work being undertaken in Universities on the use of "oxygen demand index" to determine the BOD. The method involves a similar technique to that employed for COD determination, although a lower oxidation temperature is used for a shorter time (Shriver and Young 1972).

2.1.3 Total Oxygen Demand

Definition of TOD

The TOD measurement is defined as "the amount of oxygen consumed in the catalytic combustion of the sample" (SCA 1979).

Method of Analysis

The method uses high temperature combustion and is detailed by SCA (1979).

Available instrumentation

There are currently two manufacturers of TOD equipment and on-line and laboratory instrument specification details are given in Tables 2.5 and 2.6.

2.1.4 Dissolved Organic Carbon

Definition of DOC

The DOC measurement is defined as "the total organic carbon present in the liquid phase of the sample after membrane filtration" (SCA 1979).

Methods of Analysis

There are two methods of analysis used in commercial instruments which are listed below and details are given by SCA (1979).

1. Ultraviolet

2. High temperature combustion

Available instrumentation

There are currently two instruments available which use the UV method of analysis and instrument specifications are given in Table 2.7. However, theoretically all of the TOC instruments could measure DOC, i.e. TOC on a filtered sample.

Table 2.5 On-line TOD equipment

Manufacturer	Model	Method	Range mg l^{-1} C	Accuracy	Analysis time	Ambient temp.	Flow rate	Output signal	Power required	Options	Max. particle size
Ionics	7800 TOD	High temp (900 °C) Oxygen detector	0-10 0-60,000	± 3%	3 mins	-18/38 °C	30 ml sample	4-20 mA 0-10V	115/220V 50/60 Hz 10A	None	200 µM
TORAY	TOD-810	High temp (900 °C) Oxygen detector	0-500 0-5000	± 3%	5-10 mins	0-40 °C	500 ml min^{-1}	0-10V 4-20 mA	100V 50/60 HZ 600VA	None	N/S

N/S - Not stated

Table 2.6 Laboratory TOD Equipment

Manufacturer	Model	Method	Range mg l^{-1} C	Accuracy	Analysis time	Ambient temp.	Output signal	Power required	Options	Max. particle size
Ionics	1548 TOD	High temp Oxygen detector	0-25 0-25,000	± 3%	3 mins	-18/38 °C	30 ml sample	115/220V 0-10V 50/60 Hz 10A	None	200 µM

Table 2.7 On-line DOC equipment

Manufacturer	Model	Method	Range mg l^{-1} C	Accuracy	Analysis time	Ambient temp.	Flow rate	Output signal	Power required	Options	Max. particle size
Bran & Luebbe	AC 200 DOC	Acid sparge, UV NDIR-CO_2 detector	0-20	± 5%	15 mins	10-45 °C	10-30 l h^{-1}	0-4 mA 4-20 mA RS232	110/240V 50/60 Hz 200VA	None	N/S
Maihak	TOCOR 4	Acid sparge, UV NDIR-CO_2 detector	0-3 0-30	± 2%	4 mins	0-30 °C	10 ml hr^{-1}	0-2 mA 4-20 mA	220V 50 Hz 500VA	TOC TC	500 µM

N/S - Not stated

2.2 Surrogates for BOD

Surrogate parameters include any method which measures oxygen uptake as a consequence of microbial activity. A number of parameters have been identified by Parr (1992) and are listed below with a description in the following sub-sections.

- Respirometry
- Bioprobes
- Chemiluminescence

2.2.1 Respirometry

Definition of respirometry

The principle behind respirometry is the same as that employed by BOD_5 i.e. oxygen removal from solution as a consequence of microbial respiration.

Methods of analysis

Some methods rely on the actual bacteria present in the sample, while others nurture an artificial bacterial culture within the instrument to measure oxygen removal from solution as a consequence of microbial respiration. Details regarding the methods have been described by Parr (1992) and Bealing (1988).

Available instrumentation

There are on-line respirometers available which use the methods listed previously and details of these are given in Table 2.8. There is also a commercial portable respirometer which is detailed in Table 2.9.

2.2.2 Bioprobes

Definition of bioprobes

Bioprobes consist of a layer of live immobilised microbial cells (bacterial or yeasts) secured to the exterior of a gas-permeable membrane of a dissolved oxygen probe which measures the depletion in oxygen concentration.

Examples of bioprobes

As discussed by Parr (1992), there have been a large number of bioprobes developed and applied as surrogates for BOD_5 measurement.

Table 2.8 On-line respirometers

Manufacturer	Model	Method	Resp/rate mg l^{-1} h O	Accuracy	Analysis time	Ambient temp.	Output signal	Power required	Options	Price £
Arkon	ZAW 87.1	Actual culture Oxygen electrode	0-50 0-100 0-200	± 5%	5-10 mins	-20/45 °C	0-20 mA 4-20 mA RS232	240V 50 Hz 350VA	None	13-15K
Manotherm	RA-1000	Actual culture Oxygen electrode	0-400	N/S	N/S	0-40 °C	RS232	220V 50 Hz	BOD	31K
Minworth Systems	Respirom.	Actual culture Oxygen electrode	0-50 0-100 options	± 1%	15mins	-5/45 °C	4-20 mA RS232	110/240V 50/60 Hz 50VA	Temp s.s cond.	N/S
MIT	Organic Pollution Monitor	Actual culture UV	0-50	N/S	20 secs	-10/50 °C	0-4 mA 0-20 mA RS232	90-130V 180-240V 50/60 Hz NH3, s.s	TOC, COD pH, colour temp, cond.	23K
STIP	BIOX-1000	Bio-reactor	2-10,000	N/S	3 mins.	N/S	0-20 mA 4-20 mA 20A	220/380V 50/60 Hz	None	24K
Sysco	SA400	Bio-reactor Oxygen electrodes	10-3000	N/S	5-90mins	N/S	4-20 mA	220V 50 Hz	None	N/S

N/S - Not stated

Table 2.9 Portable Respirometers

Manufacturer	Model	Method	Resp/rate mg l^{-1} O	Accuracy	Analysis time	Ambient temp.	Output signal	Power required	Options	Price £
STIP	BOD Module Portable	Bio-membrane Oxygen electrodes	2-22	N/S	3 mins	15-35 °C	RS 232	85-264V 47-62 Hz 25W	None	12K

N/S - Not stated

Available instrumentation

No commercial instrumentation is available at present only research equipment.

2.2.3 Chemiluminescence

Definition of chemiluminescence

Chemiluminescence is defined as the emission of light during a chemical reaction. Antioxidants present in the water cause a transient fall in the emission of light from the chemiluminescent reaction.

Method of analysis

The reaction involves the breakdown of luminol in the presence of hydrogen peroxide and an enhancer, horse-radish peroxidase. The light output from the chemiluminescence reaction is monitored using a conventional photomultiplier tube luminometer. The technique is comparatively rapid with a single test taking approximately five minutes, plus the system could be automated for on-line analysis.

Available equipment

This technique is not commercially available since it has been recently developed by Prof. Whitehead and Dr. Thorpe of the Wolfson Laboratory, University of Birmingham, however, it is available for evaluation.

3. SUSPENDED SOLID MEASUREMENT

Definition of suspended solids

Suspended solids consist of the non-filterable residue in water or wastewater, e.g. organic matter such as viruses, bacteria, algae, higher forms of life and industrial waste, plus inorganic matter such as clay, silt, sand and metals.

Method of analysis

A known volume of sample is filtered through a pre-weighed filter, which is then dried at 105 °C and weighed. Suspended solids are calculated from the weight of non-filterable solids collected and the volume filtered. Full details of the method are given by SCA (1980).

As stated by Parr (1992), suspended solid measurement has a number of drawbacks, including expense, it is time consuming and is not amenable to continuous monitoring, hence the NRA are interested in an alternative to the parameter.

3.1 Turbidity

Definition of turbidity

Turbidity is an expression of the optical property of a liquid that causes light to be scattered and absorbed by material suspended and dissolved in the liquid rather than transmitted in straight lines through a sample.

Methods of Analysis

Full details of methods used for turbidity analysis have been described by SCA (1981) and reviewed by Hatton (1992), however, a brief summary is given below for reference.

1. Transmitted/absorptiometry

This method measures the amount of light which passes through the sample to a detector in line with the source.

2. Scatter

This method measures the amount of light that is scattered from a light beam as a result of suspended particles in the light path, using detectors placed at an angle to the direct transmission path. There are two main classes of instruments which measure scattered light, firstly those that measure the light scattered through a chosen angle to the incident light beam and secondly those that measure forward scattering.

3. Ratiometry

This method utilizes both transmitted and scatter techniques, integrates the signal and reduces interference from colour and variations in light source intensity.

Available instrumentation

There are a large number of on-line, laboratory and portable analysers commercially available which use the methods previously described and Tables 3.1, 3.2 and 3.3 give instrument specification details.

Table 3.1 On-line turbidity equipment

Manufacturer	Model	Method	Range
Arkon	Turbidity monitor	Scatter 90°	0-1000 NTU
Aztec	T50	Scatter 90°	0-50 NTU
Belstock	977-C	Scatter 90°	0-2000 NTU
BTG	MET-3000	Scatter 90°	0-1000 FTU
BTG	MET-3010	Scatter 90°	0-4000 FTU
Dr Lange	HT1/PT1	Scatter 90°	0-200 FTU
Hach	1720C	Scatter 90°	0-100 NTU
Hach	Surface Scatter 6	Scatter 90°	0-9999 NTU
HF Scientific	Micro 200	Scatter 90°	0-100 NTU
Partech	DRT-200C	Scatter 90°	0-100 NTU
Partech	Micro-T (16-64 stations)	Scatter 90°	0.02-20 NTU
Sigrist	KTJ25	Scatter 25°	0-200 FTU

Accuracy	Ambient temp.	Flow rate	Output signal	Power required
± 1%	-20/45 °C	N/S	0-4 mA 4-20 mA RS232	110/240V 50 Hz 300VA
±1-2%	1-35 °C	50-750 ml min^{-1}	4-20 mA RS232	110V 220/240V
N/S	0-50 °C	N/S	4-20 mA	115/230V 50/60 Hz
±1%	-10 to 60 °C	N/S	0-4 mA 4-20 mA	95-130V 190-260V 50/60 Hz 10VA
±1%	-10 to 60 °C	N/S	0-4 mA 4-20 mA	95-130V 190-260V 50/60 Hz 10VA
N/S	0-40 °C	N/S	0-4 mA 4-20 mA 7VA	220V 50/60 Hz
±2-5%	0-40 °C	250-750 ml min^{-1}	0-10 mV 4-20 mA 0-1V	115/230V 50/60 Hz 135VA
±5%	0-40 °C	1-2 l min^{-1}	0-10 mV 0-100 mV 4-20 mA 0-1V	115/230V 50/60 Hz 68W
±1-5%	N/S	N/S	4-20 mA	120/220V
± 5%	0-50 °C	N/S	4-20 mA	115/230V 50/60 Hz 30VA
± 1%	N/S	0-6 l min^{-1}	4-20 mA RS232	115V 60 Hz 40VA
N/S	N/S	5-7 l min^{-1}	0-20 mA 4-20 mA	110/220V 50/60 Hz

Table 3.1 continued

Manufacturer	Model	Method	Range
BTG	SMS-3000	Ratiometric	0-1000 FTU
BTG	MEX-3	Ratiometric	0-1000 FTU
Gimat	701/702	Ratiometric	0-1000 FTU
Hach	Ratio 2000	Ratiometric	0-2000 NTU
Horiba	WATA-100	Ratiometric	0-500 FTU
Rosemount	PT Series	Ratiometric	0-1000 NTU
Rosemount	T-2120	Ratiometric	0-200 NTU
Yokogawa	8562	Ratiometric	0-2000 ppm (caolin)
Instrumark	850I/S	Transmitted	0-2000 NTU
Optek	512/TF10	Transmitted	0-200 FTU
pHox	74L	Transmitted	0-100 NTU

Accuracy	Ambient temp.	Flow rate	Output signal	Power required
N/S	-30 to 45 °C	N/S	0-4 mA 4-20 mA	90-130V 180-260V 50/60 Hz 110VA
N/S	-25 to 60 °C	N/S	0-4 mA 4-20 mA	90-130V 180-260V 50/60 Hz 8VA
N/S	-20 to 60 °C	N/S	0-20 mA 4-20 mA	110/240V 45/65 Hz 20VA
±5%	0-50 °C	100-750 ml min^{-1}	4-20 mA	100-240V 50/60 Hz 35W
N/S	-5 to 45 °C	20 l min^{-1}	0-16 mA 4-20 mA	240V 50/60 Hz 70VA
N/S	N/S	.01-5.6 l min^{-1}	4-20 mA	115V 50/60 Hz
± 2-5%	-10/50 °C	250-750 ml min^{-1}	0-4 mA 4-20 mA RS232	120/240V 50/60 Hz 11W
N/S	N/S	5-20 ml min^{-1}	4-20 mA	100/220V 50/60 Hz
±2%	0-50 °C	N/S	4-20 mA	115V 230V 50/60 Hz
N/S	N/S	N/S	0-4 mA 4-20 mA	115/230V
N/S	N/S	N/S	0-10 mA 0-20 mA 4-20 mA	120/240V 50/60Hz

Table 3.1 continued

Manufacturer	Model	Method	Range	Accuracy	Ambient temp.	Flow rate	Output signal	Power required
MIT	Organic Pollution Monitor	UV	0-100 NTU	N/S	-10/50 °C	5 l min^{-1}	0-4 mA 0-20 mA RS232	90-130V 180-240V 50/60 Hz
Partech	Turbi-Tech 20i	IR LED 950 nm	0-2000 0-10000 (mg l^{-1})	± 5%	-20/60 °C	N/S	4-20 mA	110/240V 10VA

N/S - Not stated

Table 3.2 Laboratory turbidity equipment

Manufacturer	Model	Method	Range	Accuracy	Sample size	Output signal	Power required
Hach	2100A	Scatter 90°	0-1000 NTU	±2%	25 ml	N/S	0-100 mV 50/60 Hz
Lovibond HF	TM-750	Scatter 90°	0-1000 NTU	±1%	N/S	N/S	100-140V 200-280V 50/60 Hz 30VA
Lovibond HF	TM-751	Scatter 90°	0-1000 NTU	±1%	N/S	0-1 mA 4-20 mA	100-140V 200-280V 50/60 Hz 30VA
Monitek	251	Ratiometric	0.1-1000 NTU	±0.5%	500 ml	0-100 mV	120/220V 50/60 Hz
Monitek	21	Scatter 90°	0-199 NTU	± 1	30 ml	0-1 mA	110/220V 50/60 Hz
Monitek	151	Scatter (forward)	0-199 NTU	N/S	30 ml	0-10VDC	100/260V 50/60 Hz
Orbeco Hellige	8000	Visual (Secchi)	0-150 NTU	N/S	N/S	N/S	220V 60 Hz

N/S - Not stated

Table 3.3 Portable turbidity equipment

Manufacturer	Model	Method	Range	Accuracy	Ambient temp.
BTG	MET-P	Scatter 90°	0-1000 FTU	±1%	0-40 °C
BTG	MEX-P	Scatter 90°	0-1000 FTU	±1%	5-50 °C
ELE	EL430-257	Scatter 90°	0-50 NTU	±1	N/S
Lovibond HF	TM-720	Scatter 90°	0-200 NTU	±1%	N/S
Monitek	21PE	Scatter 90°	0-1000 NTU	N/S	N/S
Ocean Systems	Aquaplex 20	Scatter 90°	0-200 NTU	±1%	5-40 °C
Orbeco Hellige	965	Transmitted	0-1000 NTU	N/S	N/S
Hach	2100P	Ratiometric	0-1000 NTU	±2-3%	N/S
Hach	DREL/ 2000	Colorimetry	0-450 FTU	±2	N/S

N/S - Not stated

4. CONCLUSIONS

The review has shown that there is a large selection of commercial equipment available for the parameters identified by Parr (1992) as possible replacements for the BOD_5 and suspended solids test.

Details of instrument specifications have shown that a variety of techniques are used in the analysis of each parameter. Conventionally the choice of instrument was limited to one or two methods which were often determined by the sample characteristics to be analysed. However, now there is a wider selection of methods to choose from, due to the development of new techniques, e.g. ozone.

5. RECOMMENDATIONS

It is recommended that selected parameters for alternatives to BOD_5 identified by Parr (1992) and described in the review are investigated. The equipment to be evaluated will be selected from this shortlist by discussions with the NRA and SNIFFER. There are a number of methods available for the analysis of each of the parameters and these will require evaluation together with the parameters. The instruments will be selected from those listed in the review and they will be operated under field operating conditions and assessed regarding their suitability as replacements for BOD_5 and suspended solids. Laboratory analysis will also be required to calibrate and check the operation of the on-line instruments. Different sites should be investigated, e.g. sewage effluent and river water to show extremes of operating conditions and highlight which method is appropriate with regard to sample conditions.

REFERENCES

Anon (1991) COD Monitoring Goes On-Line. *Process Engineering*, **72**, Nº 63.

Bealing, D. J. (1988) The five-day biochemical oxygen demand test (BOD_5) test: An appraisal and possibilities for replacement. WRc Report PRU 1954-M.

Hatton, E. (1992) Review of Turbidity. R&D Note 91, WRc Report No. NR 3160/4253.

Kinnersley Report (July 1990) Discharge Consent and Compliance Policy: A Blueprint for the Future, Water Quality Series Nº 1.

Parr, W. (1992) Possible replacements for the Biochemical Oxygen Demand (BOD) test and suspended solids as measures of effluent and water quality. WRc Report No. R&D 402/2/HO.

SCA (1979) The instrumental determination of total organic carbon, total oxygen demand and related determinands. Standing Committee of Analysts, HMSO, London.

SCA (1980) Suspended, settleable and total dissolved solids in waters and effluents. Standing Committee of Analysts, HMSO, London.

SCA (1981) Biochemical oxygen demand. Standing Committee of Analysts, HMSO, London.

SCA (1981) Colour and turbidity of waters. Standing Committee of Analysts. HMSO, London.

SCA (1983) The permanganate index and permanganate valve tests for waters and effluents. Standing Committee of Analysts, HMSO, London.

SCA (1986) Chemical oxygen demand (dichromate value) of polluted and waste waters. Standing Committee of Analysts, HMSO, London.

SCA (1988) 5 day biochemical oxygen demand (BOD_5). Standing Committee of Analysts, HMSO, London.

BIBLIOGRAPHY

Arin, M. L. (1974) Monitoring with Carbon Analysers. *Environmental Science and Technology* **8**, 898-902.

Butters, G. and Butwell, A. (1990) A review of the techniques available for monitoring of sewage effluent quality. WRc Report UM 1070. WRc Swindon., Wilts., SN5 8YR.

Chandler, R. L., O'Shaugnessy, J. C., and Blanc, F. (1976) Pollution monitoring with total organic carbon analysis. *Journal Wat. Pollution. Cont. Fed.* 48, 2791-2803.

Eckenfelder, W. W. (1970) Water quality engineering for practising engineers. Barnes and Nobel Inc., New York.

Firth, B. and Cieslek, P. (1990) Biosensing for the protection of water quality. *Tappi Journal,* **73**, Nº 4.

Galindo, E., Garcia, J. L., Torres, L. G. and Quintero, R. Characterisation of microbial membranes used for the estimation of BOD with a biosensor. *Biotechnology Techniques* **6**, 399-404.

Kalte (1990) Analysis of wastewater using ozone. IFAT Conference.

Karube, I., Matsunaga, T., Mitsuda, S. and Suzuki, S. (1977) Microbial electrode BOD sensors. *Biotechnology and Bioengineering,* **19**, 1535-1547.

Karube, I. and Tamiya, E. (1987) Biosensors for environmental control. *Pure and Applied Chemistry,* **59**, 545-554.

Karube, I. (1990) Microbial sensor. *Journal of Biotechnology* 255-256.

Kohne, M. (1985) Practical experiences using with a new on-line BOD measuring device.

Kohne, M., Siepman, F. W. and te Heesen, D. (1986) A comparison of the BODs and the Continuous short-time BOD (BOD-M3),*Korrespondenz Abwasser,* **33**(9), 787-793.

Kong, Z., Vanrolleghem, P. and Verstraete, W. (1987) Rapid IC50 estimation and on-line toxicity monitoring with the RODTOX, an activated sludge based biosensor. Awaiting publication.

Montgomery, H. A. C. and Gardiner, D. K. (1971) Experience with a bacterial inoculum for use in respirometric tests for oxygen demand. *Water Research,* **5**, 147.

Paskins, A. R.(1982) A survey of effluent quality monitors. WRc Report 125-S. WRc Swindon, Wilts, SN5 8YR.

Queeney, K. and Hoek, F. B. (1989) On-line determination of organic pollutants using TOC, TC, TOD and COD. *American Laboratory* **21**, 26-32.

Riedel, K., Lange, K. P., Stein, H. J., Kuhn, M., Ott, P. and Scheller, F. (1990) A microbial sensor for BOD. *Water Research* **24**, 883-887.

Riedel, K., Renneberg, M. and Scheller, F. (1988) A fast estimation of BOD using microbial sensors. *Applied Microbiology and Biotechnology*, **28**, 316-318.

Riegler, G., Darmstadt (1984) Continuous Short-Time BOD Measurement. *Korrespondenz Abwasser*, **31**, Nº 5, 369-377.

Sherrand, J., Friedman, A. and Rand, M. (1979) BOD: are there alternatives available? *Journal WPCF*, **51**, Nº 7.

Shriver, L. E. and Young, J. C. (1972) Oxygen demand index as a rapid estimate of biochemical oxygen demand. *Journal of Water Pollution Control Federation* **44**, 2140-2147.

Strand, S. E. and Carlson, D. A. (1984) Rapid BOD measurement for municipal wastewater samples using a biofilm electrode. *Journal Water Pollution Control Federation*, **56**, 464-467.

APPENDIX A - LIST OF MANUFACTURERS AND SUPPLIERS

MANUFACTURER	SUPPLIER
Applikon Analysers Ltd Farnborough Business Centre Eelmoor Road Farnborough Hants GU14 7QN Tel: 0252 372303 Fax: 0252 372628	
Arkon Instruments Ltd Old Station Drive Leckhampton Cheltenham Gloustershire GL53 0DL Tel: 0242 573444 Fax: 0242 221701	
Astro International Corporation 100 Park Avenue League City Texas 77573 USA Tel: 713 3322494 Fax: 713 5546795	Applikon Analysers Ltd Farnborough Business Centre Eelmoor Road Farnborough Hants GU14 7QN Tel: 0252 372303 Fax: 0252 372628
Aztec Environmental Control Ltd 8 Hawksworth Road Southmead Industrial Park Didcot Oxon OX11 7HR Tel: 0235 512000 Fax: 0235 512020	

MANUFACTURER	SUPPLIER
Belstock Controls 10 Moss Hall Crescent Finchley London N12 8NY Tel: 081 4468210 Fax: 081 4466991	
Bran & Luebba Ltd Analyzer Division Beechwood Chineham Business Park Basingstoke Hants Tel: 0256 842062 Fax: 0256 842041	
BTG Ltd 26 Breakfield GB-Coulsdon Surrey CR5 2XW Tel: 081 6685287 Fax: 081 6680509	
Carlo Erba Instruments (UK) MSE Scientific Instruments Sussex Manor Park Gatwick Road Crawley West Sussex	Fisons Instruments Sussex Manor Park Gatwick Road Crawley West Sussex RH10 2QQ Tel: 0293 561222 Fax: 0293 561980
Dr Bruno Lange GmbH Vertriebsbereich Industriemessgerate Wiesenstrasse 21 D-4000 Dusseldorf 11 West Germany	Robin Instruments Ltd Normandy House 7 Priorcroft Close Camberley Surrey GU15 LDE Tel: 0276 26987 Fax: 0276 670674

MANUFACTURER	SUPPLIER
ELE International Ltd Eastman Way Hemel Hempstead Hertfordshire HP2 7HB Tel: 0442 218355 Fax: 0442 52474	
Gimat Obermuhlstrabe 70 W-8128 Polling W Germany Tel: 0881 6280 Fax: 0881 62815	
Hach Company P.O. Box 389 Loveland Colorado 80539 USA Tel: 303 6693050 Fax: 303 6692932	Camlab Nuffield Road Cambridge CB4 1TH Tel: 0223 424222 Fax: 0223 420856
Hartmann and Braun Ltd Moulton Park Northampton NN3 1TF Tel: 0604 646311 Fax: 0604 491027	
Horiba Instruments Ltd 1 Harrowden Road Brackmills Northampton NN4 0EP Tel: 0604 765171 Fax: 0604 765175	
HF Scientific inc 3170 Metro Parkway Fort Myers FL 33916-7597 USA Tel: 813 3372116 Fax: 813 3327643	Partech Electronics Ltd Charlestown St. Austell Cornwall PL25 3NN Tel: 0726 74856 Fax: 0726 68850

MANUFACTURER	SUPPLIER
Instrumark International 485 Sinclair Frontage Road Milpitas CA 95035 USA Tel: 408 2620717 Fax: 408 2623610	Steptech Instrument Services Ltd Streptech House Primrose Lane Arlesey Bedfordshire SG15 6RD Tel: 0462 733566 Fax: 0462 733909
Ionics UK Ltd Carrington Business Park Carrington Urmston Manchester M31 4DD Tel: 061 7764550 Fax: 061 7779630	
LAB Services Eccup WTW Eccup Moor Road Leeds LS17 7RJ Tel: 0532 682135 Fax: 0532 688547	
Maihak A G Semperstrasses 38 D-2000 Hamburg 60 Tel: 040 27160 Fax: 040 2716242	Fluid Data Ltd 20 Bourne Industrial Park Bourne Road Crayford Kent DA1 4BZ Tel: 0322 528125 Fax: 0322 559022
Manotherm B.V P.O.Box 7050 3000 HB Rotterdam Tel: 010 4169011 Fax: 010 4169695	LAB Services Instrument Section Eccup WTW Eccup Moor Road Moortown Leeds LS17 7RJ Tel: 0532 682135 Fax: 0532 688547

MANUFACTURER	SUPPLIER
Measurement & Instrumentation Technology (MIT) 31 Yarmouth Close Toothill Swindon Wilts SN5 8LL Tel: 0793 872373	
Minworth Systems Ltd Kingsbury Road Minworth Sutton Coldfield West Midlands B76 9BL Tel: 021 3131709 Fax: 021 3517597	
Monitek Technologies 1495 Zephyr Avenue Hayward CA 94544 USA	Acal Aureiema Ltd 442 Bath Road Slough SL1 6BB Tel: 0628 604353 Fax: 0628 603730
Ocean Systems Ltd Unit 15 Redfields Industrial Park Redfields Lane Church Crookham Hants GU13 0RE	REN Scientific Ltd P.O. Box 53 Camberley Surrey GU16 5YU Tel: 0276 682109 Fax: 0276 64091
O.I Corporation P.O.Box 2980 College Station TX 77841-2980 Graham Road at Welbourne Road Tel: 409 6901711 Fax: 409 6900440	Eden Scientific Ltd 1 Beechrow Ham Common Richmond Surrey TW10 5HE Tel: 081 5468386 Fax: 081 5471466

MANUFACTURER	SUPPLIER
Orbeco Analytical Systems Inc 185 Marine St Farmingdale NY 11735 USA Tel: 516 2934110 Fax: 516 2938258	Labmart Ltd 1 Pembroke Avenue Waterbeach Cambridge CB5 9QR Tel: 0223 861665 Fax: 0223 861990
Partech Electronics Ltd Charlestown St. Austell Cornwall PL25 3NN Tel: 0726 74856 Fax: 0726 68850	
Pollution Control Systems AS Huths Gate 5 N-1600 Fredrikstad Norway	BTG United Kingdom Ltd 26 Breakfield Coulsdon Surrey CR5 2XW Tel: 081 6685287 Fax: 081 668 0509
Pollution & Process Monitoring Ltd Bourne Enterprise Centre Borough Green Sevenoaks Kent TN15 8DG Tel: 0732 882044 Fax: 0732 780190	
Rosemount Analytical Dohrmann Division 3240 Scott Boulevard P.O.Box 58007 Santa Clara CA 95054 Tel: 408 7276000 Fax: 408 7271601	Sartec Ltd Bourne Enterprise Centre Borough Green Kent TN15 8DG Tel: 0732 884815 Fax: 0732 885541

MANUFACTURER	SUPPLIER
Rosemount Ltd Heath Place Bognor Regis West Sussex PO22 9SH Tel: 0243 863121 Fax: 0243 867554	
Seres Jansu House 1 Harrier Terrace Berkeley Business Park Wokingham Berkshire RG11 4YJ Tel: 0734 328880 Fax: 0734 730811	
Shimadzu Europa GmbH Albert-Hahn-Strasse 6-10 4100 Duisburg 29 F.R. Germany Tel: 203 7687-0 Fax: 203 766625	Dyson Instruments Ltd Hetton Lyons Industrial Estate Hetton Houghton-le-Spring Tyne and Wear DH5 0RH Tel: 091 5260452
Sigrist Photometer Ltd 1 Pembroke Avenue Waterbeach Cambridge CB5 9QR Tel: 0223 860595 Fax: 0223 861819	
STIP Stiepmann und Teutscher GmbH Kreuzstrabe 4 D-6107 Reinheim 3 W Germany	Envitech Ltd Branton House 1a Gower Street Cathays Cardiff CF2 4PA Tel: 0222 229982 Fax: 0222 229993

MANUFACTURER	SUPPLIER
Strohlein GmbH & Co Girmeskreuzstr 55 Postbox 1460 D-4044 Kaarst 1 Germany	J & R Scientific 13 West Drive Wethersfield Braintree Essex CM7 4BT Tel: 0371 850507 Fax: 0371 851025
Sysco Analytics Ltd Broadway Market Lavington Devizes Wiltshire SN10 5RQ Tel: 0380 818411 Fax: 0380 812733	
The Tintometer Ltd Waterloo Road Salisbury SP1 2JY Tel: 0722 327242 Fax: 0722 412322	
Toray Engineering Co Ltd Instrument Marketing Dept. 3-4-18 Nakanoshima Kita-ku Osaka 530 Japan Tel: 06 4475221 Fax: 06 4485777	Acal Auriema Ltd 442 Bath Road Slough SL1 6BB Tel: 0628 604353 Fax: 0628 603730
UIC Inc P.O.Box 863 Joliet Illinois 60434-0863 Canada	Roth Scientific Ltd 11 Alexandra Road Farnborough Hants GU14 6BU Tel: 0252 513131

MANUFACTURER	SUPPLIER
WPA The Old Station Linton Cambridge CB1 6NW Tel: 0223 892688 Fax: 0223 894118	
Yokogawa Ltd Kingfisher Court Pacific Quays Broadway Salford Manchester M5 2UE Tel: 061 8737243 Fax: 061 8737234	