The Development of New Techniques for the Monitoring of Ammonia in Water

Robert Bogue & Partners

Project Report 318/5/Y

NRA

National Rivers Authority

THE DEVELOPMENT OF NEW TECHNIQUES FOR THE MONITORING OF AMMONIA IN WATER

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SUMMARY

This report concerns Phase One of a project which is intended ultimately to yield an improved ammonia sensor for use by the NRA. This study was commissioned by the NRA in recognition of the widely-held view that the performance of available ammonia sensors, such as ISEs, falls short of that required for reliable use in the hand-held water quality monitor presently being evaluated by the NRA.

The specific limitations of available ammonia sensing devices, in the context of both freshwater and marine environments, are highlighted in this report and were established through discussions with regional NRA personnel and the Plymouth Marine Laboratory.

A computer literature search was undertaken, and together with discussions with UK and overseas research groups, revealed a number of sensor technologies that offer potential to overcome these limitations. The most appropriate are identified and discussed. Several research groups were located who possess technological skills in appropriate areas who could act as sources of expertise in a collaborative sensor development programme.

Many sensor and instrumentation companies were contacted, and although none were presently undertaking ammonia sensing developments of relevance to the NRA, several are potentially well-placed to act as development contractors, in conjunction with external research establishments.

The means of structuring a collaborative sensor development programme are considered, together with details of various government and EC schemes that offer financial support for such programmes. Their respective merits and limitations are highlighted. Finally, conclusions are drawn and a number of recommendations made, concerning how best to proceed to the development phase of this project.

KEY WORDS: Ammonia, fibre optics, ammoniacal nitrogen, environment, sensors, instrumentation, analysis.

1. BACKGROUND, OBJECTIVES AND SCOPE

1.1 Background

The National Rivers Authority's many responsibilities include pollution control, managing water resources, flood defence, fisheries, conservation and navigation, and a vital function is to monitor the quality of controlled waters. This is undertaken with a combination of fixed monitors, portable and hand-held instruments and laboratory analysis.

A chemical species of particular interest to the NRA is ammonia but available sensing methods fall short of many present-day requirements. In particular, the ammonium-responsive ion-selective electrodes (ISEs) that are used in portable instruments exhibit many operational limitations, such as poor resolution and high cross-sensitivities, and fixed monitors are large, costly and difficult to operate and maintain.

In view of the planned deployment of hand-held multi-parameter water quality monitors that will be required to quantify ammonia levels, a pressing need exists for improved ammonia sensors. As a consequence of this requirement, the NRA has initiated a project which aims to develop new or improved sensors for monitoring ammonia in water.

This report summarises Phase One of this project; a phase that is intended to identify suitable ammonia sensing techniques and partners for collaborative developments. The second project phase will involve the actual development of sensors based on the most appropriate techniques.

1.2 Objectives

The four specific objectives of this phase of the project were:

* to locate and review industrial and academic research into new and improved ammonia sensors;

* to identify and assess those techniques that appear most able to yield usable devices within 2-3 years;

* to identify academic or industrial organisations to undertake the appropriate research and development;

* to suggest mechanisms that might be employed in any such developments.

1.3 Scope

1.3.1 Measurands

This study is concerned principally with ionised and un-ionised ammonia. Ultimately, it is the total ammoniacal nitrogen that is of interest to the NRA.

1.3.2 Applications and specification

The principle application considered is for a sensor for use with the NRA's hand-held multi-parameter water quality monitor. In addition, some consideration is given to the possibility of any such sensor meeting the requirements of fixed, continuous monitors. A provisional target specification for the sensor to be used in the former is included in Appendix A.

1.3.3 Environment

The freshwater environment is the primary concern of this study, but limited consideration is also given to detecting ammonia in saline waters.

2. METHOD

2.1 Overview

This study was essentially undertaken in three discrete stages, as below.

* Technical investigations;
* Survey of users' opinions and requirements;
* Identification of potential contractors for a sensor development.

Details of the methods adopted in undertaking each of these functions are provided in the following sub-sections.

2.2 Technical investigations

The technical investigations involved a literature search, and discussions with a number of academic research groups and major sensor and instrumentation companies.

The literature search included:

- a computer data-base search (undertaken through the IEE);
- a manual search of technical information at hand;
- examination of the results of a recent search undertaken by WRc.

The IEE computer search involved five data bases and gave access to a total of approximately 14 million publications. Full details of this search are included in Appendix B, but briefly, it was restricted to publications in the English language that were dated since 1986 and concerned with ammonia or ammonium sensing.

A combination of abstracts and full-form p apers were obtained as a result of the above; the latter being obtained (through the IEE) for the most relevant publications. All publications examined during this study are listed at the end of this report in Appendix E.

The academic and other research groups with whom discussions were held were either known to the author, located by the literature search, or known to the NRA. Corporate research groups were identified similarly.

2.3 Survey of user views and requirements

The survey of the users' views and needs was undertaken by:

- holding telephone discussions with key individuals from various NRA regions;
- a meeting with individuals from Plymouth Marine Laboratory (PML), to determine the needs associated with monitoring ammonia levels in the marine environment;
- a review of recent literature and reports etc.

Appendix C provides a list of the contacts from the NRA regions.

2.4 Identification of potential contractors and collaborators

2.4.1 General comments

Potential development contractors were identified from discussions with research groups and companies, located as indicated in Section 2.2, above. A full list of all such companies and research groups contacted during the course of this study is included in Appendix D.

Following an initial contact letter which provided a background to the project, telephone discussions were held which addressed a number of key factors governing whether any such groups were potentially relevant. These factors included:

- whether they would consider undertaking an ammonia sensor development on behalf of the NRA, either individually or though a collaboration with another body;

- whether they believed that such a development was technically feasible within a two or three year timescale;

- suggestions on the technological approaches that might be adopted, and whether they had direct access to potentially suitable technology;

- whether they had any direct experience with ammonia sensing, or with the water industries.

3. RESULTS

The results of the investigations considered above are summarised in the following sections.

3.1 Technical investigations

The various literature searches revealed only a relatively small number of relevant technical publications, as listed in Appendix E. The major organizations publishing were:

- Washington University, USA;
- Rutgers University, USA;
- AT&T Bell Laboratories, USA;
- Hebrew University, Israel;
- Erlangen University, Germany;
- Institute for Radiochemistry, Germany;
- Karl-Franzens University, Austria;
- Swiss Federal Institute of Technology, Switzerland;
- Various Japanese and Chinese groups (affiliations unknown).

These publications and the discussions with academic research groups (most of whom had not published in the open literature), and a number of sensor manufacturers, revealed the following technological options to determine ammonia/ammonium levels in water:

- Fibre optic sensors featuring various methods such as fluorescence, reagent colour-change and light loss etc., for ammonium and free ammonia;
- Integrated optic sensors, where surface reactions cause changes in refraction;
- Live-cell sensors featuring ammonia-oxidising micro-organisms and a dissolved oxygen sensor;
- Detection of liberated ammonia gas, following electrolytic (wet reagent-free) pH elevation, with either an ammonia gas sensor or as presently done in fixed monitors;

- Optical detection of chloramine, following the electrolytic liberation of chlorine which reacts with the ammonia;

- Use of amperometric liquid-liquid interface electrochemical sensors;

- (Unspecified) improvements to conventional ammonium-responsive ISEs;

- Use of multiple ISEs (ammonium, sodium and potassium) and micro-processors/software to compute true ammonia level.

3.2 Survey of user views and requirements

3.2.1 Ammonia detection methods within the NRA

Ammonia levels in water are determined within the NRA by several methods, including:

- ammonium-responsive ISEs (in portable water quality loggers and the hand-held meter etc.);

- ammonia-responsive gas electrodes used in conjunction with wet chemistry (in fixed monitors);

- kits using colourimetric methods (for spot measurements in the field).

It is widely recognised within the NRA that the monitoring of ammonia poses significant problems in terms of accuracy and sensor reliability (Baldwin and Ayub, 1991). The specific operational limitations associated with ISEs and gas electrodes, most frequently cited by NRA personnel, are summarised below.

Problems associated with ammonium-responsive ISEs

- high cross-sensitivity to K^+ and Na^+;

- the need for frequent calibration;

- slow response time;

- drift, when not in use;

- not particularly rugged;

- inadequate sensitivity (ie. at 1 mg/litre or less).

Problems associated with ammonia-responsive gas electrodes

- the need to be used in conjunction with wet chemistry;
- the size of a typical installation;
- the high capital, operating, maintenance and ownership costs.

3.2.2 Ammonia in the marine environment

Discussions with PML, concerning their measurements of ammonia in the sea, revealed the following points:

1. Ammonia levels are monitored in the sea and marine sediments, as part of various research programmes;

2. This is undertaken by an instrument that was developed in-house, which uses established wet chemistry combined with an optical/colourimetric detection method (Phenol Red). It was developed as no generally available analyser offered sufficient sensitivity (see 5, below);

3. This device can operate continuously, taking a reading every 40 or so seconds, and feeds into a chart recorder. It is viewed as satisfactory for the tasks for which it was intended;

4. Most measurements are in a saline environment whose pH varies from approximately 8.0 to 8.2;

5. Ammonia concentrations of interest are typically in the range 0.1 micro M/litre to around 20 micro M/litre, although figures as high as several hundred micro M/litre are encountered in marine sediments;

6. PML would like to be able to measure ammonia levels from their towed instrument packages, but their instrument is not suitable for this. They expressed an interest in any alternative method that could undertake this function. Equally, interest was expressed in any device that could take regular measurements from a fixed site such as a tethered buoy;

7. They recognised that available ammonia electrodes were unsuitable for their uses and confirmed problems with limited sensitivity, high cross-sensitivity to Na^+ and K^+, and drift etc.

3.3 Identification of potential contractors and collaborators

Following the discussions with academic and corporate research groups, several organizations were viewed as worthy of consideration as potential research/development contractors. These are discussed in section 4.3, below.

4. ANALYSIS AND DISCUSSIONS

4.1 Sensor technologies

4.1.1 Fibre optic sensors

Most of the recent research literature of potential relevance to the NRA's needs involves fibre optic sensing technology, and many differing effects and design philosophies are considered. All, however, exploit colourimetric or fluorescent reagent chemistry (wet (entrapped or metered), or immobilised), combined with optical fibres, sources and detectors.

The key design issue is the chemistry employed and whilst several devices simply rely upon ammonia penetrating a membrane and effecting a colour change in a well-established pH indicator/reagent solution (which is then detected optically), others rely on a reagent that reacts directly with ammonia (fluorescence etc.).

The key potential benefits of fibre optic methods are that sensors are likely to be small, inexpensive and rugged, but it must be stressed that fibre optic chemical sensing technology is still largely in its infancy, and several major issues must be addressed in any development. These include the identification of suitable ammonia-responsive reagents (which must be colourimetric or fluorescent, selective and reversible), the immobilisation of the reagent, the sensor's response and recovery time and its sensitivity, and a simple means of field calibration. Equally, the cost and complexity of the associated electronic signal processing must be considered.

4.1.2 Integrated optic sensors

The limited literature on integrated optical ammonia sensing suggests that this technology is far from reaching a commercial stage. Furthermore, integrated optic sensors are likely to utilise similar chemistry to that used in fibre optic sensors. This technology is not, therefore, viewed as offering particular scope in the present context.

4.1.3 Live-cell sensors

A small number of papers consider the use of immobilised ammonia-reducing micro-organisms, in conjunction with a dissolved oxygen sensor, as a means of detecting ammonia in water. Whilst live-cell sensors appear to offer scope in the context of broad-band toxicity monitoring (and, in fact, are the subject of a LINK programme between WRc (on behalf of the NRA), Luton College and the Danielson Group), it is unlikely that this technology could usefully contribute to the NRA's ammonia sensing needs.

In addition to being at a very early stage of development, several specific issues militate against this approach, for instance, questionable selectivity, uncertain field and shelf life, and potential problems with calibration and sensitivity etc. As a consequence, this technology is not viewed as being a serious contender. However, Luton College confirm that they could undertake a limited investigation on the NRA's behalf, if so requested.

4.1.4 Improvements to ion-selective electrodes

ISE technology is well developed and now mature; a fact that is widely recognized, by both the users and ISE manufacturers. The high cross-sensitivity to sodium and potassium, combined with limited sensitivity are major problems. Whilst some manufacturers maintain that further improvements could be made, these would be marginal and most unlikely to yield devices that meet the NRA's needs. Conventional ISE technology is not viewed as offering scope in this context, but the concept of microprocessor/software compensation of cross-sensitivity errors warrants brief mention.

This concept would be to deploy several ISEs (eg. ammonium-, potassium- and sodium-responsive types), and possibly also temperature and pH sensors, and employ software techniques to yield a highly sensitive and specific response to total ammoniacal nitrogen. Whilst this "smart sensor array" concept is probably feasible from a technical viewpoint, it is disregarded due to the potentially high cost and size of any such sensor assembly.

Moreover, it would not, of course, further the state-of-the-art in ammonia sensing.

4.1.5 Other techniques

An alternative to any of the aforementioned techniques involves detecting ammonia in its free form; having liberated it from solution by wet reagent-free pH elevation (Meredith, Arkon Instruments and Williams, UCL, personal communications). Various electrolytic methods of achieving this have been suggested, although none in detail, and alkaline glasses have been proposed as a source of hydroxyl ions for pH elevation. The ammonia gas could be detected by, for instance, a silicon FET (field-effect transistor) gas sensor, as developed by Thorn EMI in the UK and the Swedish company, Sensistor. This concept warrants consideration, as it could conceivably yield sensors for use in both the hand-held instrument and in fixed ammonia monitoring installations. Response time could, however, pose problems.

A somewhat similar suggestion (Briggs, City University, personal communication) involves the electrolytic generation of chlorine which would react with the ammonia to form chloramine ($ClNH_2$). The source of the chlorine could be a soluble glass (if brine were not acceptable), and the chloramine would be detected by optical absorption at 254 nm. As with the above, the response time may be unacceptable, but the technique warrants further consideration.

The dry reagent/optical sensing technology (under development by Wimpey Environmental) is interesting but is aimed primarily at fixed site monitoring applications. The irreversible nature of the reaction, however, militates against its use in the hand-held monitor.

Electrochemical amperometric sensors featuring liquid-liquid interfaces (proposed by Medisense) have not yet been investigated in any detail and the potential relevance of this technology to the NRA remains unclear. However, preliminary results indicate that reduced sensitivity to sodium can be achieved, suggesting that this method warrants further consideration.

4.2 User views and requirements

4.2.1 Uses by the NRA

Discussions with NRA personnel confirmed, in the main, the frequently voiced operational limitations of both ammonium-responsive ISEs and the fixed ammonia detectors, and it is clear that a need exists for a sensor that can improve significantly upon the performance of presently available ISEs in particular. The key operational issues are improved sensitivity, improved response time, reduced cross-sensitivity to sodium and potassium, reduced drift and simplified and/or reduced calibration requirements.

An important requirement, cited by certain regions, was monitoring discharge limits at ammonia levels of around 5-10 mg/litre, to an accuracy of +/- 0.5 mg/litre, with a high level of confidence. Ideally, any new sensor should respond down to 0.5 mg/litre or less.

It is clear that given the availability of such a sensor, it would be used widely in portable and hand-held instruments, including the "Minimonitor" being developed by Thames NRA. Estuarine measurements were also cited as playing an important role within the NRA's monitoring functions, and here, greatly reduced sensitivity to sodium is clearly a major requirement. Also, an improved sensor would ideally replace the fixed ammonia gas electrodes, whose size, operating cost and other factors prohibit their more widespread usage.

4.2.2 Marine applications

Although in the vicinity of sewage effluents ammonia levels may be high, the key operational issues here are the ability of any sensor or instrument to respond to very low ammonia concentrations (at least 100 times lower than those of interest to the NRA) and be largely unaffected by the presence of high background sodium levels.

PML's experiences are that only a custom-built detector satisfies the sensitivity requirements at the present time, and this is unsuitable for in-situ measurements due to its size and complexity. As a consequence, it is likely that an improved ammonia sensor would find several marine uses, for instance, in towed instrument packages and at fixed monitoring sites such as tethered buoys, given that it can achieve the high sensitivity required.

4.3 Research and development contractors

4.3.1 Research groups

Several academic and other research groups warrant consideration as sources of sensing expertise, as listed in Table 3.1. The respective merits and weaknesses of these are considered below.

City University

The key strengths of this university are expertise in fibre optic chemical sensing, an involvement with ammonia detection, experience with the water industry (Professors Briggs and Grattan), and experience in collaborating with industrial partners, typified by the present and potentially relevant development of an ammonia detector for Arkon Instruments. Furthermore, Briggs proposed a number of technical possibilities that warrant serious consideration in this context. Of the UK universities considered in this study, City is certainly amongst the best-placed to act as a source of technical expertise.

Dublin City University

The group of relevance is the Optical Sensors Laboratory under Dr Brian Mac Craith. The key strengths are an involvement with fibre optic sensing, a wide knowledge of fibre optic chemical sensors for environmental applications, the earlier development of a fibre optic sensor for nitrates, strong links with other academics of relevance (eg. Professor Wolfbeis, see below), and a willingness to collaborate with them, and the present collaborative development of a fibre optic methane sensor for British Gas. This group is viewed as a strong contender as a research contractor, although Dr Brian Mac Craith admits to having only limited in-house expertise in chemical technology.

Karl-Franzens University (Graz, Austria)

Professor Otto Wolfbeis has been involved with optical sensors for chemical species for five years, has published several relevant papers and was cited by a number of UK academics as an acknowledged European expert in this field. Key strengths are expertise in fibre optic sensing and chemistry, and in particular, the development to prototype stage of a fibre optic ammonia sensor. Professor Wolfbeis has positive views on the feasibility of developing a fibre optic sensor that would meet the NRA's needs and should be considered as a serious contender as the primary research contractor.

Water Research Centre

WRc has recently considered the NRA's requirement for an improved ammonia sensor and believe that fibre optic sensing technology offers the greatest potential. They have subsequently identified a UK research establishment and an individual there who apparently has been involved with an ammonia sensor development. WRc proposes that they act as managers, coordinators and advisors for a R&D programme undertaken at this (undisclosed) establishment.

UMIST (Manchester)

Although the optical sensors research unit (OSRU), has recently been disbanded, it has been involved with the development of fibre optic sensors for many ions and cations. The key strengths are that jointly, Professor Fred Alder and Dr Naryannaswami have considerable expertise in fibre optic chemical sensors and in the underlying reagent technology, including molecular modelling. The only weakness is a lack of any work on ammonia detection, although Professor Alder proposed several technical possibilities in this context. UMIST warrants consideration as a potential research contractor.

Cambridge Consultants Ltd (CCL)

The Life Sciences Group within CCL has been involved with several chemical sensor and biosensor developments, including optical biosensors for nitrate and phosphate detection, and fibre optic sensors for physical quantities. These are the key strengths of potential relevance but against these must be weighed the lack of direct experience with ammonia sensing, although this topic has been considered and discussed with the NRA (Dr J Adams). CCL is viewed as warranting further consideration.

PA Consulting

This R&D organization expressed interest in collaborating with the NRA, probably by establishing links with one or more sensor/instrumentation manufacturers, and themselves acting as technical advisors and possibly producing prototypes. The involvement with Danfoss (Denmark) is, apparently, still active, although this company's interests relate wholly to fixed, on-line detectors (personal communication). Whether PA could meaningfully contribute to any ammonia sensor development programme is unclear, and in view of their (assumed) lack of potentially appropriate in-house sensor expertise, the organization is of uncertain relevance.

University College London (UCL)

Professor David Williams, an acknowledged expert in electrochemistry and a former AEA Harwell employee, expressed an interest in this programme, and suggested that a combination of electrochemistry and an ammonia-responsive gas sensor could possibly solve the NRA's requirements. Although not involved with optical fibre sensing, Professor Williams has experience with ammonia gas sensing (through earlier work at Harwell), and this, combined with his electrochemical expertise suggests that David Williams/UCL should be considered further.

Luton College

Whilst the work at Luton College on live-cell sensors (Rawson et al 1989) is of questionable relevance (see 4.1.3, above), this establishment could certainly undertake a preliminary investigation into the role that live-cell sensing technology might play in the context of ammonia detection. Luton is ideally placed to undertake such an investigation, should it be instigated.

4.3.2 Sensor manufacturers

Several sensor manufacturers who warrant consideration as development contractors, either individually or through a collaboration with a research establishment, have been identified, as listed in Table 3.2, above. The respective merits and weaknesses of these are considered below.

Arkon Instruments

Arkon's strengths are an involvement with the water industries and ammonia detection, links with various UK and overseas university groups, and a thorough understanding of the limitations of present-day ammonia sensing methods. Also, Doug Meredith, a Director of the company, has several suggestions as to how the NRA's needs might best be solved (eg. electrolytic, reagent-free pH elevation, etc.). The major limitation of the company is its minimal internal R&D resources, but the university links could be exploited in a collaborative development programme and the company warrants consideration in this context.

EDT

The strengths of this company are an involvement with ammonia sensing (through ISE technology) and the water industry, and the Managing Director's (Rune Lundin) relationships with several overseas centres of technical/sensor expertise, including Linkoping (Sweden) and the University of Washington (US, some work undertaken on fibre optic ammonia sensors). In recognition of the limitations of ISEs, the company considers that fibre optic sensing technology is probably the best way forward, if a major improvement over the present situation is to be achieved. Whilst not in possession of any in-house advanced sensor technology, this company could act as a development contractor by collaborating with one of the aforementioned (or other) research groups, and has expressed an interest in so doing.

Unicam

Unicam (formerly Philips) is a manufacturer of ISEs and gas probes, including ammonia-responsive types, and has a strong involvement with the water industries. Although presently involved only with established ammonia detection technology, the company recognises the limitations of this and the potential offered by alternatives such as fibre optic, and has a relationship with the Swiss ETH research establishment (Professor Simon). This establishment has a reputation in the optical biosensor and chemical sensor field, and could possibly act as an external source of appropriate technology. The company expressed a strong interest in undertaking a joint programme with the NRA and should be considered as a possible development contractor.

Orion Research

The strengths of Orion are that they are major manufacturers of ISEs (arguably the technology leaders in this field), and are strongly involved with the water industries and ammonia detection. However, it is likely that any future R&D programmes undertaken by the company would be based around ISE technology and Orion would only warrant consideration, therefore, if this development route were to be pursued.

Siemens Plessey

The key potential strengths of this company are an involvement with the NRA through the manufacture of Merlin and Sherlock, access to several different sensor technologies (in-house), and an ability to draw on the extensive technical and research resources of the German parent company. Furthermore, the latter is understood to be involved with an ammonia, phosphate and nitrate sensor development through a collaboration with a Swiss research organization. Siemens Plessey warrants consideration as a potential development contractor, and could either collaborate with some external centre of expertise or possibly, with the parent company.

York Sensors

The key strength of York is their established involvement with fibre optic sensors (distributed temperature-responsive types), which are manufactured in-house. Also, the company is seriously considering the exploitation of fibre optic sensing technology in the context of chemical measurands, and has held preliminary discussions with Dublin City University (Dr B Mac Craith). The major weakness is the lack of direct experience with chemical sensors or ammonia detection, but York should be considered as a possible party in a collaborative development programme.

ABB Kent-Taylor

As manufacturers of conventional ammonia electrodes and detectors, this company clearly has a well-established knowledge of the needs of the water industries and the NRA. The Analytical Business Director (Dr H Thompson) was of the opinion that improving upon available sensing devices was the most realistic strategy to follow. In view of the widely-held view that this approach offers very limited scope, it is unlikely that this company could contribute meaningfully to solving the NRA's needs.

Thorn EMI

This company is potentially well-placed to contribute to the solving of the NRA's needs. The key strengths are direct access to a wide range of sensor technologies, extensive in-house research resources (through the Central Research Laboratories), and a former involvement with various ammonia sensing projects for WRc etc. The Deputy Director of Research (Dr B Webb), expressed a keen interest in the possibility of undertaking an ammonia sensing development, and the company is possibly unique amongst those considered, through possessing potentially relevant technical skills and resources in-house.

Medisense

Medisense, and the associated company, Ecossensor, which has close links with the University of Edinburgh (Dr Herbert Girault), proposed the use of an amperometric sensor featuring a liquid-liquid interface. Dr McAleer, who is a director of both companies, is of the view that this technology could meet the NRA's requirements. Access to this (still largely unexploited) technology is the key potential strength of Medisense/Ecossensor, and although its relevance remains uncertain, the company should nevertheless be considered further.

4.4. Research and development strategies

4.4.1 General considerations

It is clear from the previous sections that several research organizations and companies are in a potential position to contribute to solving the NRA's ammonia sensing requirements.

Of the companies viewed as warranting further consideration, only Thorn EMI has sufficient in-house technical and human resources to undertake such a development (excluding Medisense, who has in-house access to a possibly relevant technique). Thus, it is most likely that any development programme will probably involve a collaboration between a sensor or instrumentation manufacturing company, preferably with experience with the water industry and ammonia sensing, and some external centre of expertise. However, there would be considerable administrative and other advantages in choosing a single company for the development and manufacture of the sensor.

The means by which any such collaborative programmes might be configured are considered below.

4.4.2 Structuring and funding of development programmes

The development programe could be structured in any of the ways listed below. (It is understood that the NRA would make available a sum of approximately £150,000, to contribute to the R&D costs, over a period of three years).

- A development undertaken totally in-house by a suitable manufacturing company and supported financially and administratively by the NRA;
- A collaborative development involving a manufacturing company and an external source of technical expertise, supported financially and administratively by the NRA;
- As above, but with additional Governmental or EC financial support, through establishing a LINK, ETIS, Euroenviron or other relevant programme.

Of the above, the last two options are clearly the most feasible as very few companies are in a position to undertake such a programme without external technical assistance, although it might be simpler to deal with a single company.

The attraction of the second option (compared with the last), is that it could commence rapidly and would be free from any restrictions imposed by the funding body, but is reliant upon the manufacturer standing a significant part of the programme costs. Whether any company would consider this is yet to be determined, and will be governed principally by the overall programme cost and the size of the market for the end product.

The third option, that of attracting external funding (in addition to the NRA's contribution), is clearly attractive, but of course, would entail significant planning, administration and a time delay before work commenced. The schemes that are potentially relevant include: LINK, ETIS and Euroenviron, and are considered below.

The LINK scheme is the latest in a series of government programmes that are aimed at effecting technology transfer, and is intended specifically to stimulate the commercial exploitation of government-funded research. Any ammonia sensing programme would fall under the LINK molecular sensors (MS) scheme. The key features of LINK programmes are:

- They must be pre-competitive, that is, there are typically two years between the cessation of the LINK programme and product commercialization;

- They must involve a collaboration between an industrial and an academic partner (eg. university), and the latter must be from the UK;

- There must be demonstrable "additionality", for instance, the project would not commence as fast (or at all, due to the high risks involved), without DTI support;

- Financial support is limited to 50% of the total project cost. Typically, the research partner's costs are fully covered and the industrial partner receives 30-35% of their costs;

- There is no restriction on the size of the organizations involved, although small to medium-sized companies are favoured.

Typically, a LINK scheme takes six months or even up to a year set up, and the duration is usually three years.

The major disadvantages of LINK are:

- The time involved in setting up the project;

- The project duration and expected post-project period before products are ready for the market;

- The stipulation that only UK research organizations are eligible.

In view of the above, a LINK programme may not be an appropriate mechanism by which to support the proposed development. The long timescales and restrictions to UK-based academic partners are key factors militating against this strategy.

ETIS (the Environmental Technology Innovation Scheme) is funded jointly by the DoE and DTI, and aims to stimulate pre-competitive industrial research into environmental technology, and a priority activity is "Environmental monitoring - measuring emissions to and in air, water and land". As such, it is potentially relevant to the proposed development programme and the conditions are very similar to those governing LINK. Grant support of up to 50% of eligible project costs is available, but for this, three organizations must be involved of which two must be able to exploit the results commercially. The major differences are that a research institute need not be involved and the project duration can be for as little as one year. Furthermore, the negative aspects of LINK (see above) apply here also. The contact for further information is Chris Regan, ETIS Office, London, tel. 071-215-1051.

Euroenviron is part of the EUREKA programme, and is more complex than either of the above, and must involve organizations from at least two countries (EC or EFTA). The DTI will support up to 50% of the UK partners' costs but overseas partners must apply to their respective governments for support. Project durations are typically from one to three years and there is less of an emphasis on pre-competitiveness; developments that lead directly to commercial products are generally acceptable. A priority area is "Improving water quality", and the programme administrator at the DTI is Dr Sue Armfield, DTI Environmental Unit, London, tel. 071-215-2909.

5. CONCLUSIONS

1. Available means of ammonia detection, such as ISEs and gas electrodes, suffer from several operational limitations that are widely recognized within the NRA. These include limited sensitivity, the need for frequent calibration, slow response and high cross-sensitivities to sodium and potassium, and have highlighted the need for an improved ammonia sensor.

2. Such a sensor is required, in particular, to exploit fully the intended capabilities of the multi-parameter hand-held water quality monitor, and the sensor's key features should include a rapid response to ammonia levels, down to 0.5 mg/litre or less, reduced calibration requirements, small size, high reliability and reduced sensitivity to sodium and potassium.

3. Requirements exist also for improved sensors to monitor ammonia in the marine environment, where concentrations are far lower than in rivers or estuarine waters. High sensitivity to ammonia and insensitivity to sodium are the key features required from such a sensor.

4. Of the sensor technologies considered, fibre optics appear to offer the greatest scope, and techniques such as ammonia-induced fluorescence or colourimetry are likely mechanisms. ISE technology is now mature and offers little scope for improvement. Techniques such as wet reagent-free pH elevation followed by ammonia gas detection, and certain other less well-investigated methods also warrant consideration.

5. Few companies have been located that are actively involved with developing improved ammonia sensors, but several who could potentially address this issue, mostly through collaboration with an external research establishment, have been identified. The most likely include Thorn EMI, Arkon Instruments, Plessey Siemens, York Sensors, EDT, Orion Research and Unicam.

6. A number of research establishments and groups that possess potentially relevant technology and expertise have been identified, and include City University, UMIST, Dublin City University (Ireland), Karl-Franzens University (Austria), Cambridge Consultants, UCL and possibly WRc.

7. It is likely that any sensor development programme will involve a collaboration between a sensor or instrumentation manufacturer and an external centre of technical expertise, given that only a small number of companies could undertake the necessary research. The NRA would adopt a coordinating and administrative role, and be involved also with testing the sensor.

8. Various UK and wider European schemes exist whereby collaborative R&D programmes are part-supported by government (LINK, ETIS and Euroenviron), but all suffer from certain drawbacks, including restrictions on the nationalities of the academic partners, the time scales involved and in some cases, a requirement for a strong precompetitive element.

9. These factors tend to militate against the proposed sensor development programme being supported by such schemes, suggesting that all funding may need to be derived from the NRA and the industrial development contractor.

6. RECOMMENDATIONS

1. Invitations to submit outline development proposals should be sent to all of the companies listed in sub-section 4.3.2, requesting the following:
- Proposed technological approach;
- Possible external research groups for collaboration;
- Likely programme timescales;
- Anticipated programme costs;
- Whether external funding in excess of that available from the NRA would be needed;
- Agreement on the IPR;
- Any other pertinent views or comments.

2. Similar invitations should be sent to the research establishments listed in sub-section 4.3.1, above, requesting the following:
- Detailed comments on proposed technological approach;
- Possible industrial collaborators;
- Likely programme timescales;
- A preliminary assessment of costs;
- Agreement on the IPR;
- Any other pertinent views or comments.

3. Following receipt of the above, the numbers of companies and research groups should be reduced to a short-list of possibly three from each category. The key criteria governing this selection process should include the apparent feasibility of the proposed technological approaches, overall impressions of technical competence, timescales, aspects relating to the IPR, overall programme costs and any requirements for additional funding.

4. Following the above, face-to-face discussions with those organizations on the short lists should be held, with the objective of identifying the most suitable from each category and the optimal combinations.

5. Investigate further whether any of the government- or EC-funded schemes could meaningfully contribute to the proposed development programme, with a particular emphasis on the implication of the NRA's involvement.

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APPENDIX A - ABBREVIATED TARGET SPECIFICATION FOR AMMONIA SENSOR TO BE USED IN THE HAND-HELD MONITOR

Size

The probe containing the sensor should be less than 100mm in diameter and be capable of operating in 50-75mm of water.

Protection

The probe should be protected against the ingress of water to IP 68.

Temperature range

The compensated temperature range should be +5 - +35 degrees C.

Response time

A minimum of 90% of measured value should be achieved within one minute (directly or by inference).

Range, units and accuracy

Ranges	Units	Accuracy
0 - 10	mg/litre NH_4	0.5 or better
0 - 100	mg/litre NH_4	1.0 or +/- 10%
Associated with above	mg/litre NH_3	+/- 10%

Cross sensitivity

The sensor should exhibit as low a sensitivity to K^+ and Na^+ as possible. The response to all other species that can occur in river water should be minimal. Ideally, the sensor should operate also in saline environments without any detrimental effects on performance.

Calibration

The sensor should require calibration as infrequently as possible, and ideally, use a simple technique that can be undertaken in the field.

APPENDIX B - DETAILS OF IEE COMPUTER DATA-BASE SEARCH

Data bases searched	- INSPEC; - Waternet; - Chemical Abstracts; - Aquatic Science Abstracts; - Water Resources Abstracts.
Total no. of records held	- Approximately 14 million.
Subject/key words	- Ammonia/ammonium sensors/sensing/detectors.
Publication dates	- 1986-1991.
Languages	- English.
Geographical coverage	- UK, other Europe, US. (Japan excluded).
Author affiliations	- Academic, commercial, government, any other.

APPENDIX C - LIST OF REGIONAL NRA PERSONNEL WHO CONTRIBUTED TO THIS STUDY

Dr J Adams, NRA Severn Trent Region, (Nottingham).

Mr T Long, NRA Head Office, (Bristol).

Mr P Waldren, NRA Anglian Region, (Huntingdon).

Mr T Reeder, NRA Thames Region, (Reading).

Mr J Dolby, NRA Severn Trent Region, (Solihull).

Mr P Williams, NRA Wessex Region, (Bridgewater).

APPENDIX D - LIST OF RESEARCH ESTABLISHMENTS AND COMPANIES CONTACTED

Research establishments

City University
UMIST-(Manchester)
Dublin City University
Harwell Laboratory
UCL (London)
Karl-Franzens University
Water Research Centre
Cambridge Consultants
PA Consulting
Luton College of Further Education

Companies

Fisons
Unicam/Philips
Ingold
Schlumberger
York Sensors
Thorn-EMI
EDT Instruments
Orion Research
SEMAT
Radiometer
Flowline systems
Tintometer
Siemens Plessey
Arkon Instruments
ABB Kent-Taylor
Ciba Corning
ADC
pHox
Russel pH
CP Instruments
Jenway
WPA
DMP Electronics
Bran & Luebbe
Camlab
Biomedical Sensors
Wimpey Environmental
Medisense

APPENDIX E - BACKGROUND REFERENCES

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