GA Water Quality
(Box 5)

A REVIEW OF ON-LINE WATER QUALITY ANALYSERS

R W Bogue

October 1996

Consultants's report to the Environment Agency

CONFIDENTIAL

CONTENTS

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1. INTRODUCTION

1.1 Background

This study was commissioned by the Environment Agency (EA) in September 1996 and concerns the capabilities and availability of on-line instruments for the determination of a range of water-borne analytes.

The EA presently operates approximately 130 permanent monitoring stations which determine 6 or 7 variables such as pH, conductivity, turbidity, ammonia, nitrate etc. and the products considered in this report could allow this range to be significantly expanded.

1.2 Objectives

The primary objective of this report is to provide details of existing on-line analysers for a range of chemical species of interest to the EA.

Specifically, this study considers on-line sensing techniques, product performance, availability, prices, ownership costs and maintenance and support requirements. The report aims to make such information available to personnel within the EA who have an interest in the continuous or semi-continuous on-line monitoring of water-borne analytes. It should be viewed as a working document and, in view of the pace of product developments, may warrant regular updating.

1.3 Scope

This study is restricted to on-line instruments. The analytes considered are limited to those of direct or potential interest to the EA, established through discussions with Andrew Chappell (see 2.3, below) which occur in the freshwater environment. Instruments aimed specifically at oceanographic applications are excluded.

1.4 Method

The information presented in this report was derived from the following sources:

* The author's library of product literature and prices;
* Product and price information obtained during the course of this study;
* Various technical reports and conference proceedings;
* Telephone discussions with instrument manufacturers and their UK representatives.

2. EXISTING ON-LINE PRODUCTS

2.1 Analytes than can be determined on-line

On-line monitors are available for a very wide range of analytes. The following table lists those of potential interest to the EA that can be monitored continuously or semi-continuously, on-line, by commercially available instruments.

Table 2.1 - Some analytes that can be determined on-line by existing instruments

Alkalinity	
Aluminium	Manganese
Ammonia/Ammonium	Metals (trace, e.g. Cu, Pb, Cd, Zn, As)
BOD	Nitrate
Bromine	Nitrite
Chlorophyll	Oils/other organics
Chromate	Pesticides
Chloride	Phenols
Chlorine (free and combined)	pH
Chlorine dioxide	Phosphates
COD	Sulphate
Colour	Sulphide
Conductivity/salinity	Temperature
Cyanide	TOC/TC
DO	Total organics
Fluoride	Toxicity
Hydrazine	Turbidity
Iron	Volatile organics

2.2 Overview of measuring techniques

Many different measuring techniques are employed in on-line analysers. Some are particularly versatile and are used for several analytes (e.g. colourimetry, ISEs), others are analyte specific (e.g. immunoassay), and some analytes may be determined by more than one technique (e.g. ammonia, nitrates etc.).

Table 2.2 (overleaf) illustrates the more commonly used measuring techniques for a selection of the analytes listed above. The abbreviations listed overleaf are used. Note that the terms "photometry" and "colourimetry" are both used by manufacturers to describe techniques that involved quantifying the intensity of a colour following some chemical reaction. The latter term is used in this report, except where manufacturers have specifically used the former.

AAS Atomic absorption spectroscopy
C Colourimetry
FID Flame ionisation detector
GC Gas chromatography
IC Immunochemical
IR Infra-red (absorption)
ISE Ion-selective electrode
UV Ultra-violet (absorption, fluorescence)
V Voltammetry

Table 2.2 - Some measuring techniques used in on-line analysers

	ISE	UV	V	IC	C	Other techniques
Ammonia/Ammonium	*	*	-	-	*	-
BOD	-	-	-	-	-	Bioreactor, biosensor
Chlorophyll	-	*	-	-	-	-
COD	-	-	-	-	*	Oxidation plus "C" etc.
Cyanide	*	-	-	-	-	-
Fluoride	*	-	-	-	-	-
Manganese	-	-	*	-	*	-
Metals (trace)	*	*	*	-	*	AAS
Nitrates	*	*	-	-	*	-
Oils	-	*	-	-	*	Various
Organics	-	*	-	-	-	GC, IR, FID
Pesticides	-	-	-	*	-	-
Phosphates	-	-	-	-	*	-
TOC	-	-	-	-	-	Oxidation plus IR

2.3 Product details

2.3.1 Introduction

The following sub-sections provide summary technical details of products, together with listings of the better known and more reputable suppliers, for ten of the analytes listed above, namely:

- Ammonia/ammonium
- BOD
- Chlorophyll
- COD
- Nitrates
- Organics/oils
- Pesticides
- Phosphates
- Trace metals
- TOC

Note that these product and supplier listings are not definitive but representative only. In the case of several of the more commonly monitored analytes (ammonia, nitrate etc.), large numbers of manufacturers now offer on-line products. For further information on other techniques that are (or could be) used, other products and further analytes that may be determined on-line, contact the following:

Andrew Chappell (Environment Agency)	Instrument Evaluation Centre, Fobney Mead, Rose Kiln Lane, Reading RG2 0SF. Tel. 0118 953 5945, fax. 0118 931 1438.
Paul Williams (Environment Agency)	National Centre for Instrumentation and Marine Surveillance, Rivers House, Lower Bristol Road, Twerton, Bath BA2 9ES. Tel. 01225 444066, fax. 01225 469939.
Robert Bogue (Topic Advisor to Agency)	Tamar House, Tuckermarsh, Bere Alston, Devon PL20 7HB. Tel. 01822 840434, fax. 01822 841300.

2.3.2 Ammonia/ammonium

Techniques

Ammonia/ammonium may be determined on-line by various electrochemical and optical techniques, e.g. ISEs, UV spectroscopy, wet reagent-aided photometry. Examples of a selection of products based on each of these techniques are illustrated below. Note that a wide range of on-line ammonia analysers are presently being evaluated at Fobney Mead by Andrew Chappell (details above).

Performance

Technique	UV absorption spectroscopy, following addition of NaOH
Product	AM 100 (Datalink Instruments)
Ranges	0.05-100 mg/l or 5-10,000 mg/l NH_4^+
Accuracy	Not stated
Reproducibility	Not stated
Response time	< 2 min.
Output	4-20 mA, RS.232

Technique	Ion-selective electrode
Product	Monitor 90 (Bran + Leubbe)
Ranges	0-10 to 0-1000 mg/l NH_4 as N
Accuracy	± 5% of FSD
Detection limit	1% of FSD
Reproducibility	± 2% of FSD
Response time	30 sec.
Output	0/4-20 mA, RS.422A

M E M O

ENVIRONMENT AGENCY

To:

From: Andrew Chappell

Our ref:
Your ref:

Date: 22 November 1996

The following reports have now been printed and I enclose copies of either the full reports or the executive summaries for your information. (If you have received the summaries and would like a complete copy then please contact me or Chris Wright on 7-25-5945, 5973, or 5981.)

Evaluation of a Hydrolab Ammonium Ion Selective Electrode : A detailed study of the recently introduced ISE for use on DataSonde loggers

Evaluation of a YSI-6000 upg Water Quality Monitor : A detailed study of the improved YSI-6000

A Review of On-line Water Quality Analysers : A review of current commercially available instrumentation, (including a section on cost of ownership).

Please note that these reports contain specific commercial information & should not be shown to other manufacturers or sales reps.

We have also recently produced other reports which are available on request, but have not been generally distributed. They are **Evaluation of a Chelsea Instruments Aquatraka III Fluorometer** and **Tests of a Data-link FFT ammonium monitor.**

We are currently working on a Randox Aquanox Luminometer (a toxicity meter) and a number of on-line ammonia analysers.

If you have any suggestions for other instruments, determinants or studies then please contact me.

Andrew Chappell
National Centre for Instrumentation - Evaluation Laboratory

Technique	Gas diffusion ISE
Product	Model 8810 (Polymetron)
Ranges	0.1-10,000 mg/l NH_4
Accuracy	± 2%
Detection limit	0.1 mg/l NH_4
Reproducibility	< 3%
Response time	c. 5 min.
Output	0/4-20 mA

Technique	Photometry following indophenol blue reaction
Product	AMTAX Inter (Lange)
Ranges	0.01-20 mg/l or 0.1-80 mg/l NH_4 as N
Average standard dev.	5%
Response time	5-10 min.
Output	0/4-20 mA, RS.232

Availability

A large number of manufacturers now offer on-line ammonia analysers. A representative selection are listed below.

- Datalink Instruments (France, via REN Scientific Ltd.)
- Polymetron (via Sieger Ltd.)
- Lange (Germany, via Robin Instruments Ltd.)
- ABB Kent-Taylor (via ABB K-T Ltd.)
- Applikon (Netherlands, via UK subsidiary)
- pHOX Systems Ltd. (UK manufacturer)

2.3.3 BOD

Techniques

A number of products now exist that can determine BOD on-line. Those considered here actually measure biological oxygen demand, not some surrogate parameter, but of course do not measure BOD_5 but make a short-term determination. The techniques used all involve measuring the consumption on oxygen by a colony of micro-organisms and differ in terms of the nature of the organisms and how they are incorporated in the analyser. Some are true biosensors, in that the organisms are actually incorporated into a sensing membrane, whilst in others the organisms are not immobilised but contained in a "bioreactor". Correlation between the BOD values measured with these instruments and BOD_5 is often good, with figures of greater than 0.95 being quoted by STIP. However, for samples with variable composition, this correlation tends to fall. Nevertheless, it should be noted that, during a series of German inter-laboratory trials, the variations in measured BOD_5 figures from different laboratories were approximately 10 times greater than those of BOD "M3" made with STIP instruments. Note also that several products that determine dissolved organics or TOC are claimed also to determine BOD. Such claims must be treated with a healthy degree of scepticism, although in certain well defined conditions, these variables can be correlated with laboratory BOD_5 measurements.

Performance

Technique	Bioreactor/oxygen sensor
Product	SA 250 (CEMI)
Ranges	10-100 mg/l to 1000-3000 mg/l
Sensitivity	5 mg/l
Accuracy	10%
Response time	30-90 min.
Output	4-20 mA

Technique	Live cell biosensor/oxygen sensor
Product	BOD-2200 (Nissin Electric)
Ranges	0-100 to 0-500 mg/l
Sensitivity	Not stated
Reproducibility	± 3%
Response time	c. 30 min.
Output	4-20 mA, RS.232

Technique	Bioreactor/oxygen sensor
Product	BIOX-1010 (STIP)
Ranges	2-10,000 mg/l (option to 80,000)
Sensitivity	Can resolve 1-2 mg/l
Accuracy	Not quoted
Response time	3 min.
Output	4-20 mA, RS.232

Availability

The UK outlets for the above manufacturers are listed below. Note that Medingen (Germany) manufactures a BOD-responsive biosensor-based product but this is for laboratory rather than on-line applications. Also, a number of companies produce respirometers that may be used for BOD determinations, e.g. Kelma (Netherlands).

- CEMI (Italy, via Sysco Analytics Ltd.)
- STIP (Germany, via Envitech Ltd.)
- Nissin Electric (Japan, via Terra Nova Systems Ltd.)

2.3.4 Pesticides

Technique

The only technique so far exploited for the on-line determination of pesticides is an immuno-chemical reaction between an enzyme and the analyte (a "competitive immunoassay"). The reaction is monitored optically, whereby the intensity of a colour formed by the reaction is proportional to the analyte concentration. Whilst some laboratory analytical techniques such as GC have been adapted for field use, particularly in the US, this approach is not seen as technically feasible in this context, due to both the sample pre-treatment requirements and the complexity of the analytical procedures themselves (GC-MS), both of which preclude the unattended on-line deployment of such instruments.

Performance

Technique	Competitive immunoassay/colourimetry
Analytes	Triazines (atrazine, simazine, propazine)
Range	0.05-1.00 ppb
Resolution	< 0.05 ppb
Response time	c. 45 min.
Outputs	4-20 mA, RS.232

Availability

The only company known to have a product on the market is Seres (France), available through the UK subsidiary Seres (UK) Ltd.

2.3.5 Phosphates

Techniques

The main technique used to determine phosphates on-line is wet reagent-aided photometry (colourimetry), in which the intensity of the colour resulting from a reaction between the analyte and various reagents is measured. Various different implementations of this approach are employed.

Performance

Technique	Dual beam absorption photometry (vanadate-molybdate reaction), measured at 380 nm
Product	PHOSPHAX (Lange)
Ranges	0-2.0 to 0-15 mg/l PO_4 as P
Average standard dev.	5%
Response time	c. 6 min.
Output	4-20 mA

Technique	Wet reagent-aided colourimetry
Product	8242 Phosphate Monitor (ABB Kent-Taylor)
Ranges	0-60 mg/l as PO_4^{3-}, 0-20 mg/l as P
Accuracy	< ± 0.05 mg/l or < ± 5%, whichever is the greater
Reproducibility	< ± 0.05 mg/l or < ± 5%, whichever is the greater
Response time	90% step change in c. 11 min.
Output	0-10, 0-20 or 4-20 mA

Technique	Wet reagent-aided colourimetry
Product	Monitor 90 (Bran + Luebbe)
Ranges	0-2.5 to 0-100 mg/l as PO_4^{3-}, 0-0.5 to 0-20 mg/l as P
Accuracy	± 2% of FSD
Reproducibility	± 2% of FSD
Response time	c. 15 min.
Output	0-20 mA, 4-20 mA, RS.422A

Availability

Many of the major process instrumentation suppliers, as well as companies specialising in water quality monitoring, produce on-line phosphate analysers. Some of the better known are listed overleaf - there are many others.

- Bruno Lange (Germany, via Robin Instruments Ltd.)
- ABB Kent-Taylor
- Bran + Luebbe (via Bran & Luebbe (GB) Ltd.)
- Applikon (Netherlands, via Applikon Analyzers (UK) Ltd.)
- Seres (France, via Seres (UK) Ltd.)
- pHOX Systems (UK manufacturer)

2.3.6 Nitrates

Techniques

Both optical and electrochemical techniques are used to determine nitrates on-line. Optical methods are a more recent development and are usually reagentless. Most involve UV absorption although some use wet reagent-aided colourimetry (as with phosphates). Electrochemical nitrate analysers employ various ISE arrangements. Optical methods are favoured due to their rapid response, lack of wet reagents and lower running costs (compare the Lange NITRAX and ABB Kent-Taylor products' maintenance and reagent requirements in 2.4.2, below). The Seres product (see below) undertakes a spectral scan (200-800 nm, i.e. UV to visible wavelengths), compares this with stored spectra and can eliminate errors caused by interfering species (e.g. humic acids, phenols etc.).

Performance

Technique	UV absorption at 210 nm (reagentless)
Product	NITRAX (Lange)
Ranges	0-0.01 to 0-200 mg/l as NO_3, 0.01-50 mg/l as N
Average standard dev.	5%
Reproducibility	Not stated
Response time	< 60 sec.
Output	0/4-20 mA

Technique	Dual beam UV absorption (reagentless)
Product	KA 100 (Sigrist)
Ranges	0-10 to 0-200 mg/l NO_3^-
Accuracy	5% (maximum error)
Reproducibility	3%
Response time	Immediate
Output	0/4-20 mA

Technique	UV/vis scanning absorption spectroscopy
Product	Spectroflux Nitrate (Seres)
Ranges	0-10 to 0-100 mg/l NO_3
Accuracy	± 2% of full scale over 0-100 mg/l range
Detection limit	1 mg/l NO_3
Response time	4-5 sec.
Output	0/4-20 mA, RS.232

Technique	Amperometric, 3 electrode system (nitrate reduced to nitrite)
Product	Model 8893 (Polymetron)
Ranges	0-25 to 0-200 mg/l NO_3
Sensitivity	0.5 mg/l NO_3
Accuracy	< ± 2% "of middle of measuring range"
Reproducibility	As above
Response time	< 3 min. to 90% of reading
Interferences	Chlorine and residual oxidants (ozone, chlorine dioxide etc.)
Output	0/4-20 mA

Technique	Electrochemical (ISE)
Product	EIL 8236 (ABB Kent-Taylor)
Ranges	Any two consecutive decades between 0.2 and 1000 mg/l as N or 1.0 and 5000 mg/l as NO_3
Accuracy	Better than ± 5% of reading
Repeatability	± 2% of reading
Detection limit	Not stated
Response time	< 5 min. for 90% step change
Output	0-1/10/20 or 4-20 mA

Availability

As with phosphate analysers, a similarly large number of companies offer on-line nitrate analysers. Some examples are listed below.

- Bruno Lange (Germany, via Robin Instruments Ltd.)
- Bran + Luebbe (via Bran & Luebbe (GB) Ltd.)
- Sigrist-Photometer (Switzerland, via Sigrist-Photometer (UK) Ltd.)
- Applikon (via Applikon Analyzers (UK) Ltd.)
- ABB Kent-Taylor
- Polymetron (Switzerland, via Sieger Ltd.)
- Seres (France, via Seres (UK) Ltd.)
- Contronic (Sweden, via PPM Ltd.)
- pHOX Systems Ltd. (UK manufacturer)

2.3.7 TOC/TC

Techniques

TOC and TC (total carbon) are determined on-line by oxidising the carbon by various means (e.g. UV-promoted persulphate oxidation or in a high temperature oven) and detecting the resulting CO_2 by IR absorption. These instruments are, therefore, amongst the more complex of on-line analysers and are derived from their laboratory counterparts. In certain circumstances TOC can be used as a surrogate for BOD_5, in that the two variables will sometimes correlate (see 2.3.3, above). Such correlations tend to be optimal where the organic compounds are simple (e.g. sugars etc.) but vary considerably according to the species constituting the bulk of the organic load and also with particle size. Further, when the stream's composition varies with time, correlations invariably fail. Much detailed technical information on this correlation can be found in the technical literature and some is available from the TOC instrument

suppliers (see below). This issue has also been investigated by WRc and by Terry Long (Environment Agency, Twerton, details as Paul Williams, above).

Performance

Technique	VU-promoted wet chemical oxidation, CO_2 detected by NDIR
Product	Model 1800 (Astro)
Ranges	0-5 to 0-10,000 ppm C
Accuracy	Not stated
Repeatability	2% of full scale
Response time	From 2 min. to 90%
Output	4-20 mA, 0-10 VDC, RS.232
Technique	As above
Product	Model 2000 (Seres)
Ranges	0-1000 mg/l C (auto dilution for higher ranges)
Accuracy	± 2% of full scale
Detection limit	0.25 mg/l over 0-5 mg/l range, 5 mg/l over 0-250 mg/l range
Response time	7 min.
Output	4-20 mA
Technique	As above
Product	Protoc 2000 (PPM)
Ranges	0-5 ppm to 0-50,000 ppm (can determine TOC and TC)
Accuracy	Not stated
Repeatability	Better than ± 2% of full scale
Response time	2-3 min., depending on range
Output	0-1 VDC, 4-20 mA, RS.232
Technique	High temperature catalytic oxidation, CO_2 detected by NDIR
Product	Model 6800 (Ionics)
Ranges	0-5 to 0-20,000 ppm C
Accuracy	Not stated
Detection limit	0.1 ppm or 0.5% of full scale, whichever is greater
Reproducibility	± 2% of full scale
Response time	5.5 min.
Output	0-10 VDC, 4-20 mA
Notes	Requires purified CO_2-free nitrogen carrier gas, clean dry air supply and 1N sulphuric or phosphoric acid

Availability

A growing number of companies now produce on-line TOC analysers and a selection of the better known are listed below.

- Astro International (US, via Applikon Analyzers (UK) Ltd.)
- Hydro-Environnement (France, via ETI Group Ltd.)
- Seres (France, via Seres (UK) Ltd.)
- Rosemount
- Ionics (US, via Ionics UK Ltd.)
- Pollution and Process Monitoring Ltd. (PPM), manufactured in the UK

2.3.8 COD

Techniques

Although chemical oxygen demand is most often used in discharge monitoring applications it is considered here due to the growing interest in it as a means of detecting the oxygen depleting capacity of pollutants. Furthermore, COD is viewed as a key variable in the Urban Wastewater Directive. As with TOC, COD can be shown to correlate with BOD_5 in some circumstances. This issue has been investigated in detail by Terry Long (EA, Twerton).

As with TOC measurements, on-line COD determination involves oxidising the sample (e.g. with ozone, potassium dichromate and sulphuric acid, etc.) and quantifying the reaction by various means. Dichromate-based oxidation followed by colourimetric detection is most widely used, although some products employ the true Blue Book method (see Applikon product, below). In the case of the STIP product (see also below), ozone is the oxidant and the degree of oxidation is measured with two ozone sensors, one either side of a reaction chamber.

Performance

Technique	Ozone-promoted oxidation, ozone probes
Product	Phoenix 1010 (STIP)
Ranges	2-1500 mg/l COD
Accuracy	Not stated
Repeatability	Not stated
Response time	c. 3 min.
Output	0/4-20 mA

Technique	Dichromate oxidation at 150°C, colourimetric detection
Product	3400 (Ionics)
Ranges	0-100 ppm to 0-5000ppm
Accuracy	Not stated ("Precision" = 5%)
Repeatability	Not stated
Response time	10-15 min. to 2 hours, depending on sample composition
Output	0-10 VDC, RS.232

Technique	Dichromate oxidation with silver and mercury salts, microwave heating, colourimetric detection
Product	DCO (Seres)
Ranges	30-700 mg/l
Accuracy	± 3% of full scale
Repeatability	Not stated
Limit of detection	30 mg/l
Response time	5-15 min.
Output	4-20 mA, RS.232

Technique	Dichromate oxidation followed by potentiometric titration with Fe (II) solution (standard Blue Book method)
Product	ADI 2020 (Applikon)
Ranges	0-5000 mg/l
Accuracy	Not stated
Repeatability	1% or 10 mg/l, whichever is the larger
Response time	2 hours
Output	4-20 mA, RS.232

Availability

Few companies yet produce on-line COD monitors, although these are likely to increase in the future. Some of the better known suppliers are listed below.

- STIP (Germany, via Envitech Ltd.)
- Ionics (US, via UK subsidiary)
- Seres (France, via Seres (UK) Ltd.)
- Applikon Analyzers (Netherlands, via Applikon Analyzers (UK) Ltd.)

2.3.9 Chlorophyll

Techniques

Chlorophyll is invariably determined optically. Samples are illuminated by UV light and the intensity of the resultant fluorescence is measured and is proportional to the chlorophyll concentration.

Performance

Technique	UV fluorescence
Product	Chlorophyll Monitor (Turner Designs)
Ranges	5-750 µg/l
Resolution	Better than 0.1 µg/l (up to level of 50 µg/l)
Response time	Continuous output, 10 measurements/sec.
Output	4-20 mA

Technique	UV fluorescence
Product	Aquatracka III (Chelsea Instruments)
Ranges	0.01-100 µg/l chlorophyll-a
Accuracy	± 0.01 µg/l or 3%, whichever is the greater
Resolution	0.01 µg/l
Response time	Instant
Output	0-4 V

Availability

Few companies manufacture chlorophyll monitors. Details of the two considered above, and one other, are:

- Chelsea Instruments Ltd. (UK manufacturer)
- Turner Designs (US, via Steptech Instrument Services Ltd.)
- Dr Haardt (via Duncan Associates Ltd.)

2.3.10 Organics, oils and volatile organics

Techniques

A wide variety of techniques are employed to determine organics in water and vary according to the exact nature of the measurement, i.e. dissolved organics, volatile organics, specific organic compounds etc. Techniques include IR absorption, UV fluorescence, flame ionisation, chromatography etc. Some gas stripping instruments offer the ability to add a GC stage for analyte-specific determinations. Note the following abbreviations used below: BTEX - benzene, toluene, ethylbenzene and xylene; PAH - polyaromatic hydrocarbons.

Performance

Technique	UV fluorescence
Product	TD-4100 (Turner Designs)
Analytes	BTEX, fuels, PAHs, oils, aromatic solvents etc. (non-specific)
Ranges	1 ppb to > 1000 ppm
Detection limits	Vary according to species and sample matrix
Accuracy	Not stated
Response time	< 10 sec.
Output	4-20 mA

Technique	IR absorption following extraction with solvent
Product	DHIR (Seres)
Analytes	Aliphatic and aromatic hydrocarbons
Ranges	0-30 mg/l
Limit of detection	0.1 mg/l for range 0-10 mg/l
Accuracy	Not stated
Response time	11 min.

Technique	Nitrogen stripping followed by gas chromatography (specific)
Product	Model 8285 (Fluid Data)
Analytes	Wide range of organics (benzene, hexane, phenol, xylene, ethyl-benzene, chlorinated species, toluene, alcohols etc.)
Ranges	0-20 ppm nominal but no upper limits
Limit of detection	10 ppb for most species
Accuracy	c. 1%
Repeatability	± 2%
Response time	Varies with species, typically 4-9 min.
Output	0-10 VDC, 4-20 mA
Comments	Requires He (carrier gas), H_2 (fuel), and N_2 or CO_2 (stripper)

Technique	Nitrogen stripping followed by flame ionisation detection
Product	Model 8280 (Fluid Data)
Analytes	Volatile organics and hydrocarbons
Ranges	0-10 ppm to 0-2%
Sensitivity	Better than 100 ppb for most compounds
Repeatability	± 2%
Response time	30-45 sec. to 90%
Output	4-20 mA

Technique	UV absorption at 254 nm
Product	OPM 500 (pHOX Systems)
Analytes	Total dissolved organics
Ranges	0-2 AU (absorbance units). This equates to TOC ranges 0-60 to 0-250 mg/l, see note below)
Accuracy	± 5% over range 0-1.5 AU, ± 10% over range 1.5-2 AU
Repeatability	± 2%
Response time	Instant
Output	4-20 mA, RS.232
Note	Readings in AUs can be correlated empirically to TOC, BOD and COD according to the manufacturer. However, the accuracies achieved are only stated for AU measurements

Technique	Modulation of transmitted light in coated optical fibre
Product	DHP-200 (FCI Environmental)
Analytes	Petroleum hydrocarbons
Ranges	0-2000 ppm (as BTEX)
Accuracy	± 3 ppm or ± 10%, whichever is the greater
Limit of detection	3 ppm (as xylene)
Response time	5 min. to 90%
Output	Digital interface, 1200 baud

Availability

Some companies producing products as considered above are listed below. Several other manufacturers produce a variety of oil in/on water monitors. These have been reviewed in a recent EA R&D report (contact Paul Williams for details).

- Turner Designs (US, via Steptech Instrument Services Ltd.)
- Fluid Data (US, via UK subsidiary)
- pHOX Systems Ltd. (UK manufacturer)
- Cavendish Applied Technology Ltd. (UK manufacturer)
- FCI Environmental (US, no known UK outlet)

2.3.11 Trace metals

Techniques

Few techniques are used so far to determine trace metals on-line, principally voltammetry and various optical methods (with and without wet reagents). Most of these techniques offer a multi-metal sensing capability, whilst others, based on different techniques, determine just a single metal (usually Hg). Note that metal detection is the topic of much research and various new and improved techniques and technologies are under investigation. Products that determine individual metals as used in water treatment (Al, Mn, Fe) are excluded from the following summary (on-line analysers for these species invariably employ wet reagent-aided colourimetry).

Performance

Technique	Voltammetry (3 electrode system)
Product	OVA 3000 (Chemtronics)
Analytes	Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Ag, Cd, Pb, Hg, Ti, Bi
Ranges	Varies according to metal, typically up to a few thousand ppb
Detection limits	Vary according to metal, 0.1 ppm upwards
Accuracy	Not stated
Reproducibility	Not stated
Response time	Minutes
Output	4-2- mA, RS.232

Technique	UV/vis absorption spectroscopy (reagentless for some metals, e.g. Cr and Fe, complexing reagents used for others)
Product	To be launched imminently by SERES
Analytes	Cr, Cd, Fe, Cu, Ni, Pb, Zn, plus total metals
Ranges	0-500 ppb
Limit of detection	5% of range
Accuracy	± 5%
Reproducibility	Not stated
Response time	5 min.
Output	0/4-20 mA, RS.232

Technique	Atomic absorption spectroscopy following wet chemical pre-treatment
Product	Hg-Mat 1 (Seitner)
Analyte	Mercury
Ranges	0-10 µg/l to 0-30 mg/l
Accuracy	Not stated
Stability	Better than 1% of range
Response time	c. 3 min.
Output	0/4-20 mA

Availability

Relatively few companies yet produce on-line trace metal analysers. The better known are considered above. i.e.

- Chemtronics (Australia, via Sartec Ltd.)
- Seres (France, via Seres (UK) Ltd.)
- Seitner (Germany, via Windsor Scientific Ltd.)

2.4 New and alternative techniques

This section considers, albeit briefly, a number of newer techniques and those that may have a broader role in detecting pollution.

2.4.1 Electronic noses

Electronic noses (ENs) are arrays of semi-selective gas or vapour sensors, coupled to sophisticated signal processing systems, such as artificial neural networks, that can be "taught" to recognise certain characteristic odours or mixtures of compounds. To date they have found most applications in the automated quality assurance of aromatic products such as perfumes, coffee, tobacco and so forth. Research continues at a pace.

In the present context ENs may have a role to play in detecting pollution than can be characterised by its odour, rather than from the presence of specific compounds. Analysing the headspace above water samples with an EN may allow the detection of, for example, organic solvents, sewage, silage, oils and fuels, phenols etc. Two UK manufacturers of ENs are Neotronics and Aromascan.

2.4.2 Multi-sensor arrays

A number of research groups have developed arrays of sensors that respond to several water quality analytes. Perhaps the best known of these is the CENSAR development, being undertaken at the University of Southampton, with support from the EA, Siemens-Plessey and other potential users. These need to utilise fabrication technologies that are common to all of the sensors used and CENSAR uses thick film technology to determine temperature, conductivity, pH, dissolved oxygen and redox on a single substrate. Such arrays offer prospects to determine simultaneously a range of analytes and should, therefore, offer a cost-effective alternative to the use of discrete instruments for each analyte.

Research is addressing the development of arrays of other sensors, e.g. biosensors, optical sensors etc. for a broader range of analytes. In the longer term, such arrays may be configured with "smart" signal processing as used in ENs and have been dubbed "electronic tongues".

2.4.3 Biosensors

Whilst few biosensors are yet available commercially for environmental monitoring applications, and even fewer for on-line use, they offer strong longer term prospects. They have been reviewed recently in some detail by the present author on behalf of the EA (see "Biosensors for environmental monitoring: A review of capabilities and strategies for the future", November 1995). The techniques used in biosensors, such as enzyme and immunochemical reactions, can be highly sensitive and specific.

Broadly speaking future generations of biosensors offer scope to monitor certain analytes that are difficult or impossible with existing techniques, e.g. insecticides, herbicides, BOD (products already exist, see above), toxicity, phenols, PCBs, trace metals, bacteria, dioxins, cellular biomass etc.

2.4.4 Toxicity

A number of products exist that determine the toxicity of waters. Microtox is, of course, well known but various on-line instruments have emerged in recent years. Most are based on the toxicity-induced inhibition of the activity of a colony of micro-organisms are, therefore, conceptually similar to fish monitors and structurally similar to on-line BOD monitors (see above). The majority are being used to protect activated sludge treatment plants but could well have a role in detecting gross pollution of an unspecified nature, perhaps in circumstances where several plants discharge different substances to an individual water course. The major problem, other than high cost (c. £26K from STIP) and maintenance requirements, is knowing what exactly is being measured, as the organisms used invariably respond variably to different pollutants. Selecting a combination of micro-organisms that are generally present in unpolluted river water, for example, may nevertheless generate data of significant value in detecting early the presence of "broad band" pollution. STIP has sold a number of units for this type of application. Biosensors that respond to toxicity are the topic of much development and may well yield the next generation of on-line toxicity monitors.

2.4.5 Enhanced chemiluminescence

The EC technique has recently been commercialised in the water quality monitoring context and relies on a reaction between luminol and an oxidant in the presence of an enzyme catalyst (horseradish peroxidase). Light is emitted by this reaction which is inhibited by free radical scavengers. These include phenols, certain metals, amines, cyanides, compounds present in faeces and urine, and so forth. Limits of detection vary from ppb to ppm levels. EC is, therefore, another "broad band" technique and as yet, is only available in the form of a portable instrument (priced at £5K from Aztec, £6K from Randox). Predictably, perhaps, the manufacturers claim that data generated by these instruments correlate well with BOD_5 and COD (over 0.9). Trials on river water have shown that the technique can distinguish between river waters of different quality and detect and track sewage. Unsurprisingly, very few data are available concerning exactly what is being detected! Nevertheless, an on-line implementation of this technique may well have a role within the EA as an adjunct or alternative to toxicity. A portable instrument has been evaluated by Roger Sweeting.

2.4.6 Multi-analyte instruments

Finally, it should be noted that a growing number of manufacturers are producing on-line instruments that can determine more than one analyte (see also 2.5.2, above). Whilst several instruments can determine certain closely related species (e.g. nitrate and nitrite, different trace metals etc.), these respond to chemically differing species. The recently launched "DiaMons" from Bran + Luebbe is a good example. This can determine phosphate, nitrate, nitrite, ammonia and organic load, simultaneously, and employs UV absorption and wet reagent-aided colourimetry. Stored absorption spectra are used to compensate for the effects of various interfering species. The unit is priced at £21K, and although aimed mostly at industrial processes or water or sewage treatment plant, it and similar products may well offer an economically viable option to the EA where there is a requirement to determine several species at a single site.

3. COSTS AND MAINTENANCE REQUIREMENTS

3.1 Purchase prices

The majority of on-line analysers as considered above are priced in the approximate range £10-25K, although market and user pressures have recently led to some falling below the £10K barrier. Other more complex instruments are significantly more costly. Products using reagentless techniques (e.g. UV absorption) tend to be less costly than their wet reagent-based counterparts. A selection of current purchase prices are listed below. Note that these all vary somewhat according to specification, e.g. sampling system requirements, data processing and recording, number of sample streams and so forth.

Ammonia

8232 (ABB Kent-Taylor)	£7K
AM 100 (Datalink Instruments)	£13K

BOD

SA 250 (CEMI)	£25K
BIOX-1010 (STIP)	£26K

COD

Phoenix 1010 (STIP)	£29K
ADI 2020 (Applikon)	c. £35K

Chlorophyll

Chlorophyll Monitor (Turner Designs)	£14.5K
Acuatracka III (Chelsea Instruments)	c.£8-10K

Pesticides

Pesticide Analyser (Seres)	c. £20K (yet to be finalised)

Phosphates

8242 (ABB Kent-Taylor)	£8K

Nitrates

Spectroflux (Seres)	£11K
Applikon ADI	£12.5K

TOC

Protoc 2000 (PPM)	£12.7K
Astro 1900 (Applikon)	£15-19K
Ionics 6800	£14-17K

Trace metals

OVA 3000 (Chemtronics)	£30-50K, dependent on specification
Seres (no product no. yet designated)	c. £15-20K (to be finalised)
Hg-Mat 1 (Seitner)	c. £12K

Organics

OPM 500 (pHOX)	£6-6.5K
8280 (Fluid Data)	£12K
8285 (Fluid Data)	£35K

3.2 Ownership costs and product support

Purchase prices are only part of the story, as many on-line analysers require a significant degree of support which leads to high ownership costs. Those employing wet reagents, particularly where these are used to initiate chemical reactions, are amongst the most difficult and costly to maintain. Some of the key factors leading to overall ownership cost include:

- Consumable reagents (to initiate reactions)
- Consumable calibration solutions
- Consumable cleaning solutions
- Consumable gases (where required)
- Replacement components (sample tubes, filters, pump components etc.)
- Environmental control of analyser cabinets (temperature, air flushing etc.)
- Time taken for routine maintenance
- Time taken to perform calibration
- Regular visual inspections

However, recent years have seen concerted efforts my many manufacturers to reduce ownership costs and optimise up-time. This has been achieved by a number of means, e.g. automated calibration routines; reagentless sensing techniques; reduced reagent consumption by reducing the size of the measuring cell, sample volume and tube diameters; reduced servicing via self-fault diagnosis routines, etc. Many analysers that consume reagents can operate for between 2 and 4 weeks without the need for reagent replacement and in the case of some more specialised devices, this period is extended to a month or more.

No generalised statements can be made regarding maintenance, periods of unattended running or costs of ownership; these are governed by each individual instrument design. However, a flavour of these are provided by some data, derived from discussions by the author with manufacturers during 1994, discussions during this study and from recent product literature, as summarised below.

Ionics TOC Transmitter
Consumables: CO_2-free nitrogen or air, 1 gallon/week dilute sulphuric acid, 3 gallons/week deionised water.
Maintenance: Average of 1-2 man hours/week but will operate unattended for around 4 weeks.

Seres Spectroflux nitrate monitor
Consumables: No reagents needed (UV method), new flow tube required every 3 months.
Maintenance: Visual inspection and flow tube replacement every 3 months. Calibration every three months with standard solution.

Lange NITRAX nitrate monitor
Consumables: None (no active reagents, calibration standards or cleaning solutions).
Calibration: None required, factory calibrated for life.

Bran + Luebbe Monitor 90 nitrate monitor
Consumables: Standard solutions, active reagents (instrument features supply for c.2 weeks.
Calibration: Automated.

ABB Kent-Taylor EIL 8236 nitrate monitor
Consumables: Potassium di-hydrogen phosphate, di-sodium EDTA (10 litres each per month). Two calibration solutions, consumed at a rate of 50-80 ml per calibration cycle.
Maintenance: Four-weekly - replenish reagents, clean flow system; yearly - replace pump tubing, plumbing and pump capstans.

STIP Biox 1000 BOD monitor
Consumables: Electrolyte for oxygen sensor, plastic tubing.
Maintenance: c. 1 hour/week (visual inspection plus replacement of printer paper).

Fluid Data 8280 Organics monitor
Consumables: Nitrogen stripper gas, hydrogen-free and chromatographic grade - 30-60 cc/min., hydrogen fuel - 40-80 cc/min., FID combustion air - 200-300 cc/min., enclosure purge gas, air or nitrogen - 57 litres/min.

Seitner Hg.Mat 1 Mercury monitor
Consumables: $SnCl_2$ solution, calibration solution, compressed air.
Calibration: Automated.

Polymetron 8810 ammonia monitor
Consumables: Ammonium chloride (calibration), sodium hydroxide and EDTA (conditioning reagents), average consumption - 3 ml/analysis.
Calibration: Automated.
Maintenance: Reagent replacement and pump tube change each month.

ABB 8242 phosphate monitor
Consumables: Complexing reagents, calibration solution. Reagent consumption - 10 litres every 4 weeks.
Calibration: Automated or manual. Calibration solution consumption - 1 litre/4 weeks.
Maintenance: Four-weekly - replace reagents, clean flow system. Yearly - replace tubing and pump capstans.

A recent study by Severn Trent Water into the total 5-year costs of a variety of on-line monitors provides a further insight into this issue and also illustrates the great variability between manufacturers (not identified), as illustrated in Table 3.1, below. Note that both of these classes of instrument were based on wet reagent-aided photometry and, as noted above, these tend to be amongst the most costly to operate and maintain.

Table 3.1 - Five-year costs of some wet reagent-based on-line analysers

Analyte	Purchase price	Consumables	Reagents	Service	Total
Iron	£14K	£380	£1,890	£3,300	£5,570
	£8K	£300	£7,000	£4,250	£11,550
	£8K	£500	£2,325	£6,000	£8,825
	£10K	£2,400	£9,750	£4,000	£16,150
Aluminium	£9.6K	£1,490	£3,000	£7,200	£11,690
	£14K	£380	£6,500	£3,300	£10,180
	£8K	£300	£7,000	£4,250	£11,550
	£7.8K	£975	£18,900	£2,200	£22,075

As well as illustrating that 5-year ownership costs can be very significant, this table shows that purchase price bears little relation to overall operating cost; indeed, in the case of the first two iron monitors, it seems that the purchase price is inversely related to the total operating cost.

To conclude, all on-line products require a degree of maintenance support but this varies greatly from instrument to instrument. Equally, running/ownership costs vary enormously but clearly, instruments using reagentless techniques are to be preferred, even if purchase prices are higher. Manufacturers are now far more forthcoming regarding these issues than in the past, and should the Agency consider the purchase of any products, these matters should be discussed with the manufacturers or suppliers.

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