

THE ROYAL SOCIETY OF CHEMISTRY ENVIRONMENTAL CHEMISTRY GROUP



Bulletin

January 2004



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The current ECG Bulletin may be seen on the internet at <u>http://www.rsc.org/lap/rsccom/dab/</u> <u>scaf003.htm</u>

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Environment, Sustainability and Energy Forum

Recent developments within the RSC's Environment, Sustainability and Energy Forum (ESEF) include the appointment of Dr Elliot Finer as Chair of the Forum and Dr Andrea Jackson as Vice-Chair.

Elliot Finer has recently held key appointments as Director General of the Chemicals Industries Association (1996 – 2002), Head of Chemicals and Biotechnology Division, DTI (1992 – 1995), and Director General of the

Energy Efficiency Office in the Department of Energy (1988 - 1990). Andrea Jackson, who is also Chair of the Environmental Chemistry Group, is a Lecturer at the University of Leeds in the School of the Environment and her main research interest is the chemistry of the atmosphere. Dr Eimear Cotter, from the RSC, will support and manage the initiatives and activities of the Forum. Eimear's research background is also in atmospheric chemistry - before joining the RSC she spent several years in academic research and has also worked as an environmental consultant for Arthur D. Little Ltd.

With these recent appointments, activities within the Forum are beginning to gather pace. The executive committee is currently being formed and once this has been completed, the first executive committee meeting will take place in 2004 where ESEF strategy and key initiatives will be discussed and developed further.

modelling team and major UK academic research groups, with Space Agency support, to accelerate the development of methods of forecasting Earth system processes."

Prof. Jim Aiken, Plymouth Marine Laboratory

"One of the major challenges facing

Institute of Environmental Management & Assessment (IEMA)

benefits, since one of the assumptions required for the market to function is that economic agents have complete knowledge of what is being traded. Nevertheless, economists have tried to assign prices to environmental assets using two general methods:

One method infers a value from goods associated with the environmental asset: economic agents are said to reveal their preference for the environmental good in relation to the amount they actually pay for the associated good. An analysis based on the market price of houses near the environmental asset, or the amount of money spent travelling to the asset, have been suggested as examples of this method of valuation.

The other method relies on asking people what they would be willing to pay to keep an environmental asset, or alternatively what they would be willing to accept in compensation for its loss. A number of issues bedevil this approach, for instance there is the danger of inbuilt bias in the process itself producing erroneous results, and issues concerning the veracity of the answers given by respondents.

Economists are well aware of these difficulties but some feel that the exercise should still be undertaken. According to Turner, Pearce and Bateman, in Environmental economics: an elementary introduction (1994), "Economic (monetary) valuation of nonmarket environmental assets may be more or less imperfect given the particular asset together with its environmental and valuation contexts; but, invariably, some valuation... is better than none, because none can mean some implicit valuation shrouded from public scrutiny."

Others are unconvinced. Bowers *in* Sustainability and environmental economics (1997) makes the point that, when used in a straightforward cost/ benefit context, the concept of compensation for environmental degradation is meaningless because no such compensation is ever paid. He argues that prices cannot be assigned to the environment although the economic models themselves remain useful, "It is not the primary task of environmental economics to place values on environmental assets and...with many environmental assets nofw19amental

Application of ion chromatography in environmental analysis

It is probably true to say that ion chromatography has a rather low profile when compared to its more "glamorous" high performance liquid separation relatives such as LC-MS.

For example, how many local Chromatography Society meetings have been devoted to ion chromatography developments in the last 10 years? Not many I'll wager. Nevertheless, ion chromatography plays a very important part in some key areas of environmental analysis, mainly concerning natural and wastewaters. There have also been a number of important recent developments in separation and detection extending the range of analytes and sample types available to the technique.

The term "ion chromatography" strictly includes a number of high performance ion separation techniques, including ion exchange, ion exclusion, and ion pairing. But ion exchange is by far the most common system employed.

Looked at historically, ion exchange has

age of analytical instrumentation in the 1960s, when atomic spectroscopy essentially took over trace metal determinations from both ion exchange and photometric methods.

Nonetheless, there was one area of inorganic trace analysis, where atomic spectroscopy was of little help, the determination of the common non-metal anions. Helped by the renaissance in liquid chromatography in the 1970s, now commonly called HPLC, Hamish Small announced in 1975 the invention of the pellicular anion exchange resin column linked to suppressed conductivity detection for the high speed separation and determination of chloride, nitrate, nitrite, bromide, sulphate and phosphate etc. This technique became known as ion chromatography and quickly became established as the main method of anion analysis, replacing the time consuming and involved chemical methods at the time. The original patents ran out some time ago and a number of companies now offer ion chromatography instrumentation containing not only suppressed and nonsuppressed conductivity detection, but also other detection systems such as those based on UV-vis absorbance. Ion chromatography is now routinely used by many agencies such as water companies and environmental agencies to monitor the quality of potable, natural and wastewaters. Nitrate monitoring is perhaps the most well known example, where pollution from fertilized land runoff is a common occurrence.

Further developments and improvements in ion chromatography separation and detection are continuing as mentioned above to meet even more challenging environmental analyses. One such is the recent concern over the presence of bromate in drinking water produced by the oxidation of bromide during disinfecting procedures, particularly when using ozone. Bromate is considered highly carcinogenic and strict very low limits of less than 1 ppb have been set by a number of environmental agencies. Ion chromatography methods have been developed to achieve this, interestingly exploiting an old colorimetric procedure for highly sensitive and selective detection. This is accomplished using an

on-line post column reaction where the separated bromate oxidises iodide to iodine and the absorbance measured by a UV-vis detector.

Another area where ion chromatography is likely to be increasingly used is in the monitoring of trace toxic metals. Ion chromatography instrumentation is becoming smaller and can be used in areas where atomic spectrometers will be expensive or difficult to use, or even in dangerous locations such as oil rigs. The development of new separation systems involving metal chelating ion exchange materials will also allow the analysis of samples of high salt content such as seawater and estuarine water. So, 60 years after the invention of the ion exchange resin column, predominantly for metal separations, we are likely to see ion chromatography return as an important technique for trace metal determinations in environmental systems.

Dr PHIL. JONES,

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Web link: Peter E. Jackson, Ion Chromatography in Environmental Analysis. In *Encyclopedia of Analytical Chemistry*, R.A. Meyers (Ed.), pp. 2779– 2801, John Wiley & Sons Ltd, Chichester, 2000. http://www.separationsnow.com/ repository/pdfs/0835-_a.pdf

Phil. Jones' interests include the application of high-performance chelation ion chromatography, as illustrated by the following publications: Shaw, M.J., Cowan, J. and **Jones, P.** (2003) Fabrication of an aurin tricarboxylic acid immobilized chelating polymer for the ion chromatographic determination of trace metal ions in highly mineralized waters. *Analytical Letters* **36**, 423-439.

Shaw, M.J., **Jones, P.** and Nesterenko, P.N. (2002) Dynamic chelation ion chromatography of transition and heavy metal ions using a mobile phase containing 4-chlorodipicolinic acid. *Journal of Chromatography A* **953**, 141-150. Truscott, J.B., **Jones, P.**, Fairman, B.E. and Evans, E.H. (2001) Determination of actinides in environmental and biological samples using highperformance chelation ion chromatography coupled to sector-field inductively coupled plasma mass spectrometry. *Journal of Chromatography A* **928**, 91-98. **Jones, P.** (2000) Major sensitivity improvements in ion chromatography

determinations involving post-column spectrophotometric reaction detectors through elimination of pump noise using a dual wavelength monitoring procedure. *Analyst (London)* **125**, 803-806. Shaw, M.J., Hill, S.J., **Jones, P.** and Nesterenko, P.N. (2000) Determination of beryllium in a stream sediment by high-performance chelation ion chromatography. *Journal of*

Chromatography A **876**, 127-133. Shaw, M.J., Hill, S.J., **Jones, P.** and Nesterenko, P.N. (2000) Determination of uranium in environmental matrices by chelation ion chromatography using a high performance substrate dynamically modified with 2,6-pyridinedicarboxylic

acid. Chromatographia 51, 695-700.

Evaluating air quality

Concern about the environmental impact of aircraft will be a key factor in the future development of Britain's airports. But what analytical methods are available for measuring aircraft emissions? **Kim Cooke**, a committee member of the ECG, explains the use of remote optical measurement techniques for monitoring air pollution at UK airports and other urban and industrial sites.

Remote optical measurement techniques

Remote optical measurement techniques (ROMTs) have the great advantage over other more conventional techniques for measuring gaseous pollutants in that they can perform real time, in-situ gas analysis along an open path. Although there have been notable advances in ROMTs in recent years resulting in greater reliability, more portable systems and overall decrease in cost (always a very decisive factor), there is still resistance to using them for routine monitoring of emissions and air quality. The primary reason for this is that there is still no standardisation between systems. This is highlighted particularly well in the World Health Organisation's guidelines for air quality (WHO, 2000), where four out of six of the main "classic" pollutants SO₂, NO₂, CO and O₃ can be measured using remote optical sensors. However, they point out the techniques available do not conform to ISO7996 (ISO1985b), hence stress the

need to pay careful attention to instrument calibration and quality assurance to obtain meaningful data.

ROMTs have already proved their usefulness for a variety of applications, including assessing ambient air quality in urban environments monitoring concentrations of fugitive, toxic or potentially explosive gases in process plants and petrochemical sites and the measurement of motor vehicle or aircraft exhaust emissions. However, while these methods offer the advantage of being able to measure over significantly long paths, often several hundred metres, the uncertainties also associated with point measurements due to dispersion and other interfering mechanisms, become a factor. In the case of open path measurements, this has often placed doubt on the confidence in the collected data. Nonetheless, many typical applications for which remote optical sensors are used offer no superior alternative. Where the emission source is mobile and unconstrained, for example an aircraft, extractive monitoring is less attractive. A monitoring system at a runway end is a much more preferable than a measurement system fitted to each aircraft.

Remote Optical Sensing Evaluation (ROSE)

With ever more air quality legislation and national and international strategies on the horizon, governmental bodies, local authorities and industry alike are under more pressure to deploy monitoring systems in which there is a high degree of confidence in the data produced. Within the context of future standardisation legislation, a European initiative has been embarked upon to determine critical performance factors for ROMTs (CEN/TC 264/WG 18). As part of this initiative a European consortium has been formed within Framework 5's Competitive and Sustainable Growth programme to carry out a project on Remote Optical Sensing Evaluation (ROSE). The primary objectives of ROSE are the determination of "Best Practice" and performance standards, along with a firm theoretical foundation on which to support such statements (ROSE project, GR6D-CT2000-00434). It addresses the problems associated with system and certification approval by inter-comparing five diverse commercially available ROMTs under both field and laboratory conditions. The measurement techniques included differential optical absorption spectroscopy (DOAS), tuneable diode laser spectroscopy (TDLAS), Fourier transform infrared and ultraviolet spectroscopy (FTIR and FTUV), as well as differential optical absorption light detection and ranging spectroscopy (DIAL-LIDAR). Working alongside these techniques, the project also utilizes the advances in Computational Fluid Dynamics (CFD) modelling to reduce the uncertainties in the measurements induced by dispersion.

Remote optical measurement techniques used by ROSE

The ROSE project inter-compares the basic approachroscopy9(-)0iggiap8 80tive40.0001 ' comptds

Table 1: Instrument t	type and	capabilities	available to	OROSE
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Instrument	Pollutant	Beam path	Limit of detection
Polytron ToxLine (FTUV) Dräger Safety GmbH	NO_2 , NO, SO_2 , NH_3 , O_3 , benzene, toluene, ethylbenzene, xylene, (BTEX), styrene, H_2S , 1,3-butadiene	10-200m	1-30 ppm.m
Safeye 256 (IR DOAS) Spectronix Ltd	Total HC (C1-C8), calibrated for ethene	30-90m	0.2 LEL.m
Safeye 424 (UV DOAS) Spectronix Ltd	Benzene, toluene, xylene (BTX), NH ₃	30-100m	8 ppm.m
Safeye 414 (UV DOAS) Spectronix Ltd	H ₂ S	30-100m	8 ppm.m
DIAL LIDAR (IR/UV) Spectrasyne Ltd	Benzene, toluene, p-xylene, NO etc (UV), ethene, ethane, CH_4 , C_3H_8 , C_3H_6 , C_4s , HC-cocktails, cyclohexane, various chlorinated and sulphurous hydrocarbon species, etc, etc. (IR). Speciated HCs and aromatics with sorption tubes.	50-1200m (DOC)	5-50 ppb (DOC)
Unicam Mattson Research Series FTIR <i>Reading University</i>	H_2O , CO_2 , O_3 , N_2O , CO , CH_4 , NO , SO_2 , NO_2 , NH_3 , HF , HCl , SF_6 , alkanes, alkenes, and alkynes, BTX	10-100m	ppm level
Bomem 100 FTIR Sira	H_2O , CO_2 , O_3 , N_2O , CO , CH_4 , NO , SO_2 , NO_2 , NH_3 , HF , HCl , SF_6 , alkanes, alkenes, and alkynes, BTX	10-100m	ppm level
TDLAS (NIR) Norsk Elektro Optikk	$CH_{4,} NH_{3}$, HCl, HF (CO, CO ₂ , HCN, N ₂ O, H ₂ O)	Up to 100m	10-75ppm.m

(LoD: Limit of Detection; DOC: Depending on Conditions; NIR: near infrared)

Assessment of instrument performance

The diversity of remote optical techniques used in ROSE highlights the difficulty in defining comprehensive performance parameters on which to assess all the instrumentation. It therefore follows that performance parameters should be based on the application rather than the instrument itself. Performance parameters have already been defined for ambient air quality measurements by the UK certification scheme MCERTS (1998) and although ROMTs were specifically excluded, it acts as a suitable starting point. The primary performance parameters focused on by ROSE are illustrated in Table 2.

Table 2: Performance parameters

Performance parameters for ambient air quality monitoring instruments	Additional parameters for ROMTs
Laboratory and field repeatability (standard deviation)	View geometry/beam profile, including path limitations
Zero and span drift	Calibration technique/algorithm
Accuracy of measurement of known reference	Instrument lineshape (including effects of processing
concentrations	algorithms)
Detection limit and quantification limit	Effect of dispersion phenomena
Averaging of short-term fluctuations	Effect of direct solar radiation
Linear fit	Effect of obscuration phenomena (fog, smoke etc.)
Cross sensitivity to interfering substances	
Influence of atmospheric pressure and temperature	
Susceptibility to physical disturbances	

Complementary techniques

In practice, defining the performance parameters in isolation to assess ROMTs does not validate instrument performance. To be of any use, ROMTs have to be operated under real-world conditions and, in common with all monitoring techniques, are susceptible to meteorological conditions and dispersion effects, especially along the beam-path of the instrument. Thus the assessment of ROMTs has to take in to account external environmental conditions. Making complimentary meteorological measurements and carrying out numerical modelling of the site where the instrumentation is set up aids the understanding of the external parameters involved. Thus definition of 'Best Practice' in the positioning and use of remote optical sensing instruments is of paramount importance to limit the effect of environmental conditions on data obtained. Numerical and physical modelling techniques are particularly useful tools in this area.

- b. REACH should be compatible with existing and proposed international initiatives on the control of chemicals.
- c. REACH should only require data that has real value. This is particularly true for 'existing chemicals' that have been in use for many years with no apparent adverse effects.
- d. One particular concern is that REACH could lead to useful chemicals ceasing to be available because they generate insufficient profit to cover the cost of testing.
- e. The Society fully supports the principle of transparency under REACH. However, a balance needs to be found between

transparency and commercial confidentiality.

f. REACH should not inhibit innovation. If the Commission equates innovation with substitution, this strategy is unlikely to lead to true innovation.

The Environment, Health and Safety Committee is the RSC's focus for professional and policy aspects of the environment, health and safety. The committee aims to:

- Provide a service to members by answering members' e-mail, postal and telephone enquiries and by publishing guidance booklets and short papers.
- Make representations in the public

interest to ensure that public policy and legislation are based on good chemical science.

• Ensure that public awareness of

New books on the environment from the RSC

Published in 2003

S ainabili and En i onmen al Impac of Rene able Ene g So ce Issues in Environmental Science & Technology, No. 19 R. E. Hester and R. M. Harrison (eds.) £45.00 (Members' price: £29.25) http://www.rsc.org/CFbooks/ issueindex.cfm?BID=IS003019 Catalysis in Application

(Proceedings) S. D. Jackson, D. Lennon, J. S. J. Hargreaves (eds.) £99.95 (Members' price: £64.75) http://www.rsc.org/is/books/ catinapp.htm

Plasma Source Spectrometry:

Applications and Emerging Technologies (Proceedings) J. G. Holland and S. D. Tanner (eds.) £99.95 (Members' price: £64.75) http://www.rsc.org/is/books/ plasmasource.htm

Chemical Fom la ion: An O e ie of S fac an Ba ed P epa a ion U ed in E e da Life A. E. Hargreaves £23.95 (Members' price: £15.50) http://www.rsc.org/is/books/ chemform.htm

En i onmen al Radiochemical Anal i II (Proceedings) P. Warwick (ed.) £99.95 (Members' price: £64.75) http://www.rsc.org/is/books/ radiochemical.htm

To be published in 2004

H phena ed Techni e in Specia ion Anal i (RSC Chromatography Monographs)

£79.95 (Members' Price: £51.75)

Wa e Con amina ion Eme gencie : Can We Cope? (Proceedings) K. C. Thompson (ed.)

Mass Spectrometry: A Foundation Course K. Downard

Meeting report: International conference on chrysotile asbestoscement products

John Hoskins, Editor of Journal of Indoor and Built Environment, who represents the Occupational and Environmental Toxicology Group on the ECG Committee, reports on These minerals are no longer produced. The sixth mineral is a serpentine mineral chrysotile or white asbestos, which accounts for some 98% of all asbestos ever mined.

Asbestos minerals have been mined for over a century although only type, chrysotile (white asbestos), is mined today - but that still in millions of tonnes per annum. An unfortunate legacy from uncontrolled early use is an epidemic of disease resulting from exposure to, in particular, amphibole types of asbestos. The lungs are delicate organs and their physical assault by abrasive minerals can cause permanent damage that may lead to cancer. Durable mineral fibres seem particularly good at causing such damage because their morphology makes removal difficult. As a consequence amphibole asbestos types, which are extremely durable in the lungs, are now banned in most countries of the world, although interestingly not in the USA, but there are severe limitations on use. The case for banning amphibole materials is sound, that for banning chrysotile is much less so. As noted, the moves to ban all asbestos types rides ahead of so-called alternative products; cellulose and mineral wool insulants, galvanised iron and other types of corrugated sheeting, plastic pipes and a host of other products. These are invariably more expensive than similar chrysotile products, provide often inferior replacements and have a health and safety record no better, and often worse than the materials they are replacing.

In the beginning of the modern phase of asbestos mining and production the high

Meeting report: Monitoring exposure to air pollution

"... the air ... this brave o'erhanging firmament, this majestical roof fretted with bedrock) at a rate of up to 2 m^3

with the victims of Minamata disease (and those fishermen whose livelihoods suffered because of lost catches and unsellable fish) parallel changes in 'worker consciousness' in Japanese society as a whole.

Timothy George describes in great detail this struggle for compensation and much of his discussion has generic value for the interpretation of any major pollution incident. He delineates the way in which the development of the Minamata industrial base from calcium carbide manufacture to nitrogen fertilizer production, its links to cheap hydroelectric power and crucially, its role in the provision of acetaldehyde (from acetylene blown over mercuric sulfate) became nationally important for Japan's economic growth. In consequence, the Government and industry supported alternative explanations to organic mercury for the environmental effects (thallium, pesticides, explosives from WWII, red-tide). Action was therefore delayed and knowledge of the factory as the direct source of organic mercury was hidden from the mid-1950s until 1995.

Although the detailed archival evidence of the day-to-day negotiations presented in the meat of the book is somewhat tedious it is nevertheless essential for an understanding of the complexity of the legal, socio-cultural, political and economic issues that surround the environment. For instance,

"... too many scientists seem to have been in the service of money and power. Too many in the media saw it as their duty to be 'neutral' by uncritically reporting every theory, rather than investigating who sponsored them and whether they were backed by solid evidence. Too many government officials seem to have been willing to sacrifice poor fisher folk on the altar of high growth." (p70)

"From this time until the present,

diagnosis and certification of Minamata disease patients have been as much political and financial issues as medical questions." (p112)

George's final chapter ("Minamata and the Tragedy of Japan's 'Modernity'")

Elements and their Compounds in the Environment

Occurence, Analysis and Biological Relevance 2nd edition

established itself as the standard reference on this topic, and remains unmatched in the breadth of material covered.

This new edition is more clearly and concisely structured, and more emphasis is now given to nutritional aspects of the elements. It continues to provide:

- Detailed information on the environmental metals that influence the health of plants, animals and humans
- Describes the problems related to waste, soils and wildlife as well as the risks caused by the increasing output of metals from industry and households
- An extensive bibliography, numerous tables with useful data and a glossary of terms

International experts from 15 countries have pooled their knowledge and experience to create this ultimate resource giving essential information to all chemists, biologists, geologists, food scientists, toxicologists and physiologists involved in environmental research and remediation, risk assessment, food research and industrial hygiene.

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