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HUMAN HEALTH | ENVIRONMENTAL HEALTH

VOLUME 10 | October 2009
INDIA ANALYTICAL SCIENCES

Dear Readers,

We are very much thankful for the suggestions and enquiries received from your end. We have implemented the same in our immediate actions. This issue of FRESH covers the solutions related to environmental applications.

Environmental Analysis can mean lots of things: regulatory compliance, resource management, environmental protection, and workplace safety. We can help you get the most out of your instrumentation and your lab while achieving regulatory compliance. Labs performing environmental analysis are confronted with constant change: new contaminants, more rigorous measurement demands, and new or revised regulatory requirements are just three areas that put pressure on laboratories to expand their scope and expertise. You can depend on PerkinElmer as a supplier, and also as a partner.

Biomonitoring is related to both air & water analysis and industrial hygiene. But unlike these related fields, which involve the measurement of known hazards in the world in which we live, biomonitoring is broader in scope, and it looks at assessing the physiological impact of exposure to those hazards and other conditions around us.

In today's world, industrial hygiene is broad in scope encompassing everything from air monitoring at petroleum refineries to dust and particle analysis in machine shops.

How can we help? With a perspective on both chemistry and biology, PerkinElmer can offer a cross-disciplinary perspective to your biomonitoring requirements. We can help you identify the right methods, bio-hazard safety measures, and analytical procedures - plus, of course, suitable instrument systems. All with an eye focused on successful implementation, day in, and day out.

Save Environment for the cleaner future! Help to avoid Air, Water and Noise pollution during this Diwali.

WISHING YOU A HAPPY DIWALI & PROSPEROUS FESTIVE SEASON!

FOR CLEANER ENVIRONMENT FOR EVERYONE

WHAT'S Fresh inside...

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Thermal Desorption with Clarus GC to Monitor occupational Exposure

Courtesy and abstract from Application of Thermal Desorption to Occupational Exposure Monitoring
Andy Tipler; PerkinElmer Life and Analytical Sciences 710 Bridgeport Avenue; Shelton, CT 06484 USA

Simple techniques

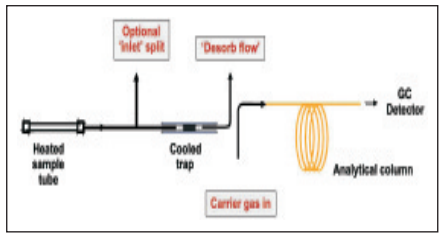
The use of air samplers, such as filters and sorbent tubes, is a universal approach to air monitoring. The collection mechanisms may employ deposition, adsorption or even derivatization on the sampler. Sampler type and analytical technique are entirely dependent on the analytes under examination. In its most basic form, analysis might be as simple as fiber counting for asbestos, gravimetry (for monitoring wood dust), or a reagent color change.

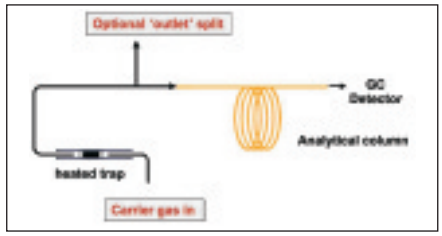
Sophisticated techniques

For the identification and quantification of complex mixtures or for biological monitoring (e.g. of breath samples) more sophisticated techniques may need to be employed. In the case of airborne volatile hydrocarbons, sampling of complex mixtures on sorbent tubes is the preferred approach, followed by thermal-desorption analysis. Key to this method is a cryofocusing stage in which analytes released during the primary desorption step are re-collected on a second sorbent bed held at a very low temperature. This enables analytes, which may have been widely distributed over the sorbent bed of the sampling tube, to be held in a tight band on the cold trap, at which point a second thermal desorption "injects" the analyte on the capillary gas chromatography (GC) column. Separation depends on the physical properties of the analytes and the type of column used. Detection methods normally include mass spectrometry (MS), flame ionization (FID) or electron capture (ECD), although other methods are possible. The benefits of MS are that co-eluting substances can be resolved and quantified with high sensitivity using ion fragments. However, in the workplace, unlike ambient monitoring, it is often the case that the substance of interest is either at a greater concentration than other contaminants, or there are no significant co-elutions. In these cases, MS may not be required and the preferred approach is the use of FID, which gives a good linear and stable response over a wide dynamic range and consequently is simple to calibrate and maintain.

Principle

An appropriate sorbent is selected for the compound or mixture to be sampled (more than one tube may be necessary). For diffusive sampling, the rate of sampling must have been validated, normally by prior calibration in a standard atmosphere. Values for sampling rates (effective uptake rate) on diffusive tubes of the PerkinElmer type are available in the standards ISO 16017-2, ASTM D6196-03, the method MDHS 80 (UK HSE) For ambient-benzene validation data, the best source is EN 14662-4. The diffusive sampler is exposed to air for a measured time period. The organic compound vapors migrate down the tube by diffusion and are collected on the sorbent. Alternatively, active pumping may be used. The collected vapors are desorbed by heat and are transferred under inert carrier gas into a gas chromatograph equipped with a suitable capillary column and a flame ionization detector.





Thermal-desorption instrumentation

The first automated thermal-desorption instrument, the PerkinElmer ATD50, was introduced in 1982 specifically to support industrial-hygiene applications. Over the last 25 years, although significant enhancements

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have been made to the technology, the fundamental principles remain the same as they were then. Technical enhancementshave been made mainly to allow thermal-desorption instrumentation to be used for a much wider range ofapplications such as environmental monitoring, materials testing, forensic work and building testing. Industrialhygiene still remains one of the most important application areas for thermal desorption and the technique continuesto have significant advantages over others. The term "thermal desorption" usually refers to the technique of two-stage thermal desorption. Step 1 involves heating the sample tube and applying a flow of carrier gas to carry the vaporized analytes into a small adsorbent trap which is usually cooled. This trap collects and focuses the analytes. In step 2, the trap is rapidly heated and carrier gas carries the desorbed analytes as a narrow band into a gas chromatograph for separation, identification and quantification. Figures 1 and 2 illustrate the main steps involved in a typical twostage thermal-desorption analysis.

Sample re-collection

Technology has been developed to enable a fraction of the original sample to be returned to the initial or a fresh sample tube. This addresses one of the major concerns of the industrial hygienist in that now it becomes possible to get a second (or further) analysis from the same tube sample.

Tube impedance testing

The packing integrity of every tube and the trap can be automatically determined at the time of analysis by measuring the pressure drop across the adsorbent bed. Any movement, crumbling, compression or loss of the packing may be detected by a change in the pressure drop for a given carrier-gas flow rate. This capability allows users to QC check the condition of the tubes as part of the normal analytical regime and make assessments as to their suitability for continued use. Further information on these and other features may be found on the following technical notes at www.perkinelmer.com/gclibrary:

Overall

As with other TD systems, there is now an opportunity to re-collect analyte, on the same tube or a new tube for analysis by modified methods, with different detectors or for storage. This last aspect is very significant for the quality and traceability requirements of legal proceedings. The pressure-balanced system accounts for changes in sample or system impedance, giving greater security in the quality of the analyses. Also, using the conditioning

feature, it is now possible to optimize available time.

Most popular TurboMatrix Thermal Desorber systems

TurboMatrix 300 TD

Incorporates PPC to provide enhanced ease-of-use, functionality and performance in a single-tube model. Upgradeable to the TurboMatrix 350 ATD.

TurboMatrix 650 ATD

Incorporates all of the performance features of the TurboMatrix 350 ATD plus the ability to re-collect sample for repeat analysis, the ability to perform dry purge without the internal standard accessory and the ability to perform tube and trap impedance measurement as a diagnostic of system performance. Provides truly outstanding analytical performance in an automated sample-tube handling system for unattended analysis of up to 50 samples.

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Analysis of Electronic Waste by Inductive Coupled Plasma Optical Emission Spectrometer (ICP-OES)

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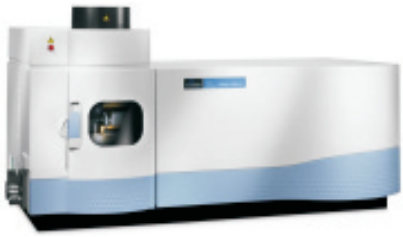
PerkinElmer Innovation Technology Centre,
Mumbai (India)

Electronic waste is major issue because it contains number of toxic or nontoxic metals in very high concentration. These wastes can be reprocess and reuse in new electronic components. The study was carried out to show the capability of PerkinElmer® ICP-OES instrument which is useful for determination of metal contain in high matrix sample like electronic waste.

A motherboard and the connectors of an old CPU were selected for the study. The electronics components were removed first and some of them were selected for the analysis. Each part was cut into small pieces and mixed thoroughly to form a composite

Fig. Old CPU before & after segregation/grinding



Optima 7000 DV ICP-OES

sample. The approximately weighted samples were kept in different beakers for acid digestion using hot plate. The temperature of hot plate was control to avoid the loss of the volatile elements. Plastic parts were digested in aqua regia (3:1,HCl:HNO3) and other electronic parts in conc. HNO3. Digested solutions were transferred into sample vessels and diluted to 50 ml using ASTM type I water. To check the performance of the method of digestion, some samples were digested in duplicate at different interval. Working calibration standards were prepared from PerkinElmer Single-element ICP standards (1000 mg/L) by volume by volume dilution in a matrix of 2% HNO3 (Suprapur (65%), Merck, Germany).

The digested samples were analyzed on the PerkinElmer® Optima™ 7000 DV ICP-OES instrument (PerkinElmer, Inc., Shelton, CT, USA) equipped with WinLab32™ for ICP, Version 4.0 software for measurement of all analyte wavelengths of interest. It was carried out using Concentric Glass nebulizer and Cyclonic spray chamber. Yttrium at 1 ppm concentration was used as an internal standard to compensate for viscosity and surface tension effects between clear standards and samples.

To ensure the effectiveness of the sample preparation stage and to further validate the method developed, a post digestion spike recovery was performed at 1 mg/L. The spike recovery results were well within the 80-120% range.

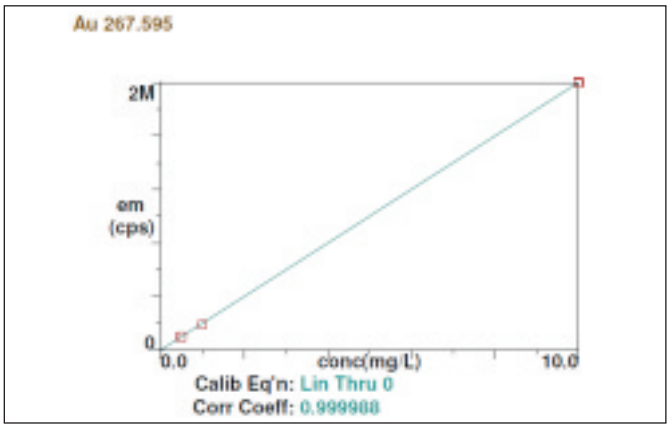
Table 1

Element	Mother board base	PCI slot	Hard disk drive connectors	Power connector Slot	PCI Express Slot Duplicate	PCI Express	Data Cable (white)
Aluminum	882.2	6705.1	75.9	205.5	159.7	356.4	N.D.
Antimony	N.D.	15647.9	383.3	N.D.	471.4	944.2	N.D.
Barium	406.9	46.4	N.D.	N.D.	42.5	46.5	N.D.
Cadmium	60.8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Chromium	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Copper	212456.1	163813.6	167687.4	146065.8	108930.8	105632.9	227694
Lead	5453.1	13211.3	N.D.	12325.0	11507.4	10444.9	788
Nickel	733.9	993.2	1352.2	1217.0	834.6	770.0	N.D.
Tin	9750.1	29769.7	N.D.	20982.7	27728.6	27302.6	2222
Zinc	342.2	44.7	86694.0	51798.5	41728.1	39723.7	N.D.

N.D.: Not Detected. Results given are in mg/Kg

In this study the Gold and Silver determination was also done for some parts like Microprocessor, Sound card and Hard Disk Drive connectors. The results of analysis are given in milligrams of gold or silver present in whole component.

The Optima 7000 DV ICP-OES proved as an effective tool to analyze the metal content in difficult matrices such electronic waste. It provides good repeatability and reproducibility for such high matrix samples.
Calibration graphs: Au, Ag



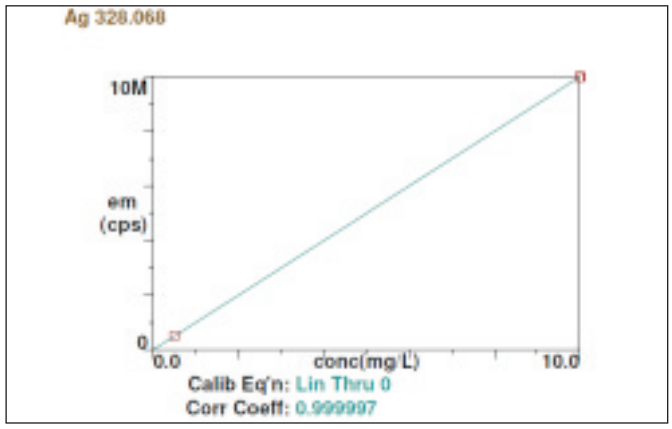


Table 2

Element	Microprocessor	Sound Card	Hard Disk Drive Connector
Gold	4.53 mg	1.96 mg	0.26 mg
Silver	N.D.	N.D.	N.D.

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The Determination of Total Mercury in Coal And Coal Fly Ash by SMS 100 Mercury analyzer

Coal-fired power plants are by far the largest source of mercury pollution. Through the coal-combustion process, they emit approximately 50 tons of mercury particulates into the atmosphere every year (EPA, 2005 data). When the mercury falls back to earth it is deposited on the land and gets into the water ecosystem, where it is converted into the highly toxic organo mercury compound, methyl mercury (CH3Hg+) by anaerobic organisms. This toxicant enters the aquatic system food chain, and eventually ends up in the shellfish and seafood we consume.

Mercury is an undesirable constituent in lignite and bituminous-type coals used in coal-fired power stations. These low-grade coals are typically high in pyrite (iron sulfide) content, in which the mercury is chemically bound. The EPA mercury rule will therefore translate into a significant requirement for measuring the mercury content of all coal used in power plants. In addition, coal combustion products (CCP), such as coal fly ash will also have to be monitored for mercury, because of its widespread use for the manufacture of concrete products.

Because there is no sample dissolution required, this novel approach can determine the total mercury content of a coal related sample in less than five minutes, which is significantly faster than the traditional wet chemical reduction method (EPA Method 7473 and ASTM Method 6722-01)

Instrumentation

The SMS 100 mercury analyzer (PerkinElmer, Inc., Shelton, CT) was used for this study. This is a dedicated mercury analyzer for the determination of total mercury in solid and liquid samples using the principle of thermal decomposition, amalgamation and atomic absorption described in EPA Method 7473 and ASTM Method 6722-01. The SMS 100 uses a decomposition furnace to release mercury vapor instead of the chemical reduction step used in traditional liquid-based analyzers. Both solid and liquid matrices can be loaded onto the instrument's autosampler and analyzed without acid digestion or sample preparation prior to analysis. Because this approach does not require the conversion of mercury to mercuric ions, lengthy sample pretreatment steps are unnecessary. As a result, there is no need for reagents such as highly corrosive acids, strong oxidizing agents or reducing chemical, which means, no hazardous waste to be disposed of. An additional benefit of this technology for coal-related samples is that it allows for the stack gas monitoring of mercury with

sorbent traps, such as those described in the EPA methods, 40 CFR,Part 60, Appendix B, "Specification and Test Methods for Total Vapor Phase Mercury Continuous Emission Monitoring Systems in Stationary Sources" and 40 CFR Part 75, Appendix K, "Quality Assurance and Operating Procedures for Sorbent Trap Monitoring Systems"

SMS 100 Automated Mercury Analyzer

The SMS 100 is a full function, stand alone, automated mercury analyzer for EPA method 7473 and also ASTM 6722-1. It employs thermal decomposition, gold amalgamation and cold vapor atomic absorption spectrometry designed for sensitive measurement of mercury in solid samples eliminating the need for elaborate sample preparation. Standardization can be accomplished using aqueous standards.

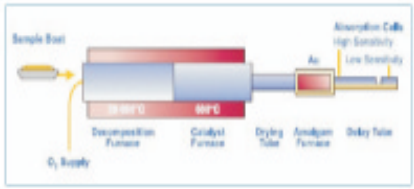
The SMS 100 requires a computer workstation (available separately), included autosampler capable of holding 42 samples, standards, or check samples. Also included are accessories for set-up, calibration and verification of system performance.

SMS 100 Software

Comprehensive mercury analyses software based on Windows™ XP. It offers a unique graphical display of Hg signals to simplify optimization of method parameters. A wide range extended calibration (about 10X over other systems) is included allowing measurements over a wide concentration range. User features are included which help guide the analyst through method setup and sample analysis for an efficient workflow. On-line maintenance diagnostics provide users with efficient resources to keep the SMS 100 operating at high sensitivity and peak performance. Acquired data can be easily transferred to a variety of third-party software packages such a EXCEL™

Autosampler

Included with every SMS 100 is a modular full-function random access autosampler operating under the versatile automation of SMS 100 Software. Includes all interconnecting cables, sample tray, and sample injector. Samples can be loaded onto racks of 14 samples (three racks are supplied) to a maximum capacity of five racks (70 samples). Once the samples in the rack are analyzed they move to a park position and can then be removed and refilled and added back to the autosampler when the analysis of large numbers of samples is required.



Schematic of SMS100 Mercury Analyzer

The SMS 100 is a full function, stand alone, automated mercury analyzer. It employs thermal decomposition, gold amalgamation and cold vapor atomic absorption spectrometry designed for sensitive measurement of mercury in solid samples eliminating the need for elaborate sample preparation. Standardization can be accomplished using aqueous standards

Principles of Operation

A small amount of the coal or fly ash sample (0.05-1.00 gms, depending on the mercury content) is weighed into a sample boat (typically nickel). The boat is heated in an oxygen rich furnace, to release all the decomposition products, including mercury. These products are then carried in a stream of oxygen to a catalytic section of the furnace. Any halogens or oxides of nitrogen and sulfur in the sample are trapped on the catalyst. The remaining vapor is then carried to an amalgamation cell that selectively traps mercury. After the system is flushed with oxygen to remove any remaining gases or decomposition products, the amalgamation cell is rapidly heated,

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releasing mercury vapor. Flowing oxygen carries the mercury vapor through an absorbance cell positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance is measured at the 253.7 nm wavelength as a function of the mercury concentration in the sample. Adetection limit of 0.005 ng (nanogram) of mercury is achievable with a 25 cm path length cell, while a 2 cm cell allows a maximum concentration of 20 µg (microgram) of mercury. A schematic of the SMS 100 is shown in Figure above.

Calibration

Calibration graphs of 0-50 ng and 50-500 ng of mercury were generated from 0.1 and 1.0 ppm aqueous standards in 10% nitric acid respectively, by injecting different weights into a nickel sampling boat. The 0-50 ng calibration was obtained using the high sensitivity 25 cm optical path length cell, while the optional 2 cm cell was used for the 50-500 ng.

Results

The SMS 100 results for experiment 1 are shown in Table 2. The SMS 100 results for experiment 2 are shown in Table 3,while the wet chemical data for the same coal samples using the traditional wet digestion and chemical reduction/atomic absorption technique (ASTM Method D6414-99) are shown in Table 4

Table 2. Measuremernt of mercury in an SRM coal and fly ash sample using the SMS 1OO.

Sample	SRM	Mercury Certificaite Value (µg/g)	Mercury Measurecl Value (µg/g)	% Recovery
Brtuminous Coal	HC-35 15O	O.176	O. 177	1OO.6
Bituminous Fly Asn	NIST 1633b	O.143	O. 132	92.3

Table 3. Determination of mercury in five separate portions of two different coal samples (with precision data), using the SMS 100.

Portion #	Sample 1 (ng of mercury)	Sample 2 (ng of mercury)
1	80.4	3.1
2	77.5	2.8
3	84.1	2.4
4	77. 1	2.5
5	75.0	2.3
Average	78.8	2.6
Std Dev	3.54	O.32
% RSD	4.5	1 2.3

Table 4. Determination of mercury in five separate portions of two different coal samples (with precision data), using the traditional wet digestion and chemical reduction/atomic absorption technique.(Note: ND =Not Detected)

Portion #	Sample 1 (ng of mercury)	Sample 2 (ng of mercury)
1	81.5	ND
2	85.O	ND
3	75.2	ND
4	79.0	NO
5	81.3	ND
Average	8O.4	ND
Stci Dev	3.62	ND
% RSD	4.5	ND

Conclusion:

The study confirms that the reproducibility of this approach is equivalent to the wet chemical technique, keeping in mind that coal samples are notorious for not being homogeneous in their chemical composition. The added benefit of the SMS 100 for coal-related samples is that because the analysis is done directly on the solid, the detection capability is significantly lower than with traditional atomic absorption based mercury analyzers.

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Application Note

Environmental

Indian Standard 3025 Part 39 Determination of Oil and Grease in Water with a Mid Infrared Spectrophotometer

Author

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Introduction

The concentration of dispersed oil and grease (OG) is an important parameter for water quality and safety. Regulatory bodies worldwide set limits in order to control the amount of OG entering natural bodies of water or reservoirs through industrial discharges, and also to limit the amount present in drinking water. The Indian standards (IS 10500 specification) for discharge of OG into inland surface water and public sewers are 10 mg/L and 20 mg/L, respectively. However, the established method is based on hexane as an extraction solvent, which as a hydrocarbon-containing solvent, can interfere with the infrared analysis determination of OG.

This paper presents the method development for the analysis of OG in water using Mid-IR in accordance with standard method 'IS 3025 part 39' using carbon tetrachloride as an extraction solvent. Carbon tetrachloride is proved to be a suitable alternative to hexane and the method is shown to be sufficiently sensitive for monitoring OG discharges in surface waters or in the drinking water network as per the operative range specified in the method IS 3025 part 39.

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Experimental

Instrumentation and operating conditions

The absorbance measurements were performed using the PerkinElmer® Spectrum™ 400 FT-IR/FT-NIR spectrophotometer in mid-IR mode and equipped with a DTGS detector (PerkinElmer, Inc. Shelton, CT USA), shown in Figure 1. Other instrument models with similar configurations such as the Spectrum One or Spectrum 100 can also be used. The software used to acquire the spectra was Spectrum version 6.3. Spectra were collected in transmission mode using a glass cell with 10 mm pathlength. Spectra were acquired over the range 3200 - 2700 cm-1 at 4 cm-1 resolution with ~1 minute acquisition time, and ratioed against a spectrum of pure solvent. The peak maximum between 2930 and 2926 cm-1 was determined and used in the linear regression described below. A linear baseline fit through the points at 3100 and 2800 cm-1 was subtracted before measuring the peak height.

Apparatus and reagents

The reagents, chemicals, standards were prepared as described in the standard method BIS 3025 part 39. Reagents and standards used were of ACS grade.

Apparatus:

- Separating funnel – 1 liter capacity with stopcock.
- Analytical balance – Sartorius® five-decimal analytical balance.
- Pipette – Eppendorf® micropipettes.

Reagents:

- Hydrochloric acid – 1:1
- Carbon tetrachloride (spectroscopy grade): used as a solvent
- Sodium sulphate
- Calibration reference oil: mixture of 37.5% iso-octane, 37.5% hexadecane and 25% benzene.

Procedure

The calibration reference oil was prepared by mixing iso-octane, hexadecane and benzene in the ratio 3:3:2, and stored in a sealed container to avoid evaporative loss. The calibration stock solution was prepared by weighing about 1 gm of calibration reference oil into a clean and dry 100 mL volumetric flask and diluting up to the mark with solvent, i.e., carbon tetrachloride. From the calibration stock solution, a series of standard solutions were prepared using the volumetric techniques in the range 1-40 mg/L with 9 calibration points.

Sample Preparation: Samples were prepared as follows:

1. Acidification of 1 liter of sample using hydrochloric acid to pH 2.0.
2. Extraction of above sample with 30 mL of carbon tetrachloride three times (i.e., 1 x 3 times)
3. Filtration of extract through 10 g of sodium sulfate and dilution of combined collected extract up to 100 mL with solvent.
4. Measurement of the solution at the absorbance maximum near 2930 cm- 1.

Results and Discussion

Calibration – Linearity

Over the calibration range excellent linearity was observed; with a correlation coefficient (R2) of 0.9997 (see Figure 2). A standard error of prediction of 4 mg/L was obtained.

Spike recovery studies

A recovery study has been performed at 6 mg/L concentration in three replicates. The results are summarized in Table 1. As seen in the table, the recoveries are excellent, ranging from 90 to 95 percent. This indicates that the solvent extraction recovers nearly all of the OG and introduces only a small negative bias to the reported result.

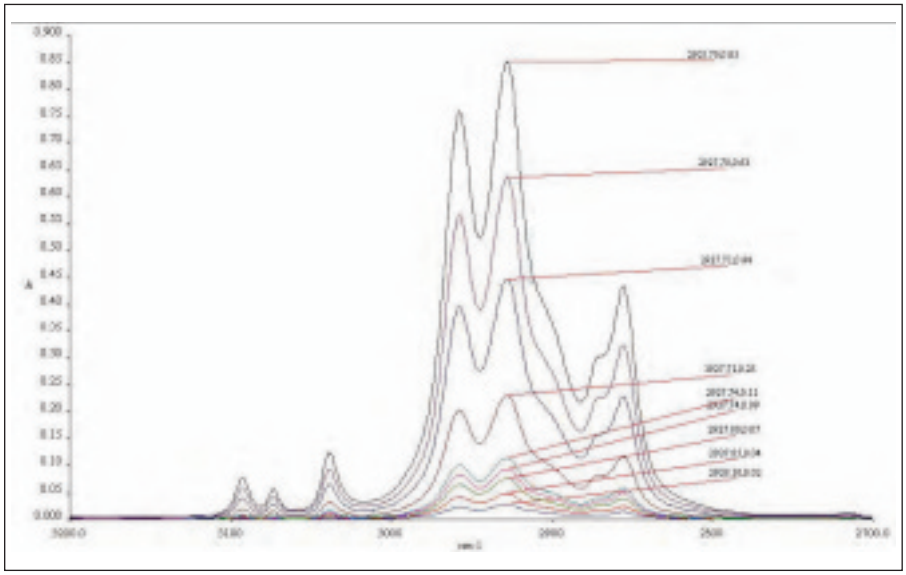
Table 1: Replicate spike recoveries.

Sample %	Recovery
Sample 1 (6.51 mg/L)	92.3
Sample 2 (6.23 mg/L)	94.3
Sample 3 (5.54 mg/L)	92.9

Precision

A precision study has been carried out at 7.0 mg/L concentration in six replicates. Standard deviation is found to be 0.062. This is well within the expected precision for this technique.

Figure 1. The Spectrum 400 FT-IR/FT-NIR.



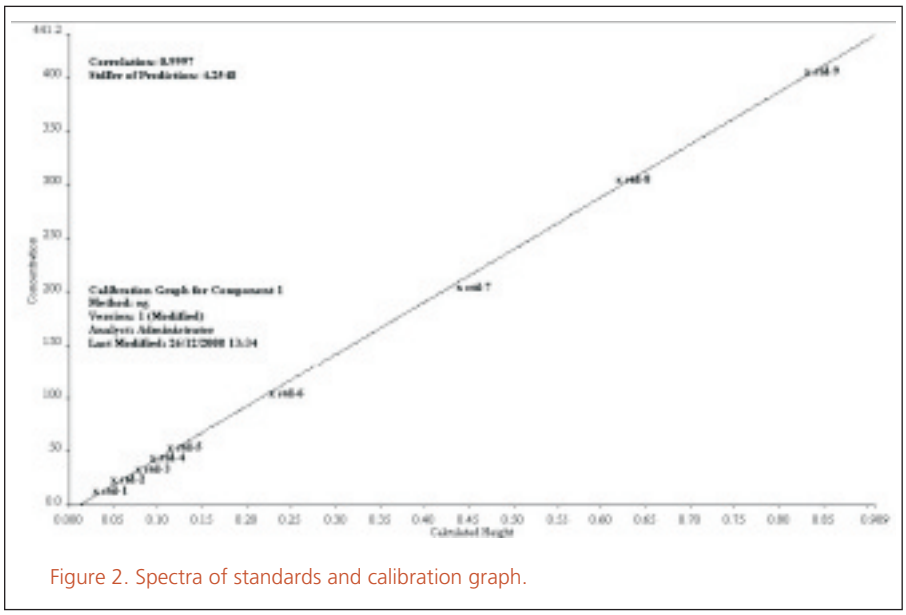


Figure 2. Spectra of standards and calibration graph.

Table 2: Replicate precision data.	
Sample	Concentration (mg/L)
Sample 1	6.92
Sample 2	6.95
Sample 3	6.85
Sample 4	6.81
Sample 5	6.81
Sample 6	6.91
Standard Deviation	0.06

Conclusion

The Spectrum 400 Mid FT-IR/FT-NIR, Spectrum 100 or Spectrum One series of spectrophotometers can be utilized successfully for determination of OG in water samples as they show linearity with good correlation coefficient up to concentration of 1 mg/L, good percent recovery and good precision.

The standard method IS 3025 part 39 works well with carbon tetrachloride as an extraction solvent. The working range specified in the method is 4 mg/L to 40 mg/L but concentrations between 1 mg/L to 40 mg/L may be satisfactorily determined using this method.

References

1. IS 3025 (part 39): 1991, Reaffirmed 2003. (Indian standard Methods of sampling and test for water and waste water – Oil and Grease)

2. IS 10500: Indian standard specification for drinking water.

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Low-level Selenium Determination

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Introduction

Selenium is an essential element to human health at low levels (20-80 µg/L), but becomes toxic at elevated levels. Selenium exists in different forms that determine its toxicity and bioavailability. Current research is now focusing on the determination of individual selenium species or selenium- containing compounds. This can be done using ICP-MS as a seleni- um-specific detector for a chro- matographic separation of the compounds. Since the critical levels of the individual com-pounds will be significantly less than the total selenium concentra-tion, it is becoming more necessary to be able to make very low level selenium determinations. This application note discusses the use of the ELAN® Dynamic Reaction Cell™ (DRC™) ICP-MS for making low-level selenium determina- tions.

With conventional quadrupole ICP-MS, the most abundant isotope of selenium (80Se) cannot be used for the determination due to the interfering 40Ar2+ dimer from the argon plasma which occurs at the same mass-to-charge ratio (m/z). As a result, selenium is normally determined using the 82Se isotope, which is only 8.7% abundant. This limits the detection capability for selenium to the 0.5-10 µg/L range by conventional ICP-MS.

Using the ELAN DRC ICP-MS, this limitation can be overcome by removing the 40Ar2+ interference. This allows the most abundant isotope of selenium, 80Se, to be used in the determination, result- ing in detection limits that are on the order of a thousand times better than those obtainable by conventional ICP-MS.

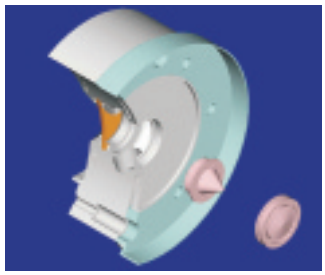
Experimental

The instrument used was the ELAN DRC ICP-MS. The ELAN DRC eliminates the Ar2+ back- ground, so that selenium can be determined at levels below 100 ppt. The background reduction described in this application note was achieved using methane as the reaction gas. The flow rate of the reaction gas was optimized using the automated routines in the ELAN software to maximize selenium signal transmission while minimizing the 40Ar2+ background. In addition, the dynamic bandpass tuning parame-ters of the quadrupole inside the reaction cell were adjusted to eliminate any unwanted secondary reaction products.

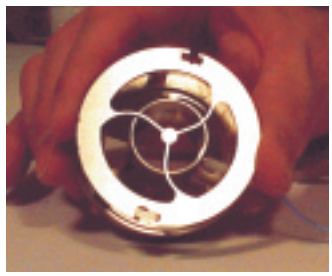
Choice of ICPMS

Elan 9000, DRC-e and DRC II ■

- PlasmaLok control
- High performances ion optical train
- 40 MHz Free-running RF generator
- AutoLens
- Fast, powerful quadrupole
- On-the-fly resolution
- Simultaneous automatic extended dynamic range detection system]
- DRC capability (ELAN DRC-e and DRC II)



Skimmer & Sampler cone



Single Shadow stop

Quadruple mass filter

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Results

Figure 1 shows the mass spectrum of 50 ppt selenium in 1% nitric acid compared with the theoretical isotope ratios. The accurate agreement of theoretical and measured abundance of all isotopes indicates that the Ar2+ is virtually eliminated. Further evidence of this reduction is seen in Figures 2 and 3, which show 80Se and 78Se calibration curves using 1, 5, 10, and 20 ng/L standards. The linearity of these low-level curves further verifies the removal of the Ar2+ interference. The detection limits obtained using DRC ICP-MS are presented in Table 1.

The quantitative determination of selenium in a Certified Reference Material (CRM), Trace Metals in Drinking Water (High-Purity Standards, Charleston, SC) is shown in Table 2. The CRM was diluted 1,000 times to reduce the selenium concentration to 10 ng/L. Accurate recoveries for selenium were obtained at the 10 ng/L level for both the 78Se and 80Se isotopes. Further evidence of the accuracy in other matrices is shown in Table 3. The data in Table 3 illustrate that the DRC ICP-MS technique is also applicable to chloride-containing matrices. Excellent recoveries for a 50 ng/L spike were obtained in 1000 mg/L NaCl.

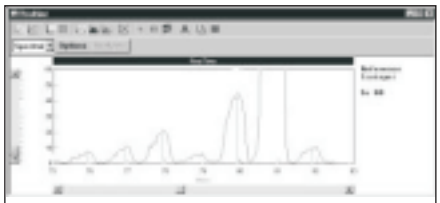


Figure 1. Spectrum of 50 ng/L Se in 1% HNO_3.

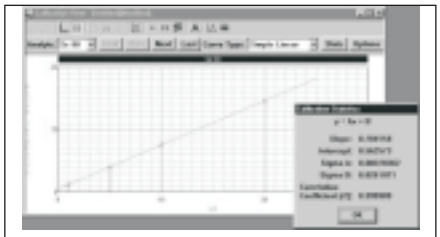


Figure 2. Calibration curve for 80Se.

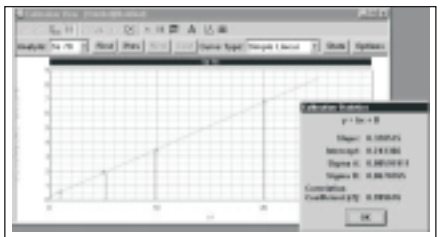


Figure 3. Calibration curve for 78Se.

Table 1: Detection Limits in 1% HNO_3

Spike Level (ppt)	80Se IDL (ng/L) DRC Mode	78Se IDL (ng/L) DRC Mode	82Se IDL (ng/L) Standard Mode
1	0.7	1.2	131
5	0.9	1.5	Not Determined
10	1.7	1.5	Not Determined

Table 2: Analysis of 10 ng/L Se in High-Purity Standards SRM - Trace Metals in Drinking Water

	80Se (ng/L)	78Se (ng/L)
Replicate 1	9.77	11.80
Replicate 2	9.26	9.24
Replicate 3	10.68	10.83
Mean	9.90	10.62
Standard Deviation	0.72	1.29

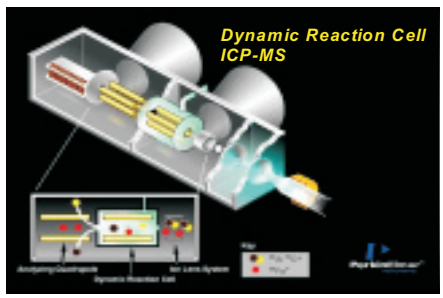
Table 3: 50 ppt Se Spike Recoveries in 1000 mg/L NaCl

	80Se (% Recovery)	78Se (% Recovery)
Replicate 1	93	101
Replicate 2	98	98
Replicate 3	101	90
Mean	97	96
Standard Deviation	4	6

Conclusions

The results of this study indicate that the ELAN DRC ICP-MS can accurately determine low selenium levels with a detection limit of 1 ng/L or less. This is achieved by the complete elimination of the Ar2+ interference using Dynamic Reaction Cell ICP-MS with a methane reaction gas and tunable DRC bandpass. Calibrations using 1, 5, 10 and 20 ppt selenium standards showed excellent linearity. Results for 10 ppt selenium reference material and spike recoveries for 50 ppt spikes in a NaCl matrix were both excellent.

The analysis time per sample using DRC ICP-MS was less than 30 seconds per sample. In addition, DRC mode elements can be determined in the same analysis as standard mode elements for analyte lists containing multiple elements. The ELAN DRC will automatically switch between DRC mode and standard mode during the data acquisition, so the sample tube is only sampled once by the autosampler. This means that productivity is not sacrificed when using DRC mode in an analysis.



Fresh

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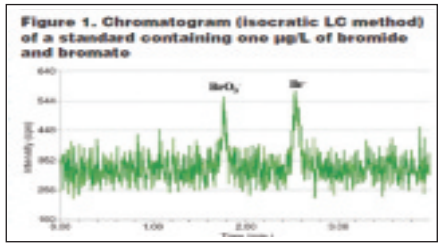
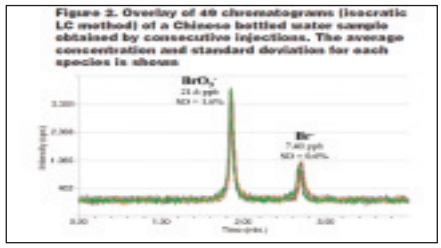
For the Better

Analysis of disinfected water for public consumption.

Zoe A. Grosser Ph.D. and Kenneth Neubauer Ph.D.

Safer drinking water is the prime right of every one. Water for public consumption must be purified prior to distribution or bottling. Chlorine is commonly used for disinfection, but may create hazardous disinfection by-products, depending on the residual organic content of the water supply. Treatment with ozone is another disinfection alternative. While this method is effective, ozonolysis can also convert bromide (Br-), a natural component of many waters into bromate (BrO3-), a carcinogen. Therefore, the need exists to measure bromate in drinking waters, which means that it must be measured separately from other forms of bromine. In addition, each form is usually present at low concentrations. Current methods for measuring bromate and bromide involve separating the bromine containing components by liquid chromatography (HPLC) and using inductively coupled plasma mass spectrometer(ICP-MS) as a detector and are described in US EPA Drinking Water Method 321.8. Bromate has been limited to 10 µg/L (parts- per-billion) in drinking water. The US FDA also adopted the same standard for bottled water exposed to ozonation for disinfection. Similar levels are regulated in Europe for a variety of water types.
Primary drinking water contaminants are generally measured by a single technique, such as HPLC or GC for





organic components and ICP-MS for inorganic components. The use of a combined technique for inorganic speciation has only recently become routine and is still rapidly advancing in developments devoted to speed and ruggedness.

Speciation Studies

Development of a speciation method needs the technology and expertise of the chemist in organic separation sciences and inorganic analysis. Bridging the gap is key to creating the best method for analysis. For example, chromatographers must consider minimizing the use of glass, organic solvents and the total dissolved solid content of the mobile phase. These areas do not need to be considered for 'normal' HPLC analyses, but can cause problems for inorganic detection (i.e., glass is dirty with respect to inorganic elements and glass components and may cause high results).

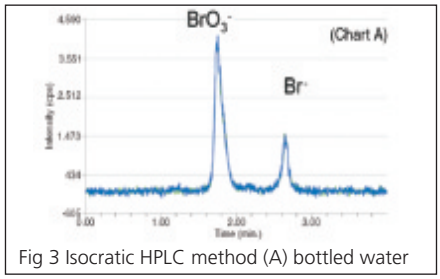
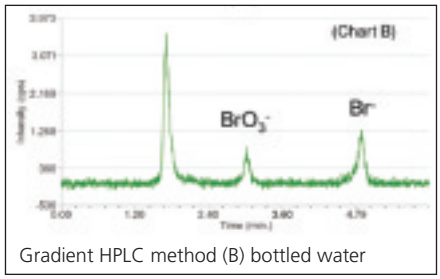


Fig 3 Isocratic HPLC method (A) bottled water



Gradient HPLC method (B) bottled water

ICPs do not handle highly organic solvents very well under normal sample introduction conditions, although modifications can be made to accommodate samples with high organic content. Finally, high total dissolved solids (TDS) can deposit on various components within an ICP-MS, leading to drift over time and frequent maintenance. The inorganic chemist must also have proper expectations about HPLC method development, which is more complex and time consuming than the ICP-MS method. Major variables include the mobile phase composition and various column

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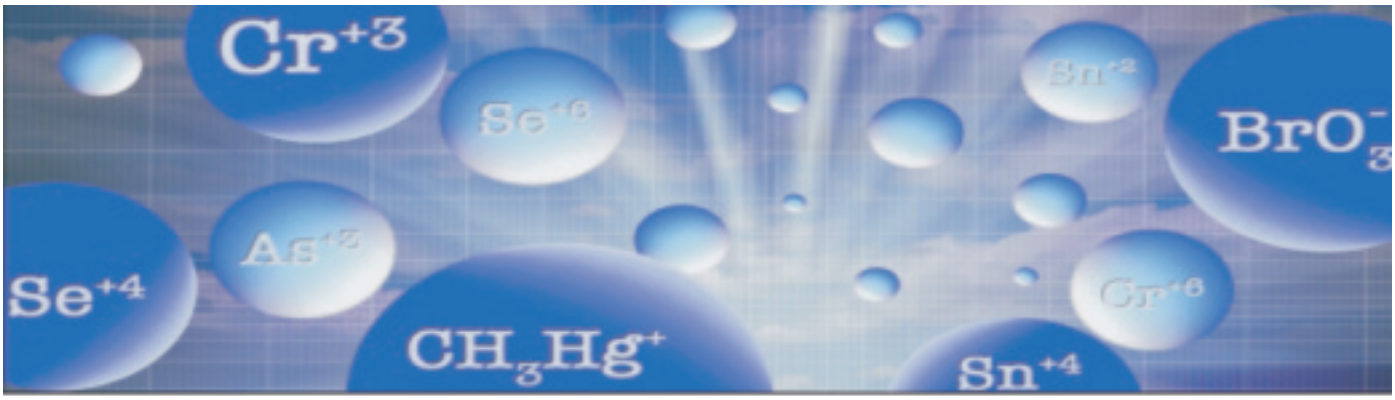

characteristics, such as packing material, particle size and length. HPLC method development involves real chemistry and may take weeks. These are some of the challenges in developing speciation methods.

Table 1. Quantitative determination of bromide and bromate in bottled and tap water samples confirmed with a gradient HPLC method (All units in µg/L)

Samples	BrO_3^-	Br^-
Water A	--	38.1
Water B	--	7.94
Water C	--	23.5
Water D	37.4	17.3
Water E	76.0	--
Water F	3.03	9.36
Water G	--	8.97
Water H	--	224
Water I	20.8	7.41
Water J	16.1	11.9
Tap Water K	--	380
Water L	14.0	11.8
Tap Water M	--	64.6

Advancements in bromate measurement

Since the development of US EPA Method 321.8 in 1998, advances in speciation have taken place, allowing the method to be improved for ruggedness and speed. Figure 1 shows a chromatogram of one µg/L of bromate, showing that even at very low concentrations it can be distinguished from the background levels. Note that time for analysis is less than three minutes, whereas the Method 321.8 chromatographic separation takes eight minutes. Figure 2 shows overlaid chromatograms of a bottled water analyzed multiple times over the course of several hours to examine the short-term precision, which is better than 2%.

For some samples additional method development was done to ensure the analyte of interest was adequately separated from any other components that might mistakenly contribute to the bromate measurement. A gradient HPLC method, although slightly longer than the isocratic method developed for routine use, showed several peaks overlapped the bromate peak in some samples. Advanced interference correction on the ICP-MS showed that the additional peaks did, in fact, contain bromine. Their identification was not investigated further. Figure 3 shows the chromatogram for a bottled water purchased in Thailand showing an additional peak, uncovered with the gradient separation method. Table 1 shows the concentrations of bromide and bromate for a variety of bottled and tap water samples. The samples with suspect peaks or bromate concentrations above the regulatory limit were confirmed with the developed gradient HPLC separation to ensure that only one peak was present at the retention time expected for bromate

Summary

Speciation development continues in this improvement of existing methodology. The separations are accomplished in less than three minutes and proved to be repeatable from injection to injection and over several days. For those waters containing additional bromine-containing species, a gradient HPLC method was established. The isocratic separation method scheme can serve as a rapid screening method; those samples which contain additional bromine species can then be confirmed using the longer gradient method.

Although bottled water may contain less bacteria than tap water, it may not contain safe levels of disinfection byproducts (DBPs) such as bromate. Many countries are increasing regulations to ensure safe drinking water.