

# Atomic Spectrometry Update— Industrial Analysis: Metals, Chemicals and Advanced Materials

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Atomic  
Spectrometry  
Update

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## SUMMARY OF CONTENTS

### 1. Metals

1.1 Ferrous Metals and Alloys

1.2 Non-ferrous Metals and Alloys

Table 1. Summary of the Analyses of Metals

### 2. Chemicals

2.1 Petroleum and Petroleum Products

2.1.1 Crude oil and fractions

2.1.2 Fuels

2.1.3 Lubricating oils

2.2 Organic Chemicals and Solvents

2.2.1 Chemicals

2.2.2 Solvents

2.3 Inorganic Chemicals and Acids

2.4 Nuclear Materials

Table 2. Summary of Analyses of Chemicals

### 3. Advanced Materials

3.1 Polymeric Materials and Composites

3.2 Semiconductor Materials

3.3 Glasses

3.4 Ceramics and Refractories

3.5 Catalysts

Table 3. Summary of Analyses of Advanced Materials

This Atomic Spectrometry Update is the latest in an annual series appearing under the title 'Industrial Analysis'. The structure of the review is broadly the same as in previous years.

Direct analysis of solid samples continues to be a prime objective for industrial atomic spectrometry and laser sampling techniques (for both MS and AES) are becoming increasingly common, especially in the field of metals analysis. More traditional approaches using glow discharge sources are, however, still undergoing development and are frequently applied to the determination of elemental depth profiles. A novel sampling system has even been described which permits elemental mapping over many tens of square centimeters of a sample surface at one time using GD-AES. The development of rf GD sources is beginning to extend the applications of GD-MS and GD-AES to non-conductive samples and may be particularly useful in the field of advanced materials. However,

although seldom reflected in the volume of published literature, XRF still often remains the method of choice within industry for direct analysis of solid samples. The capabilities of the technique have recently been extended to include spatially resolved analysis, through the development of instruments with microbeam capabilities and of software packages that are capable of carrying out the analysis of small, irregularly shaped particles, and this is now beginning to be exploited. TXRF continues to become more established within the semiconductor industry for the determination of contaminants on wafer and device surfaces and the applications of the technique have recently been extended to include the analysis of light elements (*e.g.*, Al, C, F, Mg, N, Na and O). It has been estimated that there are now over 100 TXRF instruments in use within the semiconductor industry, and the possibility of establishing an industry wide ISO standard method based around the technique has been discussed at a recent conference. XRF is also frequently the method of choice for many process control applications. In the field of catalyst analysis, however, traditional solid sampling techniques such as SIMS, XPS and electron microscopy (usually in combination with XRD) continue to dominate.

Rapid multi-element techniques, such as ICP-MS, are becoming more widely available and the capabilities are being exploited for a diverse range of 'fingerprinting' applications (precious metal identification, oil-source rock correlations, origin of illicit drugs, archaeological artefact correlations, *etc.*). The range of elements covered by ICP-MS is being extended to include 'difficult' elements (*i.e.*, those which suffer from molecular ion interferences) through the use of novel sample introduction techniques and/or cool plasmas. Reports on the application of high resolution ICP-MS are starting to appear in the literature and it is clear that this technique offers very high potential, particularly for applications in the nuclear industry and for the analysis of advanced materials. At the moment, however, the number of such reports is relatively small, due to the limited availability and high cost of the instrumentation. In cases where multi-element capability is not required, it is often difficult to justify expensive instrumentation such as that described above, and so many workers are developing innovative approaches to improve sensitivity and eliminate interferences with cheaper alternatives such as FAAS and ETAAS. A large proportion of such work has to some extent been stimulated by the commercial availability of robust and automated sample preparation and sample introduction equipment (ultrasonic nebulizers,

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thermosprays, direct injection nebulizers, on-line matrix separation/preconcentration systems, hydride generation/desolvation systems, etc). Direct injection nebulization (DIN) appears to offer particular advantages for ICP-AES and ICP-MS analysis, since it allows direct analysis of samples containing volatile analytes (e.g., As, Hg and P in organic feedstocks), and when combined with flow injection, can allow extremely rapid analysis (up to 240 samples per hour).

Every year sees a growing awareness regarding the impact of industrial products and processes on the environment and this is the driving force for much of the research in the field of atomic spectrometry at the current time. Methods for determination of total element concentrations are fairly well established, although developments in ICP-AES (e.g., axially viewed plasma, ultrasonic nebulization) have meant that this technique may be starting to undergo something of a renaissance, as it can now be used for applications which, a few years ago, would have required the use of a more sensitive technique such as ICP-MS or ETAAS. The extension of the UV wavelength range of some newer ICP-AES instruments to allow determination of chlorine down to ppm levels also increases the attractiveness of the technique for environmental applications. In many cases, however, determination of total element concentrations in environmental samples is not sufficient, since it is well known that toxicity can vary enormously depending on the chemical form of the element. Methods for element speciation are much less well developed than those for total element concentrations and so the former is a very active field of research at the present time. Most of the work reported is concerned with development of methods for extracting, and if necessary derivatizing, chemical species prior to measurement using a chromatographic system coupled with an atomic spectrometric detector. In view of the complexity of these problems, it seems likely that this will remain an active area of research for many years to come.

## 1. METALS

The analysis of ferrous metals, non-ferrous metals, and their alloys by analytical atomic spectrometry is covered in this section. A summary of the analytical methods reported for metals in the time period under review is given in Table 1.

### 1.1. Ferrous Metals and Alloys

A review (60 references) of analytical atomic spectrometric methods involved in the iron and steelmaking industries was published (96/1385), as was a similar review (16 references) comparing spark emission and X-ray fluorescence spectrometry for process control in steelmaking plants (95/4420).

A number of papers focusing on *laser solid sampling* appeared in the literature during this review period. *In situ* laser sampling for ICP-AES (95/4725) was accomplished by placing a solid steel sample 1 mm below the plasma by a direct system insertion system. The laser directly above the plasma ablated the metal sample directly into the plasma, thus minimizing sample loss, and produced a very fast transient signal (0.7–1.7 ms compared with 1 s for a conventional laser ablation system). Improvements in sensitivity were reported. A time of flight mass spectrometer was used as a detector in an ICP-MS system to measure the transient Pb signal generated from a laser pulse impinging upon a cast iron standard (96/3017). Pulse to pulse variations were virtually eliminated by ratioing signals from two Zn isotopes that were simultaneously acquired. A 10 ppb limit of detection (LOD) was reported for Pb in iron. A 'nominally' non-destructive sampling method was reported (95/4173) in which the metal/alloy surface was polished with a diamond lapping disk, following which the metal transferred onto the disk was analysed by laser ablation (LA) ICP-MS. The determination of trace elements agreed

with certified values of steel standards and detection limits varied between 1 and 10 µg g<sup>-1</sup>.

Interest continues in *laser-induced plasma atomic emission spectrometry* (LIP-AES) or *laser-induced breakdown spectrometry* (LIBS). *Sulfur in steel* was determined by this spectroscopic method (96/2813) with the plasma generated by 7 ns pulses of a Q-switched Nd:YAG laser operating at 20 Hz. Wavelengths below 180 nm were used for detection. The monochromator was filled with nitrogen to prevent light absorption by oxygen. No noticeable matrix effects were observed. This method was also used for *depth profiling studies of coatings on steel* (96/1039). Good precision was reported for 2.7–7.2 µm coatings of Zn–Ni and 0.38 to 1.48 µm of Sn. An ultra-thin coating of Cr (20 nm) was also detected on a steel sample. The main advantages of this method appear to be the profiling performance and rapid measurement times (<60 s). A CO<sub>2</sub> laser was used to induce a shock wave plasma for atomic emission spectrometric *determination of Cr and Ni in steels* with an iron emission line as an internal standard (95/3837). A high speed steel was vaporized by this more energetic laser (700 mJ at 5 Hz); however, W in this steel could not be determined.

A number of papers on *glow discharge sources* were published. A method of *quantitative depth-profile analysis* by GD-AES based on matrix independent emission yields was proposed (95/4714). It was tested by profiling an Al–Ni–Cr-steel thin film system. The determined thickness of the Ni–Cr layer of sample was in agreement with the known value. The thickness of the Al layer was low biased by 1.8 µm and the reasons for this are not known. A study (95/4186) of discharge conditions, for in-depth profile analysis of thin films using an Al–Zn coated steel, showed that the internal diameter of the anode, etching rate with the rf power and the gas pressure were important in optimizing GD-AES measurements.

There were a moderate number of research papers involving *atomic emission spectrometry*. Most of these investigated different methods of liquid sample pre-treatment prior to presentation to the emission source (commonly an ICP). These are conveniently summarized in Table 1. An interesting comparison was made between ICP-AES and flame heated quartz tube AAS for the determination of selenium in steels with matrix separation by hydride generation (95/4700). Although Se was determined by both methods, ICP-AES showed lower detection limits by a factor of 1.5 to 3 depending on the sample type and had reduced matrix interference. Experiments indicated that these are gas phase interferences and are most likely due to the presence of As and Sn hydrides. The determination of *boron in steels* continued to be a topic of investigation by on-line separation and pre-concentration, flowing into a microwave plasma emission source (96/2801). In the flow injection system described, the sample passed through a strongly acidic cation exchange column and then through a strongly basic anion exchange column. The microwave plasma excitation source was pursued because of its lower cost (compared with ICP), but since it suffers from matrix interferences, the described sample pre-treatment was necessary. The accuracy of the method was verified with certified materials and the precision varied from 3.6 to 4.7% RSD for B concentrations ranging from 12 to 100 µg g<sup>-1</sup>.

ICP-MS is becoming an increasingly common method for the *determination of trace elements in high purity iron and steels*. However, molecular ion interferences originating from matrix elements can be troublesome. Mass spectral interferences (above 69 m/z) from matrix components in high purity iron, and low and high alloy steels (e.g., Cr, Fe, Mn, Mo, Ni and W) in combination with different acids have been experimentally determined (96/2436). It was recommended that prior knowledge of the material before analysis would aid in anticipating potential interferences. A direct flow injection manifold

**Table 1** SUMMARY OF THE ANALYSES OF METALS

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
Ag	Au–Ag jewellery alloys	XRF;—;S	No sample pretreatment reported. Determination range was 1–99.99% m/m	95/3504
Ag	Nickel-based alloys and steels	AA;ETA;L	Samples (1 g) dissolved in 25 ml HF–HNO <sub>3</sub> –H <sub>2</sub> O (1:1:1), diluted to 100 ml with water and then 10 ml of solution mixed with 10 ml 50% HNO <sub>3</sub> and diluted to 100 ml. Resulting solutions (0.5 ml) mixed with 0.5 ml of 0.6% ammonium dihydrogenphosphate–0.5% Ni solution prior to analysis using ETAAS. (Detection limit 0.06 µg l <sup>-1</sup> )	95/4696
Ag	Copper	AA;F;L	Copper (0.3 g) dissolved in 15 ml HCl–HNO <sub>3</sub> (4:1) then diluted to 50 ml with water. Detection limit was 0.017 µg ml <sup>-1</sup> and precision 2.7–6.3% (RSD)	96/389
Al	Zinc and zinc alloys	AA;F;L	Samples (1 or 2 g) dissolved in 20 or 40 ml of HCl, boiled with H <sub>2</sub> O <sub>2</sub> (1 or 2 ml) then diluted to 100 ml with water. N <sub>2</sub> O–C <sub>2</sub> H <sub>2</sub> flame used. Limits of interfering components quoted	95/3421
Al	Copper alloys	AA;F;L	Sample solutions adjusted to pH 3.8 and shaken with 5 ml 0.16% <i>N</i> -nitrophenylhydroxylamine–lead in benzene for 1 min. Al determined indirectly by measurement of Pb in aqueous phase which was displaced by Al. Linear calibration up to 5 µg ml <sup>-1</sup> . (RSD <2.6%; LOD 0.0048 µg ml <sup>-1</sup> )	96/358
As	Cadmium	AA;ETA;L	Most of the cadmium distilled off at 360 °C under vacuum. Residue dissolved in 0.2 ml of 50% HNO <sub>3</sub> and diluted to 2 ml with water. Pd nitrate matrix modifier added if As concentration <0.01 µg ml <sup>-1</sup> . (Detection limit 4 ng g <sup>-1</sup> ; RSD 0.34 at 5 µg g <sup>-1</sup> )	95/3431
As	Caesium	AA;F;L	As for P	95/4401
As	Nickel alloys and copper metal	AA or AE;F;L	Interferences from nickel and cobalt removed by adding DTPA. Solution made alkaline with NaOH and filtered to remove copper hydroxide. Tetrahydroborate was added and resulting solution mixed with HCl in continuous-flow hydride generation system	96/2883
Au	Au–Ag jewellery alloys	XRF;—;S	As for Ag	95/3504
B	Steels	MS;ICP;L	Steel dissolved in <i>aqua regia</i> within high pressure microwave vessels. Be added as internal standard. Discrete volume (220 µl) introduced using flow injection system. (Detection limit 0.2 µg g <sup>-1</sup> and RSD <1.5% for 100 ng B in 0.5% Fe)	95/3557
B	Steel	AA;F;L	Dissolved samples treated to form ionic complex Cu(phenyl) <sub>3</sub> <sup>2+</sup> –B–phenylhydroxyacetic acid. Complex extracted into MIBK and B content determined indirectly by measuring Cu concentration in solution	95/3785
B	Steels	AE;MIP;L	Aliquot of dissolved sample passed through two on-line anion exchange columns (one strongly acidic and the other strongly basic) in series to remove interferences. RSD was 4.2% at 0.2 mg l <sup>-1</sup> and detection limits were 0.0055 mg l <sup>-1</sup> at 45 samples h <sup>-1</sup> and 0.0018 mg l <sup>-1</sup> at 20 samples h <sup>-1</sup>	96/2801
B	Cobalt-based alloys	AA;ETA;L	Samples (30 mg) mixed with 2.5–3.0 ml <i>aqua regia</i> at room temperature for 1 h; heated in a water-bath (70 °C), mixed with 0.2% HNO <sub>3</sub> and diluted to 20 ml. A 5 ml aliquot was mixed with 1.5 ml 20 g l <sup>-1</sup> Ni and diluted to 10 ml. 10 µl aliquot plus 20 µl 2000 mg l <sup>-1</sup> Zr injected into atomizer. (RSD 3.3%)	96/2975
Be	Aluminium-based alloys	AE;ICP;L	Alloy samples (100–300 mg) dissolved in 6 mol l <sup>-1</sup> HCl and then diluted to 50 ml with water. Aliquots of 10 µl were mixed with 10 µl of a <i>o</i> -phenanthroline solution, dried at 110 °C, loaded into tungsten boat furnace and 15 µl 0.9 mol l <sup>-1</sup> ethylmagnesium bromide in THF added prior to vaporization into ICP. (LOD 1.1 pg)	96/302
Bi	Copper-based alloys	AA;F;L	Comparison between flame and hydride generation with and without a slotted tube atom trap	95/4261
Bi	Nickel-based alloys and steels	AA;ETA;L	Samples (1 g) dissolved in 25 ml HF–HNO <sub>3</sub> –H <sub>2</sub> O (1:1:1) and diluted to 100 ml. Aliquots (0.5 ml) mixed with 0.1 ml Ni–Hf solution (15:2 m/v) and 0.15 ml 25% tartaric acid. (Detection limit 1 µg l <sup>-1</sup> )	95/4696

**Table 1** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
Bi	Zinc metal	MS;ICP;L	Sample dissolved in 7 mol l <sup>-1</sup> HNO <sub>3</sub> and evaporated to near dryness. Residue re-dissolved in 0.5 mol l <sup>-1</sup> HNO <sub>3</sub> and injected into a carrier stream of 0.1 mol l <sup>-1</sup> KI onto anion-exchange mini-column. Analytes eluted with 2 mol l <sup>-1</sup> HNO <sub>3</sub> directly into ICP-MS. Calibration linear to 10 ng ml <sup>-1</sup> and detection limit 0.014 ng ml <sup>-1</sup>	96/1309
Cd	Cobalt	AA;ETA;L	Sample (0.1 g) dissolved by heating with 10 ml 50% HNO <sub>3</sub> and diluted. A 20 µl aliquot injected into the atomizer, dried, and atomized (without pyrolysis). Precision varied between 1 and 7%	95/3386
Cd	Zinc and zinc alloys	AA;F;L	Samples (1 g) dissolved in boiling H <sub>2</sub> SO <sub>4</sub> -HNO <sub>3</sub> , cooled, mixed with 10 ml urea (10 g l <sup>-1</sup> ), diluted to 100 ml and mixed with 3 ml NaI solution (750 g l <sup>-1</sup> ). Resulting solution extracted with 25 ml tri-n-octylamine (10 ml l <sup>-1</sup> ) in n-butyl acetate and analysed by AAS. (Concentration range 0.0001–0.02 m/m Cd)	95/3425
Co	Steels	AA;F;L	Sample solution (500 µl) injected into flow injection manifold and mixed with an acetylacetone-buffer solution at 1.5 ml min <sup>-1</sup> . Precipitated Co-acetylacetone was collected on in-line filter and dissolved with 80 µl MIBK and passed directly to the spectrometer. Precision was 2.5% (RSD) for concentrations < 25 ng ml <sup>-1</sup>	96/1280
Co	Zircaloy	MS;ICP;S	Pulsed Nd: YAG laser (1064 nm) operated at 150 mJ with sampling depth of 12 mm for LA-ICP-MS. Good agreement reported for analysis of reference materials. (RSD 1.5%)	96/2352
Cr	Aluminium	AE;ICP;L	Aliquots (10 µl) of dissolved sample and 10 µl of 8-hydroxyquinolinolate (0.10 mol l <sup>-1</sup> ) mixed, dried in a tungsten cuvette and loaded into a tungsten boat furnace. Sample vaporized at 950 °C into ICP torch. Results agreed with certified Cr concentrations for standard reference samples. (RSD 4.6% for 2.5 ng Cr)	96/1433
Cu	Zinc and zinc alloys	AA;F;L	Samples (2 g) boiled in 35 ml H <sub>2</sub> SO <sub>4</sub> -HNO <sub>3</sub> , cooled, mixed with 10 ml 10 g l <sup>-1</sup> urea, diluted to 100 ml and mixed with 3 ml NaI (750 g l <sup>-1</sup> ). Cu was extracted using 15 ml tri-n-octylamine (10 ml l <sup>-1</sup> ) in n-butyl acetate. Concentration range was 0.0001–0.0025% m/m Cu. Results from inter-laboratory comparison given	95/3422
Cu	Zinc and zinc alloys	AA;F;L	Samples (1 g) boiled in 60 ml 50% HNO <sub>3</sub> and diluted to 100 ml with water. Analysis followed further 10 fold dilution with water. Applicable to concentration range 0.25–1.25% m/m Cu. Results from inter-laboratory comparison given	95/3423
Cu	Tungsten alloys	XRF;—;L	Samples (3 g) dissolved in 10 ml of 50% HCl and Co internal standard added. Solution was decanted from undissolved tungsten powder which was then washed with water. The solutions and washes were combined and diluted to 25 ml. Aliquots of 400 µl absorbed on a piece of filter-paper, dried and analysed by XRF.	96/2926
Ge	Low-alloy steel	AA;ETA;L	Samples (0.2 g) dissolved in 5 ml aqua regia, diluted to 100 ml with 1 mol l <sup>-1</sup> HNO <sub>3</sub> and filtered. A 1 ml aliquot was injected into hydride generator (1% NaBH <sub>4</sub> and a carrier of H <sub>3</sub> PO <sub>4</sub> and L-cysteine). Volatile Ge hydride was collected <i>in situ</i> on heated Zr coated graphite tube or platform. (RSD 2% at 1 µg l <sup>-1</sup> ; LOD 9–18 pg)	96/291
Mg	Zinc and zinc alloys	AA;F;L	Samples (0.5 g) dissolved in 20 ml HCl and 1 ml H <sub>2</sub> O <sub>2</sub> , then diluted to 200 ml with water and analysed by AAS at 285.2 nm using an N <sub>2</sub> O-C <sub>2</sub> H <sub>2</sub> flame. Method is applicable to Mg concentrations of 0.002–0.1% and can tolerate up 5% Al content. Results from an inter-laboratory comparison presented	95/3420

**Table 1** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
Mn	Copper alloys	AA;F;L	Chips, millings or turnings (0.75 g) dissolved in 10 ml HNO <sub>3</sub> and 0.5 ml HF, mixed with 10 ml H <sub>3</sub> BO <sub>3</sub> (30 g l <sup>-1</sup> ) and diluted to volume with water. Mn in resulting solutions determined by AAS at 279.48 and at 403.08 nm, for Mn < 3% and Mn > 3%, respectively. Results from inter-laboratory comparison given	95/3427
Mo	Zircaloy	MS;ICP;S	As for Co. Precision was 7% (RSD)	96/2352
N	Steels	AE;—;S	Comparison of results from 6 laboratories	96/1099
Ni	Magnesium alloy	AA;F;L	Alloy chips 0.5 g (or 1.0 g) wetted with 10 ml (or 20 ml) water, then 40 ml (or 20 ml) of 50% HCl added. Dissolution began cold then 10 (or 5) drops conc. HNO <sub>3</sub> added and solution boiled for 1–2 min. After cooling samples were made up to 100 ml. Standard additions used to verify Ni concentrations	95/3428
O	Steel	XRF;—;S	None	96/624
O	Titanium	SIMS;S	Cs <sup>+</sup> primary ion beam used for the local quantification of surface oxygen	96/2316
P	Caesium	AA;F;L	Sample reacted with ethanol, treated with 50% H <sub>2</sub> SO <sub>4</sub> and evaporated to near dryness. Residue dissolved in water and mixed with 2 mol l <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub> –0.2 mol l <sup>-1</sup> Na <sub>2</sub> MoO <sub>4</sub> –0.1 mmol l <sup>-1</sup> malachite green and diethyl ether. Total P and As were determined by measuring the Mo in organic phase. P alone determined by including 2 mmol l <sup>-1</sup> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	95/4401
Pb	Zinc and zinc alloys	AA;F;L	As for Cd. Determination by AAS with 283.3 and 217.0 nm for 0.0001–0.005% and 0.005–0.03% Pb, respectively	95/3424
Pb	Copper alloys	AA;F;L	Copper alloys dissolved in HNO <sub>3</sub> and HF and mixed with H <sub>3</sub> BO <sub>3</sub> . Solution diluted to volume with water and analysed by AAS at 217.0 and 283.3 nm for 0.0001–0.005% and 0.005–0.03% Pb, respectively. Results from inter-laboratory comparison given	95/3426
Pb	Aluminium	AA;ETA;L	Aluminium matrix dissolved with HNO <sub>3</sub> –HF–HClO <sub>4</sub> . Residue (containing Pb) dissolved in 5 ml 50% HNO <sub>3</sub> and diluted to volume with water. Precision and recoveries were 2.6% (RSD) and 101–106%, respectively	95/4561
Pt	Au–Ag jewellery alloys	XRF;—;S	As for Ag	95/3504
S	Steel	MS;ICP;L	Iron matrix was removed by solvent extraction with 4-methylpentan-2-one. Samples analysed using ETV-ICP-MS with calibration using isotope dilution. RSD was 10% at 2 µg g <sup>-1</sup> and detection limit 0.05 µg g <sup>-1</sup>	96/2805
S	Steel	AE;laser;S	Samples cut to fit into sample chamber (filled with N <sub>2</sub> ). RSD 5% for S concentration > 0.05%	96/2813
Sb	Copper	AF;F;L	Dissolved samples treated with 0.1% L-cysteine in 0.5 mol l <sup>-1</sup> HCl to convert Sb <sup>V</sup> to Sb <sup>III</sup> . Discrete samples injected into continuous flow hydride generation system with detection by AFS. Calibration was linear to 1 µg ml <sup>-1</sup> and detection limit was 22 pg ml <sup>-1</sup>	96/274
Sb	Copper	AA;ETA;L	Large excess of copper acted as matrix modifier for determination of Sb	96/1079
Se	Nickel-based alloys	AA;ETA;L	Selenium hydride generated from dissolved sample and preconcentrated within a palladium coated graphite tube. Precision was 5.4–6.1% (RSD) and recoveries 97–110%	95/3382
Se	Nickel and steel	AA;F;L	Analysis using hydride generation with high concentrations (up to 8000 mg l <sup>-1</sup> ) of Ni <sup>2+</sup> and Co <sup>2+</sup> masked by EDTA or DTPA. Tartarate was an effective masking agent for up to 5000 mg l <sup>-1</sup> for Fe <sup>3+</sup> and Cr <sup>3+</sup> . (Detection limits 0.1 µg g <sup>-1</sup> for nickel and 0.3 µg g <sup>-1</sup> for steel)	95/4699
Se	Nickel and steel	AA or AE;F or ICP;L	Comparison between AA and ICP-AES for determination of Se using hydride generation. The detection limit was lower by 1.5–3 times when ICP-AES was used	95/4700

**Table 1** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
Se	Steels and nickel based alloys	AA;ETA;L	Variety of dissolution schemes presented for one gram sample depending on other metals in sample. Se was precipitated by adding 2–3 g ascorbic acid and 5 ml 0.6 g l <sup>-1</sup> Pd. Precipitated Se was dissolved in HNO <sub>3</sub> –HCl, then diluted to 10 ml for analysis. Ascorbic acid (3%) was used as a matrix modifier. RSD was 0.8%	96/59
Si	High temperature alloys	AA;ETA;L	Samples (0.05 g) dissolved in 4 ml <i>aqua regia</i> , then diluted to 25 ml with water. Aliquot treated with 2.5 mg La and 1 mg Ca, then made up to 5 ml with water. Detection limit was 2.3 µg g <sup>-1</sup>	95/3632
Sn	Iron and steels	AA;F;L	Samples dissolved in HCl, cooled and filtered. Filtrate mixed with ascorbic acid and KI, diluted and then Sn extracted using 10 ml trioctylphosphine oxide (50 g l <sup>-1</sup> ) in IBMK. Analysis by AAS at 235.5 nm using an N <sub>2</sub> O–C <sub>2</sub> H <sub>2</sub> flame. Inter-laboratory comparison data reported	95/4470
Te	Nickel-based alloys	AA;ETA;L	Samples (0.05 g) dissolved with 4 ml <i>aqua regia</i> and 0.5 ml HF. Residue boiled with 5 ml 6 mol l <sup>-1</sup> HCl for 40 min and diluted to 5 ml with water. Solution diluted 5 fold and reacted with stream of 10% KBH <sub>4</sub> . Generated hydride preconcentrated <i>in situ</i> onto Pd-coated graphite tube at 200 °C. (Linear calibration to 1.5 ng ml <sup>-1</sup> )	95/3637
Te	Steels and nickel based alloys	AA;ETA;L	As for Se; (RSD 1.4%)	96/59
Te	Zinc metal	MS;ICP;L	As for Bi. (Detection limit 0.16 ng ml <sup>-1</sup> )	96/1309
Te	Nickel alloys and copper metal	AA or AE;F;L	As for As	96/2883
Te	Tungsten alloys	XRF;—;L	As for Cu. Calibration linear from 1–3%. (RSD 2.61% and recovery 99.76%)	96/2926
Zn	Aluminum alloys	AA;F;L	Zn in dissolved sample reacted with 4-(2-pyridylazo)resorcinol (PAR). The Zn–PAR complex anion was adsorbed onto trioctylmethylammonium–bromate ion-pair material supported on biphenyl and then dissolved in DMF	95/3813
Various (15)	Unalloyed steels	MS;ICP;L	Sample solutions made with Be, Ti and Rh internal standards. Discreet volumes were introduced into ICP using flow injection manifold. (RSD <3% for analyte concentrations >1 µg ml <sup>-1</sup> )	95/3056
Various (5)	High purity zinc	MS;ICP;L	Samples (5 g) dissolved in 9 mol l <sup>-1</sup> HCl, evaporated to near dryness, then re-dissolved in 50 ml 2 mol l <sup>-1</sup> HCl. Aliquot (170 µl) passed through anion-exchange column (BIORAD AG1-X8) where Zn was retained and analytes passed directly to ICP-MS. (RSD <5% RSD for 10 ng ml <sup>-1</sup> concentrations)	95/3531
Various (10)	High purity selenium	MS;ICP;L	Etched selenium dissolved in 80 ml 2 mol l <sup>-1</sup> HCl, 7 ml 4.8% thiourea added and then solution heated, cooled and filtered. Nitric acid (10 ml) was added to the filtrate and then heated until SO <sub>3</sub> appeared. Samples diluted to 100 ml with water prior to analysis. (LODs <0.1 µg g <sup>-1</sup> )	95/3532
Various (7)	Tungsten	MS;GD;S	Direct analysis of tungsten filaments	95/3572
Various (10)	Steel	XRF;—;S	None	95/3877
Various (4)	Aluminium	AE;laser;S	Direct sample analysis. (Detection limits about 10 µg g <sup>-1</sup> for most analytes)	95/3880
Various (8)	Steels	MS;ICP;S	Sample surface polished with diamond lapping disc and solid material transferred onto the disc was analysed directly using LA-ICP-MS. (RSD <10% for elements in reference materials and detection limits 1–10 µg g <sup>-1</sup> )	95/4173
Various (3)	Copper alloys	AE;laser;S	Solid samples analysed with minimal sample preparation. (Detection limits 20, 10, and 1 µg g <sup>-1</sup> and RSD 4, 7 and 3%, for Fe, Ni and Ag, respectively)	95/4182
Various	Precious metals	AE;GD;S	Direct solid analysis. Calibration curves linear over 2–3 orders of magnitude. Analyte signal ratioed to spectral background (RSDs 1% and 5% for short- and long-term, respectively)	95/4347

**Table 1** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
Various	Zircaloys	MS;ICP;L	Dissolved samples (by $\text{HNO}_3\text{-HF}$ ), pH adjusted to 1.5–2, then extracted with 50% bis-(2-ethylhexyl)orthophosphoric acid in toluene. The organic phase with Zr was further extracted with 6 mol l <sup>-1</sup> $\text{HNO}_3$ and dioctyl alcohol and all aqueous phases were analysed for trace elements. Isotope dilution was used for calibration	95/4491
Various (4)	NdFeB permanent magnet alloy	AE;ICP;L	Sample (3 g) dissolved in 15 ml 3 mol l <sup>-1</sup> HCl and a few drops of $\text{HNO}_3$ , then heated till $\text{HNO}_3$ fuming stopped. Nd determined by direct nebulization. Rare-earth elements (Sm, Pr, Ce and La) determined after preconcentrating on a column of sulfopropyl SI-100 and gradient elution with 0.06–0.19 mol l <sup>-1</sup> $\alpha$ -hydroxyisobutyric acid	95/4530
Various	Molybdenum and molybdenum silicide	AA;ETA;S	Powdered samples weighed directly into either graphite cup or a boat/platform then placed into the atomizer	95/4594
Various (4)	Gold/silver fire assay beads	MS;ICP;S	Trace elements preconcentrated in fire assay beads from geological samples and spark sampled in a specially designed solid-sampling cell. Signal precision from continuous sampling of 5 replicates was <6% (RSD). Applicable to metal analysis	95/4595
Various	Low-alloyed steels	MS;ICP;S	Solid sampling by spark ablation. (Detection limits 0.08–0.32 $\mu\text{g g}^{-1}$ with $^{58}\text{Fe}$ internal standard)	95/4708
Various (5)	Furnace slag and roaster feed	XRF;—;S	Samples dissolved in lithium tetraborate flux containing oxidizing agent and set in platinum–gold crucibles. Fused glass discs/beads presented to spectrometer for analysis	96/355
Various (4)	Ferro-alloys	XRF;—;S	Samples fused with lithium tetraborate and lithium carbonate to form glass discs/beads	96/407
Various (5)	Crudely refined gold	AE;ICP;L	Samples (0.25 g) heated in 5 ml of $\text{HNO}_3$ , cooled, 20 ml HCl was added and then re-heated (process repeated until samples fully dissolved). Aliquots (500 $\mu\text{l}$ ) injected into water carrier stream using flow injection system. LODs were <0.7 $\mu\text{g ml}^{-1}$ (or <0.08% m/m).	96/417
Various (4)	Steels	AE;laser;S	Depth profiling studied using laser-induced plasma emission spectrometry. Precision of 3.5% RSD reported for Zn–Ni coatings (2.7–7.2 $\mu\text{m}$ ) and for Sn coatings (0.38–1.48 $\mu\text{m}$ ). Thin coating of Cr (20 nm) also detected. (Analysis time was reported to be <60 s)	96/1039
Various	Copper	XRF;—;L	Portions (5 $\mu\text{l}$ ) of dissolved copper samples placed on quartz plate and evaporated. Spectra taken before and after irradiation with spallation neutrons (<700 MeV) or monoenergetic protons (590 MeV). Difference spectra (irradiated <i>versus</i> non-irradiated) analysed for peak areas	96/1223
Various (5)	High-purity iron	MS;ICP;L	Aliquot (200 $\mu\text{l}$ ) of dissolved sample (50 mg ml <sup>-1</sup> in 2 mol l <sup>-1</sup> HF) loaded onto anion-exchange column (Dowex 1X8–100). Analytes eluted from column with 200 $\mu\text{l}$ of solution consisting of 0.7 mol l <sup>-1</sup> $\text{HNO}_3$ –0.5 mol l <sup>-1</sup> HCl–0.05% $\text{H}_2\text{O}_2$	96/1503
Various	Scandium	MS;ICP;L	Scandium extracted into bis(2-ethylhexyl)orthophosphate in toluene, leaving analytes in the aqueous phase	96/1573
Various	Gold	MS;ICP;S	Solid sampling by laser ablation (Nd: YAG) with calibration using gold reference materials. Detection limits were <0.18 $\mu\text{g g}^{-1}$ . Crudely refined gold from different geological sites could be differentiated using unique elemental fingerprint	96/1723
Various	Aluminium	Various	Comparison of ICP-AES, FAAS, ETAAS and HGAAS for determination of various elements. Results from a round-robin survey presented	96/1811
Various	Ferromolybdenum and ferroniobium	XRF;—;S	Samples prepared by re-melting with iron (15 g FeMo alloy + 25 g iron and 12 g FeNb + 28 g iron). Calibration standards prepared either by re-melting pure metals with iron or by re-melting a known ferro-alloy with iron. (RSD <0.6%)	96/2653
Various (23)	Tungsten	AE;ICP;L	Samples dissolved by microwave dissolution in HF and $\text{HNO}_3$ . Line selection and spectral interferences studied. (Average precision 1% RSD)	96/2889

**Table 1** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
Various (4)	Zinc	AE;ICP;L	Zinc dissolved in $\text{HNO}_3$ , taken to dryness and dissolved in dilute $\text{KI-HNO}_3$ . Solution passed through column packed with BIORAD AG1-X8 anion-exchange resin. Analytes eluted with 3 mol $\text{l}^{-1}$ $\text{HNO}_3$ , evaporated to dryness and then re-dissolved in 5 ml $\text{HNO}_3$	96/2891
Various (7)	Steels	AE;ICP;L	Steel (3 g) dissolved with $\text{HCl-HNO}_3-\text{HF}$ and heated to dryness with $\text{HClO}_4$ . Residue taken up in 50% HCl and then 1% benzophenylhydroxylamine in IBMK used to extract interfering species into organic phase. Rare-earth analytes remained in aqueous phase for analysis	96/2906

\* HG indicates hydride generation and S, L, G and SL signify solid, liquid, gaseous or slurry sample introduction, respectively. Other abbreviations are listed elsewhere.

was used for ICP-MS determination of 15 elements in unalloyed steel samples (95/3056). Chloride interferences were eliminated by sample dissolution in nitric acid using high pressure (closed vessel) microwave dissolution. Elements were accurately determined in reference material samples with calibration solutions that contained only 2% (m/v)  $\text{HNO}_3$  and Be, Tl and Rh used as internal standards. The forward power of the plasma was adjusted to 1.5 kW and the nebulizer flow rate was optimized at 1.1 ml  $\text{min}^{-1}$  for this analysis.

Different sample introduction systems were used with *ICP-MS*. *Spark ablation (SA) ICP-MS* was used for determining Al, B, Co, Mn, Nb, P, Sb, Si, V and Zr in low-alloyed steels (95/4708). The spark generated aerosol particles passed through a newly designed cyclone chamber which was reported to deliver more uniform sized particles ( $<1.0\ \mu\text{m}$ ) to the plasma. Calibration was effected with solid steel reference materials and  $^{58}\text{Fe}$  was used as an internal standard. Low detection limits were reported ( $<0.3\ \mu\text{g g}^{-1}$  for most elements except Si, B, and P) and the precision at 10 times the LOD was  $<2.5\%$  RSD. A comparison was made between SA-ICP-MS and GD-MS with the same mass detector (95/4596). It was reported that shorter analysis times were obtained by the spark ablation system, whereas the glow discharge system had lower detection limits.

*Sulfur in steel* was determined by *ETV-ICP-MS*. Matrix components greatly affected the analyte signal (96/2805). This was overcome by the use of isotope dilution calibration and the removal of Fe (the major matrix component) by solvent extraction with 4-methylpentan-2-one. A precision of 10% (RSD) at S levels of  $2\ \mu\text{g g}^{-1}$  was reported and the LOD was estimated to be  $0.05\ \mu\text{g g}^{-1}$ .

*Hydride generation-electrothermal atomization atomic spectrometry (HG-ETAAS)* was applied to the determination of germanium in low alloy-steel (96/291). Volatile elements were also determined in steels and nickel alloys by directly inserting solid samples into a conventional atomizer for determination by ETAAS (96/C712). Aqueous calibration was successful for the determination of Pb and Bi. Incomplete analyte release required that solid reference material pieces be used for the determination of Sn and Se.

A less common approach was taken in determining trace elements in steels by *synchrotron XRF* (95/3877) focused on a  $1\ \text{mm}^2$  spot on the sample surface. The results were reported to be in agreement with values obtained by PIXE. *Calcium in steel* was determined by *secondary-ion mass spectrometry (SIMS)* in an area of  $500 \times 700\ \mu\text{m}^2$  (95/3887). This appears to be a good semi-quantitative tool, with the limit of detection estimated to be  $0.5\ \mu\text{g g}^{-1}$ . Papers using FAAS and XRF

mainly focused on sample preparation and are summarized in Table 1.

## 1.2. Non-Ferrous Metals and Alloys

A considerable number of abstracts appeared in the literature during this review period dealing with different spectrometric methods for the analysis of a wide variety of non-ferrous metals. The majority of papers deal with innovations in sample preparation prior to spectrometric analysis and are summarized in Table 1. In general, there has been a sustained interest in the development of *direct solid sample analysis* for metal samples, especially for pure metals and precious metal alloys.

An overview (95/3800) of *laser-induced breakdown spectrometry (LIBS)* was given with respect to the quantitative determination of metal alloy components in solid samples. Elements in aluminium were determined by LIBS using two different experimental procedures (96/1078). The emission from the aluminium matrix was used as an internal reference for elements whose emission lines are in close proximity to the matrix emission wavelength (such as Mg and Mn). However, for elements such as Ti, the background emission intensity was taken as a reference emission because there are no aluminium emission wavelengths in the spectral region of the required Ti wavelength. A report of time-resolved LIBS was published (95/4180) in which a plasma was formed by using a low energy (10 mJ, 10 ns) Q-switched Nd: YAG laser in atmospheric air. Au, Ag, and Cu were determined in jewel etalons by measuring the intensity ratios Cu:Ag, Ag:Au and Cu:Au at different wavelengths for alloys of known composition. Ratioing is required because the amount of material ablated by each laser pulse varies considerably. The application of low energy laser pulses minimized the amount of material taken from the sample. In another report, quantitative analyses and plasma characteristics were studied for the determination of trace elements in aluminium and copper matrices with LODs observed in the order of  $10\ \mu\text{g g}^{-1}$  for most elements (95/3880, 95/4182).

*Solid sampling from a glow discharge* for either atomic emission spectrometry (GD-AES) or mass spectrometry (GD-MS) was the focus of a number of abstracts. A novel sampling system has been developed which permits elemental mapping by GD-AES of a solid surface (many tens of square centimeters) at one time (96/647). This was accomplished by sustaining multiple discharges simultaneously over a Macor restrictor plate with sampling holes set in at regular intervals (in a grid pattern). Emissions were selectively multiplexed by Hadamard spatial transform imaging and sorted out by a

matrix multiplication process. Trace elements in a variety of precious metal samples (Au, Pt, Ag and sterling Ag) have been determined by radiofrequency GD-AES (95/4347). A significant feature of this work was that the analyte signal intensity was ratioed with the spectral background adjacent to the analytical wavelength. Detection limits were in the range of tens of ppb and were considerably lower than other direct solid sample spectrometric methods. An alternative detection scheme for GD-MS was presented (96/C2044), whereby secondary mass species such as  $M^{2+}$ ,  $M\text{Ar}^+$  and  $M_2^+$  were used for element determination, which may be useful in overcoming isobaric interferences and gaining more useful information from the sample. Relative errors in the range of 15% were shown for element concentrations greater than 1% in aluminum reference materials.

The determination of elements in gold by LA-ICP-MS was shown to be quite successful ( $\text{LOD} < 0.18 \text{ ppm}$ ) provided one has adequate reference materials for calibration (96/1723). It was also determined that semi-quantitative elemental fingerprints of crudely refined gold hold sufficient information to distinguish between samples originating from different mines. A special device has been constructed for solid sampling of fire assay beads (gold/silver alloys) by SA-ICP-MS (95/4595). For samples containing 100 ppm of Pt, Pd, Rh and Ir, good precision was reported (3–6% RSD). The accuracy of the method was verified with fire assay beads prepared from a geological reference material and LODs varied from 0.6–1.2 ppm. This device appears to have potential in determining trace elements in small samples of precious metals in general. A comparison was made between SA-ICP-AES and LA-ICP-MS for determining trace elements in fine gold and silver for assaying purposes (95/4574). Better LODs were obtained by LA-ICP-MS for most elements (except Fe, Mn and Zn). However, SA-ICP-AES was preferred due to ease of operation, long term stability, high sample throughput and relative flexibility in sample shape and size.

Flow injection ICP-MS was applied to the determination of a variety of elements in high purity zinc (95/3531, 96/1309), whereby a discrete volume of the dissolved sample was passed through an anion-exchange column then eluted directly into the ICP-MS instrument. It has been shown that polyatomic ion interferences in ICP-MS, arising from the presence of chloride ions from the dissolution of gold in *aqua regia*, can be overcome by dissolving the gold using hydrobromic acid in place of hydrochloric acid (96/C2215) and by flow injection hydride generation ICP-MS, whereby the analytes are separated from the chloride containing solution (96/C762).

A direct flow injection manifold was used in conjunction with ICP-AES for the determination of base metals in crudely refined gold (96/417). Concentrated hydrochloric acid was required to maintain high levels of silver in solution. The flow injection manifold was used to minimize the total amount of acid introduced into the nebulizer system and a vented sample introduction hood was designed to isolate the spectrometer and peristaltic pump from corrosive fumes from the samples. Chromium was determined in aluminium by complexation with 8-hydroxyquinolinate and vaporized via a heated tungsten cuvette for determination by ICP-AES (96/1433). In this case the dissolved aluminium matrix appears to be acting as a carrier for the vaporized chromium, thereby improving sensitivity and slightly lowering the absolute LOD (0.05 ng) in comparison with the absence of the matrix. A solution/suspension of metal samples was made by laser probe sampling of a metal immersed in a reagent solution and then analysed by ICP-AES (96/C918). This was reported to be applicable to a flow injection system. A report of elemental fingerprinting by spark excitation AES (96/1299) claims that information on microhomogeneity and production technology can be gained from interpretation of the data.

A method for determining components in a metal melt for process control was developed using wavelength dispersive X-ray spectrometry (96/598). The spectrometer was designed for this industrial environment and was reported to significantly reduce the time of analysis. An iteration equation (95/3400) was designed for calculation of elements in a sample by standardless wavelength dispersive XRF and was applied to the analysis of an aluminium alloy. A review (182 references) of different XRF analysis techniques and applications in a variety of sample types was published (95/4529).

The majority of abstracts involving atomic absorption spectrometry tend to discuss sample preparation and are summarized in Table 1. However, some novel approaches warrant mention. Arsenic in cadmium was determined by ETAAS, with the bulk of the cadmium distilled off under vacuum prior to dissolution (95/3431). Apparently, the As loss was negligible during dissolution. Trace impurities in molybdenum and molybdenum silicide were determined by direct weighing solid sample ETAAS with different atomizer types (95/4594). The LODs were reported to be at the sub- $\text{ng g}^{-1}$  level and the determined values were in agreement with values from solution sample preparation. Solid samples (96/C238) were also introduced into a graphite furnace by deposition of the particle aerosol generated by laser ablation of metal samples with subsequent determination by ETAAS. Phosphorus was determined indirectly in caesium by FAAS after an elaborate sample preparation ending with determination of Mo from a molybdo-phosphate complex (95/4401). The recoveries for P were reported to be 95–103%. Work with the slotted tube atom trap (STAT) continued from the last review period (95/4261). The determination of Bi in copper-based alloys was compared with/without STAT for nebulized solutions and for hydride generation. The application of STAT generally increased sensitivity and lowered the detection limit by a factor of two.

There were some interesting abstracts in this review period involving less common methods. Oxygen in titanium was reported to be quantitatively determined in a localized area by SIMS using  $\text{Cs}^+$  as the primary ion and  $^{16}\text{O}^-$ ,  $^{64}\text{TiO}^-$ , and  $^{96}\text{Ti}^{2+}$  as the secondary ions (96/2316). Atomic fluorescence spectrometry was used to determine Sb in copper with continuous flow hydride generation (96/274). Precision was 1.2% (RSD) for Sb at 5  $\text{ng ml}^{-1}$  and the reported LOD was 22  $\text{pg ml}^{-1}$ . Precious metals in silver were determined with ETA laser induced fluorescence (96/C251).

Of special note were two articles which compared various spectrometric methods (and other types). One was a review for determination of precious metals (96/2992) in various samples (785 references). The other compared the determination of trace elements in aluminium by ICP-AES, FAAS and ETAAS (96/1811) for the certification of reference materials. The results of a round-robin survey were also discussed.

## 2. CHEMICALS

### 2.1. Petroleum and Petroleum Products

This section of the review covers analysis of crude oil and fractions, refinery feedstocks and products, fuels and lubricants. Also included are analyses of some inorganic materials (e.g., fluid inclusions and environmental samples) where these are clearly related to oil exploration, refinery operations or the use of petroleum products. A summary of the literature for the review period is given in Table 2.

#### 2.1.1. Crude oil and fractions

In the field of oil exploration and production, an understanding of reservoir diagenesis is as important as a knowledge of the over-all physical structure of the reservoir itself. In order to gain an understanding of reservoir history, source maturity and generation potential and oil/source rock correlations,

**Table 2** SUMMARY OF ANALYSIS OF CHEMICALS

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>PETROLEUM AND PETROLEUM PRODUCTS—</b>				
Al	Lubricating oil	MS;ICP;L	ETV sample introduction used to obviate oxygen addition to plasma and reduce molecular ion interferences originating from organic matrix	96/2342
As	Naphtha	AE or MS;ICP;L	Direct Injection Nebulizer (DIN) used to eliminate problems due to selective volatilization. (Detection limits >2000 and 0.011 ppb for AES and MS, respectively)	96/C2294
As	Refinery products	AE or MS;ICP;L	Direct Injection Nebulizer (DIN) used to eliminate problems due to selective volatilization	96/C2834
C	Crude oil	MS;—;L	Stable C isotopic analysis of bulk and alkane fractions of Eldfisk crude oils—showed evidence for at least two phases of reservoir filling	95/3568
C	Various	MS;—;G	Performance and optimization of combustion interface for isotopic ratio monitoring GC-MS	96/1025
C	Various	MS;—;L	Carbon and nitrogen isotopic ratios measured by coupling microanalyser with mass spectrometer. (Standard error of 0.2% reported based on >1000 analyses)	96/1540
C	Petroleum source rocks	MS;—;S	GC-isotopic ratio MS used to study compositional fractionation between extractable and covalently bound aliphatic hydrocarbons in source rocks	96/1726
Ca	Lubricating oil	AA;F;L	Sample (10 g) ignited, ashed at 900 °C (3 h) and residue dissolved in 20 ml 6 mol l <sup>-1</sup> HCl. Resulting solution concentrated to about 5 ml (water-bath), 6 ml La <sup>III</sup> or Sr <sup>II</sup> solution (10 mg g <sup>-1</sup> ) added and mixture diluted to 20 ml with H <sub>2</sub> O	96/2978
Cl	Lubricating oil	AE;F;L	Sample combusted in propane-air flame in presence of Cu. Measurement of CuCl molecular emission allowed specific determination of organochlorine compounds (ionic Cl compounds did not give emission signal)	95/4468
Cl	Waste oil	AEP;ICP;L	Nitrogen purged spectrometer with magnesium fluoride optics used to measure VUV Cl lines at 134.724, 138.969 and 138.957 nm	96/C730
Cl	Feedstocks and products	AE;ICP;L	Recent developments in ICP optics allowed measurement using VUV lines (<190 nm)	96/C2195
Cl	Lubricating oil	AE;ICP;L	Spectrometer with patented nitrogen purge system permitted use of VUV wavelengths down to 120 nm. (Limit of detection for Cl in oil <1 ppm)	96/C2196
Cl	Waste oil	XRF;—;L	Samples analysed directly by XRF after 5-fold dilution in mineral spirits and presentation to spectrometer as thin film (to eliminate problems with particulate settling.) Comparison with XRF and ion chromatography results after combustion of sample in oxygen bomb	96/2644
F	Oils and greases	XRF;—;L	Samples analysed directly using He purged spectrometer	96/519
Fe	Fuel; lubricating oil; crude oil	AE;ICP;L	10 fold dilution with tetralin containing 5 mg kg <sup>-1</sup> Sc internal standard [Detection limit 5 ng kg <sup>-1</sup> ; RSD <1% (short term) and <2% (long term) at 1 mg kg <sup>-1</sup> ]	96/380
Fe	Lubricating oil	MS;ICP;L	As for Al	96/2342
Hg	Natural gas	AA;CV;G	Mercury species trapped on Au-Pt wire and then Hg thermally desorbed and measured using CVAAS. Quantitative recoveries for Hg <sup>0</sup> and (CH <sub>3</sub> ) <sub>2</sub> Hg if collector heated to 80 °C, sampling rates <2 l min <sup>-1</sup> and sample volumes at least 10 l. (Detection limit 30 ng m <sup>-3</sup> )	95/4694
Hg	Naphtha	AE or MS;ICP;L	As for arsenic (detection limits 20 and 0.011 ppb for AES and MS, respectively)	96/C2294
Hg	Refinery products	AES or MS;ICP;L	As for Arsenic	96/C2834
Li	Lubricating greases	AA;F;L	Sample (0.5–1 g) dissolved in 50 ml xylene (50 °C), transferred to extraction unit and boiled with 25 ml conc. HCl for 15 min. Acid fraction was drained off, combined with washings and made up to 100 ml with H <sub>2</sub> O prior to analysis by AAS at 670.8 nm	96/324
Mg	Lubricating oil	MS;ICP;L	As for Al	96/2342
Mg	Lubricating oil	AA;F;L	As for Ca	96/2978
N	Various	MS;—;L	As for C	96/1540
Ni	Fuel; lubricating oil; crude oil	AE;ICP;L	As for Fe [detection limit 12 ng kg <sup>-1</sup> ; RSD <1% (short term) and <2% long term) at 1 mg kg <sup>-1</sup> ]	96/380

**Table 2** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>PETROLEUM AND PETROLEUM PRODUCTS—</b>				
Ni	Oil; asphaltene; bitumen	XRF;—;L	Internal standard solution (1 ml 40 µg ml <sup>-1</sup> Pb in chloroform) added to sample (0.01–0.02 g) and resulting solution pipetted onto mylar film and dried prior to determination of Ni and V using EDXRF. (Detection limit 2 ppm; RSD 7%)	96/405
Hg	Naphtha	AE or MS;ICP;L	As for arsenic (detection limits 300 and 0.34 ppb for AES and MS, respectively)	96/C2294
Pb	Refinery products Gasoline	AES or MS;ICP;L AE;ICP;L	As for arsenic Emulsion prepared by vortex mixing sample with tetralin, Triton X-100 and H <sub>2</sub> O (2 min); 3% iodine solution in toluene and 10% Aliquat 336 in decalin added with mixing (5 min) to decompose volatile Pb species. (Concentration range 0–10 mg kg <sup>-1</sup> Pb)	96/C2834 96/1430
Pb	Roadside soils	AA;F;L	Study of impact of emissions of Pb from gasoline engines on roadside soils. Samples homogenized, dried and sieved prior to digestion using HCl-HNO <sub>3</sub> (3:1)	96/1979
Pb	Gasoline	AE;F;L	Determination of tetraethyllead in gasoline by gas chromatography with a surface emission flame photometric detector. (Detection limit 0.3 ng; RSD 0.7%)	96/2902
S	Petroleum products	XRF;—;L	Measurement based on ratio of sulfur X-ray fluorescence to X-ray scattering intensity. Simulated material consisting of Mo substrate and X-ray absorber used as standard	96/521
S	Petroleum products	XRF;—;L	Review (no refs) of XRF for on-line sulfur measurement in refinery processes and products	96/1208
S	Waste oil	XRF;—;L or AE;ICP;L	As for Cl but comparison also with results obtained by oxygen bomb combustion followed by ICP-AES	96/2644
Se	Refinery waste waters	MS;ICP;L	Total, dissolved and particulate Se determined by digesting samples with H <sub>2</sub> O <sub>2</sub> and HNO <sub>3</sub> . Selenite, selenite and selenocyanate determined using ion chromatography coupled with ICP-MS	96/C2276
V	Fuel; lubricating oil; crude oil	AE;ICP;L	As for Fe [detection limit 2 ng kg <sup>-1</sup> ; RSD <1% (short term) and <2% long term) at 1 mg kg <sup>-1</sup> ] As for Ni. (Detection limit = 5 ppm)	96/380 96/405
Zn	Oil; asphaltene; bitumen	XRF;—;L	As for Ca	96/2978
Various	Lubricating oil Fuel oil	AA;F;L MS;ICP;L	Sample (250 mg) heated with 7 ml 65% HNO <sub>3</sub> and 3 ml 30% H <sub>2</sub> O <sub>2</sub> in high pressure PTFE vessel using a 10-step microwave oven process, cooled in a water-bath and then diluted to 25 ml. (Detection limits for most elements in range 0.02–0.2 mg kg <sup>-1</sup> )	95/3731
Various (wear metals)	Lubricating oil	AE;ICP;L	Samples diluted 1:100 or 1:10 with deodourized kerosene. (Limits of detection 0.002–0.07 mg l <sup>-1</sup> and RSD <1% for integration time >500 ms)	95/3839
Various	Used oil	XRF;—;L	Determination of Cd, Cl, Hg, Pb, S and Ti in used oil feedstocks for cement kilns. Calibrated using multielement standards prepared from organometallic compounds, base oil and xylene	95/C4201
Various (10)	Heavy oil	AA;ETA or CV;L	As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and V determined using GFAAS or CVAAS after digesting sample with HNO <sub>3</sub> -H <sub>2</sub> SO <sub>4</sub> . Good recoveries for all elements except Hg (70%). (Detection limits 0.004–0.046 mg kg <sup>-1</sup> )	95/4262
Various	Lubricating oil	AA;F;L and/or AE;ICP;L	Sample ultrasonically treated with 5.5 mol l <sup>-1</sup> HCl and several drops H <sub>2</sub> O <sub>2</sub> for 15–20 min, diluted with xylene or toluene and stirred at 60 to 70 °C for 30 min. Aqueous phase analysed by AAS for Ca, Cr, Cu, Fe, Mn and Zn and ICP-AES for preceding elements plus P and S	95/4495
Various	Oil and wax	AE;ICP;L	High temperature nebulizer used to introduce samples directly without solvent dilution. Applicable to most organic materials provided viscosity can be reduced to about 10 cP by heating	96/C203
Various (11)	Crude oil	MS;ICP;L or NAA;—;L	Study of contribution of formation water, produced water, drilling fluid and rocks to trace element concentration of a range of exploration samples. Highlighted importance of washing and filtering oils prior to analysis if appropriate oils are to be correlated with each other	96/336

**Table 2** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>PETROLEUM AND PETROLEUM PRODUCTS—</b>				
Various	Petroleum products	XRF;—;L	Viscosity of sample increased by chilling with liquid N <sub>2</sub> or mixing with eicosane prior to forming into disc for analysis by pouring into central well (15 mm diameter × 1 mm deep) of Al foil covered plastic disc	96/411
Various (additive elements)	Synthetic lubricating oils	AE;ICP;L	Study of matrix effects caused by synthetic oils prepared from poly-alpha olefins and trimethylol propane esters, cf. standards prepared in mineral oil	96/C728
Various	Vehicle exhaust particulates	MS;ICP;L	Airborne particulates collected with low-volume air sampler. Elements of interest (Cd, Cu, Ni, Pb, Tl and Zn) separated from interfering matrix elements by solvent extraction with dithizone	96/956
Various	Crude oil/water emulsions	AA;F;L	Homogenized sample (3 g) heated for 30 min with 0.3 g alkylbenzenesulfonic acid and 15 ml ethanol, ignited and heated with 1 ml HNO <sub>3</sub> until brown vapour eliminated. Residue ashed at 550 °C and then cooled ash dissolved in 2 ml HCl-HNO <sub>3</sub> (1:1) and diluted to 50 ml	96/1300
Various (additive elements)	Lubricating oil	AE;ICP;L	Study of effectiveness of methods for elimination of matrix effects caused by viscosity modifiers. Use of internal standard (Y) provided best alternative, with errors reduced to ±2% relative (cf. –8% if no internal standard used)	96/C2237
Various	Crude oil	AE;ICP;L	Plasma diagnostics used to study effect of introduction of organic emulsified samples. Whereas emulsions of solvents such as xylene perturbed the plasma, crude oil in water emulsions had similar effect to aqueous solutions	96/2468
Various (11)	Crude oil	XRF;—;L	EDXRF used to assess effects of weathering (2, 7 and 14 d outdoors) on trace element concentrations and ratios. Attempt made to assess applicability of V:Ni ratio for passive tagging. (Concentration ranges 0.02–182 ppm)	96/2559
Various	Lubricating oil and grease	XRF;—;L	Solidification agent used for sample preparation	96/2640
<b>ORGANIC CHEMICALS—</b>				
Al	Commercial formulations	AA;F;L	Determination of fosetyl Al in commercial formulation 'Aliette'. Comparison with ion chromatographic method utilizing measurement of phosphonate anion	96/1945
As	Dimethylarsenate	AA;ETA;L	Automated thermospray interface used to couple HPLC with ETAAS for arsenic speciation studies. Total thermal cycle of 40 s feasible (15 s furnace cycle plus 25 s cooling time). Detection limits 5, 8 and 15 ng ml <sup>-1</sup> for As <sup>III</sup> , As <sup>V</sup> and dimethylarsenate, respectively	95/3459
As	Organometallic compounds	MS;ICP;L	Speciation of organoarsenic, organoiron and organotin compounds using SFC-ICP-MS	95/3561
As	Monomethylarsonic acid and dimethylarsenic acid	MS;ICP;L	Speciation of above compounds plus As <sup>III</sup> and As <sup>V</sup> using micellar liquid chromatography with ICP-MS. Samples containing protein could be injected without pre-treatment and no interference due to chloride was found. (Detection limits 90–300 pg)	95/3610
As	Methylarsonic acid and dimethylarsinic acid	AA;F or ETA;L	Study of effects of mobile phase, buffer composition and the presence of Na or Ni sulfate in the mobile phase, on As <sup>III</sup> , As <sup>V</sup> , methylarsonic acid and dimethylarsinic acid retention times using Hamilton PRP-X100 anion exchange column. (Detection limit 10 ng)	95/3653
As	Wood preservatives	AA;F;L	Study of leaching of chromated copper arsenate preservatives from treated softwoods submerged in sea-water	95/3930
As	Monomethylarsonic acid and dimethylarsinic acid	AF;F;L	Speciation of above compounds plus As <sup>III</sup> and As <sup>V</sup> by HPLC using ultrasonic nebulization, atomic fluorescence detection. (Concentration range 250–2500 ng As)	95/4176
As	Organoarsenic compounds	AA;ETA;L or AE;ICP;L	Comparison of LC-HG-quartz cuvette AAS with LC-HG-ICP-AES for speciation of arsenite, arsenate, monomethylarsonate and dimethylarsinate in aqueous samples	95/4386

**Table 2** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>ORGANIC CHEMICALS—</b>				
As	Organometallics	XRF;—;S	Organometallic compounds preconcentrated from ground and waste water samples using Zr-loaded activated charcoal. Optimum pH 3–7. (Recoveries >98% for 1 mg l <sup>-1</sup> analyte)	95/4481
As	Wood preservatives	AE;ICP;L	Study of release of As, Cr and Cu into rain water from wood treated with preservatives, using ion exchange chromatography and ICP-AES	96/104
As	Organometallic compounds	AE;MIP;L	Inorganic and organometallic As and Hg compounds separated using vesicle mediated HPLC and metals introduced to MIP by volatile species generation. (Detection limits 1–6 ng ml <sup>-1</sup> As)	96/283
As	Arsenobetaine and arsenocholine	AE;ICP;L or AA;ETA;L	On-line UV photolysis used to decompose organoarsenic compounds prior to hydride generation in LC-HG-ICP-AES and LC-HG-quartz cuvette AAS	96/1103
As	Organometallics	MS;ICP;L	SFC-ICP-MS used to determine five organometallic compounds containing As, Hg and Sb. Limits of detection 2–3 orders of magnitude lower than with flame ionization detector (FID)	96/1637
(Bi)	Pesticides	AA;F;L	Indirect method for determination of organophosphate pesticide malathion. Sample hydrolysed to form dimethylidithiophosphate, complexed with Bi <sup>III</sup> and extracted into IBMK. Bi determined using FAAS	96/121
Br	Haloforms	AA;DCP or MIP;L	Wavelength double modulation, diode laser AAS in modulated low pressure DCP or MIP used for element selective GC determination of haloforms (detection limit 45 pg Br)	95/4169
Br	Organic compounds	AE;MIP;L	GC carried out on fused silica column coated with HP-5, with 2 ml min <sup>-1</sup> He carrier gas. Stationary phase burned off final 2 cm of column which was used as (350 kHz) plasma tube. Addition of 10–15 ml He make-up gas enhanced detection (4 pg s <sup>-1</sup> ) and reduced tailing	96/1434
C	Pesticides	AE;MIP;L	Solid-phase microextractor consisting of silica fibre coated with polydimethylsiloxane used to adsorb pesticides from water. Trapped analytes thermally desorbed into GC-MIP-AES and determined using C and S emission lines. (Concentration range 2–200 µg l <sup>-1</sup> )	95/3474
C	Phenols	AE;MIP;L	Study of responses for C, Cl and O in a set of phenolic compounds	96/1077
C	Organic compounds	MS;—;L	Combustion elemental analyser interfaced to IRMS via ConFlo interface for measurement of C and N isotopic abundances on a single sample	96/1713
Ca	Analgesic tablets	AA;F;L	Determination of Ca in calcium carbonate coated tablets	95/3938
Cd	Ferritin	MS;ICP;L	Capillary electrophoresis—ICP-MS used to separate metallothionein isoforms and ferritin. Detection limit 4 fg Cd (for 74 nl injections)	96/1495
Cl	PCBs and methylsulfonate metabolites	AE;MIP;L	PCBs and their methylsulfonyl metabolites determined in plasma and seal blubber using GC-MIP-AES after appropriate GPC-HPLC clean-up procedures (detection limits 0.22–0.25 ng g <sup>-1</sup> for PCBs in plasma, and 5 to 10 ng g <sup>-1</sup> for methylsulfonyl PCBs in seal bladder)	95/3479
Cl	Haloforms	AA;DCP or MIP;L	As for Br (concentration ranges 1–5000 ng ml <sup>-1</sup> for CHCl <sub>3</sub> and CCl <sub>4</sub> and 0.01–100 ng ml <sup>-1</sup> for dichlorotetrafluoroethane using MIP. Corresponding ranges for the DCP were 1–10 000 and 0.1–10 000 ng ml <sup>-1</sup> )	95/4169
Cl	Methanol	AE;SCP;L	Determination of chlorinated organic compounds using graphite furnace to introduce samples to stabilized capacitively coupled He Plasma (SCP)	95/4591
Cl	Halocarbons	AA;MIP;L	Element selective detection of Cl in capillary GC by wavelength modulation diode laser AAS of excited, metastable Cl atoms in an MIP. (Detection limits 1 mg l <sup>-1</sup> or 80 pg s <sup>-1</sup> )	96/640
Cl	Phenols Organic compounds	AE;MIP;L AE;MIP;L	As for C As for Br	96/1077 96/1434

**Table 2** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>ORGANIC CHEMICALS—</b>				
(Co)	Anionic surfactants	AA;F or ETA;L	Indirect method for determination of sodium dodecylsulfate in toothpaste, liquid detergents and waste water by formation of ion pair with bis-(2-benzoylpyridinethiosemicarbazone)cobalt <sup>III</sup> . (Detection limit 18 mg l <sup>-1</sup> )	95/4057
Cr	Wood preservatives	AA;F;L	As for arsenic	95/3930
Cr	Wood preservatives	AE;ICP;L	As for arsenic	96/104
Cr	Wood preservatives	AA;F;L	Alkali extraction and acid digestion used for speciation and quantification of chromium species (Cr <sup>VI</sup> and total Cr) in chromated copper arsenate treated building timbers	96/126
Cu	Copper citrate	AA;ETA;L	Cu nitrate and Cu citrate determined at different pH levels using ETAAS following a range of solid phase extraction procedures. Results compared with those predicted by NSPEC computer speciation program	95/3454
(Cu)	Nitrophenols	AA;F;L	Indirect method for determination of nitro and nitrophenols using solvent extraction of ionic associates involving bipyridylocopper(II) or phenanthrolinocopper(II) complexes. (Concentration range 0.01–0.1 mg l <sup>-1</sup> nitrophenol)	95/3842
Cu (Cu)	Wood preservatives Dithiocarbamate fungicides	AA;F;L AA;F;L	As for arsenic Indirect FI method for determination of dithiocarbamate fungicides (e.g., Ziram), based on IBMK extraction of complex with Cu <sup>II</sup> . (Detection limit 0.07 μmol)	95/3930 95/4084
Cu	Traditional Chinese medicines	AA;F;L	Sample (3 g) heated (100 °C) for 3 h with 20 ml of 10% v/v HNO <sub>3</sub> , filtered and then diluted to 50 ml with H <sub>2</sub> O. (Detection limit 0.2 mg kg <sup>-1</sup> )	95/4168
Cu (Cu)	Wood preservatives Salicylic acid	AE;ICP;L AA;F;L	As for arsenic Indirect FI-AAS method for determination of salicylic acid in pharmaceuticals (dissolved in water or ethanol solutions) by reaction with copper carbonate incorporated in polyester resin beads. (Concentration range 4–75 mg l <sup>-1</sup> )	96/104 96/1384
Cu	Cocaine and heroin	AA;ETA;L	Samples dissolved in nitric acid (35%) and solutions diluted to 10 ml with H <sub>2</sub> O. Pd–Mg nitrate used as chemical modifier. (Detection limit 3.9 mg kg <sup>-1</sup> )	96/2017
Fe	Organometallic compounds	MS;ICP;L	As for arsenic	95/3561
Fe	Pharmaceuticals	AA;F;L or XRF; —S or L	Comparison of methods for determination of Fe in pharmaceuticals	96/1136
Fe	Ferritin	MS;ICP;L	As for Cd. Detection limit 184 fg Fe (for 74 nl injections)	96/1495
Gd	Polyaminopolycarboxylic complexes	AE;ICP;L	Analysis of gadolinium polyaminopolycarboxylic complexes and thermal degradation products using HPLC-ultrasonic nebulizer-ICP-AES	96/1035
Ge	Organogermanium compounds	AE;ICP;L	Liquid chromatography–hydride generation-ICP-AES used for determination of inorganic and organometallic species of Ge in saline matrix (μg l <sup>-1</sup> concentrations)	95/3851
Hg	Organometallics	MS;ICP;L	GC interfaced to ICP-MS using heated interface. (Detection limit 120 fg Hg)	95/1478
Hg	Organic compounds	AA;CV;L	Combination of Wickbold combustion and cold vapour AAS used for determination of Hg in organic compounds	95/3662
Hg	Organometallic compounds	AE;MIP;L	Simultaneous determination of organotin, organolead and organomercury in environmental samples using GC-MIP-AES after pentylation of ionic compounds using pentylmagnesium bromide. (Concentration range 2.5–10 000 μg l <sup>-1</sup> )	95/3670
(Hg)	Aldehydes	AA;CV;L	Indirect method for determination of lower aldehydes by reduction of mercuric ion to elemental Hg and measurement using cold vapour AAS. (Concentration range 10–100 nmol methanal; 20–250 nmol ethanal and propanal)	95/3674
Hg	Alkylmercury compounds	AE;MIP;L	Alkylmercury compounds in water preconcentrated on sulphydryl cotton column, eluted with 3 mol l <sup>-1</sup> HCl, phenylated using sodium tetraphenylborate and extracted into hexane prior to determination of methyl and ethyl mercury using GC-AES. (Detection limits 10 ng l <sup>-1</sup> )	95/3852

**Table 2** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>ORGANIC CHEMICALS—</b>				
Hg	Organometallic compounds	AE;MIP;L	Evaluation of three different derivatization methods for determination of Hg, Pb and Sn compounds in environmental samples by GC-AES	95/3855
Hg	Organomercurials	AE;MIP;L	Chromatographic conditions optimized for determination of methylmercury in environmental samples using commercial GC-AES instrument. (Detection limit 1.2 pg; linear range 1–40 µg l <sup>-1</sup> methylmercury)	95/3947
Hg	Traditional Chinese medicines	AA;CV;L	As for Cu. (Detection limit 0.03 mg kg <sup>-1</sup> )	95/4168
Hg	Methylmercury	MS;ICP;G	Measurement of mercury methylation in sediments by using enriched stable mercury isotopes with methylmercury determination by GC-ICP-MS. (Detection limit 1 pg Hg, or 0.02 ng g <sup>-1</sup> dry sediment)	95/4178
Hg	Methylmercury	AF;CV;L	Evaluation of different sample pretreatment procedures (extraction into methylene chloride, distillation under N <sub>2</sub> flow and alkali digestion) for determination of methylmercury in environmental samples by ethylation-GC-CV-AFS	95/4360
Hg	Alkylmercury compounds	AAS;HG;L	HG procedure for speciation of Hg <sup>n</sup> , monomethylmercury cation, dimethylmercury and diethylmercury using heated quartz furnace with AAS	95/4363
Hg	Organometallics	XRF;—;S	As for arsenic. Optimum pH for adsorption <10	95/4481
Hg	Organometallic compounds	AE;MIP;L	As for arsenic (detection limits 0.15 ng ml <sup>-1</sup> for inorganic Hg and 0.35 ng ml <sup>-1</sup> Hg for methylmercury)	96/283
Hg	Organometallics	MS;ICP;L	As for arsenic	96/1637
Hg	Methylated metal species	AE;MIP;L	Methylated metal species in water samples volatilized from solution after ethylation using sodium tetrtaethylborate, preconcentrated on a cryogenic trap and then thermally desorbed into GC-AES. (Detection limit 0.6 ng l <sup>-1</sup> for 10 ml sample)	96/1806
Hg	Organomercury compounds	AF;CV;G	Organomercurials extracted from soil and water samples using dithizone and determined using HPLC-AF. Differentiation between gaseous organomercury and metallic mercury achieved by adsorption on Carbotrap and gold filters, thermal desorption and AF detection	96/1990
Hg	Organomercury compounds	AF;—;S	Continuous microwave assisted pervaporation-atomic fluorescence used for speciation of inorganic and organic mercury compounds in solid samples. (Concentration range 10–500 µg kg <sup>-1</sup> )	96/3015
La	Texaphyrins	MS;ICP;L	Determination of La and Lu in metal-containing texaphyrins and in tissue samples following treatment with texaphyrin photosensitizers	96/1456
Lu (Mn)	Texaphyrins Drugs	MS;ICP;L AE;DCP;L	As for La Indirect method for determination of hydrochlorides of antazoline, hydralazine and amiloride and quinine sulfate, based on precipitation of ion pairs with [Mn(SCN) <sub>4</sub> ] <sup>2-</sup>	96/1456 95/4166
N	Organic compounds	AE;plasma;L	350 kHz He plasma used for N, O and P selective AES detection in capillary GC. CH <sub>4</sub> -O <sub>2</sub> or CH <sub>4</sub> -N <sub>2</sub> used as plasma gases for N and O detection. (Detection limits 50 pg s <sup>-1</sup> )	95/3799
N	Organic compounds	AE;MIP;L	Optimum conditions established for simultaneous GC detection of <sup>15</sup> N and <sup>14</sup> N at 420.17 and 421.46 nm, respectively. (Linear range 1.5–19 ng and detection limit 1.9 pg s <sup>-1</sup> for <sup>15</sup> N)	96/1268
N Ni	Organic compounds Heroin and cocaine	MS;—;L AA;ETA;L	As for C Cocaine (500 mg) dissolved in 2 ml 35% HNO <sub>3</sub> and solution diluted to 10 ml with H <sub>2</sub> O. Heroin (250 mg) dissolved in 5 ml H <sub>2</sub> O, 400 µl 35% HNO <sub>3</sub> added and solution diluted to 10 ml with more H <sub>2</sub> O. Mg(NO <sub>3</sub> ) <sub>2</sub> used as matrix modifier. (Concentration range 0.8–40 ng l <sup>-1</sup> )	96/1713 96/282
O O P	Organic compounds Phenols Organic compounds	AE;plasma;L AE;MIP;L AE;plasma;L	As for N As for C As for N, but H <sub>2</sub> -CH <sub>4</sub> used as plasma dopant (detection limit 39 pg s <sup>-1</sup> )	95/3799 96/1077 95/3799

**Table 2** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>ORGANIC CHEMICALS—</b>				
P	Organic compounds	AE;ICP;L	Sample combustion in oxygen followed by collection of combustion products in dilute hydrogen peroxide used for determination of P using ICP-AES	96/1338
Pb	Organometallics	MS;ICP;L	As for Hg. (Detection limit 100 fg Pb)	95/1478
Pb	Organometallic compounds	AE;MIP;L	As for Hg. (Concentration range 2.5–2500 $\mu\text{g l}^{-1}$ )	95/3670
Pb	Ionic organolead compounds	AA;ETA;L	Determination of ionic organolead compounds using FI-HG-ETAAS. (Calibration range 0.1 to 5 $\mu\text{g l}^{-1}$ ; detection limit 7 ng $\text{l}^{-1}$ )	95/3790
Pb	Organolead compounds	AA;F;L or AE;MIP;L	Study of interferences in ultratrace speciation of organolead and organotin compounds by GC with atomic spectrometric detection	95/3808
Pb	Tetraethyllead	AA;ETA;L	Use of quartz tube atomizer with packed column, or capillary GC-AAS for determination of organolead and organotin compounds. (Detection limit 1.1–1.2 pg Pb for tetraethyllead)	95/3847
Pb	Trimethyllead species	AA;ETA;L	Trimethyllead species in rain water or roadside dust derivatized using sodium tetraethylborate, and determined using purge and trap GC-AAS	95/3854
Pb	Organometallic compounds	AE;MIP;L	As for Hg	95/3855
Pb	Traditional Chinese medicines	AA;F;L	As for Cu. (Detection limit 4 mg kg $^{-1}$ )	95/4168
Pb	Sludge; paint; fuel	MS;ICP;S	Use of slurry sampling (10% m/v), continuous flow, microwave digestion, isotope dilution ICP-MS for determination of Pb in environmental samples. (Concentration range $\text{pg g}^{-1}$ to $\text{ng g}^{-1}$ )	95/C4312
Pb	Tetramethyllead and tetraethyllead	AA;F;L	Optimization of quartz tube atomizer for GC-AAS determination of alkyllead compounds	95/4685
Pb	Trialkyllead compounds	MS;ICP;L	Inorganic lead, trimethyllead and triethyllead extracted from urban particulate using 1% $\text{HNO}_3$ , separated using HPLC and determined using hydride generation-ICP-MS. (Concentration range 0.01–5 ng ml $^{-1}$ )	96/213
Pb	Alkyllead compounds	MS;ICP;L	Inorganic lead, trimethyllead and triethyllead determined using HPLC-hydride generation-ICP-MS. (Detection limits 0.6–6 ng $\text{l}^{-1}$ Pb)	96/273
Pb	Illicit drugs	AA;ETA;L	Cocaine (0.5 g) dissolved in 2 ml $\text{HNO}_3$ (35% v/v) and then diluted to 10 ml with $\text{H}_2\text{O}$ . Heroin (0.5 g) dissolved in 10 ml $\text{H}_2\text{O}$ containing a few drops of 35% $\text{HNO}_3$ . Palladium used as matrix modifier. (Detection limit 31.4 $\mu\text{g kg}^{-1}$ )	96/309
Pb	Methylated metal species	AE;MIP;L	As for Hg. (Detection limit 0.2 ng $\text{l}^{-1}$ for 10 ml sample)	96/1806
(Pb)	Glycyrrhizic acid	AA;F;L	Indirect method for determination of glycyrrhizic acid in glycyrrhiza based on reaction with lead nitrate at pH 6.5–7 and measurement of Pb in the precipitate	96/2555
Pd	Fosinopril sodium	MS;ICP;L	Samples dissolved in 25% v/v 2-butoxyethanol-water. Minimum quantifiable limit 1 ng ml $^{-1}$ Pd (in analyte solution)	96/1653
S	Pesticides	AE;MIP;L	As for C	95/3474
S	PCBs and methylsulfonate metabolites	AE;MIP;L	As for Cl	95/3479
Sb	Organometallics	MS;ICP;L	As for arsenic	96/1637
Se	Organometallics	XRF—;S	As for arsenic. Optimum pH for adsorption = 8	95/4481
Se	Selenide drugs	MS;ICP;L	Characterization of selenide drugs and their metabolites by HG-ICP-MS and HPLC-ICP-MS	96/2362
Si	Wool	AA;F;L	Specific method for determination of cross-linked silicones on wool (insensitive to silica or silicates) based on depolymerization of cured silicone by aminolysis with anhydrous <i>n</i> -propylamine and extraction into IBMK	95/4096
Sn	Organometallics	MS;ICP;L	As for Hg. (Detection limit 50 fg Sn)	95/1478
Sn	Organotin compounds	AE;MIP;L	Soil or sediment samples amended with diethylammonium diethyldithiocarbamate, extracted with supercritical $\text{CO}_2$ modified with 5% methanol, pentylated using pentylmagnesium bromide and organotin compounds determined using GC-AES	95/1866

**Table 2** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>ORGANIC CHEMICALS—</b>				
Sn	Organotin compounds	MS;ICP;L	Chlorides of dimethyltin, trimethyltin, dibutyltin, tributyltin, diphenyltin and triphenyltin completely separated within 20 min using micellar liquid chromatography. (Concentration range $10^{-3}$ to $10 \text{ mg l}^{-1}$ )	95/2394
Sn	Organometallic compounds	MS;ICP;L	As for arsenic	95/3561
Sn	Organometallic compounds	AE;MIP;L	As for Hg. (Concentration range $2.5\text{--}2500 \mu\text{g l}^{-1}$ )	95/3670
Sn	Butyltin compounds	AA;F;L	Determination of butyltin compounds in water, suspended particulate matter, soil, sediment, fish and air using GC-AAS after butylation-hexane extraction using sodium tetraethylborate (detection limit $25 \text{ pg Sn per } \mu\text{l injected volume}$ )	95/3691
Sn	Organotin compounds	AA;F;L or AE;MIP;L	As for Pb	95/3808
Sn	Organotin species	AE;MIP;L or MS;ICP;L	Comparison of analytical strategies using supercritical fluid extraction (SFE) with GC-AES, SFC-ICP-MS and other techniques for determination of organotin compounds in aqueous and solid matrices	95/3822
Sn	Tetraethyltin	AA;ETA;L	As for Pb. (Detection limit $2\text{--}3.7 \text{ pg Sn for tetraethyltin}$ )	95/3847
Sn	Organometallic compounds	AE;MIP;L	As for Hg	95/3855
Sn	Alkyltin compounds	AE;MIP;L	Triphenyltin and butyltin compounds determined in marine biomaterials using tetramethylammonium hydroxide solubilization, enzymatic hydrolysis and derivatization using sodium tetraethylborate. (Detection limits $2 \text{ ng g}^{-1} \text{ Sn}$ )	95/3905
Sn	Organotin compounds	AE;MIP;L	Organotin compounds in environmental samples determined using GC-MIP-AES after derivatization (pentylation). (Detection limit $0.8 \text{ pg Sn using } 326.23 \text{ nm line}$ )	95/3948
Sn	Organotin standards	AA;ETA;L	Guidelines for synthesis, purity control and quantification of pentylated organotin standards for calibration of GC-quartz furnace-AAS and GC-AES	95/4362
Sn	Alkyltin compounds	MS;ICP;L	ICPMS with ultrasonic nebulizer used as reversed-phase LC detector for determination of inorganic tin, trimethyltin, triethyltin, tripropyltin, tributyltin and triphenyltin. (Detection limits $2.8\text{--}16 \text{ pg Sn}$ )	96/58
Sn	Tributyltin	AA;HG;L	Tributyltin extracted from sea food samples using $0.1 \text{ mol l}^{-1} \text{ HCl}$ in methanolic solution. Sn determined using hydride generation-cold trapping and on-line quartz furnace AAS	96/74
Sn	Methylated metal species	AE;MIP;L	As for Hg. (Detection limit $0.15 \text{ ng l}^{-1}$ for $10 \text{ ml sample}$ )	96/1806
Sn	Pentylated organotin compounds	AE;MIP;L	Interlaboratory study involving 10 laboratories. Good chromatographic performance achieved but electronic pressure control required to achieve acceptable chromatography for tetracyclohexyltin and tetraphenyltin. (Inter-laboratory precision 10–40% RSD)	96/1911
Sn	Alkyltin compounds	MS;ICP;L	Speciation of organotin compounds using HPLC-ICP-MS (application to EC Measurement and Testing certification programme)	96/2021
Sn	Organotin compounds	MS;ICP;L	GC-ICP-MS interface described and used for determination of organotin compounds	96/2433
Sn	Alkyltin compounds	AA;F;L or AE;MIP;L	Alkyltin compounds leached from sediments using polar solvent containing complexing agent. Compounds derivatized prior to determination using GC-AES or GC-AAS	96/3029
Various	Petrochemicals; pharmaceuticals	AE;MIP;L	Overview of GC-AES applications	95/3368
Various	Surfactants	AE;ICP;L or AA;CV or ETA;L	Vesicular mobile phases of the surfactants didodecyldimethylammonium bromide (DDAB) or dihexadecyl phosphate (DHP) used for determination of several species of As, Hg, Se and Sn using HPLC coupled with atomic spectrometry	95/3475
Various	Organic compounds	MS;Penning cell;G	Variation of discharge current in low pressure Penning ion source allowed selection of degree of molecular fragmentation, from electron impact (EI) type spectra through to highly fragmented small molecules and even single atoms (e.g., Br, C, Cl, F and O)	95/3563

**Table 2** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>ORGANIC CHEMICALS—</b>				
Various	Balm oil	MS;—;L	Coupled GC-isotope ratio-MS used to evaluate origin and authenticity of balm oils	95/3574
Various	Volatile organic compounds	AE;GD;G	Gas sampling glow discharge used for continuous determination of C, Cl, F and S in molecular gases and vapours by optical emission spectrometry using He discharge gas. (Detection limits low ng s <sup>-1</sup> )	95/3881
Various	Bromoperoxidase	AE or MS;ICP;L	Purification of novel metal containing non-heme bromoperoxidase from <i>Pseudomonas putida</i> and determination of Co, Fe, Ni and Zn prosthetic metal compounds in the enzyme	95/3912
Various	Cured epoxy resins	AE;MIP;L	Pyrolysis GC combined with MS, FTIR and AES detectors, used for characterization of major resin constituents and minor compounds (e.g., coupling agents) in cured epoxy resins	95/3924
Various (15)	Ginseng	AE;ICP;L	Determination of essential and toxic elements in various types of ginseng using ICP-AES. (Concentration range 1–1000 mg kg <sup>-1</sup> approx.)	95/3952
Various (10)	Cotton	AA;F;L	Determination of Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Pb and Zn reported. (Concentration range 1 to 6500 mg kg <sup>-1</sup> )	95/4095
Various	Organic compounds	AE;plasma;L	Low resolution, near-IR monochromator used with plasma atomic emission for element specific (Br, Cl, F, I, P and S) detection in capillary GC. (Element to carbon selectivities 1000–10 000)	95/4415
Various	Forensic samples	XRF;—;S	Grazing incidence XRF applied to forensic samples—counterfeit 100 dollar bill, polyvinyl tape fragments, semen trace, illegal drugs, fingerprints and fake brandy	95/4503
Various (11)	Pharmaceuticals	AA;ETA;L	Analgin, Nivalin and amidophen dissolved in water (5% m/v); aspirin (5% m/v) dissolved in water with a few drops of ammonia solution (20%); paracetamol (5% m/v) dissolved in acetonitrile after heating on a water-bath. No matrix modifier added	95/4698
Various	Methamphetamine	MS;ICP;L or AA;F;L	Seized methamphetamine samples (20 mg) dissolved in 20 ml water. Ba, Br, Cu, Pd, Sb, Sr and Pd determined using ICP-MS and Na determined using AAS. Na and Br concentrations found useful in classifying samples into groups	96/101
Various (heavy elements)	Organic materials	XRF;—;S or L	Use of Barkla polarized X-ray radiation for EDXRF analysis of organic materials. (Detection limits <1 mg kg <sup>-1</sup> )	96/621
Various	Oxalic acid	AA;ETA;L or AE;ICP;L	Column solid-phase extraction used as preconcentration for trace-element (Cd, Co, Cu, Fe, Hg, Ni and Pb) determinations using ETAAS or ICP-AES. (Detection limits 0.1 ng g <sup>-1</sup> to 1 µg g <sup>-1</sup> )	96/1030
Various	Organic compounds	AE;MIP;L	Review (69 refs) of element selective GC detection using plasma AES	96/1046
Various	Various	Various	Review (126 refs) of element-specific chromatographic detection by AAS, ICP-AES, MIP-AES, ICP-MS and MIP-MS. The chromatographic techniques HPLC, GC, SFC and field flow fractionation are considered	96/1075
Various	Paper	XRF;—;S	Determination of fillers (e.g., kaolinite, Ca carbonate, TiO <sub>2</sub> , talc, muscovite and sodium aluminosilicate) in commercial papers	96/1165
Various	Drugs	XRF;—;S	Review (19 refs) of applications of XRF in drug percutaneous absorption measurements	96/1194
Various (22)	Organic waste	AE;ICP;L	Use of axially viewed ICP for determination of analytes in waste samples subjected to toxicity characteristic leaching procedure (detection limits 0.03–5 ng g <sup>-1</sup> , cf. 0.3–700 ng g <sup>-1</sup> for radially viewed plasma)	96/1259
Various	Organic compounds/ organometallics	AE;MIP;L	Review (124 refs) on determination of trace elements by chromatographic methods employing atomic plasma emission spectroscopic detection	96/1401
Various (35)	Heroin	MS;ICP;L	Statistical evaluation of trace element composition of drug seizures for tracing origin and method of manufacture	96/1535
Various	Polyimides	AA;ETA;L	Determination of Ca, Cu, Fe, K, Na and Si after dissolution in organic solvent. (Detection limits 0.5, 2, 5, 2 and 25 ng g <sup>-1</sup> , respectively)	96/1814

**Table 2** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>ORGANIC CHEMICALS—</b>				
Various	Organic compounds	AE;MIP;L	Review of GC-MIP-AES (45 refs)	96/1857
Various	Drugs	MS;—;L	Review (8 refs) of use of isotope ratio MS in drug research and development	96/2453
Various	Paper	AE;laser;S	Coating coverage, coatweight distribution and 3-dimensional distribution of paper coating pigments determined using AES from laser generated plasma	96/2500
Various	Paper	XRF;—;S	Review (6 refs) of applications of EDXRF for determination of additives and contaminants present in pre- and post-consumer paper products	96/2770
Various	Herbicides	AE;MIP;L	Samples extracted with $\text{CH}_2\text{Cl}_2$ and concentrated in a Kuderna-Danish flask prior to measurement by GC-MIP-AES using element specific detection (Br, Cl, I, N and S)	96/2918
<b>INORGANIC CHEMICALS AND ACIDS—</b>				
Ag	Lead sulfide concentrate	AA;F;L	The AA method was compared with the fire assay procedure. The precision was comparable but the accuracy was greater	96/1286
As <sup>III/V</sup>	Coal fly ash	MS;ICP;L	1 g of fly ash was extracted with 20 ml of He purged $\text{H}_2\text{O}$ under nitrogen. The pH was varied from 1–12. Samples taken at periods of 3 hr–3 d at temperatures ranging from 18–55 °C were examined. As <sup>III</sup> /As <sup>V</sup> were separated using HPLC	95/4175
Au	Plating bath solutions	AA;F;L	Influence of the bath composition on precision was studied	95/4077
B	Fertilizers	AE;ICP;L	An investigation of the best analytical wavelengths for the determination of B in various fertilizer compositions was reported. Multiple linear regression in conjunction with experimental design was employed to determine the best B wavelength to use for a given sample matrix	96/120
B	Trichlorosilane	MS;ICP;L	Manitol was used as a chemical modifier for ETV sample introduction. An eighty-four fold increase in sensitivity was reported using the modifier	96/272
Ba	Common salt	AA;ETA;L	Ammonium nitrate, Si and $\text{V}_2\text{O}_5$ modifiers employed to control interferences. Pyrolysed and Zr coated tubes used to improve graphite tube lifetimes	96/4043
Bi	—	AE;ICP;L	Sodium di-n-propylthiophosphinate tested as means of improving the sorption properties of activated carbon. Optimization of this procedure for the recovery of Bi prior to ICP-AES determination	96/3001
Br	Activated carbon	XRF;—;S	Sample ground and a portion (0.5 g) of known particle size placed in the sample cell; 2.5 ml of ethanal were added and the sample suspended and then measured	96/2984
Ca	Ca compounds	AA;F;L	Speciation of Ca in ternary mixtures of Ca compounds	95/3462
Ca	Tungstic Acid	AA;F;L	5–10 ml of $\text{H}_2\text{O}$ were added to the sample solution and the resulting solution heated. 5 ml of pyrogallol were then added and the solution diluted to 50 ml	96/2927
Ca	—	AA;F;L	Interference study on the effects of cations and organics. KCN used to control interferences	96/3814
Cd	Passivation solution (Cd plating)	AA;F;L	Cd extracted with IBMK + KI. Effects of acidity and concentration of reducing agents were studied	95/3781
Cd	Fertilizers/soils	AE;ICP;L	Application of closed pressure digestion systems reported	95/4078
Cd	Tobacco	AA;F;L	0.2 g sample decomposed using $\text{HNO}_3\text{--HClO}_4$ (4+1), solution evaporated, $\text{H}_2\text{O}$ added and solution centrifuged. 1 ml of 20 mg $\text{ml}^{-1}$ $\text{SrCO}_3$ and 2 ml of sodium acetate-acetic acid buffer + 1 ml of 10% $\text{Na}_2\text{CO}_3$ added and the solution centrifuged after 30 min. Precipitate dissolved in few drops HCl and diluted to 5 ml Cd used as internal standard, LOD = 15 mg $\text{l}^{-1}$	96/3621
Cl	Photographic developer solutions	WDXRF;—;L		95/2298
Cl	Di-isocyanates	XRF;—;L	Samples spiked with monochlorobenzene and sonicated for 10 min	95/3493
Cu	Electrolytic cell solution	XRF;—;L	A portable EDXRF spectrometer was interfaced to the electrolytic cell to allow on-line control of cell Cu concentration	96/487

**Table 2** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>INORGANIC CHEMICALS AND ACIDS—</b>				
Cu	Coal Ash	AA;—;L	Sample decomposed using a mixture of HCl-HF-HClO <sub>3</sub> and extraction of Cu-diethyldithiocarbamate complex with Bu acetate at pH 9	96/1065
Cu	Industrial wastewater	AA;F;L	Cu separated by TLC and the spot from the plate removed, treated with 2 mol l <sup>-1</sup> HNO <sub>3</sub> , filtered, and the filtrate dissolved in 1 mol l <sup>-1</sup> HCl	96/2921
Cr	Various	MS;ICP;L	Reversed phase ion-pair HPLC used for speciation of Cr <sup>III/VI</sup> . Optimization of separation conditions described. LOD = 24 µg l <sup>-1</sup> Cr <sup>III</sup> , 40 µg l <sup>-1</sup> Cr <sup>VI</sup>	96/1024
Cr	Galvanic baths	AE;ICP;L	Ion Chromatography used for Cr speciation	96/1319
Cr	Plating liquors	EDXRF;—;L	Two-stage procedure for separation of Cr <sup>III</sup> /Cr <sup>VI</sup> involving adsorption of Cr <sup>VI</sup> onto Zr-loaded activated charcoal followed by co-precipitation of Cr <sup>III</sup> with Fe <sup>III</sup> hydroxide and adsorption of the precipitate onto activated charcoal. (LOD = 0.0042 mg l <sup>-1</sup> Cr <sup>III</sup> , 0.0013 mg l <sup>-1</sup> Cr <sup>VI</sup> )	96/2024
Fe	High purity phosphoryl chloride	AA;ETA;L	Direct injection of the analyte solution to the graphite tube	95/4355
Fe	Caustic soda	AA;F;L	FIA sample preparation/introduction system. Fe precipitated as hydroxide	95/4421
Fe	Electrolytic solutions (Zn-bromide batteries)	AE;ICP;L	Zr carrier added to the analyte solution, pH adjusted with NH <sub>4</sub> Cl-NH <sub>4</sub> OH, solution heated and then cooled to coprecipitate FeOH. The precipitate was filtered, washed and dissolved in HCl	96/3640
I	—	AE;ICP;L	HNO <sub>3</sub> and the sample solution as the iodide were mixed in a hydride generation system. Iodine gas formed as a result was introduced directly into the ICP. A hundred-fold increase in sensitivity was reported	95/3783
Hg	Phosphate/carbonate food additives	AA;—;L	—	96/144
Hg	—	AA;ETA;L	Use of chemical modifiers investigated. PdCl <sub>2</sub> , Ce(NH <sub>4</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> , thioacetamide, and H <sub>2</sub> O <sub>2</sub> -HCl were compared. The performance of the modifiers were dependent on acid concentration. (LOD = 0.1 mg kg <sup>-1</sup> Hg)	96/290
Hg	Sulfuric acid	AA;—;L	Oxidation with KMnO <sub>4</sub>	96/930
Hg	Flue gases	AE;MIP;G	Method applied to artificial flue gases. No interferences were observed from trace amounts of CO, HCl, SO <sub>2</sub> and NO	95/3373
Hg	Zn-MnO <sub>2</sub> dry battery	AA;—;L	Bread crumbs extracted with H <sub>2</sub> O and the filtered extract applied to three 3 ml SAX bond elutes in series. After addition of H <sub>2</sub> O and 0.2 mol l <sup>-1</sup> ammonium acetate, KBrO <sub>3</sub> was eluted with 0.5 mol l <sup>-1</sup> ammonium acetate. A 50 µl portion was separated using ion chromatography and the eluent introduced to the ICP-MS	95/4015
K	KBrO <sub>3</sub> (Flour improver)	MS;ICP;L	—	95/3843
Mg	Fertilizer	AE;ICP;L	Effect of matrix composition on 4 Mg wavelengths was examined. Multiple linear regression was employed to evaluate the influence of matrix composition. Mg <sup>I</sup> 83.826 was considered the best line	96/1910
Mo	Tetrathiomolybdate	AA;F;L	10 ml of sample was digested with 4.5 ml HNO <sub>3</sub> -HClO <sub>4</sub> -H <sub>2</sub> SO <sub>4</sub> . After cooling the digest was neutralized with 4 mol l <sup>-1</sup> NaOH. The solution was then treated with 5 ml of 0.56 mol l <sup>-1</sup> NH <sub>4</sub> OH, 1.2 mol l <sup>-1</sup> HNO <sub>3</sub> , 0.32 mol l <sup>-1</sup> H <sub>3</sub> PO <sub>4</sub> and 300 mg l <sup>-1</sup> aluminium nitrate	95/3374
Ni	Synthetic diamond	XRF;—;S	Synchrotron source employed, XRF imaging used to look at single diamond crystals. A novel quantification technique for Ni was described	96/1215
Pb	Post-abatement dust	EDXRF;—;S	Dust was collected on Teflon filters	96/1196
Sb	Cu electrolyte solutions	AE;ICP;L	HPLC procedure used to separate Sb <sup>III</sup> /Sb <sup>V</sup> LOD = 0.003 g l <sup>-1</sup> Sb <sup>III</sup> , 0.005 g l <sup>-1</sup> Sb <sup>V</sup>	96/1042
Se	High salt waste waters	AA;ETA;L	100 ml of sample was made 1 mol l <sup>-1</sup> in HCl and the solution treated with 5 g of hydrazine sulfate and boiled for 30 min. The inorganic Se <sup>IV</sup> and Se <sup>VI</sup> were coprecipitated with 25–500 µg of Te and the precipitate collected on a nitrocellulose filter	96/2895

**Table 2** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>INORGANIC CHEMICALS AND ACIDS—</b>				
Sb	Pb/Zn concentrates	AA;F;L	Sample (0.5–1 g) heated with 1 g $\text{KHSO}_4 + 10 \text{ ml H}_2\text{SO}_4$ , cooled and 10 ml of $\text{H}_2\text{O} + 1 \text{ g hydrazine}$ added. Mixture was heated, then 20 ml of 7.5 mol $\text{l}^{-1}$ HCl and 1 ml of $\text{NaNO}_3$ added and mixture extracted with di-isopropyl ether. Organic extracts partitioned with 0.5% $\text{NaHSO}_3$ and aqueous portions analysed	96/2983
Zn	Ammoniacal ore leaching solutions	XRF;—;L	—	95/2845
Various (4)	Gaseous hydrogen chloride	AA;ETA;G	Automated sampling system for sample introduction. Calibration against aqueous standards. (LOD 1–40 pg)	96/292
Various (40)	Coal	MS;ICP;L	Microwave digestion procedure employed	96/376
Various (10)	Shale	AE:laser;S	Laser spectrometer combining both flame and electrothermal atomization employed. LOD in the 1–10 fg level	96/413
Various (6)	Soil pollutants	EDXRF;—;—	Methods described for the monitoring of Sn pollutants around Sn mining and smelting operations	96/468
Various (6)	Rare earth molybdate crystals	EDXRF;—;S	Composition of crystals grown by the gel method determined	96/498
Various	Cement	XRF;—;S	A review of the use of XRF in production control	96/539
Various (3)	Silicone grease	XRF;—;S	Several foils and crystal analysers were examined for the analysis of light elements. (LOD = 100 ppm for Cl, S)	96/1177
Various (55)	Coal fly ash	MS;ICP;L	0.25 g sample and 0.5 g of lithium tetraborate placed in Pt crucible, fused at 1000 °C for 45 min and then 25 ml of $\text{HNO}_3$ added. Solution was heated 10–15 min at 50–60 °C and transferred to a 250 ml polypropylene flask. Procedure was repeated with second aliquot of $\text{HNO}_3$ and then made up to volume	96/1281
Various (2)	Trichlorosilane	MS;ICP;L	Analytes preconcentrated from matrix by addition of copper(I) chloride and analysed using ETV-ICP-MS	96/1308
Various (9)	Potassium titanylphosphate	AA;F;L	200 mg of sample mixed with 2 ml of conc. $\text{H}_2\text{SO}_4 + 6 \text{ ml of } 40\%$ HF. The mixture was heated until the sample dissolved and the excess HF had been removed. After cooling, $\text{H}_2\text{O}$ was added and the solution heated until the appearance of $\text{SO}_3$ fumes. Solution diluted with 2–3 ml $\text{H}_2\text{O}$ and 0.4 ml $\text{H}_2\text{O}_2$ added	96/1382
Various (4)	Brine	AE;ICP;L	Analysis of impurity elements in brine used in chlor-alkali membrane electrolyzers	96/2019
Various	Ni oxide	SSMS;—;S	Dry NiO mixed with graphite (1:1), presparked for 30 min to remove impurities. Experimental sensitivity factors determined using NIST 673 NiO FIA sample introduction employing preconcentration of analytes by coprecipitation with $\text{Fe(OH)}_3$	96/2359
Various (2)	Caustic soda	AA;F;L	FIA sample introduction employing preconcentration of analytes by coprecipitation with $\text{Fe(OH)}_3$	96/2552
Various (3)	Alkali salts	AA;F;L	—	96/2554
Various (7)	Air filter	XRF;—;S	A comparison of impurities in five materials commonly used to make air filters	96/2654
Various (17)	Ammonium tungstate	AE;ICP;L	0.5 g sample digested with 10 ml aqueous $\text{NH}_3$ for 4 h in covered PTFE vessel. The digest was treated with 5 ml of $\text{H}_2\text{O}_2$ and boiled for 30 min. This procedure was repeated and 5 ml of HCl or $\text{HNO}_3$ added to resulting digest and the solution heated to near dryness. The residue was dissolved in HCl	96/2929
Various (5)	Scandium oxide	AE;d.c. arc;S	90 mg of sample added to 10 mg carrier (C, $\text{AgCl}$ and $\text{Ga}_2\text{O}_3$ ) (2+2+1) and the resulting mixture formed into an electrode	96/2912
Various (11)	Titanium disilicate	AE;ICP;L	10 ml $\text{H}_2\text{SO}_4-\text{HNO}_3 + 3 \text{ ml HF}$ added dropwise to powdered sample and heated. $\text{H}_2\text{O}$ was added and solution filtered. Residue ashed in Pt crucible, placed in a PTFE vessel with 3 ml $\text{H}_2\text{SO}_4$ (1:1)+3 ml $\text{HNO}_3-\text{HF}$ (1:9) and heated at 180 °C for 16 h. Resulting solution combined with filtrate and diluted	96/2879
Various (8)	W products	AE;ICP;L	Method for separation of analytes from matrix using cellulose collector	96/C2828

**Table 2** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>INORGANIC CHEMICALS AND ACIDS—</b>				
Various (29)	Electrofilter ashes	MS;ICP;L	Results obtained from three standard reference materials compared	96/3239
Various	Mongolian coal	XRF;—;S	Coal sample pressed into pellets 2.5 cm diameter (2–3 tons dynamic pressure)	96/3408
Various	—	—	A review of the use of MS methods in inorganic chemistry (7 refs)	95/3544
Various	Inorganic gases	ICMS;—;—	A review/discussion on isotopic chromatographic spectral analysis of inorganic gases	95/3652
Various (6)	Silica gel	AA;ETA;slurry	Stability of slurries investigated. Standard addition used for quantification	95/3660
Various (18)	High purity chemical reagents	AE;—;—	MOS grade HCl, HF and HNO <sub>3</sub> analysed by emission spectroscopy. (LOD = 0.2–4 ng ml <sup>-1</sup> )	95/3666
Various	Fertilizer	—	Review of the analysis of fertilizers by atomic spectrometry	95/4009
Various (6)	Zirconium tetrafluoride	AA;ETA;L	Sample decomposed in autoclave and residue dissolved in HCl	95/4411
Various (4)	Nickel carbonyl	AA;F;L	0.1 g sample dissolved in HCl by heating to near dryness. The residue was mixed with 5 ml HNO <sub>3</sub> and treated with 0.5 ml HF and evaporated to near dryness. The resulting residue was mixed with 5 ml of HClO <sub>4</sub> and heated to fuming before dissolving in 10 ml of HCl (1:1)	95/4521
<b>NUCLEAR MATERIALS—</b>				
Ag	Uranium	AE;ICP;L	Ag separated from U using triisobutylphosphine sulfide in xylene and back extracted into 5% NaHSO <sub>3</sub> . Solutions measured using ICP-AES	96/2979
<sup>14</sup> C	Air	AMS;S	Airborne <sup>14</sup> C was collected from two Swedish reactors, one BWR and one PWR, and measured using accelerator mass spectrometry. Results obtained compared well with liquid scintillation counting	96/2412
Fe	Zirconium oxide	XRF;—;S	Powdered zirconium oxide was pressed on boric acid and irradiated under He medium to determine Fe. Calibration graphs were linear over the range 10–2500 mg kg <sup>-1</sup> Fe	96/299
Fe	Zirconium	TIMS;L	Sample dissolved and spiked with <sup>54</sup> Fe, zirconium removed by ion exchange and Fe further purified by back extraction. A silica gel–boric acid ionization enhancer was used to obtain stable Fe <sup>+</sup> currents. Fe determined to ppm levels	96/1618
I	Environmental samples	MS;ICP;L and NAA	Water samples filtered and measured directly, detection limit of 0.2 ng ml <sup>-1</sup> obtained. Soil and plant were heated in an oxygen stream and the evolved I trapped in Na <sub>2</sub> SO <sub>3</sub> ; <sup>125</sup> I added as a tracer. Detection limit in soils 0.02 mg kg <sup>-1</sup> . Problems with the measurement of <sup>129</sup> I discussed	96/C2034
Pu	Uranium matrix	MS;ICP;L	Ion chromatography used to separate interfering actinides prior to measurement of Pu by ICP-MS	96/C2265
<sup>79</sup> Se	Radioactive waste	MS;ICP;L	Hydride generation used separate <sup>79</sup> Se from <sup>79</sup> Br and polyatomics prior to measurement using high resolution ICP-MS	96/C2076
<sup>99</sup> Tc	Rainwater	MS;ICP;L	Losses of Tc during preconcentration with and without addition of nitric acid, hydrochloric acid, sodium hydroxide or ammonia	95/4556
<sup>99</sup> Tc	Environmental	MS;ICP;L	High resolution ICP-MS used to determine ultra trace <sup>99</sup> Tc after dissolution and separation from <sup>99</sup> Ru	96/2409
<sup>99</sup> Tc	Rainwater	MS;ICP;L	Preconcentrated rainwater extracted with trioctylamine–xylene and Tc back extracted into 1 mol l <sup>-1</sup> K <sub>2</sub> CO <sub>3</sub> ; Ru removed by extraction with cyclohexanone. Detection limit 0.04 ppt	96/2410
Th U	Sea-water Rainwater	TIMS;L MS;ICP;L	<sup>230</sup> Th and <sup>232</sup> Th determined in Norwegian sea-water. High resolution ICP-MS and ultrasonic nebulizer used to determine U to 0.06 pg l <sup>-1</sup> for <sup>235</sup> U. <sup>238</sup> U– <sup>235</sup> U ratios calculated	96/2394 95/3601
Various (actinides)	Waste streams	XRF;—;L	On-line process control of actinide waste streams from ion exchange processes using EDXRF	96/382
Various (actinides)	Waters	MS;ICP;L	Off-line preconcentration of actinides using selective polymer beads. Pneumatic or ultrasonic nebulization and ICP-MS used to determine actinides in a variety of waters	96/C676

**Table 2** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>NUCLEAR MATERIALS—</b>				
Various (REE)	Actinide matrix	AES;ICP;L	Use of a 200 µl volume microcolumn to separate and preconcentrate Ce, Eu, La, Nd, Pr, Sn, Sr and Y in lithium chloride–potassium chloride matrices containing uranium. Using the microcolumn, a 100 fold preconcentration was achieved	96/1343
Various (actinides)	Soils	MS;ICP;L	Long-lived actinide isotopes determined in soil leachates. Use of an ultrasonic nebulizer improved detection limits to 50 mBq l <sup>-1</sup> for <sup>239</sup> Pu and 2 µBq l <sup>-1</sup> for <sup>235</sup> U. Extraction chromatography used to separate and preconcentrate the actinides prior to measurement	96/1658
Various (halides)	Biological samples and radioactive waste	MS;ICP;L	Br, Cl, and I determined in biological reference material using HR-ICP-MS. <sup>129</sup> I measured in radioactive wastes. Iodine introduced to the plasma in elemental form to improve detection limits	96/C2077
Various (REE)	Plant tissue	MS;ICP;L	Microwave digestion compared with conventional dissolution. Detection limits found to be in the ppt range for REE determined	96/3013

\* HG indicates hydride generation and S, L, G and SI signify solid, liquid, gaseous or slurry sample introduction, respectively. Other abbreviations are listed elsewhere.

petroleum geochemists are increasingly making use of isotopic ratio measurements in addition to identification of biomarkers (typically measured using GC-MS). In one such study carried out during the review period (95/3568), the authors measured both biomarker and carbon isotopic data from the bulk and n-alkane fractions of 27 oils from the Eldfisk and satellite North Sea fields and provided evidence for at least two phases of reservoir filling. In interpreting isotopic data, however, great care must be taken to ensure that fractionation effects do not influence results. For example, Love *et al.* (96/1726) have shown that significant compositional fractionation effects can occur between the free molecular (bitumen) phase and those covalently bound to the insoluble kerogen network in immature source rocks, such that the former is not necessarily a low relative molecular mass indicator of the constituents of the bulk kerogen. For measurements of this type, gas chromatography-isotope ratio mass spectrometry (GC-IRMS) is generally the preferred approach. An interface has been described for on-line combustion of GC effluents and removal of water vapour prior to introduction (of produced CO<sub>2</sub>) to an IRMS instrument (96/1025). Combustion was carried out using tubular reactors packed with CuO or NiO and water vapour was removed (from the combustion products) using Nafion tubing. The simultaneous measurement of carbon isotopic ratios and GC-MS spectra (e.g., for biomarker measurement) using an IRMS and ion trap MS connected in parallel to one GC has also been reported (95/3562).

In the past, several attempts have been made to use trace element fingerprints in addition to biomarkers and isotopic data to gain additional information on oil classifications and source rock correlations (see for example 96/416). However, most of these studies have been hampered due to contamination from formation-produced waters, drilling fluids and reservoir rocks. Olsen and co-workers (96/336) have used NAA and ICP-MS to carry out a detailed study of contaminants introduced to a series of crude oils from these sources. It was shown that oil samples must be water washed and filtered to remove barite contributions to Cu, Fe, Ga, Mn and Pb and formation-produced water contributions to As and Br concentrations in the oils. Also, elements such as Cd, Pb and Zn were picked up by oils migrating through ore bodies of these metals. Prior to examining the contributions of water, barite and migration, oils could only be classified according to their Co,

Ni and V concentrations but the new understanding acquired from this work has extended the range of useful elements to include As, Bi, Co, Fe, Mn, Mo, Ni, Sb, V and Zn.

Understanding of formation water chemistry also plays a key role in building up a picture of reservoir diagenesis. Unfortunately, elemental analysis of bulk formation water rarely gives direct information regarding the composition of the fluids at the time of reservoir formation due to migration, ingress of meteoric/sea-water, complex water–rock interactions and contamination from drilling fluids and produced water. One largely untapped source of information regarding original formation water composition are the fluid inclusions often found trapped inside the reservoir rocks. Although several methods have been applied for bulk analysis of a number of fluid inclusions (e.g., thermal decrepitation, crushing and leaching), analysis of the elemental composition of individual fluid inclusions has proved elusive. An attempt has been made to measure Sr concentrations in individual fluid inclusions using synchrotron XRF (8 × 12 µm beam size), but difficulties in correcting for inclusion geometry gave rise to large errors (10–39% standard deviation) and necessitated analysis of numerous inclusions within the same population in order to minimize errors (96/1251). True analysis of individual fluid inclusions has, however, been achieved by Shepherd and Chinery (96/1250) using UV laser ablation-ICP-MS. Use of a quadrupled Nd:YAG operating at 266 nm allowed spatial resolutions below 2 µm to be achieved and permitted analysis of single aqueous inclusions of diameter 10–100 µm and up to 60 µm below the sample surface. Calibration using synthetic microwells or NIST SRM 611 glass was shown to be suitable for determination of element concentrations relative to strontium (95/1803). RSDs of around 25% were achieved for element ratios. In addition to elemental ratios as discussed above, Rb-Sr isotopic ratios can provide further information on age, provenance and chemical interaction history of the ancient fluids trapped in the inclusions. An evaluation of bulk extraction procedures for these analyses has been carried out using synthetic fluid inclusions (96/1249). Accurate determination of <sup>87</sup>Sr:<sup>86</sup>Sr was achieved with both methods (crushing and leaching and thermal decrepitation and leaching) but only the former method was found to give accurate results for <sup>87</sup>Rb:<sup>86</sup>Sr due to the reaction of Rb with glass at temperatures above 500 °C. Analyses of the bulk composition of the reservoir

rocks themselves are also obviously critical factors in understanding the structure and diagenesis of the reservoir. Sams *et al.* have carried out validation of a geochemical logging tool for major element analysis in boreholes by comparison with analyses of core samples carried out using ICP-AES (96/331). Statistically significant biases were observed ( $-55\%$  to  $+5\%$ ).

*Mercury in natural gas* is not only a potential environmental problem, but perhaps even more seriously, it can also catalyse corrosion/fracturing of downstream aluminium components (a particularly serious problem for heat exchangers). Mercury in natural gas can be determined by trapping the mercury compounds in strongly oxidizing solutions and measuring by cold vapour AAS or AFS. However, the reagents used in these methods can give rise to relatively high blank levels and the method is not ideally suited to field applications (e.g., offshore) due to the hazardous reagents used. An alternative approach is to trap the mercury on a solid collector (usually involving amalgamation of the Hg with noble metals) prior to thermal desorption into an AAS or AFS instrument. Studies have been carried out to evaluate the efficiency of various noble metal collectors for trapping of mercury compounds (95/4694). Collectors filled with Au-Pt wire were found to be more efficient than those filled with Au or Pt wire and quantitative sampling for metallic mercury and dimethylmercury was achieved using the former collector heated to  $80^\circ\text{C}$ , at sampling rates less than  $2\text{ l min}^{-1}$ , provided sampling volumes of at least  $10\text{ l}$  were used. Precision for field measurements was  $8\text{--}15\%$  RSD and the limit of detection was  $30\text{ mg m}^{-3}$  for a  $10\text{ l}$  sample. Mercury can also cause problems if present in other light feedstocks (e.g., naphtha) due to poisoning of downstream catalysts as well as environmental and corrosion problems, as discussed above. Other elements which can form relatively volatile species (e.g., As and P) can also cause similar problems. *Determination of volatile trace elements in light feedstocks* is problematical because of potential losses during digestion procedures and problems with selective volatilization if conventional nebulization is used for direct sample introduction for atomic spectrometry (e.g., ICP-AES or ICP-MS). An elegant solution to this problem has been reported by Botto (96/C2294) which uses a *direct injection nebulizer* (DIN) for direct sample introduction to ICP-AES and ICP-MS. Oxygen was added to the auxiliary plasma gas to prevent build-up of carbon on the injector tip. Detection limits for ICP-AES were disappointing ( $>2000$ ,  $20$  and  $300\text{ ng g}^{-1}$  for As, Hg and P, respectively) due to background interference from the organic matrix, but those obtained using ICP-MS ( $0.011$ ,  $0.011$  and  $0.34\text{ ng g}^{-1}$ , respectively) were very good. The method can potentially be extremely fast since it has been claimed that using a DIN for direct sample introduction to a plasma it was possible to analyse samples at rates up to  $240$  per hour (96/C2834).

*X-ray fluorescence* is commonly used throughout the petroleum industry for determination of Ni, V and S in crude oil and fractions. However, for some heavy fractions, solubility in common solvents can be limited and this can give rise to problems due to settling of material on the cell windows (particularly if the samples are not freshly prepared prior to analysis). One possible solution to this problem which was reported, involved increasing the sample viscosity by chilling with liquid nitrogen or mixing with eicosane prior to forming into a disc for analysis using a plastic dish with a central well covered with aluminium foil (96/411). An alternative approach involved homogenizing the sample ( $0.01$  to  $0.2\text{ g}$ ) with  $1\text{ ml}$  of internal standard solution ( $40\text{ mg l}^{-1}$  Pb in chloroform), pipetting a portion onto a Mylar foil, evaporating the solvent and analysing using EDXRF (96/405). Detection limits of  $5$  and  $2\text{ mg kg}^{-1}$  were obtained for V and Ni, respectively, but the precision of the method was relatively poor ( $7\%$  RSD). Measurement of sulfur concentrations in refinery products and

processes is becoming increasingly important, particularly in the light of increasingly stringent environmental legislation. XRF is ideally suited to on-line measurement of sulfur in these products and can potentially give significant advantages due to the ability to monitor critical streams continuously. A review (no references) has been published dealing with advances in *on-line measurement of sulfur in petroleum products* and includes a discussion on installation and commissioning of equipment (96/1208). XRF has also been used to carry out trace metal analysis in fresh and weathered (2, 7 and  $14\text{ d}$ ) crude oils (96/2559). An attempt was made to assess the applicability of V:Ni ratios for passive tagging of oils.

*Speciation of selenium in petroleum refinery and municipal waste waters* has been carried out using ion chromatography-ultrasonic nebulization-ICP-MS (96/C2276). Selenite, selenate and selenocyanate were determined with limits of detection in the  $0.6\text{--}0.8\text{ mg l}^{-1}$  range using a gradient programme involving ammonium borate and ammonium perchlorate. The method was used to study oxidative conversion of selenocyanate in refinery waste water to selenite and subsequent coprecipitation with iron hydroxide. A method for determination of gaseous nitrogen in natural gas using low pressure MIP-AES has also been reported.

### 2.1.2. Fuels

The measurement of concentrations of *trace metals in atmospheric samples* is gaining in importance, reflecting the growing world-wide concern over levels of atmospheric pollution. A method has been reported for the determination of six elements (Cd, Cu, Ni, Pb, Ti and Zn) in atmospheric particulate samples using isotope dilution ICP-MS (96/956). Although isotope dilution effectively eliminates multiplicative interferences such as matrix suppression, the method can still be prone to additive type interferences caused by isobaric or molecular ion overlaps in the mass spectrum. The authors successfully eliminated this problem by solvent extraction with dithizone, which had a low affinity for interfering elements (e.g., Mo, Sn, Ti, V and alkali and alkaline earth elements) but a high affinity for the heavy metals of interest. The method was tested using a *Vehicle Exhaust Particulates* CRM. One of the main contributors to over-all concentrations of lead in the atmosphere is undoubtedly Pb expelled by engines running on leaded gasoline. A study has been carried out on the impact of traffic volume and distance from roads on agricultural soils (96/1979). By using conventional acid digestion (3:1 HCl-HNO<sub>3</sub>) in a closed pyrex container and AAS, the authors showed that Pb concentration in soils close to roads was dependent on traffic volume, distance from road and depth from which the sample was taken. Owing to the impact of leaded gasoline emissions on the environment, the amount of lead in gasoline is being regulated and gradually replaced with unleaded fuels. Thus, it is necessary to determine the concentration of Pb in gasolines at lower concentrations than previously required. This can readily be achieved using solution techniques such as AAS or ICP-AES, provided that labile lead species are first converted to non-volatile lead compounds. A common approach is to use iodine to decompose the alkyllead compounds followed by complexation with Aliquat 336 (tricaprylmethylammonium chloride). However, even when this approach is used, problems can still occur with direct introduction of the resulting gasolines into ICP-AES owing to the high concentrations of volatile organic compounds reaching the plasma (carbon deposition, plasma overload, background emission, etc.). Brenner *et al.* (96/1430) have reported a novel solution to this problem involving introducing the gasoline to the plasma in the form of an emulsion. Gasoline samples were vortex mixed with Triton-X and water for  $2\text{ min}$ ,  $5\%$  iodine solution in toluene was added with mixing for  $5\text{ min}$  and  $10\%$  Aliquat 336 in

decalin was added. The method was suitable for the determination of Pb at the  $\text{mg kg}^{-1}$  level and gave good agreement for NIST standard reference fuels. The method is also suitable for use with gasoline spillage cases, where the samples may consist of mixtures of fuel and water or water emulsified fuels. Where determination of the chemical form of lead in gasoline is required (e.g., tetramethyl or tetraethyllead), it is common practice to utilize a combination of GC with an atomic spectrometric detector (e.g., GC-AAS, GC-AES, GC-ICP-MS). Determination of tetraethyllead in gasoline by GC with a home-made surface emission flame detector has been reported during the review period (96/2902). The reported RSD was 0.7% and the detection limit was 0.3 ng.

Although it is clear that vehicle exhaust emissions can make a significant contribution to atmospheric pollution, an even larger contribution for many elements is emissions from thermal power plants. In Germany and Italy, maximum emission levels of various metals from fuel oil fired power plants have recently been set according to the relative toxicity of the elements. Although concentrations of nickel, sulfur and vanadium are routinely measured in fuel oils, determination of other trace elements has generally been less extensively studied. In view of the increasing interest in these other trace elements (because of their potential contribution to environmental pollution and also their potential ability to poison upgrading catalysts), some effort has been devoted towards development of suitable analytical methodology. Bettinelli *et al.* (95/3731) have reported a method for determination of 20 elements in fuel oil by ICP-MS after acid mineralization in a microwave oven. Samples (250 mg) were digested with 7 ml 65%  $\text{HNO}_3$  and 3 ml  $\text{H}_2\text{O}_2$  in a high pressure PTFE vessel, using a 10 step microwave oven programme. After cooling, the samples were made up to 25 ml with water prior to analysis. Detection limits were generally in the range 20–100  $\text{ng g}^{-1}$ . Results were in good agreement with certified values (where available) and with results obtained using NAA. Even better limits of detection have been reported for determination of 10 elements in fuel oil using GFAAS and CVAAS after more conventional sulfuric acid–nitric acid digestion in a round-bottomed flask fitted with a condenser. The principle reason for the improvement in detection limits in this case was the use of a larger sample size (5 g in a final volume of 100 ml, *cf.* 250 mg in a final volume of 25 ml for 95/3731). The main disadvantage with this method, however, was that the reaction had to be carried out slowly (3 h), otherwise a ‘violent and harmful reaction was induced’! Good recoveries were reported for As, Cd, Co, Cr, Cu, Mn, Ni, Pb and V, although problems were experienced with Cd and Pb in distillate samples due to high background signals in GFAAS. Recovery for Hg was only 71%. In recent years, some power plants have been utilizing a novel fuel oil replacement based on water–oil emulsions (e.g., Orimulsion). However, since these are normally manufactured from very heavy oils or bitumens, levels of trace elements can be particularly high, potentially resulting in high levels of metallic emissions if clean up procedures (e.g., precipitators) are not used. A method for determination of metallic elements in crude oil–water emulsions has been reported (96/1300). The method involved heating a homogenized sample (3 g) for 30 min with 0.3 g of alkylbenzenesulfonic acid and 15 ml of ethanol in a quartz dish, igniting and heating with 1 ml of nitric acid until brown fumes were eliminated. The residue was transferred to a muffle furnace and heated at 550 °C to burn off carbon. The cooled ash was dissolved with a few drops of  $\text{H}_2\text{O}$  and 2 ml of  $\text{HCl-HNO}_3$  (1:1), and the resulting solution diluted to 50 ml with water prior to analysis using flame AAS.

### 2.1.3. Lubricating oils

Every year sees more papers published describing the determination of additive and/or wear metals in lubricating oils using

ICP-AES. The most common approach is to use straightforward dilution with an organic solvent (e.g., 95/3839), and standard methods [e.g., American Society for Testing and Materials (ASTM) and Institute of Petroleum (IP) methods] exist for these determinations. However, it is increasingly being realized that significant errors can occur with these methods due to the presence of viscosity modifiers in modern, multi-grade oils. Carey and Mattern (96/C2237) have studied various methods for reducing these interferences—use of an internal standard, matrix matching, microwave digestion and ultrasonic nebulization. Use of an internal standard (in this case yttrium) proved to be the most effective and practical method and successfully reduced errors to within 2% relative (*i.e.* similar to the precision of the method). A similar conclusion has been reached by ASTM, who are currently changing their standard methods to make minimum 20-fold dilution and use of an internal standard mandatory. Analysis of synthetic motor oils (e.g., made from poly-alpha-olefins and trimethylol propane esters) can pose an additional challenge since these compounds can affect plasma conditions in addition to the changes in nebulization efficiency commonly caused, for example, by viscosity index improvers and surfactants in the oil (96/C728). Careful choice of internal standard(s) is therefore likely to be required if these materials are to be analysed. Although direct solvent dilution is by far the most convenient method for determination of additive elements in lubricating oils, problems such as those described above can sometimes affect results. It is therefore often useful to check results using a total digestion method in order to eliminate completely the interference effects caused by the organic compounds. A fairly conventional approach has been described which involved ashing 10 g of sample, dissolving the ash in 20 ml of 6 mol  $\text{l}^{-1}$  HCl, concentrating to 5 ml, adding 6 ml of 10  $\text{mg g}^{-1}$  La<sup>III</sup> or Sr<sup>II</sup> solution (to eliminate interference from phosphate) and diluting to 20 ml prior to the determination of Ca, Mg and Zn using air-acetylene FAAS (96/2978). Although this may be a useful method, it is always preferable, if possible, to use one of the standard reference methods (published, for example, by ASTM or IP). Another problem with direct solvent dilution methods is that if wear particles in the samples are larger than a few microns, 100% recovery will not be achieved (incomplete sample transport and atomization). In order to achieve 100% recovery for samples containing larger wear particles, it is necessary to include a digestion step. One such method has been published during the review period which involved ultrasonically treating the oil with 5.5 mol  $\text{l}^{-1}$  HCl and several drops of  $\text{H}_2\text{O}_2$  for 15–20 min, diluting with toluene and stirring for a further 30 min at 60–70 °C and then analysing the aqueous phase using AAS or ICP-AES (95/4495). Using ICP-AES, the method was successfully applied to the determination of Ca, Cr, Cu, Fe, Mn, P, S and Zn. However, for most condition monitoring applications it is the trends in wear metals which are more important than the absolute concentrations themselves, and so provided the measured concentrations correlate well with degree of wear, obtaining 100% recovery is not critical. This is the case for most normal wear processes and the extra time and effort associated with the use of digestion techniques can rarely be justified on a routine basis where very large numbers of samples must often be analysed within a short period of time.

Whereas additive and wear metals in lubricating oils are most commonly determined using ICP-AES, *determination of chlorine concentrations* normally requires the use of alternative techniques, such as XRF or microanalytical combustion techniques (because of the inability of conventional ICP-AES instruments to measure Cl concentrations down to  $\text{mg kg}^{-1}$  levels). The requirement to measure chlorine concentrations in oils (particularly waste oils) is becoming increasingly important with the current emphasis on reduction of chlorinated

hydrocarbons in the environment and the ability to measure Cl simultaneously with a wide range of other elements using ICP-AES is therefore an attractive prospect. Several newer commercial instruments allow extended wavelength coverage in the UV/VIS down to 120 nm, permitting the use of sensitive Cl lines in the 130–140 nm region (96/C2195 and 96/C2196). Detection limits of less than 1 mg kg<sup>-1</sup> have been reported and so the method is potentially suitable for the *analysis of waste oils*, although consideration must be given to the variety of chlorine compounds which can be encountered in these samples and their respective volatilities (96/C730). The presence of particulates and/or emulsified water in waste oil samples can also cause problems with direct ICP-AES analysis, although combustion in an oxygen flask prior to analysis using ICP-AES and ion chromatography has been shown to be an effective method for determination of S and Cl in these waste oils (96/2644). This approach is relatively time consuming, however, and so direct analysis using XRF may be a more attractive option. The authors have shown that problems with settling of particles could be largely overcome by using a thin film method for sample presentation to the XRF spectrometer. The use of XRF for rapid determination and control of Cd, Cl, Hg, Pg, S and Ti concentrations in used oil feedstock to a cement kiln has been reported (95/C4201). In some cases, it may be necessary to distinguish between organic and inorganic chlorine compounds. Galkin and Karyakin (95/4468) have described a novel method for determination of *organochlorine compounds in lubricating oils* using molecular emission of Cu<sup>II</sup> chloride formed by combustion of the compounds in a propane-air flame in the presence of copper (95/4468). Inorganic chlorine compounds did not give an emission signal.

## 2.2. Organic Chemicals and Solvents

This section of the review covers the analysis of organic chemicals and solvents. Also included is work dealing with the determination of organic and organometallic compounds in environmental samples where these are related to industrial processes or products. A summary of work published during the review period is given in Table 2.

### 2.2.1. Chemicals

Environmental considerations form an integral part of overall business strategy within a modern industrial company and, in recent years, significant progress has been made in minimizing the environmental impact of industrial processes and products. Unfortunately, in the past, environmental considerations were not always given as high a priority as they are today and, over the years, there is no doubt that industrial products and by-products have been a significant source of environmental pollution. Examples include pesticides, fungicides, chlorinated hydrocarbons (e.g., PCBs), Cr and As from wood preservatives, Hg from several industrial sources such as mercury cells used in the chloralkali industry, Sn from antifoulants and Pb from a number of sources including gasoline additives and paint. Methods for determination of total concentrations of most elements in environmental samples are fairly well established and so few of the papers published during the review paper dealt solely with these applications. One recent development, however, is the availability of axially viewed ICP-AES instrumentation. Limits of detection for these instruments are typically an order of magnitude lower than those attainable using conventional radial viewing of the ICP and this opens up the possibility of carrying out determinations using ICP-AES which would previously have required use of alternative techniques such as GFAAS or ICP-MS. Alavosus *et al.* (96/1259) have evaluated an *axially viewed ICP-AES spectrometer* for determination of 22 elements in *toxicity characteristic leaching procedure* samples from a landfill site.

Limits of detection ranged from 5 (K) to 0.03 (Mg) ng ml<sup>-1</sup>, compared with 700 (K) to 0.3 (Be) ng ml<sup>-1</sup> for a radially viewed plasma.

For *environmental samples*, determination of the total concentration of elements is rarely sufficient, since it is well known that toxicity can vary enormously depending on the chemical form of the element. Methods for *chemical speciation* are generally much less well developed than for total concentrations and this is therefore currently one of the most active areas of research in atomic spectrometry. The most common approach for chemical speciation is to combine chromatographic separation with atomic spectrometry. A review (126 references) has been published which covers the principles of element-specific chromatographic detection using atomic absorption, emission and mass spectrometry with applications drawn from the environmental, petrochemical, geochemical agricultural and chemical fields (96/1075). Due to the relatively widespread availability of robust commercial instrumentation, one of the most common of these hybrid techniques is GC-AES. Several reviews have been published during the review period (95/3368, 96/1046, 96/1401, 96/1857) covering applications of GC-AES for chemical speciation of analytes which are relatively volatile (or which can be made volatile by derivatization). Pedersen-Bjergaard and Griebrokk have described a system in which a 350 kHz plasma was sustained inside the end of a 0.32 mm i.d. capillary column and used for element specific detection of Br, Cl, N, O and P by AES (95/3799, 96/1434). Owing to the small volume of the detector cell, the energy density of the plasma was high and the plasma could be sustained using only 2–3 ml min<sup>-1</sup> of helium GC carrier gas. However, it was found to be advantageous to add 10 to 15 ml min<sup>-1</sup> of helium make up gas to stabilize the plasma and reduce peak tailing. For N and O specific detection, it was also necessary to use methane mixed with oxygen or nitrogen as plasma dopant. Even with this high level of doping, however, nonspecific responses from eluting hydrocarbons were observed and element to carbon selectivities were only 100:1 (N) and 40:1 (O). For phosphorus-selective detection, use of hydrogen-methane as plasma dopant provided a selectivity of 2300:1 and a detection limit of 39 pg s<sup>-1</sup>. GC-AES has been used for the determination of nitrogen-containing herbicides in water (96/2918), polychlorinated biphenyls (PCBs) and methylsulfonyl metabolites in seal blubber and plasma (95/3479) and organophosphorus pesticides in environmental waters (95/3474). In the latter application, a novel approach was adopted which involved adsorbing the analyte onto a silica fibre coated with 100 µm polydimethylsiloxane (placed in the water sample for 20 min) and then thermally desorbing (205 °C) into the GC. Carbon and sulfur selective chromatograms were recorded at 193 and 181 nm, respectively, and provided linear calibrations over the range 2–200 ng ml<sup>-1</sup>. As discussed in last year's review (96/416), *AAS detectors based on wavelength modulated diode lasers* have been shown to have extremely low limits of detection for determination of halogens and appeared to offer high potential for use as relatively low cost, sensitive, *halogen specific detectors* for GC. Niemax and co-workers (96/640) have described application of this technique for Cl specific GC detection using a helium microwave induced plasma. Limits of detection were, however, very disappointing (1 mg l<sup>-1</sup> or 80 pg s<sup>-1</sup>). The problem was found to be due to slow fluctuations of background absorption and, in more recent work, the authors were able to eliminate the problem through additional modulation of the absorption, obtained by switching the plasma on and off with a frequency of a few kHz (95/4169). Using the latter approach, limits of detection below 3 ng ml<sup>-1</sup> were obtained for species such as chloroform and carbon tetrachloride using splitless injection of 0.5 µl samples. Other relatively low-cost halogen specific detectors that have been reported during the review period include a gas sampling

GD-AES (95/3881) and a low power He SCP based instrument utilizing a fibre optic link and an interference filter AES spectrometer (95/4591). In the former application, molecular gases and organic vapours were introduced into an exponential dilutor and carried by support gas through a silica capillary and into the GD (limits of detection were in the  $\text{ng s}^{-1}$  range for C, Cl, F and S). In the latter application, chlorinated hydrocarbons (including pesticides) were introduced into the plasma by electrothermal vaporization of methanol solutions.

*Chromated copper arsenate (CCA)* is commonly employed as a wood preservative. All three metals can, however, be leached into the environment under varying conditions. The release of As, Cr and Cu species into simulated rain water (96/104) and in a marine environment (95/3930) have been studied using ICP-AES and AAS, respectively. Specific determination of  $\text{Cr}^{VI}$  using alkaline leaching followed by AAS has also been reported (96/126). Fortunately, although the samples studied contained 0.3–0.4% m/m total chromium, less than  $100 \text{ mg kg}^{-1}$  was found to be in the more toxic  $\text{Cr}^{VI}$  form. The various chemical forms of arsenic can exhibit wide ranging levels of toxicity, e.g.,  $\text{As}^{III}$  and  $\text{As}^V$  species are toxic, whereas, arsenobetaine and arsenocholine are virtually non-toxic. Determination of the chemical form of arsenic in environmental samples is therefore an essential consideration. The ion chromatographic behaviour of arsenite, arsenate, methylarsonic acid (MMA) and dimethylarsinic acid (DMA) on a Hamilton PRP-X100 anion exchange column has been studied using FAAS and GFAAS detectors (95/3653). All the species were effectively separated in a few minutes and could be detected at arsenic levels above about 10 ng (100  $\mu\text{l}$  injection). Unfortunately, ion-exchange columns can have limited lifetimes and so reversed phase HPLC can be a more attractive option. Woller *et al.* (95/4176) have described use of a modified  $C_{18}$  Rutin HPLC column with a  $20 \text{ mmol l}^{-1}$   $\text{Na}_2\text{HPO}_4$  buffer solution of pH 6 containing 0.5% of methanol and 0.1% of  $10 \text{ mmol l}^{-1}$  didodecyltrimethylammonium bromide as the mobile phase for determination of the above arsenic species using a cool flame AFS detector, with sample introduction using an ultrasonic nebulizer (95/4176). Limits of detection were 35, 50, 20 and 20 ng for  $\text{As}^{III}$ ,  $\text{As}^V$ , DMA and MMA, respectively for a 250  $\mu\text{l}$  injection. Even lower detection limits have been obtained by coupling reversed phase HPLC with ETAAS using an automated thermospray interface (95/3459). The interface consisted of a fused silica capillary inserted into a heated stainless steel tube, through which effluent from the HPLC was injected for 2 s onto the pre-heated ( $150^\circ\text{C}$ ) graphite furnace platform. A total thermal programme of 40 s was possible and limits of detection were 5, 8 and 15  $\text{ng ml}^{-1}$  for  $\text{As}^{III}$ ,  $\text{As}^V$  and DMA, respectively. Low limits of detection (90–300 pg) for determination of arsenic species have also been reported using ICP-MS in combination with micellar liquid chromatography (95/3610). This method had the further advantage that samples containing protein (e.g., urine) could be injected without pre-treatment and showed no interference due to chloride. The use of ICP-MS with SFC for multi-element (As, Hg and Sb) determination of organometallic compounds has also been reported (96/1637). Although ICP-MS probably represents the ultimate in sensitive detectors for arsenic speciation, it is rather expensive for many laboratories to use on a routine basis. Simpler, low-cost detectors are therefore often more appropriate. Hydride generation coupled with quartz tube AAS has been demonstrated to be a suitable method for determination of  $\text{As}^{III}$ ,  $\text{As}^V$ , MMA and DMA in aqueous samples, and can be considered cheap enough to be applied in most laboratories (95/4386). Some arsenic species however, e.g., arsenobetaine and arsenocholine, cannot be determined using this approach without first being transformed into simpler species which are able to form hydrides. On-line photolytic decomposition has been shown to be suitable for this purpose (96/1103). Hydride generation

has also been used with MIP-AES for HPLC determination of arsenic compounds (96/283). In this case, vesicle forming surfactants were used as mobile phase and provided signal enhancements of 75–100%. The method was applied to As speciation in natural water and human urine and detection limits for the toxic arsenic compounds  $\text{As}^{III}$ ,  $\text{As}^V$ , DMA and MMA were in the range  $1\text{--}6 \text{ ng ml}^{-1}$ . The method was also applied to the speciation of mercury compounds (using cold vapour generation with  $\text{SnCl}_2$ ) and gave limits of detection of 0.15 and  $0.35 \text{ ng ml}^{-1}$  for inorganic Hg and methylmercury, respectively.

Whereas speciation of metallic species in liquid samples can be fairly readily achieved using a combination of chromatographic separation and atomic spectrometric detection, speciation in solid samples can be more problematical since there is no guarantee that species will necessarily be preserved during sample digestion. Direct speciation in solid samples is therefore preferred where possible but, unfortunately, few methods exist for carrying out these determinations. A novel method has been reported for *mercury speciation in solid samples* which involved continuous microwave assisted pervaporation with atomic fluorescence detection (96/3015). The solid sample was placed in a pervaporation cell and either  $\text{SnCl}_2$  (for inorganic mercury), or oxidizing solution followed by  $\text{SnCl}_2$  (for total mercury), was added using a syringe. The cell was placed in a microwave device and the Hg produced swept to the fluorescence detector via a gas–liquid separator. The linear range was  $10\text{--}500 \text{ ng g}^{-1}$  and a sampling frequency of 10–12 samples per hour was claimed. Contaminated soils can contain not only metallic and ionic mercury, but also various forms of alkylmercury. Thus it is necessary to distinguish not only between organic and inorganic mercury, but also to determine the various forms of alkylmercury. The behaviour of eight *organomercury compounds in contaminated soils* has been investigated using lysimeter experiments (96/1990). Organomercury compounds in the soil and percolating water samples were determined using dithizone extraction followed by HPLC-AFS while differentiation between organic and metallic mercury in gaseous samples (air above the soil) was accomplished by adsorption on Carbotrap and gold filters, thermal desorption and atomic fluorescence detection. Evidence was observed for transformation of organic to inorganic mercury. An increasingly common method for the *speciation of organomercurials in environmental samples* is GC-AES. Using this approach, low limits of detection (1.2 pg) and linear range of  $1\text{--}40 \text{ ng ml}^{-1}$  has been reported for methylmercury in marine tissue samples (95/3947). Generally, these methods require a derivatization step to convert non-volatile compounds into more volatile compounds, which can be successfully separated on a GC column. A comparison has been carried out of three different derivatization techniques (direct aqueous phase ethylation or phenylation and chelation extraction followed by Grignard reaction) for determination of Hg, Pb and Sn compounds in tissue samples using GC-MIP-AES (95/3855). Procedures for sample pre-treatment prior to ethylation (solvent extraction, distillation under nitrogen and alkali digestion) have also been evaluated for the determination of methylmercury in various aqueous and solid environmental samples using GC-CV-AFS (95/4360). An extremely sensitive method for the determination of alkylmercury compounds in water samples using GC-MIP-AES has been reported by Mena *et al.* (95/3852). Alkylmercury compounds were pre-concentrated on micro-columns of sulphydryl cotton, eluted using  $3 \text{ mol l}^{-1}$  HCl, treated with buffer solution, phenylated using sodium tetraphenylborate and then extracted into 1 ml of hexane. Detection limits of  $10 \text{ ng l}^{-1}$  were reported for methyl- and ethylmercury. The rate of mercury methylation in sediments has been studied using enriched stable mercury isotopes with measurement of isotopic ratios using GC-ICP-MS (95/4178). Methylmercury ion was

separated from the sediments by distillation, converted to methylethylmercury using sodium tetraethylborate and analysed after purge and trap collection on a Tenax absorber and thermodesorption into the GC column. A limit of detection of  $0.02 \text{ ng g}^{-1}$  for Hg in dry sediment sample was obtained. More than 3% of the mercury added to the lake sediment was methylated within 21 days and evidence suggested that the system was still not in equilibrium after this period.

Major sources of *organotin compounds in the environment* include fungicides, anti-fouling paint biocides, thermal stabilizers for PVC and catalysts used for production of silicones and polyurethane foams. Of these, tributyltin leached from antifouling paints is one of the most significant contributors to the pollution of marine environments. The tributyltin degrades to other alkyltin compounds, principally mono- and dibutyltin and can be concentrated up in fish tissues with bioconcentration factors of several thousand fold. Although the toxic effects of butyltin compounds on different organisms are well established, the genotoxic potential has received less attention. Kuballa *et al.* (95/3691) have studied the genotoxicity of various butyltin compounds and have carried out determination of the distribution of these compounds between water, suspended particulate matter, soil, sediment, fish tissues and air in the highly polluted River Elbe in Germany, using GC-quartz tube-AAS. A simple analytical procedure was presented based on ethylation with sodium tetraethylborate and extraction into hexane. No pre-extraction steps were apparently required and limits of detection of  $25 \text{ pg Sn}$  per microlitre injected volume were reported. Other workers have reported that limits of detection for GC-AAS can be reduced to around  $2\text{--}5 \text{ pg Sn}$  by optimization of the quartz tube atomizer (95/3847). For determination of the butyltin compounds in marine biotissues, Kuballa *et al.* used solubilization with tetraethylammonium hydroxide prior to ethylation. A similar approach has also been used for the determination of triphenyltin and butyltin in these materials using GC-MIP-AES (95/3905) and gave limits of detection of  $2 \text{ ng g}^{-1}$  (as Sn). With sediment samples, however, it has been shown that monobutyltin can have a strong affinity for the sediment and that polar solvents and strong acidic conditions, in combination with a suitable complexing agent, may be necessary in order to achieve good extraction efficiencies (96/3029). Complexation (diethylammonium diethyldithiocarbamate) has also been used with SFE ( $\text{CO}_2$  modified with 5% ethanol) for determination of 13 alkyltin compounds in sediment and soil samples using GC-MIP-AES (95/1866). Limits of detection were approximately  $1 \text{ ng ml}^{-1}$  of Sn (corresponding to approximately  $0.2 \text{ ng}$  of compound per gram of sample), but even with the use of the complexing agent, monoalkyltin compounds could not be recovered from the samples. The use of SFE with GC or SFC using various atomic spectrometric detectors for the determination of organotin compounds in aqueous and solid matrices has been reviewed by Bayona and Cai (95/3822). Simultaneous determination of organotin, organolead and organomercury compounds in environmental samples using GC-MIP-AES (95/3670) has been reported, and a new arrangement in which an MIP was directly coupled to the GC (without interface) and quartz fibres used to transmit emitted light to the spectrometer, has been applied to the speciation of organotin compounds (95/3948). Simultaneous determination of methylated species of tin, lead and mercury in water by purge-and-trap injection GC-MIP-AES has also been reported (96/1806). In the last case, limits of detection of  $0.15$ ,  $0.20$  and  $0.60 \text{ ng l}^{-1}$  were achieved for methylated tin, lead and mercury species, respectively. A GC-MIP-AES method for determination of selected organotin compounds has been developed by the US Environmental Protection Agency and as part of an evaluation exercise, an interlaboratory study has been carried out using pentylated organotin compounds

(96/1911). Ten laboratories participated in the study and each received 5 pentylated organotin standards, 3 pentylated soil or sediment extracts and 1 pentylation blank. Of 720 individual results, 60 (8.3%) were identified as outliers (with two laboratories accounting for most of the outliers!). It was found that electronic pressure control on the injection inlet was required in order to achieve acceptable chromatography for tetracyclohexyltin and tetraphenyltin. The intralab precision of the method ranged from 1.3 to 22% RSD, depending on the compound, and the interlab precision ranged from 11 to 40% RSD over the concentration range tested. Guidelines for the synthesis, purity control and quantification of pentylated organotin standards have also been published (95/4362). For the ultimate in detection limits for the determination of organometallic species, derivatization GC techniques can be applied with ICP-MS detection (95/1478, 96/2433). In the former study, limits of detection of 50, 100 and  $120 \text{ fg}$  were reported for Sn, Pb and Hg compounds, respectively. ICP-MS has also been used with reversed phase HPLC for the determination of inorganic tin, trimethyltin, triethyltin, tripropyltin, tributyltin and triphenyltin in harbour sediment and water samples (96/58). Using an ultrasonic nebulizer to introduce the carrier solution into the plasma, limits of detection of  $2.8\text{--}16 \text{ pg}$  tin were obtained for the various species. The application of HPLC-ICP-MS within the EC Measurement and Testing programme for production of organotin certified reference materials has been discussed by Rivas *et al.* (96/2021).

Reversed phase HPLC-ICP-MS has also been applied to the determination of trimethyllead (TML) and triethyllead (TEL) (degradation products of tetraalkyllead gasoline additives) in urban particulate material (96/273). Coupling of the HPLC to the ICP was achieved by mixing the mobile phase with  $6\%$   $\text{H}_2\text{O}_2$  and  $0.08 \text{ mol l}^{-1}$  HCl and reacting with  $10\%$   $\text{NaBH}_4$  in  $0.01 \text{ mol l}^{-1}$  NaOH to form volatile lead hydride, which was swept into the plasma by a stream of argon (*via* a gas-liquid separator). Limits of detection (6, 0.6 and  $1 \text{ ng ml}^{-1}$ , respectively, for  $\text{Pb}^{II}$ , TML and TEL) and repeatability were comparable to, or better than, those for an LC-ICP-MS system with a conventional pneumatic nebulizer. As with other organometallic species, involatile alkyllead compounds can be converted into more volatile materials suitable for gas-phase separations by derivatization. Craig *et al.* (95/3854) have described a method for the determination of trialkyllead species in rain water and roadside dust which involved derivatization with sodium tetraethylborate, purging the derivatized species from solution and trapping in a silanized quartz U-trap packed with 10% OV101 on Chromasorb W-HP and cooled by liquid nitrogen. The derivatized alkyllead compounds were driven from the trap by heating at  $63^\circ\text{C}$ , separated according to their volatility and detected using AAS. Alternatively, as with alkyltin compounds, derivatized species can be determined using GC-MIP-AES, although interferences due to matrix coextractives and reagent impurities introduced during sample preparation can sometimes cause problems (95/3808). Although identifying the source and form of lead in contaminated soils is an important consideration, the ultimate fate of the lead contamination is perhaps even more important. Bacon *et al.* (95/4285) have addressed this issue by using isotope ratio mass spectrometry to analyse grass samples grown on soils spiked with isotopically enriched lead. Up to 50% of the lead in unwashed grass grown on the spiked soils had its origin within the soil and at least 10% of this remained after washing. Furthermore, approximately 10% of the lead measured in grass grown on adjacent unspiked soil was found to have originated from the spiked soil. A major problem in the field of chemical speciation determinations has been lack of availability of suitable certified reference materials. Over recent years however, some steps have been taken to try to address this problem. A review (23 references) of certified

reference materials for specific chemical forms of elements has been published by Quevauviller (95/4473), with particular emphasis on the work carried out under the EC Measurement and Testing Programme (formerly BCR).

Several innovative *indirect methods for determination of organic compounds using atomic spectrometry* have been published during the review period. The most common approaches have involved solvent (typically IBMK) extraction of analyte–metal complexes and determination of the concentration of metal in the solvent using FAAS. These have included methods for: determination of malathion pesticide, involving reaction of the hydrolysis product dimethylthiophosphate with Bi<sup>III</sup> (96/121), determination of dithiocarbamate fungicide (Ziram) by complexation with Cu<sup>II</sup> (95/4084) and determination of some nitrophenols (not monosubstituted) involving complexation with bipyridylcopper(II) or phenanthrolinecopper(II) (95/3842). Improvements in sensitivity for this type of method can be obtained using GFAAS or cold vapour AAS in place of the more conventional FAAS approach. Both FAAS and GFAAS have been used with an indirect method for the determination of anionic surfactants (sodium dodecylsulfate) in toothpaste, commercial liquid detergents and waste water samples by formation of an ion pair with bis-(2-benzoylpyridine)semithiocarbazone)cobalt(III) and extraction of the complex into isopentyl acetate-isopentanol (8.5:1.5) mixture (95/4057). A method based on cold vapour AAS has been described for the determination of nanomole quantities of lower aldehydes (95/3674). The method was based on the oxidation of aldehydes to the corresponding acids by the mercury(II) ion which was, in turn, reduced to elemental mercury and determined using CV-AAS. The method was reported to be highly selective and could be used for the determination of methanal, ethanal and propanal in the presence of ketones, alcohols, acid esters, ethers, organic chlorides and epoxides.

*Indirect methods* are commonly applied for the *determination of active and other organic components in pharmaceuticals* since the matrices are usually known and generally highly controlled, reducing the likelihood of unexpected interferences. A flow-injection FAAS method has been reported for determination of salicylic acid in pharmaceuticals (96/1384). The method was based on reaction of the analyte with copper carbonate entrapped in polyester resin beads (preparation described) and determination of the released Cu<sup>II</sup> using FAAS. The calibration graph was linear over the concentration range 4–75 mg l<sup>-1</sup> and a sample throughput of 257 per hour was claimed by the authors. Interferences from foreign compounds were investigated and tabulated. A method has also been described for determination of the hydrochlorides of antazoline, hydralazine, and amiloride and quinine sulfate in pharmaceutical preparations based on precipitation of the complexes with manganese thiocyanate and determination of Mn in the filtrates using DCPAES (95/4166).

*Determination of trace elements in drugs* is an important area in its own right, which has received considerable attention during the review period. In cases involving seized *illicit drugs*, trace element fingerprints can provide useful information regarding the *geographical origin* of the drugs. The most commonly applied approach is GFAAS. Barrejo-Barrera and co-workers have studied various matrix modifiers for the determination of Cu (96/2017), Ni (96/282) and Pb (96/3090) in cocaine and heroin using this technique. By using appropriate chemical modifiers, it was possible to carry out the above determinations using a simple dissolution technique (water for heroin and 35% nitric acid for cocaine) with no sample pre-treatment. Limits of detection obtained were 3.9, 32 and 31 µg kg<sup>-1</sup>, respectively, for Cu, Ni and Pb. Arpadjan and Alexandrova (95/4698) however, have claimed that many drugs (*e.g.*, aspirin, Analgin, paracetamol, Nivalin and ami-

dophen) can effectively fulfil the role of chemical modifier, obviating the use of additional modifiers. *Universal temperature programmes for modifier free ETAAS* of 11 elements in pharmaceuticals were presented. It was noted, however, that As and Sb could not be determined in all medicines without use of chemical modifiers. In general, origin tracing of illicit drugs requires statistical evaluation of the concentrations of a large number of trace elements. ETAAS, being generally a single element technique is therefore not ideally suited to this application and rapid multi-element techniques such as ICP-MS are preferred. Use of *ICP-MS for origin tracing of seized methamphetamine and heroin* has been reported (96/101, 96/1535). The application of ICP-MS for the measurement of La and Lu texaphyrin photosensitizers in liver homogenates (96/1456), determination of Pd in fosinopril sodium (96/1653) and for the characterization of selenide drugs and their metabolites using hydride generation ICP-MS and HPLC-ICP-MS (96/2362) have also been described. Other publications which may be of interest to workers in the pharmaceutical field include a discussion on the use of IRMS in drug research and development (96/2453), a comparison of analytical methods for the determination of iron in pharmaceuticals and a review covering applications of XRF in drug percutaneous absorption measurements (96/1194).

## 2.2.2. Solvents

Introduction of *organic solvents* to plasma sources can be problematical due to both plasma stability and carbon build-up on the plasma torch and, in the case, of ICP-MS, on the interface cones in particular. In addition to prohibiting direct analysis in some cases, the organic solvent can also give rise to spectral and molecular ion interferences. These problems have limited the use of conventional solvent extraction sample preconcentration procedures. Increasingly, however, new sample introduction approaches, which allow *solvent removal* prior to *sample introduction to the plasma*, are being applied to allow direct analysis of a wide range of organic solvents. An ultrasonic nebulizer-membrane separation interface has been evaluated for the analysis of chelated trace metals by ICP-AES and ICP-MS (96/C2285). The possibility of using oil-based standards in chloroform for universal calibration was investigated and the role of membrane desolvation on analyte recovery and on the level of molecular ion intensity was reported. It was found that in order to minimize analyte losses due to chelate volatilisation, the boiling-point of the extraction solvent should be as low as possible. The use of this system resulted in reduced spectral interferences and improved detection limits. The possibility of using a universal calibration for the ICP-AES analysis of multiple organic solvent systems for use in the petrochemical industry has been investigated (96/C2247). An ultrasonic nebulizer coupled to a microporous membrane desolvator (MMD) was employed for the direct introduction of organic solvents. In order to achieve universal calibration the following conditions were required: the volumetric flow to the nebulizer had to be constant, matrix effects due to residual solvent loading had to be negligible and the nebulization efficiencies of the sample and solvents relative to the calibration sample had to be known. Using this system with a 140 mm MMD direct analysis of pentane was possible at uptake rates of 1.3 ml min<sup>-1</sup> providing detection limits comparable to those obtained for aqueous solution using the ultrasonic nebulizer. The performance of a commercial membrane tubular desolvation system (Cetac Technologies Inc.) and a flat sheet membrane desolvation system have been compared (96/C733). The parameters examined included both analyte transport and desolvation efficiencies.

The application of flow injection to the determination of Cu, Mn, Fe, and Pb in *organic solvents* by *ICP-OES* has been

reported (95/4520). Solvents studied were: methanol, ethanol, isoamyl alcohol, formaldehyde, acetone, cyclohexanone, ethyl acetate, 1,2-dichloroethane and cyclohexane; a double capillary nebulizer was employed for sample introduction. The effect of the organic solvent on plasma stability, analyte signal intensity and carbon build-up on the plasma torch were investigated. The effects of organic solvents on the determination of Se by ICP-MS with both pneumatic nebulization and flow injection sample introduction, coupled with hydride generation, have been studied (95/4709). The addition of alcohols reduced the polyatomic interference and gave rise to a ten-fold enhancement of the Se signal. The effect of ethanol loading of a 40 MHz ICP has been investigated (96/3022). A comparison was made between aqueous and organic solution with ethanol added. The electron density increased as the ethanol content of the aqueous solutions increased and the addition of ethanol led to an increase in sensitivity. In contrast, the addition of ethanol to the organic solvent (xylene) gave a reduction in electron density and a corresponding reduction in sensitivity. Signal enhancements in ethanol for the determination of Se and As by ICP-MS have also been reported (96/2395). The effects of both plasma power and nebulizer flow rate on the magnitude of the signal enhancement were studied. A study has been carried out on the effects of organic solvent load on the radial emission profiles for MgI, MgII, Cl and CN (96/592). Zones in the plasma were identified in which the emissions of these species were proportional to solvent load and plasma excitation conditions.

### 2.3. Inorganic Chemicals and Acids

As with previous reviews a recurring theme concerns efforts to improve methodology associated with the *analysis of samples with high dissolved solids*. Three main approaches dominate: direct introduction of solutions through improvements in nebulization techniques (and optimization of resulting analyte response); direct introduction of solids; and matrix elimination either prior to analysis or coupled on-line *via* FIA or chromatographic techniques. Cluster analysis has been applied to the analysis of high saline and serum solutions by ICP-MS (95/3444). The degree of signal suppression depends on the ionization potential and mass of the elements in question and compromises the choice of a single internal standard. A matrix of signal suppressions for 25 elemental responses in serum ( $9 \text{ g l}^{-1}$  NaCl) and saline solutions ( $5 \text{ g l}^{-1}$  NaCl), under various conditions, were compared using the cluster analysis technique. Four groups of elements exhibiting the same behaviour were identified and for each group a suitable internal standard was chosen. This approach significantly improved the accuracy and precision of the analyses compared to when a single internal standard was used. The combined use of emission and MS detection (plasma optical emission mass spectrometry, POEMS) has been investigated for the analysis of solutions containing high dissolved solids. The combination of a relatively large sampler and skimmer cones in the mass spectrometer coupled with a novel sample introduction system allowed determination of analyte levels from ppt to % levels using the same instrument (96C876). In order to achieve this remarkable dynamic range, however, memory effects in both the sample introduction system and in the ICP-MS interface must be controlled. The interference effects of Ca, Sr, Mg on the determination of Li in brine solutions by flame atomic emission spectrometry have also been reported (95/3833). Three types of interference effects were described; band emission due to Sr and Ca compounds, scatter of Li emission and Li ionization. Interferences were investigated using both factorial and univariate approaches, with the factorial design method providing the most satisfactory optimization conditions.

A large number of abstracts describing developments in *improved sample introduction techniques* were received during the review period. Activity in this subject area has increased substantially and perhaps reflects the availability of commercial systems applied to real-world applications. A comparison has been made between analytical figures of merit obtained using pneumatic, ultrasonic and thermospray sample introduction systems in conjunction with three different ICP-AES systems (95/4581). A Leeman Labs air-path echelle spectrometer coupled to a 27 MHz ICP was used with an ultrasonic nebulizer and a fused  $\text{SiO}_2$  aperture thermospray. For low dissolved solids, ultrasonic and thermospray nebulizers gave similar LOD improvements (a factor of twenty) over conventional pneumatic nebulization. For *solutions containing high dissolved* solids the thermospray showed similar optimized conditions to those obtained for solutions containing low dissolved solids. In contrast, the ultrasonic nebulizer required changes in both power and gas flow to maintain a stable discharge. Consequently, these changes degraded the LODs achieved with this nebulizer for high dissolved solids compared with those obtained at lower solids concentrations. As a result, the improvement over conventional pneumatic nebulization under these conditions was only a factor of four. In another study the analytical characteristics of a thermospray sample introduction system coupled to ICP-MS were investigated and compared with a conventional pneumatic system and with the same pneumatic system coupled to the desolvating unit normally employed with the thermospray (95/4171). In the presence of salts [ $\text{NaNO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ] analyte ion signal suppressions were more severe in the former than for the other two arrangements. Conversely, in the presence of mineral acids ( $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ) the systems gave similar suppressions. Ultrasonic and Meinhard high efficiency nebulizers have been adapted for the analysis of corrosive samples by ICP-MS (96/2407) with nebulization efficiencies ranging from 10–60%. The authors described a desolvation and condensation assembly which allowed on-line thermal separation of analyte/matrix and reduced all major acid components (HF, HCl,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and methanol) by 90–98%. The analyte:matrix ratio that could be tolerated increased by a factor of 5–25 fold and detection limits improved by a factor of 2–20. Non-metals (B, Si, Se, Br, I) were washed out and could not be determined in the  $\text{ng g}^{-1}$  range. For 68 other analytes, recoveries were in the order of 95%. The application of ultrasonic nebulization to the analysis of mineral acids, surfactants and petrochemical solvents using ICP-MS has been described (96/C791). Polyatomic ion formation was studied as a function of instrument operating parameters for the various sample matrices. In another paper (95/4393), the performance of six different types of nebulizer were compared in terms of their long-term stability for aerosol generation from multielement solutions containing differing salt concentrations.

The need to couple efficiently *small volume sample introduction devices* with atomic spectrometry techniques has become increasingly important as the use of coupled techniques (required for determining speciation information) has become more prevalent. The performance characteristics of two spray chambers with small internal volumes (10 ml) have been assessed (96/C2280). Peak broadening is a significant factor when coupling FI or HPLC to ICP-MS at a variety of flow rates. The solution uptake rate of high efficiency nebulizers such as the Meinhard design may have a significant influence on the performance of available spray chamber designs. In this study a range of sample uptake rates were examined. To match the optimal flow rate of a capillary column (0.32 mm id) a sample uptake rate of 3–5  $\mu\text{l}$  was required. The performance of the spray chambers was assessed, considering factors such as peak width and shape, dispersion and sensitivity. Arsenic, Sn and Hg species were determined in environmental samples.

*Direct deposition of a liquid sample* in the form of an aerosol has been applied as a means of both high efficiency sample introduction and analyte preconcentration for *ETV-ICP-MS* analysis (95/4703). For the eight elements studied, a two minute deposition, at a flow rate of  $0.25 \text{ ml min}^{-1}$ , gave an improvement of two orders of magnitude over conventional nebulization/spray chamber sample introduction. The effect of varying several parameters on both the ICP and deposition process were reported. The deposition and insertion procedures were automated and RSD values at the  $1 \text{ mg l}^{-1}$  concentration level were reported to be around 5%. Good agreement was obtained for the analysis of a number of standard reference materials using this system. The direct introduction of samples for ICP-MS analysis of semiconductor grade chemicals has been described (96/1745). Given the high purity specification required for these chemicals, directly analysing the sample is advantageous as it eliminates the possibility of contamination, which may be caused if sample pretreatment steps are required. Both direct nebulization using an anti-corrosive injection system and introduction by ETV were evaluated for the analysis of HF, HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>. For the analysis of HF, limits of detection for elements which were affected by molecular ion interferences (*e.g.*, Cr, Ni, Zn) were in the  $0.5 \text{ ng ml}^{-1}$  range. For elements not affected by such interferences (Li, Be, Mg, Mn, and Ga) detection limits were in the  $0.1 \text{ ng ml}^{-1}$  range. Iron could not be determined by conventional nebulization due to interference of argon oxide. However, using ETV sample introduction, detection limits for Fe were  $0.2 \text{ ng ml}^{-1}$ .

ICP-OES has been applied to the *on-line analysis of elemental pollutants in gaseous effluents* (95/4185). A thermodynamic study established the need to control the water content of the gas and a torch design able to withstand changes in thermal conductivity was developed. Calibration was achieved using an aerosol produced from a standard solution injected through a batch-type ultrasonic nebulizer and a desolvation unit. Detection limits were reported for a number of environmentally significant elements, from  $25 \mu\text{g m}^{-3}$  for As, to around  $1 \mu\text{g m}^{-3}$  for Cu, Cr, Mn, Ti and Zn. These detection limits are below the threshold limits allowed in gaseous effluents for many industrial processes.

The requirement to *separate analytes from complex materials* prior to analysis is an all too familiar requirement for most atomic spectrometry techniques. Traditionally separations have been based on off-line procedures. However, in recent years developments in *on-line sample preparation systems* have resulted in sample preparation methodologies being modified or developed for use in such systems.

An *on-line matrix removal method* for the determination of trace metals in highly salted waters using anion and cation exchange cartridge columns has been reported (96/C2142). The pH of the samples were adjusted by the addition of appropriate amounts of HNO<sub>3</sub> or NH<sub>3</sub> solutions. A chelating reagent APDC or 8-hydroxyquinoline was added to the sample and heavy metals were neutralised by complexing with the chelates; 50 µl of this solution were injected into a stream of pure water using a six-way valve. Potential interfering cations and anions, such as Na<sup>+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, which did not form chelates, were retained in the ion exchange cartridges, whilst the neutral chelates of the heavy metals passed through the columns and were introduced to the ICP. This system allowed rapid matrix removal but did not pre-concentrate analyte elements of interest. Some chelates of heavy metals were also adsorbed onto the columns as a result of non-selective hydrophobic interactions between the column support materials and the chelates. A novel iminodiacetate chelating agent immobilized onto a controlled pore glass support, has been used as a method of analyte matrix separation for ICP-MS (96/2809). This reagent was used with a commercial automated system and has been shown to be effective for the

analysis of effluent samples. A sampling frequency of 10 per hour was reported and calibrations from pure and saline solutions demonstrated good linearity, indicating that retention of analytes was unaffected by matrix loading on the column. A wash cycle between samples was required to remove residual matrix elements from the column. An on-line system for separation and preconcentration of noble metals (Au, Pd, Pt, Ir) with both flame and electrothermal atomic absorption spectrometry has been reported (96/C1411). An aminopyridine resin was used for the extraction stage. The choice of eluent was found to be a critical parameter. Flow injection micro-sampling dilution has been combined with the zone penetration technique to produce an on-line system capable of achieving 27 000-fold dilutions with a sampling frequency of 45 per hour (95/3809). The method was applied to the direct determination of Mg in the  $\text{g l}^{-1}$  range in brines without sample dilution. A multi-purpose dialyser unit designed for use in flow injection analysis has been applied to the determination of copper in industrial effluents by atomic absorption spectrometry (95/4687). The advantage of using this system was the ability to deal with the wide variation in copper levels present in the samples and the removal of particulate matter from the sample, which eliminated the possibility of nebulizer blockages. The system was claimed to be capable of analysing 120 samples per hour.

As with previous reviews, abstracts describing the *analysis of acids* continue to be received. The abstracts tend to fall into two classes; the actual determination of elements in samples of interest, *e.g.*, contaminants in semiconductor grade acid, or where acid solutions are used to test the performance of sample introduction devices or to study interference effects. In the present review period, the abstracts tended to fall into the latter of these two classes. The mechanism of mineral acid interferences in ICP-AES has been investigated (95/4270). Fundamental studies describing pneumatic generation and aerosol transport for five mineral acids (HCl, HNO<sub>3</sub>, HClO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>) have been described. The parameters investigated included: analyte signal response; sample uptake rate; primary and secondary droplet size distributions; total analyte transport rates; and excitation temperature. A reduction in the analyte transport rate and the reduction of the plasma temperature were implicated as principal causes of interference. However, the magnitude of the contribution of each of these factors is dependent on the type of acid and the uptake mode. The origin of the differences in interference effect is related to the physical properties of the acids which modify both the sample uptake rate and/or the droplet size distribution of the aerosols. The influence of aerosol formation and transport in acid solutions in ICP-OES has been investigated by other workers (95/4718). In this study, the role of ionization and excitation from that of sample introduction was separated by maintaining the plasma operating conditions such that the atom:ion ratio of Mg was kept constant. Perchloric acid up to a concentration of 50% v/v was used as the test acid. Several types of pneumatic nebulizers were compared: a concentric nebulizer (Meinhard); a Perkin-Elmer cross flow nebulizer; and a Perkin-Elmer cone spray nebulizer. Signal depression resulting from the acid depended on the nebulizer type, the carrier gas flow rate and the spray chamber design. At perchloric acid concentrations higher than 1% v/v, results obtained suggested that the depressive effect on the Mg atom line intensity (MgI 285 nm) could not be explained by changes in aerosol density alone, but also by a variation in the analyte concentration in the fraction of analyte that reached the plasma. The results obtained with the pneumatic nebulizers were compared with those achieved using an ultrasonic nebulizer with a desolvation system. Acid effects were more significant when the ultrasonic nebulizer was used, which was explained on the basis of a reduction in the production of aerosol using the former systems. The effect of

nitric and hydrochloric acids on rare earth elements (REE) intensities in ICP-AES has been reported (95/4721). In the presence of nitric acid, the response observed from the group of REE studied did not show any particular trend with increasing acid concentration. In contrast, in the presence of hydrochloric acid the REE responses were comparable. Both pneumatic concentric and ultrasonic nebulizers (with desolvation) were employed in the study. These effects were similar irrespective of the type of nebulizer used. However, the magnitude of the interference observed for  $\text{HNO}_3$  was reduced when the ultrasonic nebulizer was employed due to the removal of the  $\text{HNO}_3$  by the desolvation stage. The excitation temperature measured for increasing  $\text{HNO}_3$  concentrations varied from about 7500 K for aqueous solution to 7000 K in  $7 \text{ mol l}^{-1}$   $\text{HNO}_3$ , whilst no appreciable difference in excitation temperature was observed with HCl concentrations upto  $10 \text{ mol l}^{-1}$ . It was concluded that the effects observed for HCl were related to physical effects in the aerosol transport system although when the ultrasonic nebulizer was used the measured excitation temperature decreased by 500 K. In the case of the nitric acid no direct correlation was observed between thermal and spectral characteristics and the depressive effect of the acid nor could it be attributed to any transport effects.

The increasing importance of identifying and quantifying *chemical species* rather than total amount of element present is reflected in the significant increase in the numbers of abstracts received detailing developments in this area. Medical, biological and environmental applications have all been reported on during the current review period. The toxicity of arsenic species is greatly dependent on its chemical form. The methylation of arsenic acid to monomethylarsenic acid significantly lowers its toxicity. To provide an accurate evaluation of the risk of environmental As exposure it is necessary to quantify all As species present. Assessments based on total As levels do not give a true picture and may overestimate the risk, since it is the level of the more toxic forms of As, not the total amount, that is significant. As discussed in Section 2.2, the low limits of detection provided by ICP-MS make it an ideal technique to couple with chromatographic techniques for the determination of low levels of As species. However, the use of ion chromatography, which provides a good separation method, has difficulties when coupled with ICP-MS since the salt content of the eluents normally employed can lead to blockage of the sampling cones of the ICP-MS interface. This can be avoided if the hydride generation technique is adopted, because this allows introduction of the gaseous hydride to the plasma without the dissolved solids. This introduces an additional problem, in that the hydrochloric acid employed in the generation step can be transported to the plasma *via* conventional gas-liquid separators to manifest itself as  $\text{ArCl}$ , which interferes in the determination of monoisotopic As. This can also be avoided if a microporous membrane, such as PTFE is employed in the gas-liquid separator. The evaluation of microporous tubing for use in speciation of As compounds by ion chromatography with ICP-MS detection utilizing hydride generation sample introduction has been reported (96/C2300). The studies centred on the design of the phase separator and its incorporation into the hydride generation system, long-term stability of the membrane and selection of an appropriate membrane. An on-line ion exchange preconcentration system has been developed for the separation and determination of the As species monomethylarsonate (MMA) and  $\text{As}^{\text{V}}$  by ICP-AES (96/60). A strongly basic anion exchange resin AG1-X8 was employed for the separation of the two As species. The pH and flow rate of the eluent were optimized to achieve quantitative retention elution conditions. By using an ultrasonic nebulizer, the detection limits obtained were in the  $\text{ng l}^{-1}$  range. The speciation of  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  in coal fly ash using coupled HPLC-ICP-MS has also been reported

(95/4175). The concentration of these species released into water from coal fly ash was found to be dependent on the pH of the extracting solution and the type of coal fly ash (location collected, type of coal and combustion conditions). A small amount of conversion of  $\text{As}^{\text{III}}$  to  $\text{As}^{\text{V}}$  was found, particularly at lower pH extraction conditions. This was thought to be partially caused by the grinding conditions. The use of an ultrasonic nebulizer in the determination of As speciation has been reported to cause a shift in the As oxidation state from  $\text{As}^{\text{III}}$  to  $\text{As}^{\text{V}}$  (95/3055). This was determined by collecting aerosol fractions and analysing them by ion chromatography. This analysis indicated that the  $\text{As}^{\text{III}}$  might be oxidized to  $\text{As}^{\text{V}}$  as the aerosol traverses the ultrasonic nebulizer. Treatment of samples with  $1 \text{ mg l}^{-1}$  sodium hypochlorite was found to remove this effect. A liquid chromatography method coupled with ICP-MS detection has been reported for the speciation of methylmercury, mercury(II) chloride and ethylmercury in sea-water (96/1439). A mobile phase of 1% v/v acetonitrile and 0.005% mercaptoethanol in  $0.006 \text{ mol l}^{-1}$  ammonium acetate was used. An off-line sample preconcentration step using dithiocarbamate was required for the analysis of sea-water samples. An on-line procedure for the determination of inorganic Sb species by HPLC-hydride generation ICP-MS has been described (95/4701).  $\text{Sb}^{\text{III}}$  and  $\text{Sb}^{\text{V}}$  were separated on a strong anion exchange column using phthalic acid as the mobile phase. Optimization studies to establish the best conditions for both separation and hydride generation were reported.  $\text{Sb}^{\text{III}}$  and  $\text{Sb}^{\text{V}}$  have also been determined in electrolyte solutions used for Cu refining by HPLC-ICP-OES (96/1042). In this procedure, the sample solution was introduced into a cation exchange column using a  $0.1 \text{ mol l}^{-1}$  thiourea mobile phase.  $\text{Sb}^{\text{III}}$  was retained on the column, whilst  $\text{Sb}^{\text{V}}$  was eluted. The mobile phase was then changed to  $1 \text{ mol l}^{-1}$  lithium chloride to elute  $\text{Sb}^{\text{V}}$ . The eluents were sequentially introduced to the ICP. Using this system, four samples per hour could be analysed with LODs of  $0.003 \text{ g l}^{-1}$   $\text{Sb}^{\text{III}}$  and  $0.005 \text{ g l}^{-1}$   $\text{Sb}^{\text{V}}$ . A procedure for the determination of trace amounts of  $\text{Se}^{\text{V}}$ , which combines hydride generation AAS with on-line flow injection pre-concentration, has also been reported (96/2488).

## 2.4. Nuclear Materials

Traditionally neutron activation analysis and  $\alpha$ ,  $\beta$  and  $\gamma$  spectrometry have been used in the analysis of nuclear materials; however, *inductively coupled plasma mass spectrometry* (ICP-MS) is becoming the method of choice for the determination of the long-lived radioisotopes. A comparison of alpha spectrometry and ICP-MS has been made (96/C2859) and a new preparative strategy developed to allow either measurement technique to be used. Comparison of both techniques indicated that, for many applications, the two techniques are interchangeable. A review has been written (96/1742) detailing the determination of isotopes of I, Np, Pu, Ra, Tc, Th and U. The determination of  $^{239}\text{Pu}$  in ocean sediment has been investigated (96/1762). When using alpha spectrometry counting times of around 1000 min or more were required but ICP-MS reduced the total analysis time significantly, resulting in a cost and turnaround saving. A review of bioassay techniques for the actinides has been undertaken (96/2922) and the various analytical measurement techniques were described and assessed in the light of the ICRP recommendations for monitoring workers in the nuclear industry. The authors concluded that ICP-MS does not yet have the sensitivity required for this type of analysis but does show promise.

*Electrothermal vaporization* (ETV) has been used as a sample introduction technique for ICP-MS to improve the detection limits for uranium and radium (95/3366). Further sensitivity enhancement using sample preparation techniques, such as multiple deposition, pre-concentration and chemical modifi-

cation, were described. The vaporization and atomization of uranium from a graphite tube atomizer have been investigated using *electrothermal atomization atomic absorption spectrometry* and ETV-ICP-MS (95/4739). The ETA-AAS studies indicated that uranium atoms formed above 2400 °C but the ETV-ICP-MS studies indicated an appearance temperature of 1100 °C for uranium, which means that uranium oxide was vaporized at this lower temperature. Addition of Freon to reduce the formation of uranium carbide is also recommended.

Use of *actinide selective polymer beads* to pre-concentrate and separate uranium, thorium and uranium progeny in water samples (spring, lake, river and tapwater) has reduced the detection limits to below 1ppq with *ultrasonic nebulization ICP-MS* (96/C676). Iodine is an important environmental indicator and ICP-MS has been used for the *measurement of natural iodine and <sup>129</sup>I in environmental samples* (96/1661 and 96/C2034). Water samples were treated with sodium sulfite and iodine (and other halides) were measured directly using ICP-MS. Soils and plants were more complicated since the iodine had to be extracted prior to measurement by heating the sample in an oxygen stream and collecting the iodine in a suitable medium. Detection limits obtained for <sup>129</sup>I were limited by the presence of <sup>129</sup>Xe impurity in the plasma gas (argon). ICP-MS has also been used for the determination of <sup>99</sup>Tc in rainwater (95/4556). <sup>95</sup>Tc was used as a tracer to investigate possible losses of Tc during pre-concentration by evaporation. The losses were negligible providing the sample was not heated to dryness. A further pre-concentration step, which involved extraction with trioctylamine in xylene, gave an instrumental detection limit of 0.04 ng l<sup>-1</sup> (96/2410). The Tc was back extracted in two stages and the final measurement solution was deionized water. <sup>99</sup>Ru was removed by extraction with cyclohexanone.

Various *tandem techniques* have been reported for the *measurement of the actinides using ICP-MS*. *Flow injection* (FI) ICP-MS has been used for the measurement of uranium in environmental samples (96/2340). A 30-fold pre-concentration and separation of the matrix was achieved using TRU, a commercially available resin; however, only data for groundwater was presented. Ion chromatography linked with ICP-MS has been used to determine Pu in waste streams (96/C2265). It is extremely difficult to measure <sup>239</sup>Pu in the presence of uranium because of interference from uranium hydride. This method describes the separation of uranium from plutonium using cation exchange (CS10, Dionex, USA) prior to measurement using ICP-MS.

The superior sensitivity advantage of *high resolution ICP-MS* (HR-ICP-MS) should improve the detection limits attainable for the determination of the actinides in many sample types but relatively few abstracts have been received. This is probably due more to the limited number of instruments in use than to shortcomings in the technique. Uranium has been determined in rainwater using HR-ICP-MS fitted with an ultrasonic nebulizer sample introduction system (95/3601). An ultimate detection limit of 0.06 pg l<sup>-1</sup> was obtained for <sup>235</sup>U and <sup>235</sup>U:<sup>238</sup>U ratios were calculated. Low levels of <sup>99</sup>Tc in marine algae and sediment have been measured using HR-ICP-MS (96/2409). The samples were leached with nitric acid and three extraction procedures were employed to separate and pre-concentrate the Tc. HR-ICP-MS has also been used to determine the halides (Cl, Br and I) in biological standard reference materials and <sup>129</sup>I in radioactive waste samples (96/C2077). A better detection limit for iodine was achieved by introducing the analyte to the ICP-MS in elemental form. A novel hydride generation HR-ICP-MS technique has been used to determine selenium-79 in radioactive waste samples (96/C2076). Hydride generation improves the sensitivity and also helps overcome some of the isobaric and molecular ion interferences.

*Thermal ionization mass spectrometry* (TIMS) has been used for the determination of <sup>230</sup>Th and <sup>232</sup>Th in seawater (96/2394). Depth profiles of both isotopes were determined and were characterized by a surface minimum, a subsurface maximum and intermediate concentrations that progressively decreased towards the bottom of the sea. Isobaric interference from <sup>238</sup>Pu on the determination of <sup>238</sup>U has been investigated and three different methodologies for overcoming this interference were presented (96/2399). Use of a multicollector detection system was also investigated (95/4645) and the application of this to synthetic samples was described. *Isotope dilution* and TIMS have also been used to determine trace amounts of Fe in zirconium (96/1618). Signal suppression and interference caused by the zirconium matrix was avoided by use of a two-stage purification process. Using this procedure it was possible to determine mg g<sup>-1</sup> levels of Fe in zirconium metal and other applications are possible.

An increasing number of papers are appearing using *resonance ion mass spectrometry* (RIMS) for the analysis of the long-lived radioisotopes. The technique is based on stepwise excitation and ionization of atoms with resonant laser light followed by mass analysis. This technique has been limited to a small number of research institutes owing to the complexity of the experimental set-up; however, a review (with 20 references) of the determination of radionuclides has been published (96/1716). Three different experimental approaches have been developed to address the different requirements of each radioisotope's different physical, chemical and environmental properties (96/1719). For example, the actinides were measured using triple resonance ionization and time-of-flight mass spectrometry, while a high efficiency laser ionization source was used to determine Tc isotopes and collinear fast beam spectroscopy for the quantitative determination of strontium-90 and strontium-89 in environmental samples. An ion exchange technique for the separation of Pu from a polycarbonate filter and subsequent measurement using RIMS has been developed (96/1479). Several types of filaments have been investigated for the determination of Pu using RIMS (96/1480). The best results were obtained from use of tantalum as a backing and titanium as a covering. Ultra-trace analysis of long-lived radioisotopes in the environment using alpha, beta and gamma spectrometry, ICP-MS and accelerator mass spectrometry (AMS) has been discussed and the use of RIMS proposed for the analysis of Tc to approximately  $2 \times 10^6$  atoms detection limit (96/1468).

A review, with 64 references, detailing the principles, performances and applications of *laser spectroscopy* to the *analysis of actinides and radioisotopes* has been published (95/4143). The advantages and drawbacks of each of eight laser techniques were discussed and compared with ICP-MS. The *determination of uranium series isotope ratios using mass spectrometry* (TIMS and ICP-MS) has been reviewed (95/3599). Good agreement was found for the determination of plutonium isotope ratios (<sup>240</sup>Pu/<sup>239</sup>Pu) in sediment cores from the Irish Sea using ICP-MS and TIMS (96/2411). *Accelerator mass spectrometry* has been used to determine Pu to detection limits around  $10^{-15}$  g, which is equivalent to  $10^{-5}$  Bq of <sup>239</sup>Pu; this is better than alpha spectrometry and technical improvements to the accelerator should reduce these detection limits by a further ten-fold (95/C4301).

*Inductively coupled plasma atomic emission spectrometry* (ICP-AES) still continues to be used for the analysis of nuclear materials; however separation of uranium was important to remove potential spectral interference. This technique has been used for the determination of Ti, V and Mo in nuclear quality uranium oxide. The uranium was removed by ion exchange and the three analytes measured using ICP-AES (95/4459). Detection limits were around  $0.08\text{--}0.6 \times 10^{-6}$  g with a recovery of 94–99%. Ion exchange using a micro-column has been used

to separate and pre-concentrate, by around 100 times, some of the rare earth elements and Sr and Y from salt matrices containing uranium (96/1343). Silver was separated from uranium using tri-isobutylphosphine sulfide in xylene and determined using ICP-AES, a detection limit of  $20 \mu\text{g g}^{-1}$  was obtained (96/2979). An interesting alternative to conventional ICP-AES is coupling a laser to the system and analysing samples using laser ablation (96/954 and 96/1096). The main advantage of this approach is that the sample does not need to be dissolved prior to measurement, which means that handling of active samples is minimized (95/3403). This technique has been used to determine major and minor elements in various matrices (uranium-zirconium fuel, beryllium, plutonium, etc.). It has also been used to determine uranium isotope ratios, using a two monochromator ICP-AES instrument. Laser ablation was compared with conventional nebulization and the isotope ratios obtained confirmed using TIMS.

X-Ray fluorescence spectrometry (XRF) was used to measure iron in zirconium oxide by pressing the powdered zirconium oxide onto a boric acid substrate and irradiating in a helium medium at 50 mA and 50 kV (96/299). On-line analysis of process anion exchange eluates for actinides and other analytes has been carried out using a commercial energy dispersive XRF (96/382). The analysis was only semiquantitative but pre-concentration to lower detection limits and a more rigorous calibration protocol to provide more quantitative data was envisaged.

### 3. ADVANCED MATERIALS

#### 3.1. Polymeric Materials and Composites

Like a bad penny, the analysis of *Pb in paints* continues to turn up in this review and this year is no exception. The driving force for much of the published work this time around has been the development of *portable or field screening test instruments*. XRF has traditionally been popular in this area and Driscoll *et al.* (96/314) have reported a field method using a SEFA-Pb portable XRF instrument with a high resolution ( $\text{N}_2$  cooled) Si(Li) detector and a 10 mmCi  $^{57}\text{Co}$  source. No detection limits were given for Pb in paints but results correlated well with low resolution instrument data. An alternative portable, battery-powered, tungsten coil AAS has been reported (96/2505, 96/C886). The finished spectrometer could be powered by a normal 12 V car battery and had dimensions of  $19 \times 8 \times 3$  in. Instrument characteristics included a limit of detection of 20 pg of Pb, linear range covering 2 orders of magnitude, RSD of around 5% and accuracy of 95–97% (NIST SRM 1579a). The workers concluded that the most limiting parameter was detector noise and that performance could be improved by increasing the optical throughput of the system. A portable laser-induced breakdown spectroscopy instrument has also been developed (96/2507). The instrument weighs just 14.6 kg, and operates from 115 V. Fibre optics are used to collect the light produced from a hand-held laser probe. Disappointing limits of detection (0.8% m/m) for Pb in paint were quoted because the instrument uses the less sensitive 220.35 nm PbII line due to interferences on the stronger 405.78 nm PbI line. The use of ICP-MS for the determination of Pb isotopic ratios has also attracted attention. Hall (96/C2304) has reported some interesting work on the identification of old white Pb-based paints. Problems encountered included the fact that the source lead carbonate was usually mixed with other Pb-based pigments. Using a two source Pb mixing equation, ICP-MS Pb isotope data could be used to identify the manufacturer of old paint samples. One step further on from this is the use of Pb isotopes to detect the exposure source of Pb (96/C702). Experimental details included the observation that Th, if used as an internal standard,

degraded within-run precision for isotope ratio measurements. The workers suggested that Pb exposure in a number of subjects was a result of aerosol dust which, in turn, was a composite of disturbed paint surfaces. Other workers have concentrated on the quality control of this type of analysis. Protocols for preparing method evaluation materials from real-world, Pb-containing paints and dusts has been reported (96/1192). The materials have been used in a round-robin exercise involving techniques such as AAS, ICP-AES and XRF. Such performance exercises have been reviewed by Harper *et al.* (96/1189). The report includes a summary of method performance evaluations, both for laboratory based methods and field measurement techniques. A comparison of Pb paint field screening test methods has also been published (95/4054).

If the number of abstracts is anything to go by, XRF is one of the most utilized analytical techniques for the *analysis of polymeric materials*. A method for the direct determination of Ga on polyurethane foam has been developed (95/3402). Gallium chloride is easily extracted from 6 mol  $\text{l}^{-1}$  HCl on to comminuted polyether-type polyurethane foam. Ga was detected to  $(\pm)60 \text{ ng ml}^{-1}$  with a linear range of  $0.1\text{--}2.33 \mu\text{g ml}^{-1}$ . The procedure was successfully applied to the determination of Ga in a variety of aluminium, bauxite and industrial residue samples. A variation on this theme has been developed for the analysis of Au by XRF after absorption onto a polyurethane foam disc (96/365). Water traces were, however, found to affect the Compton scattering background intensity. A linear range of 0–300  $\mu\text{g}$ , limit of detection of 0.4  $\mu\text{g}$  and RSD of 1.52% were reported. Good agreement to certified reference values was obtained.

A quantitative method for the determination of *cotton fibre maturity by XRF* has been published (96/537). Samples were prepared by grinding (100 mg) and pressing at 20 kpsi into a 31 mm diameter pellet. The prepared pellet was analysed using Rh continuum excitation and a Ti secondary target (20 kV, 1 mA) in a He atmosphere. An Li drifted Si detector was used. Calibration was achieved using NIST SRM apple leaves diluted with cellulose powder. Significant relationships between cotton maturity parameters and Ca concentration were found.

The *analysis of plastics by AA and AE* methods continues to appear. A short review of the latest dissolution techniques for AAS and ICP-AES detection has been compiled (95/3935). Trace amounts of Sb, Mn and Co have been determined in poly(ethylene terephthalate) (PET) films by solid sampling ETAAS (95/3380). The temperature program was critical to avoid fusion of the PET film, which would interfere with the complete charring of the sample. Standard additions had to be used for quantification purposes. Results were in good agreement with those from traditional acid digestion with FAAS detection, although the solid sampling techniques demonstrated poorer precision. Tin has been determined in unplasticized poly(vinyl chloride) pipes by Zeeman ETAAS (95/3684). Samples were suspended in 4% acetic acid using  $\text{Ca}(\text{NO}_3)_2$  as a matrix modifier. Recoveries of 95–106% with RSDs of 3.4% are reported.

Finally, an interesting report by Forsyth *et al.* (95/C4330) on the determination of organotin leachates from chlorinated poly(vinyl chloride) pipes caught this reviewer's eye. Drinking water samples collected from CPVC pipes were analysed for organotins by solid phase extraction followed by GC-AAS detection. Dialkyltin levels of approximately 30–100  $\text{ng g}^{-1}$  have been found, depending on the water temperature. Monoalkyltin was also identified.

#### 3.2. Semiconductor Materials

Several reviews on the use of *total reflectance X-ray fluorescence* for the *analysis of semiconductor materials* have been published (96/2607, 96/1119, 96/2609) in the last year. Hockett (96/2792)

estimates that there are approximately 100 TXRF instruments in use in the semiconductor industry. TXRF is ideally suited to the determination of trace element contamination on semiconductor surfaces, has detection limits of between  $10^9$  and  $10^{10}$  atoms per  $\text{cm}^2$  and the depth of analysis is typically in the tens of nanometers (96/511). An interesting comparison of TXRF with radiochemical methods has been made by Fester *et al.* (96/2564). The authors used both techniques to monitor contamination levels of Co, Cr, Fe, Ni and U under various preparation conditions. They found that the results were comparable at levels of  $10^{11}$ – $10^{13}$  atoms per  $\text{cm}^2$ , providing the surface distribution was homogeneous, but that the differences became more significant close to the detection limits. It was reported that radiochemical analysis of Co, Cr and Fe has detection limits of at least an order of magnitude lower than *vapour phase deposition* (VPD) TXRF. A review of standardization issues for TXRF and VPD-TXRF has been published (96/1150). Reference samples are required for quantitative TXRF and VPD-TXRF analysis and the approaches to making and using these reference samples varies among manufacturers and users worldwide. Some of the basic issues are reviewed and summarized in this paper. Yoshihiro *et al.* (96/1153, 96/2766) have published two papers on the preparation of calibration samples for TXRF. The technique involves immersion of the silicon wafers in intentionally contaminated alkali hydrogen peroxide solution; they found that the metal ions were adsorbed on the surface oxide layer with a thickness of approximately 1 nm. The authors examined adsorption isotherms, depth profiles and stability of wafers prepared for Ca, Co, Fe, Mn, Ni and Zn. The possibility of TXRF as a candidate for the ISO standard for determination of contaminant element content of silicon wafers was discussed at a recent conference (96/C2851). Several round-robin tests have been carried out and the results of the most recent were discussed. Cleaning of the silicon wafer is one of the most frequent processes in the manufacturing sequence for integrated circuits. The purpose of the cleaning procedure is to remove contaminants and the industry uses the highest purity chemicals available to limit the possibility of adding contaminants from the chemicals themselves. The chemicals are usually well characterized and analysed to exacting standards, prior to use in the process stream. However, over 50% of the yield losses in integrated circuit manufacture are thought to be due to contamination left on the wafer surface after cleaning. Sees and Hall (96/581) have used TXRF to investigate metallic impurities on silicon wafers after cleaning with ultra-pure and standard grade chemicals. They concentrated on the cleaning procedure with SC-1, an ammonia solution–hydrogen peroxide mix, and found that ultra-pure chemicals gave less contamination, as expected. TXRF with a special energy dispersive spectrometer has been used to measure the light elements such as Al, C, F, Mg, N, Na and O on silicon (96/1154). The angular dependence of the fluorescence signal from low atomic number atoms implanted in silicon, excited by monoenergetic radiation of various energies, was calculated. The excitation energy in the experiments was monochromatized Cr-K $\alpha$  radiation. Yakushiji *et al.* (96/1158) have reported spurious peaks such as Fe-K $\alpha$  and Ni-K $\alpha$  radiation observed during the determination of trace determination of metal impurities on silicon wafers. The intensity of the spurious peaks varied with changes in the incident azimuth angle and intensity of the primary X-ray beam and was found to be due to impurities along the path of the X-rays. The use of *synchrotron X-ray sources* for TXRF (SR-TXRF) offers an improvement in sensitivity by one or two orders of magnitude. A sensitivity of  $3 \times 10^8$  atoms  $\text{cm}^{-2}$  for the third row transition metals was recently demonstrated using this technique (96/1155). SR-TXRF has been reviewed and a new quantification method for the determination of such low levels of analytes, based on

relative sensitivity factors, proposed (96/1151). Ni was determined on a silicon wafer surface using SR-TXRF (96/1216). A detection limit of 13 fg was obtained for Ni at a beam current of 73 mA.

*Secondary ion mass spectrometry* is another important technique in the analysis of semiconductor materials. A review of both TXRF and SIMS for the determination of ultra-trace contaminants on silicon surfaces has been written (96/2458). The basic principles of SIMS and its application to semiconductor analysis have been reviewed (96/1690, 96/4653, 96/2320). Contamination during ion implantation has also been investigated using SIMS (96/1751). Routine detection limits of  $<10^{13}$  atoms  $\text{cm}^{-2}$  have been obtained for the determination of boron in antimony-doped silicon using SIMS (96/3718). The technique was not affected by the high levels of antimony present and, based on the statistics obtained from a control sample, the analytical precision was approximately 8% at a boron concentration of  $1.7 \times 10^{14}$  atoms  $\text{cm}^{-2}$ . Oxygen flooding of the surface during SIMS measurement provides a technique capable of detecting  $10^{10}$  atoms  $\text{cm}^{-2}$ , or less, of many surface elemental contaminants (96/1681). SIMS depth profiling experiments have been used to determine the layered structure, impurity distribution and current induced changes in polymeric light emitting diodes (LEDs) (96/2389). Two systems were studied and results indicated evidence of current induced degradation effects. A new procedure to obtain accurate SIMS depth profiles of Na in silicon dioxide was investigated (96/2396). The silicon samples were treated with HF to etch off some of the oxide and the surface analysed by SIMS after coating with Ag. The Na depth profile was obtained by plotting the  $\text{Na}^+$  intensity at the Ag/SiO<sub>2</sub> interface against the etched depth.

*Electrothermal atomization atomic absorption spectrometry* is still an important tool in the determination of ultra-trace analytes in semiconductor samples. Impurities on silicon wafers have been determined by ETAAS (96/1093, 96/2894) after dissolution of the surface layer in a droplet of hydrofluoric acid. Detection limits of  $10^8$ – $10^9$  atoms  $\text{cm}^{-2}$  for a 6 in wafer were obtained, which are similar to those currently quoted for TXRF. Silicon has been determined in photoresist using ETAAS (95/4370). Pre-conditioning of the furnace with calcium improved the Si response by 50% and gave a detection limit of 0.02 ng. High purity gallium was analysed for Sb and Fe content by dissolving the sample in nitric and tartaric acids and measuring the resulting solutions using ETAAS (95/3430). Zeeman background correction ETAAS and a L'vov platform was used to determine In in gallium arsenide (95/4255). The use of the L'vov platform, Zeeman background correction and standard additions helped overcome interference from the gallium arsenide matrix. Chemical modification and ETAAS were used to determine Tl in telluride thermoelectric material (95/4693). The modifier used was a mixture of tartaric acid–ascorbic acid–magnesium nitrate (1:2:1) and the detection limit for Tl was calculated to be 0.6 ng  $\text{ml}^{-1}$ .

A few papers on the application of *inductively coupled plasma mass spectrometry* to semiconductor analysis have been published. A combination of VPD and ICP-MS was used to measure around 60 elements on wafer surface by Tan *et al.* (96/1746). Detection limits of  $<10^8$ – $10^{10}$  atoms  $\text{cm}^{-2}$  for bare wafers and 10 ppb to 10 ppm on dielectric oxide layers were found. Accuracy was demonstrated by spike recovery studies and by intercomparison of methods with Japanese laboratories. Correlations were made between the trace metals content of cleaning chemicals (SC-1) and metal contaminants on wafers. Tan (96/2951) used VPD and a combination of ICP-MS with a capillary nebulizer, and ETAAS to determine nine elements on wafer surfaces. *Electrothermal vaporization* (ETV)-ICP-MS offers better sensitivity of measurement and also requires very small sample volumes and therefore should offer advantages

over nebulization ICP-MS for the analysis of silicon wafer surfaces. Hub and Amphlett (95/3550) have used ETV-ICP-MS for the determination of eight elements in hydrofluoric acid and buffered oxide etch, two chemicals used routinely in semiconductor manufacture and on silicon wafers. For wafer analysis, the surface oxide coating is dissolved by VPD or DSE (droplet surface etching) and the dissolved analytes measured using ETV-ICP-MS. Using this protocol, they obtained detection limits of  $0.2\text{--}2 \times 10^9$  atoms per  $\text{cm}^2$  for eight elements on 6 in wafers. The authors pointed out that ETV-ICP-MS combines the sensitivity benefits of ETAAS and the simultaneous multi-element analytical advantage of TXRF, with the possibility of being able to measure the light elements such as Al, Mg and Na, which are difficult to determine using TXRF. Isotope dilution (ID) ETV-ICP-MS has been used to determine Cu, Zn and Pb on wafer surfaces (96/2354). The wafer surface was etched with  $200\text{ }\mu\text{l}$  of a mixture of nitric and hydrofluoric acids and the impurities determined at  $3 \times 10^8\text{--}8.7 \times 10^9$  atoms per  $\text{cm}^2$  in the resulting solution using ID-ETV-ICP-MS. Other workers (96/1457) have used a *microconcentric nebulizer* (MCN) to introduce the small sample volumes obtained from VPD or DSE to the ICP-MS instrument. Detection limits of 1 ppt for Cr and 25 ppt for Al were obtained, with detection limits for Mo, Zn, Ni, Na, W and Cu falling between. The authors were also able to determine K to 10 ppt, Ca to 28 ppt and Fe to 13 ppt using cold plasma conditions in the same multi-element run. Two recent conference papers (96/C2222, 96/C757) also describe a combination of cool or reduced power plasma conditions with and without a microconcentric nebulizer and ICP-MS for the analysis of semiconductor materials. The cool plasma is reported to overcome polyatomic interference on low mass analytes and hence allow the measurement of  $^{39}\text{K}$ ,  $^{56}\text{Fe}$  and  $^{40}\text{Ca}$  in semiconductor process solutions.

*Inductively coupled plasma emission spectroscopy* (ICP-AES) is used for the analysis of semiconductor materials when speed of analysis is required and the instrument can meet the industry's detection limit requirements. Impurities in quartz sand and silicon powder have been determined using ICP-AES (96/1058). The sample was dissolved in hydrofluoric and nitric acids and buffered with boric acid before measurement. Interference from silicon was also investigated. ICP-AES has been used to determine Ag, Al, As, Cd, Cu, Fe, Ni, Pb, Sn, Te and Zn in high purity indium (96/1370). The same group of workers presented the data for the determination of Al, Ca, Cd, Cr, Cu, Fe, In, Mg, Mn and Zn in gallium arsenide using ICP-AES at a recent conference (96/C943). Gallium was separated from the impurities by extracting with diethyl ether saturated with hydrochloric acid.

*Glow discharge mass spectrometry* (GDMS) has been used to perform high sensitivity (ppt) measurements of semiconductors and metals (96/1800). The advantages of this technique are the ability to analyse solid samples directly and depth profiling capabilities. However, the main disadvantage, in semiconductor analysis, is that the sample is used as the cathode in a d.c. glow discharge and therefore must be conducting to some extent, which presents major difficulties in the analysis of silicon wafers. Use of a radiofrequency source for GDMS has been presented as means of overcoming this limitation of the technique (96/C859). A radiofrequency glow discharge ion source has been optimized and characterized for a high resolution mass spectrometer (95/4715) and has been used to analyse gallium arsenide wafers (96/2386).

The potential use of *accelerator mass spectrometry* (AMS) to the analysis of semiconductor samples has been explored in two papers published during the review period (95/4617, 96/1701). This technique is reported to be more sensitive than SIMS for some elements because it is capable of electron stripping molecular ions which can cause interference effects

when using SIMS. It will be interesting to see how AMS develops for semiconductor and other analysis. *Analysis of cleanroom air* has been undertaken using ETAAS, ICP-MS and ion chromatography (96/1048). Impurities were trapped in an impinger and measured using the most appropriate technique.

### 3.3. Glasses

Since its introduction laser ablation has been a very popular sample introduction technique for the spectrometric analysis of glass. However, for the period under review nothing of real significance has caught this reviewer's eye. One paper (96/374) using LA-ICP-MS studied the homogeneity of 4 NIST glass standard reference materials. Within the reported analytical uncertainty, NIST 611, 612 and 614 are apparently homogeneous whereas NIST 1834 is inhomogeneous on a scale of 100 mg with respect to several trace elements.

Thankfully, workers in the field of *X-ray fluorescence* (XRF) seem to have been more productive. Most effort has been concentrated on sample preparation or direct analysis of individual glass particles. A fast (45 min) preparative procedure, which consisted of casting the glass melt directly into a pre-heated graphite mould followed by annealing for 30 min at 500 °C, has been described (96/484). Element X-ray intensities were found to be highly reproducible (<1%). The workers claim that the method is suitable for vitrification process control purposes, permitting on-site monitoring of glass composition. An alternative method has been reported (96/522) using a Pt sample vessel and a multiple melt-cool cycle. It was claimed that the method is particularly useful for samples from which gas bubbles are formed during melting. Other crucibles consisting of Pt–Au–Rh mixtures have been utilized for XRF glass sample preparation (96/1125).

Most of the preparative methods described were used to overcome problems in sample homogeneity. Rindby *et al.* (96/2751) reported using the intensity correlations between pairs of elements for detecting topological variations between solid samples by *micro-beam XRF*. The method was used to analyse *irregularly shaped millimetre sized glass fragments*. A mathematical model for fluorescent correlation has been formulated from the data. Another approach to the problem has been reported by Lankosz and Pella (96/1010, 96/1011). The method described used polychromatic X-ray micro-beam excitation for the quantitative analysis of individual particles ( $50\text{--}160\text{ }\mu\text{m}$ ) by XRF. The coherent and incoherent tube target lines scattered from the sample were used to calculate the average atomic number and mass thickness of the sample. Irregularly shaped particles were analysed using a known equation usually applied to flat samples of intermediate thickness. The procedure has been tested on glasses of known composition with good accuracy and RSDs of between 4 and 25% for spherical particles.

Finally, the field of archaeometry has become a fruitful area for the analysis of glass materials. For example, one application reported during the review period involved use of secondary neutral mass spectrometry (SNMS) to study glass corrosion phenomena (96/2382). Using the recently developed high frequency mode (HFM) of the electron gun SNMS, the workers were also able to obtain 'fingerprint' mass spectra for ceramic samples. The study of ancient glasses has also become popular: Roman (96/1830), Mediaeval (96/2998), early Thuringian (95/4038) and ancient (95/4039) glasses have been analysed by ICP-AES, X-ray microprobe and XRF, respectively.

### 3.4. Ceramics and Refractories

Since its introduction over a decade ago, *inductively coupled plasma mass spectrometry* has penetrated practically all areas

of elemental analysis. Ceramic materials have proved to be no exception although this year most of the reported work has been confined to conference presentations. *High resolution-inductively coupled plasma mass spectrometry* instruments are now making an appearance with the analysis of  $\text{Al}_2\text{O}_3$  ceramic powders being reported (96/C2221). After dissolution by pressure digestion with HCl, the solutions were diluted to an equivalent  $\text{Al}_2\text{O}_3$  content of  $400 \mu\text{g ml}^{-1}$ . A suite of elements were determined at low resolution ( $m/\Delta m = 300$ ) whereas  $^{51}\text{V}$ ,  $^{52}\text{Cr}$ ,  $^{55}\text{Mn}$ ,  $^{56}\text{Fe}$  and  $^{69}\text{Ga}$  were performed at high resolution ( $m/\Delta m = 3000$ ) to overcome polyatomic interferences. Good agreement was obtained when compared with a low resolution quadrupole ICP-MS method which involved a matrix removal stage based on hexamethylene dithiocarbamate (HMDC). Other reports included the use of ICP-MS for the analysis of *silicon carbide* powders for 35 elements (95/3554). The method was extended to Mg, Ca, Sc and Ti by employing matrix removal by evaporation after high pressure acid decomposition in a mixture of  $\text{HNO}_3-\text{H}_2\text{SO}_4-\text{HF}$ .

Ceramics and refractory materials can be notoriously difficult to digest and with these materials, efficient sample preparation/dissolution is critical for a successful analysis. One way around this problem is to use direct sampling techniques such as *electrothermal vaporization* coupled with ICP-AES or ICP-MS, although as yet these techniques may not have been fully exploited, mainly owing to problems with reproducibility. In this vein, a novel ETV-ICP-AES configuration has been reported (95/4724, 96/C221). The system was based on in-line resistive heating of a graphite crucible with powdered SiC mixed with a  $\text{CoF}_2$  and BaO modifier in a 1:1:1 proportion. The transport path to the base of the torch, considered critical in this type of device, has been kept down to 9 mm. Detection limits were reported to be in the pg range for Al, Fe, Ti and V. A disposable graphite cup system has been developed (95/4593) for ICP-AES using  $\text{PdCl}_2$  as a matrix modifier. The aspect of calibration has been addressed by several workers (95/3433, 96/C663), as well as the use of Freon-12 ( $\text{CF}_2\text{Cl}_2$ ) to aid volatilization.

Advances in the analysis of *silicon carbide thin films* have continued. The analysis is important as the structure of the films radically alters their physical properties. The use of SIMS and XPS has been studied for the characterization of hydrogenated amorphous SiC thin films (95/4624). All the  $a\text{-Si}_{1-x}\text{C}_x:\text{H}$  films studied consisted of a homogeneous layer on a c-Si substrate. The analysis also provided values of the dielectric function of the layered material. A multi-technique approach has been utilized for the study of porous silica membranes (95/4652). Techniques used included SIMS, Raman scattering, FTIR, XPS and AES. Matrix effects on the SIMS analysis of ceramic-copper powder pellets has also been published (95/4106).

The field of *archaeometry* is fast growing and the analysis of ancient ceramics by spectroscopic methods has become very popular. Neutron activation analysis has traditionally been the method of choice in the past but, with the advent of fast, reliable digestion procedures, e.g., microwave methods, and sensitive instrumentation (e.g., ICP-AES and ICP-MS), spectroscopic techniques are catching up (96/2323). Lithium borate (both meta and tetra) fusions are the sample dissolution methods of choice with either Pt crucibles (96/2485) or graphite crucibles (96/2876) at 1000–1100 °C, followed by dissolution using  $\text{HNO}_3$ . Elemental content has been used to track movements of materials (96/C911) and trace trade routes (96/1998), as well as for the identification of different types of pottery (96/1831, 96/1834). Other workers have used XRF to study kiln sites (96/1163, 96/2578).

The analysis of *non-conducting materials* by both *rf-GDMS* and *d.c.-GDMS* has been reviewed and compared (95/1489). Work has concentrated on sample preparation, with several

schemes being reported. The use of secondary cathodes has been evaluated for d.c.-GDMS (96/1520). Optimum discharge conditions and analytical characteristics were reported. The electrical resistivity of the sample was found to be an important factor determining the capabilities of the technique, especially with respect to detection power. De Gendt *et al.* (95/4188) reported the quantitative analysis of Fe-rich samples by GDMS. Various iron ore reference materials were mixed 1:7 with either Cu or Ag powder as a conducting host matrix. Internal repeatability was less than 6%, with external repeatability less than 10% for flat electrodes. Variation in sensitivity factors for various non-conducting materials (iron ores, sinters, firebrick and bauxite) was better than 25%. Another approach has been direct analysis of non-conducting samples by rf-GDMS (95/3524). Parameters such as discharge pressure, orifice distances and cryogenic cooling were optimized to deliver semi-quantitative results within a factor of 2 of the certified concentrations for reference materials.

Several matrix separation and removal methodologies have been published for a variety of sample matrices. *HPLC-ICP-MS* has been used for the interference-free analysis of all rare earth elements in rock samples (95/4368) using a cation exchange column (not specified) and a 2-hydroxy-2-methylpropanoic acid mobile phase. Detection limits of 0.4–30 ng  $\text{ml}^{-1}$  for all REEs were obtained. Traces of Ca and Mg in *rare earth oxides* by *flow injection analysis* coupled with fluorescent detection using calcein (95/3643) have been determined. To discriminate between Ca and Mg, 8-hydroxy-quinoline (for Mg) and EGTA (for Ca) were used as masking agents. Matrix concentrations of up to 500 mg  $\text{l}^{-1}$  could be tolerated, with detection limits of 0.1 mg  $\text{g}^{-1}$  for Ca and 0.04 mg  $\text{g}^{-1}$  for Mg. Ten trace elements have been quantified in EuO by using di-(2-ethylhexyl)phosphonic acid-resin and a dilute  $\text{HNO}_3$  mobile phase with ICP-AES detection (95/4447). The removal of SbO matrix has been achieved by hydride vaporization using HBr, allowing the interference free analysis of Th and U by ICP-MS (96/1534). As in previous years, numerous papers described methods for the analysis of *rare earth elements in oxide matrices*. A summary of these methods is provided in Table 3.

*Slurry samples*, when coupled with ETAAS, continue to play a part in the analysis of refractory materials. Trace metals in  $\text{ZrO}_2$  slurries were analysed by suspending 5–150 mg of sample in 10 ml of  $\text{H}_2\text{O}$  (96/2955). For Ca, Fe and Na, the slurry was diluted up to 100-fold, while for Al, Cd and Si  $\text{H}_3\text{BO}_3-\text{HF}$ , diammonium hydrogen phosphate–magnesium nitrate and calcium nitrate modifiers were added, respectively. Detection limits for a range of elements were 1–20 ng  $\text{g}^{-1}$  for a 20  $\mu\text{l}$  injection. Modifiers seem to be just as important for slurry-ETAAS as for conventional ETAAS analyses, with a mixture of  $(\text{NH}_4)_2\text{HPO}_4-\text{Mg}(\text{NO}_3)_2$  being used for the determination of *silicon nitride powders* (95/3767). However, the use of modifiers can be avoided by using a cup and boat solid sampling technique (95/4594). In this case, Ca, K, Mg, Na and Zn in high purity Mo metal and Mo silicide powders for microelectronic applications were determined. Since contaminant levels were significantly reduced using this approach, detection limits of 0.06 ng  $\text{g}^{-1}$  for Zn and 0.5 ng  $\text{g}^{-1}$  for Na could be achieved.

The analysis of *cement and concrete* type materials continues to attract attention. A new fusion agent consisting of oxalic acid,  $\text{Li}_2\text{B}_4\text{O}_7$  and  $\text{Li}_2\text{CO}_3$  (1:1:1) has been utilized (96/1383). Fusion was carried out in a Pt crucible for 10 min at 925 °C, followed by dissolution of the fusion cake in 10% HCl prior to determination of Al, Fe, K, Na, Si and Ti by AAS. Ca and Mg could only be analysed after addition of lanthanum(III) nitrate. A substantial number of reports on the use of XRF for the analysis of cement and related materials have been published this year (96/1185, 96/1238, 96/2623, 96/2656).

**Table 3** SUMMARY OF ANALYSES OF ADVANCED MATERIALS

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>POLYMERIC MATERIALS AND COMPOSITES—</b>				
Au	Polyurethane	XRF;—;S	Au absorbed on polyurethane discs. (Linear range 0–300 µg, LOD 0.4 µg and RSD 1.52%)	96/365
Ga	Polyurethane	XRF;—;S	Gallium chloride extracted from 6 mol l <sup>-1</sup> HCl on to polyurethane foam and quantitatively determined by XRF	95/3402
Mg	Acrylonitrile–butadiene–styrene	MS;ICP;L	Semi-quantitative analysis carried out on acid digests of the polymeric materials. (LOD 50 µg kg <sup>-1</sup> )	96/1571
Mn	Polymer aluminium chloride	AA;F;L	1 g of sample boiled with 1 ml of HNO <sub>3</sub> before addition of 5 ml of 0.5 mol l <sup>-1</sup> sulfosalicylic acid. Mn was directly determined by acetylene–air flame AAS	95/3388
P	Poly( <i>p</i> -phenylenebenzoxazole)	XRF;—;S	Sample cut into 1.25 in discs and analysed by XRF. The instrument was operated at 8 kV, 0.05 mA, with a Ru tube for excitation. LOD was 40 mg kg <sup>-1</sup> , RSD 5.8%, recoveries 90.6–113.6% and linear range 150–4100 mg kg <sup>-1</sup>	95/3399
P	Polymers	AF;ET-LEAFS;S	A novel dissolution method that utilized trifluoroacetic acid and toluene was used for validation purposes. RSDs of 11–12% were obtained for the solid sampling method	96/2472
Pb	Paint	XRF;—;S	A high resolution portable XRF instrument was developed. For Pb in paint the lines detected were K <sub>α</sub> <sub>1</sub> and K <sub>α</sub> <sub>2</sub> lines at 75 and 72.8 keV	96/314
Pb	Paint	MS;ICP;L	Pb based paints were characterized by the Pb isotope ratio data obtained from ICP-MS. Pb isotope ratio ‘fingerprints’ of paint manufacturers have been identified	96/C2304
Pb	Nitrocellulose paint	AA;—;L	The pigments in paint were selectively separated by propylene glycol ether–butanone solvent mixture followed by determination using AAS and dithizone spectrometry	96/1987
Pb	Paint	AA;W-coil;L	Development of a portable AAS instrument is described. LOD was 20 pg (20 µl sample volume)	96/2505
S	Rubber	AA;F;L	Samples were microwave digested in HNO <sub>3</sub> –H <sub>2</sub> O <sub>2</sub> and treated with BaCl <sub>2</sub> . S was determined indirectly by determining the excess Ba	96/2982
Sb	Polyethylene terephthalate	MS;ICP;L	As for Mg (LOD <1 mg kg <sup>-1</sup> )	96/1571
Sn	PVC	AA;ETA;L	Sample suspended in 4% acetic acid. Ca(NO <sub>3</sub> ) <sub>2</sub> used as matrix modifier. Recoveries were in the range 95–106%	95/3684
Sn (organo-)	Chlorinated poly(vinyl chloride)	AA;F;L	Drinking water samples were collected from CPVC pipe and analysed by solid-phase extraction followed by GC-AAS. Dialkyltin and monoalkyltin compounds were identified in leachate waters	95/C4330
Te	Plasticizers	AE;ICP;L	Volatile hydride was generated by NaBH <sub>4</sub> reduction. The 214.282 nm line was used giving LOD of 4 ng ml <sup>-1</sup>	95/3897
Various	Polymers	MS;ICP;L	Microwave digestion in concentrated HNO <sub>3</sub> and H <sub>2</sub> SO <sub>4</sub> . Indium used as internal standard	95/1670
Various (3)	Poly(ethylene terephthalate)	AA;ETA;S	Co, Mn and Sb were analysed by solid sampling ETAAS. Concentrations in PET films ranged from 10 <sup>-8</sup> to 10 <sup>-4</sup> g g <sup>-1</sup>	95/3380
Various	Rubber	XRF;—;S	Rubber samples, either vulcanized or pulverized by using liquid N <sub>2</sub> , were analysed by application of two different radioactive sources. Method was verified by NAA	95/C4203
Various (6)	Polyimides	AA;ETA;L	Samples were dissolved in 10 ml purified <i>N</i> -methylpyrrolidone or dioxane for solid samples. LODs of 0.5–25 ng g <sup>-1</sup> were obtained for Ca, Cu, Fe, K, Na and Si	96/1814
<b>SEMICONDUCTORS—</b>				
B	Silica and silicon	SIMS;S	Detection to <10 <sup>13</sup> atoms B cm <sup>-2</sup> on Sb doped Si substrates using SIMS. Precision and accuracy acceptable	95/3718
Cu	Silicon wafers	MS;ICP;L	Isotope dilution and ETV-ICP-MS used to determine Cu, Zn and Pb on silicon wafers. Detection limits 3 × 10 <sup>8</sup> to 8.7 × 10 <sup>9</sup> atoms cm <sup>-2</sup>	96/2354

**Table 3** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>SEMICONDUCTORS—</b>				
Eu	A <sub>4</sub> B <sub>6</sub> thin films	AF;ICP;L	An etching solution and electrochemical oxidation were used to remove layers of 0.5 to several microns. PbEuTe–PbTe and PbEuSe–PbSe heterostructures investigated. Eu removed measured using ICP-AFS	95/3789
Fe	Gallium arsenide	XRF;—;S	Depth profiling of Fe on GaAs was performed using TXRF. Detection limit of $10^{11}$ atoms $\text{cm}^{-2}$ on GaAs surfaces obtained	96/2794
Fe	Gallium	AA;ETA;L	Gallium dissolved in nitric–tartaric acid mixture ETAAS detection limits obtained were 5 ng $\text{ml}^{-1}$ Sb and 1.5 ng $\text{ml}^{-1}$ Fe	95/3430
In	Gallium arsenide	AA;ETA;L	Zeeman background correction, standard additions and L'vov platform used to overcome matrix interference. Recovery of 96–97.4% and detection limit of 2.5–3 ng $\text{ml}^{-1}$ obtained	95/4255
K	Phosphorus diffusion source	AA;F;L	Microwave digestion of sample and flame AAS measurement of Na and K. Standard additions used to overcome interferences from Al and P <sub>2</sub> O <sub>5</sub>	96/395
Na	Phosphorus diffusion source	AA;F;L	As per K	96/395
Na	Silica/Silicon	SIMS;S	Depth profiling of Na in SiO <sub>2</sub> on a silicon substrate. Surface coated with silver and depth profile obtained using SIMS	96/2396
Ni	Silicon wafers	XRF;—;S	Synchrotron radiation excited TXRF used to determine Ni to a detection limit of approximately 13 fg	96/1216
O	GaN	SIMS;S	Surface of GaN exposed to oxygen and monolayer of oxide on surface studied using SIMS	95/3716
Sb	Gallium	AA;ETA;L	As per Fe	95/3430
Si	Photoresist	AA;ETA;L	Furnace pre-conditioned by addition of calcium which was dried and ashed at 590 °C before addition of the sample. The Ca improved the sensitivity by about 50% to give a detection limit of 0.02 ng	95/4370
Tl	Monocrystals of Bi <sub>2</sub> Te <sub>3</sub>	AA;ETA;L	Tartaric acid, ascorbic acid and magnesium nitrate added as modifiers. Detection limit of 0.06 ng $\text{ml}^{-1}$ obtained	95/4693
Various	Silicon wafers, HF and BOE	MS;ICP;L	Analysis of Al, Mg, Na, Fe and other analytes on silicon wafers, HF and buffered oxide etch (BOE) using ETV-ICP-MS. Detection limits 0.2–2 × 10 <sup>9</sup> atoms $\text{cm}^{-2}$ . Main advantage is analysis of Fe where KI is used as a modifier	95/3550
Various (3)	Semiconductor process chemicals	MS;ICP;L	Cold plasma conditions used to overcome polyatomic interference and permit measurement of Ca, Fe and K by ICP-MS	96/C757
Various (7)	Silicon wafers	XRF;—;S	A special energy dispersive spectrometer described for TXRF analysis of light elements ( <i>viz.</i> , Al, C, F, Mg, N, Na, and O)	96/1154
Various (11)	VPD droplets	MS;ICP;L	Microconcentric nebulizer (MCN) and cold plasma conditions used to determine Ca, Fe and K, and MCN and normal plasma conditions to determine Al, Cr, Cu, Mo, Na, Ni, W and Zn to low ppt detection limits in VPD droplets	96/1457
Various (60)	Silicon wafer	MS;ICP;L	Vapour phase deposition used to remove surface layer and solution obtained measured using ICP-MS. Detection limits for silicon wafers <10 <sup>8</sup> to 10 <sup>10</sup> atoms $\text{cm}^{-2}$ and 10 ppb–10 ppm for dielectric oxide layers	96/1746
Various	Semiconductor process chemicals	MS;ICP;L	Combination of microconcentric nebulizer and cold plasma conditions to determine a suite of analytes in SC-1, SC-2 and TMAH	96/C2222
Various (6)	Silicon wafers	XRF;—;S	Standard sample procedure described for TXRF analysis of Ca, Co, Fe, Mn, Ni and Zn on silicon wafers	96/2766
Various (9)	Silicon	MS;ICP;L and AA;ETA;L	VPD used to remove surface layer and resulting solution measured using ETAAS and ICP-MS (magnetic sector). Sensitivity of both techniques similar	96/2951
<b>GLASSES—</b>				
As	Glass	XRF;—;S and SEM;S	Samples were K <sub>2</sub> O–CaO glass containing approximately 8% As <sub>2</sub> O <sub>3</sub>	95/4038

**Table 3** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>GLASSES—</b>				
Cu	Borate glass	AA;F;L	Cu <sup>II</sup> was determined by d.c. polarography. Total Cu was measured by AA using air–acetylene flame. After HCl digestion Cu <sup>I</sup> was determined by difference	96/2882
Fe	Borate glass	AA;F;L	10 mg sample was dissolved in 2 mol l <sup>-1</sup> HCl under N <sub>2</sub> and diluted with H <sub>2</sub> O. Total Fe was determined using air–acetylene flame after addition of 7 m mol l <sup>-1</sup> –alizarine red sulfonate	96/2896
K	Glass	AE;laser;S	XeCl excimer (20 ns, 25 mJ) was focused on glass samples at reduced pressure (1–10 Torr)	96/2815
Li	Glass	AE;plasma;S	XeCl excimer (20 ns, 25 mJ) was focused on glass samples at reduced pressure (1–10 Torr)	96/2815
Si	Glass fibres in rat lungs	AA;—;—	Rats were exposed to glass fibre and sacrificed at weekly intervals. Amount of glass fibre in the lungs increased linearly with time to about 0.3 mg	96/115
Sn	Tin coatings for glass	XPS;S	Depth profiling was achieved using Ar <sup>+</sup> and HF etching as well as mechanical abrasion. Sn speciation was determined from the Sn 3d, 4p, 4d and Sn <sub>MNN</sub> Auger peaks	96/C175
Various	Glass	AE;ICP;L and XRF;—;S	Following grinding, the samples were fused with Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> at 1000 °C with subsequent dissolution in HNO <sub>3</sub>	95/4039
Various	High-B borosilicate glass	AE;ICP;L	Samples were dissolved in HF or HF–HClO <sub>4</sub> mixture. For multicomponent glass a sodium borate–carbonate fusion was used	95/4364
Various	Glass	MS;ICP;S	Calibration curves for LA-ICP-MS were achieved using a series of geochemical reference standards. Ce, Y and Zr calibrations were non-linear. Internal standards (usually a low abundance isotope of a major element) were used to normalize raw intensities	95/4674
Various	Glass reference materials	MS;ICP;L	Samples were powdered under acetone and digested with HNO <sub>3</sub> –HF (1+9) (7 d at 150 °C). The residue was taken up in 8 mol l <sup>-1</sup> HNO <sub>3</sub>	96/374
Various	Waste glasses	XRF;—;S	Glass discs were prepared in 45 min by casting the melt directly into a graphite cast and annealing for 30 min at 500 °C	96/484
Various	Glass	XRF;—;S	Average atomic number and mass thickness were calculated from incoherent scatter data. Irregularly shaped particles could be analysed using a well known equation usually used for flat particles	96/1011
Various (4)	Borate glass	AA;F;L	Signal depressing interference from matrix was eliminated by using alizarin red sulfonate which forms a stable metal–alizarinate complex	96/1037
Various (10)	Vehicle headlight glass	XRF;—;S	Powered sample was suspended in EtOH, filtered and fixed with an aqueous collodion solution. As, Fe, K, Na and Zr showed correlation to different glass types	96/1235
Various	Glass fragments	XRF;—;S	Quantitative method based on correlation graphs between the intensities from different fluorescent lines. The method could be used study inhomogeneous samples	96/2751
<b>CERAMICS AND REFRACTORIES—</b>				
Al	Silicon carbide	AE;ICP;S	Direct analysis using LA-ICP-MS. Since no reference materials were available a standards additions method based on interpolation was used	96/C2821
Ba	Fly ash	XRF;—;S	Sample preparation process did not involve hazardous solvents. Ba and Sr could be used to ‘fingerprint’ for the presence of fly ash	96/1185
Ca H	Bismuth trioxide Carbon fibres	AA;F;L SIMS;—;S	RSDs of 2.78–2.98% quoted SIMS showed that H content of the core was greater than in the coating. (Strength of a C–H material increases with H content)	95/3832 95/4110
Mg Oxide phases Pb	Bismuth trioxide Y–Ba–Cu–O system Rare earth compounds	AA;F;L MS;laser;S MS;ICP;L	As for Ca Quantitative phase analysis of inhomogeneous oxide materials in the Y–Ba–Cu–O system using LIMS Isotope ratios <sup>207</sup> Pb: <sup>206</sup> Pb and <sup>208</sup> Pb: <sup>206</sup> Pb were measured by ICP-MS. The initial composition and origin of the samples by ‘fingerprint’ method was demonstrated	95/3832 96/1648 95/3553

**Table 3** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>CERAMICS AND REFRactories—</b>				
Pb	Ceramic glazes	XRF;—;S	Qualitative analysis of Pb by $^{109}\text{Cd}$ -induced XRF. For housewares Pb identification did not always correspond to Pb leachability	95/3869
Sc	Red mud	AE;ICP;L	Sample was fused with $\text{NaKCO}_3\text{--Na}_2\text{B}_4\text{O}_7$ at 1100 °C. 25 ml was passed through a Dowex 50W-X8 column. The eluate was extracted with 0.05 mol l <sup>-1</sup> di(2-ethylhexyl)phosphoric acid (pH = 0). Sc was stripped from the organic phase with NaOH	96/2875
Sr	Fly ash	XRF;—;S	As for Ba	96/1185
Ti	Silicon carbide	AE;ICP;S	As for Al	96/C2821
Th	Antimony(III) oxide	MS;ICP;L	Antimony matrix was removed by halide vaporization using HBr. Detection limit was 0.03 ng g <sup>-1</sup>	96/1534
U	Antimony(III) oxide	MS;ICP;L	As for Th. (Detection limit 0.02 ng g <sup>-1</sup> )	96/1534
Various (4)	Silicon carbide	AE;ICP;S	A modifier of $\text{CoF}_2\text{--BaO}$ (1:1) was used to decompose the SiC for the analysis of Al, Fe, Ti and V using ETV-ICP-MS	95/3433
Various (10)	Tantalum carbide/nitride	AE;ICP;L	The carbide was decomposed in $\text{HNO}_3\text{--H}_2\text{O}_2\text{--HF}$ mixture in a PTFE bomb and treated with $\text{H}_3\text{BO}_3$ . The nitride needed HF-H <sub>2</sub> O <sub>2</sub> and was treated with $\text{H}_3\text{BO}_3\text{--HNO}_3$ Ca, Co, Cr, Fe, Mg, Mn, Nb, Ti, W and Zr were determined	95/3438
Various (12)	Titanium oxide	AE;ICP;L	0.25 g sample was treated with 10 ml of $\text{H}_2\text{SO}_4$ and boiled. The cooled mixture was filtered and the residue ashed in a Pt crucible and dissolved in HF-HNO <sub>3</sub>	95/3439
Various (36)	Silicon carbide	MS;ICP;L	Dissolution was achieved by $\text{HNO}_3\text{--H}_2\text{SO}_4\text{--HF}$ mixture. For all 36 elements the detection limits were improved with matrix removal by evaporation of the dissolved solution	95/3554
Various (14)	Yttrium oxide	MS;ICP;L	Fourteen rare earth impurities were determined. Detection limits were 0.003–0.02 ng ml <sup>-1</sup>	95/3566
Various (14)	Lutetium oxide	MS;ICP;L	Suppression of analyte signal was observed in the presence of the Lu matrix. This was overcome by the use of In as an internal standard. Recoveries were 90–103% and RSDs 1.4–4.2%	95/3617
Various (9)	Silicon nitride	AA;ETA;S	Silicon nitride powders were slurried in $\text{H}_2\text{O}$ . Ammonium dihydrogenphosphate-magnesium nitrate modifier and slurry were placed sequentially into the graphite tube. Radiotracers showed that Si was retained (80%) at 2200 °C but was removed at 2500 °C	95/3767
Various	Scandium oxide	AE;—;L	Hydroxylamine hydrochloride and carbon powder were used as buffers which improved the vaporization process of REE impurities upon chlorination	95/3787
Various (14)	Europium oxide	AE;ICP;L	Instrumental parameters optimized. Recoveries were between 88–112% and RSDs better than 11%	95/4245
Various	Boron nitride	AE;ICP;L	0.3 g sample decomposed with HF-HCl mixture at 200 °C for 16 h. Remaining solid phase was treated with $\text{H}_2\text{SO}_4$ at 2300 °C for 16 h. (Detection limits ranged from 0.1 ppm Ca to 18 ppm Si)	95/4505
Various	Aluminium nitride	AE;ICP;L	0.3 g sample decomposed with 15 ml HCl in a PTFE pressure vessel at 200 °C for 24 h. (Detection limits ranged from 0.1 ppm for Ca to 4 ppm for Si)	95/4505
Various (14)	Yttrium oxide	AE;ICP;L	0.2 g sample was dissolved in HCl, evaporated to dryness then dissolved in 5% HCl. Detection limits were 0.0002–0.01% for REEs. Recoveries were 83–120% with RSDs 3.2–9.8%	95/4549
Various (4)	Silicon carbide	AE;ICP;S	Disposable graphite cups with $\text{PdCl}_2$ modifier used for determination of Al, Fe, Ti and V using ETV-ICP-AES	95/4593
Various (6)	Molybdenum metal	AA;ETA;S	Using a cup and boat method, contamination was considerably reduced. Cu, K, Mg, Mn, Na and Zn were determined with detection limits 0.06–4.5 ng g <sup>-1</sup>	95/4594
Various	Strontium titanate	MS;ICP;L	The sample was decomposed with HCl-HF mixture in PTFE pressure vessel. Au was used as an internal standard. Impurities in the $\text{SrTiO}_3$ at the sub $\mu\text{g ml}^{-1}$ level were detected	95/4634
Various (REE)	Rare earth oxides	MS;ICP;L	10 mg sample was heated with 50% $\text{HNO}_3$ . Internal standards (In, Rh, Cs and Rh) were added	96/366

**Table 3** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>SEMICONDUCTORS—</b>				
Various	Superconductors	AE;ICP;L	Carrier gas flow was shown to be critical in lowering detection limits for alkaline earth analyses	96/371
Various (4)	Slag cements	XRF;—;S	A double briquetting technique with correction constants was used to improve accuracy for both enhancement and absorption effects. Al, Ca, Mg and Si were determined	96/1169
Various (4)	Lanthanum oxide	AE;DCP;L	0.1 g was dissolved in 5 ml HCl and 5 ml Li solution ( $40 \text{ g l}^{-1}$ ) was added. (Ce, Nd, Pr, and Sm determined with detection limits of 0.012, 0.021, 0.012 and $0.009 \mu\text{g ml}^{-1}$ , respectively)	96/1326
Various (6)	Cement	AA;—;L	Samples fused with oxalic acid– $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_2\text{CO}_3$ at $925^\circ\text{C}$ in Pt crucible and then dissolved in HCl. (Al, Fe, K, Na, Si and Ti were determined)	96/1283
Various	Europium oxide	MS;ICP;L	Sample solutions were prepared containing $1 \text{ g l}^{-1}$ Eu and $10 \mu\text{g l}^{-1}$ internal standard ( $^{155}\text{In}$ for lighter REEs and $^{205}\text{Tl}$ for heavier REEs)	96/1502
Various (8)	Gadolinium oxide	MS;spark;L	Samples were analysed for Ce, Ho, La, Lu, Pr, Tb, Tm and Y by isotope dilution–SSMS. (Recoveries were 85–114% and RSDs 4–21%)	96/1566
Various (10)	Silicon carbide	AE;ICP;L	A mixture of $\text{Na}_2\text{O}_2$ and $\text{LiBO}_2$ in conjunction with microwave digestion was used. Problems with Ni contamination were encountered. (Al, Cu, Cr, Fe, Mg, Mn, Ni, Ti, V and Zn determined)	96/C2046
Various	Solid oxide fuel cells	MS;ICP;S	Direct analysis using LA-ICP-MS. Due to lack of standards a stoichiometric mixture of high purity $\text{La}_2(\text{CO}_3)_3$ , $\text{SrCO}_3$ , $\text{MnO}_2$ and ultrapure graphite was prepared	96/C2125
Various (14)	Aluminium oxide	MS;ICP;L	Samples were decomposed by pressure digestion with HCl. B, Ba, Co, Cu, Ga, La, Ni, Ti, Zn and Zr were determined in low resolution. $^{52}\text{Cr}$ , $^{56}\text{Fe}$ , $^{69}\text{Ga}$ and $^{55}\text{Mn}$ determinations were performed using high resolution ( $m/\Delta m = 3000$ )	96/C2221
Various (50)	Ceramics	MS;ICP;L	High-pressure microwave digestion with HF– $\text{HNO}_3$ mixture was used. Data for 23 elements was plotted against INAA concentrations. Correlation coefficients were >90%	96/2323
Various (8)	Zeolites	AE;ICP;S	Freon-12 was used as a gas-phase halogenation reagent to stop carbide formation in ETV-ICP-MS determination of Ca, Cd, Cu, Mn, Pb, Ti, V and Zn	96/2503
Various (13)	Europium oxide	MS;ICP;L	Severe interferences observed at matrix concentrations above $1 \text{ mg ml}^{-1}$ . Tm was not quantified due to $^{153}\text{Eu}^{16}\text{O}^+$ spectral interference	96/C2837
Various (9)	Ceramics	AE;ICP or flame;L	Powdered samples were fused with $\text{LiBO}_4$ in graphite crucibles at $1100^\circ\text{C}$ for 30 min and then dissolved in 10% $\text{HNO}_3$ . K and Na were determined by FAES	96/2876
Various	Zirconium dioxide	AA;ETA;S	For Ca, Fe or Na the slurry was diluted 100-fold while for Al, Cd and Si, modifiers ( $\text{H}_2\text{BO}_3$ –HF, diammonium hydrogenphosphate–magnesium nitrate and calcium nitrate, respectively) were added	96/2955
<b>CATALYSTS—</b>				
Mo	Activated carbon	XPS;S and SIMS;S	Surface and bulk structure determined by XPS, TOF-SIMS and XRD. TOF-SIMS and XPS valence bands showed presence of polymeric Mo species	96/2314
Noble metals	Catalyst film on C electrodes	XRF	Samples of predetermined size irradiated and analysed by XRF	96/2666
Pb	Auto catalysts	MS;ICP;L	Samples digested using $\text{HNO}_3$ , HCl, HF and $\text{HClO}_4$ in PTFE beakers on a hotplate	96/1497
Pd	Auto catalysts	MS;ICP;L	Samples digested using HCl– $\text{HNO}_3$ in Carius tubes and undissolved residues treated with HF. Final analysis by ID-ICP-MS	96/1497
Pd	Spent catalysts	AE;MIP;L	For surface and sludge determinations $2\text{--}2.5 \text{ mol l}^{-1}$ HCl extraction was used. For solid samples, a mixture of HCl– $\text{HNO}_3$ plus $\text{HClO}_4$ , under pressure at $120^\circ\text{C}$ , was required (PTFE vessel)	96/2027
Pt	Auto catalysts	MS;ICP;L	As for Pd	96/1497
Rh	Auto catalysts	MS;ICP;L	As for Pd	96/1497
V	Cracking catalysts	SIMS;S	Measurement of distribution of V on composite catalyst particles. Results consistent with cracking activity data	95/3712

**Table 3** (continued)

Element	Matrix	Technique; atomization; analyte form*	Sample treatment/comments	Reference
<b>CATALYSTS—</b>				
W Various	W- $\gamma$ -Al <sub>2</sub> O <sub>3</sub> Platinum catalyst	EPMA;S AE;ICP;L	Determination of W concentration depth profile 250 mg sample dissolved in 10% HCl. Y added as internal standard	96/982 95/3624
Various	Catalysts	AA;F;L	Microwave assisted digestion using HNO <sub>3</sub> -HF. Fluoroboric acid (60% v/v) added to final solutions	95/3650
Various	Ni-Mo catalysts	AE;ICP;L	Comparison of H <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> and HClO <sub>4</sub> micro-wave digestion methods. All mixtures gave similar results	95/3884
Various	Catalysts	SIMS;S	Review (182 refs.). Applications of SIMS in catalyst analysis. Comments on phenomena such as sputtering and ionization	95/4618
Various	Catalysts	SIMS;S	Review. Use of various post-ionization techniques to reduce matrix effects and to increase sensitivity for surface analyses	96/2346

\* HG indicates hydride generation and S, L, G and SL signify solid, liquid, gaseous or slurry sample introduction, respectively. Other abbreviations are listed elsewhere.

*On-line process control by XRF* methods are also popular, with reports of automated system control (96/1224) and on-stream XRF analysers (96/2605).

The characterization of *high temperature superconductor* (HTSC) materials, both for elemental content and surface/interface properties has become a major application for spectroscopists (96/4108). Depth profiling by SNMS (96/1768) and studies of the binding energies of various components in Bi-based cuprate superconductors, *e.g.*, Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+δ</sub>, by SIMS (96/4123) have been reported. In the latter report, results were compared with those of similar measurements of BiO<sub>3</sub>, CuO and CaCO<sub>3</sub> samples to ascertain detailed information on the surface binding energies for these compounds. ICP-AES has been used for the analysis of high temperature superconductors (96/371). If the sample carrier gas flow was optimized for the analysis of alkali metals, detection limits of  $1 \times 10^{-3}$ – $9.7 \times 10^{-4}$  with respect to the dissolved solid could be achieved.

*Laser ablation* as a means of solid sampling for atomic spectrometry has the potential to be universally applied to all materials of the ceramic or refractory type. *Laser-induced vaporization-mass spectrometry* (LIMS) has been used to measure the vapour pressure of refractory materials, especially for various U-O vapour species (96/2428). The total vapour pressure at 4300 K was deduced to be 3.9 atm. LIMS has also been used to study the oxide phases in the Y-Ba-Cu-O system (96/1648). The formation of polynuclear ions (clusters) as a result of the laser sputtering of oxides was examined and from this it was possible to carry out quantitative analysis of inhomogeneous oxide materials. Lasers (under various guises and couplings) have also been used for fundamental studies, such as to identify ablation products from (BC<sub>2</sub>N)<sub>n</sub> materials (96/4124), to characterize charged species from Pb(Ti<sub>0.48</sub>Zr<sub>0.52</sub>)<sub>3</sub> targets (96/1628), to prove the existence of Rydberg state atoms (96/2415) and finally to study the synthesis of lanthanide oxide clusters (96/1629).

### 3.5. Catalysts

As has been shown by previous ASU reviews, *secondary ion mass spectrometry* has been, and continues to be, the most popular analytical tool for the analysis and characterization of industrial catalytic materials. This year, the strength of the technique in this area has been underlined by the publication of a comprehensive review (182 references) by Borg and Niemantsverdriet (95/4618). Technical details such as sputtering, ion emission, ionization and neutralization was discussed.

The application of SIMS to gain information about catalytic interactions with gas promoters and poisons was also described, as well as surface reactivity studies, adsorption and surface reactions. This last, and extremely important, aspect of catalytic functionality has also been addressed by Cherepin (96/2346). The author provides an overview of progress in instrumentation and ion formation, with particular emphasis on the sensitivity and lateral and depth resolution capabilities of various post-ionization techniques, such as electron beam, plasma and multiphoton ionization (resonant and non-resonant). In a more specific paper Chao *et al.* (95/3712) used SIMS to study *vanadium passivation* on composite cracking catalyst particles comprising REE exchanged zeolite mixed with calcium-exchanged clay. The results obtained were consistent with cracking activity data and show that vanadium preferentially accumulated on the clay material.

A wide range of techniques has been utilized by Rondon *et al.* (96/2314), such as *X-ray diffraction*, *X-ray photon spectroscopy* and *time-of-flight SIMS* for the characterization of Mo-C catalysts. A series of Mo-C catalysts were prepared by adsorption of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O on to activated carbon. It was found that pH was the driving mechanism for Mo adsorption. Surface and bulk analysis of the Mo-C catalysts by XPS and XRD indicated the presence of a highly dispersed mono-layer-like Mo phase. ToFSIMS, however, showed that the catalysts contained polymer Mo species, which was consistent with the predicted speciation based on Mo solution chemistry.

Obtaining *concentration profiles in heterogeneous catalysts* has always been a problem for workers in this field. A technique using *electron-probe microanalysis* has been developed by Viturro *et al.* (96/982) for measuring the W concentration on rough spherical material of a W- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support catalyst. Using a large number of experimental points, accurate information about the depth profiles of W could be obtained in a short time. The workers discuss the possibility of the technique being extended to metallurgical and mineralogical materials.

As in other sectors of analytical chemistry the utilization of *microwave digestion* techniques for the dissolution of catalytic materials continues to receive attention. Comparisons of different dissolution procedures continue to be popular. Ali (95/3884) has compared different acid media for the microwave digestion of Ni-Mo hydrotreating catalysts. It was found that H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> destroyed the matrix better than *aqua regia* and that Mo required higher power and longer exposure in order to be efficiently dissolved. A mixture of nitric and

hydrofluoric acids has also been used for the analysis of oil and petrochemical catalysts (95/3650). Elemental analysis of the resulting solutions was carried out using AAS, with greater than 96% recoveries for a variety of elements being reported.

The accurate analysis of precious metals and contaminants in auto-catalysts continues to attract attention (96/1497). A mixture of  $\text{HNO}_3$ ,  $\text{HCl}$ , HF and  $\text{HClO}_4$  was used to analyse for Pb by isotope dilution ICP-MS. Pt and Pd were also

determined using ID-ICP-MS but after a  $\text{HCl}-\text{HNO}_3$  dissolution in Caruis tubes. Rh was quantified using In internal standardization. Correction had to be made for mass bias, drift of mass bias and relative sensitivity factors. A round-up of other noble group determinations include analysis of Pd in spent catalysts by MIP-AES (96/2027), Pd and Rh (plus 11 other elements) in platinum catalysts by ICP-AES after HCl dissolution (95/3624) and Pt and Ru in catalyst film on carbon electrodes by XRF (96/2666).

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Abbreviated forms of the literature references quoted (excluding those to Conference Proceedings) are given on the following pages for the convenience of the readers. The full references, names and addresses of the authors and details of the Conference presentations can be found in the appropriate issues of *JAAS* cited above.

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