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Atomic spectrometry update. Industrial analysis: metals, chemicals and advanced materials

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This Atomic Spectrometry Update is the latest in an annual series[1] under the title 'Industrial Analysis'. The writing team has remained unchanged this year, although the writing duties have been re-arranged slightly. The general structure of the review is fundamentally the same as in previous years, but in an attempt to keep the review focussed on atomic spectrometry, there have been a few omissions. Included in these omissions are numerous papers that have described the derivatization of a commercial resin with an organic functional group, so that analytes may be pre-concentrated and/or separated from the matrix. Although the chemistry is interesting in such papers, it was thought that this does not really count as being analysis of an organic chemical nor, in most cases, was it a serious advance in knowledge of atomic spectrometry. The use of SIMS as a depth-profiling tool is still extremely common. Many papers however give little detail on the atomic spectroscopy side and inclusion of all the papers would lead to an enormous number of references whilst adding very little in the way of detail. Therefore, only a few papers have been chosen to give the reader a taste of what research is being performed.

The use of LIBS appears to be gaining popularity, especially in the area of metals analysis, although applications for polymers, ceramics and semi-conductors have also appeared.

Much of the methodology reported in the organics section, is similar to that described in previous reviews with only relatively minor tweaks but in some areas, e.g. oils, the introduction of more advanced techniques have been reported. This is a function of the more ambitious analyses being performed requiring more imaginative techniques to be employed to ensure success.

1 Metals

1.1 Ferrous metals and alloys

Interest continues in the application of laser induced breakdown spectrometry (LIBS). Improvements in the figures of merit for the determination of C in steel were reported using a vacuum ultraviolet detector system (40–160 nm) for the pulsed laser emissions.[2] A fast scanning LIBS instrument was used to characterize non-metallic inclusions in steels.[3] High peak intensities for single elements correlated with the location of specific inclusion types. The same system was applied by Kuss *et al.* to depth profiling and ablation of metals.[4]

Minor elements in steels (Mo, Nb, Si and Ti) were determined by LIBS.[5] A long-term precision of 5% RSD (relative standard deviation) was observed for these elements. Thin films produced by pulse laser deposition were analyzed using LIBS.[6] The single laser shot emission intensities detected from the films were 16 times higher than emissions from the equivalent bulk material. The authors concluded that the ablation process from films is more efficient than from the bulk. Beddows and co-workers have determined the analytes Cr, Mn and Si in steel under water by single-pulse LIBS using a single fibre light delivery system.[7] A 20 inch probe delivered a buffer gas (Ar, N_2 or air) to the sample surface during analysis and transmitted both the laser light pulse and the emitted light. Analytical figures of merit were similar for samples in air and under water. The application of LIBS to element determination in high temperature steel pipes in real-time plant operation has been studied by Bulajic *et al.*[8] Simulations were constructed to predict problems with pipe steels and the laser head was designed to overcome problems related to high temperature and vibration. Accuracy was verified through the analysis of steel reference materials.

LIBS has proved to be useful in studying other laser-based techniques. The effect of laser de-focusing for laser ablation (LA) ICP-AES was studied using LIBS.[9] It appears that Fe emission increases initially but then decreases as the laser was de-focused (as the surface is ablated). The material parameters such as texture, hardness, conductivity, and heat capacity were

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found to influence the amount of material ablated. The application of internal standards to the analysis of low alloy steel by LA-ICP-MS was studied by Ohata by comparing Fe^+ ion, Ni^+ ion and Fe emission from laser induced plasma emission.[10] In general, using the matrix ions Fe^+ and Ni^+ as internal standards resulted in better precision than when Fe emission intensity was used. Using Ni^+ ion as an internal standard also yielded a better correlation coefficient for the calibration than did the other two internal standards.

The determination of C and N by spark atomic emission spectrometry was compared with the traditional combustion methods with infrared detection.[11] The spark emission method is slightly faster than the combustion method and has comparable limits of detection (1 and 4.5 $\mu g\ g^{-1}$ for C and N, respectively). The precision was reported to be $\pm 1\ \mu g\ g^{-1}$ at 25 $\mu g\ g^{-1}$ for C and N. Kuss and co-workers studied inclusions in steel using three different spark optical emission spectrometers.[12] The data distribution was examined and two procedures were developed to correlate the effect of inclusion concentration to the size of partial area of the inclusions.

Radiofrequency glow discharge atomic emission spectrometry (RF-GD-AES) with bias-current introduction was used by Wagatsuma to determine Sn in steels.[13] The 317.504 nm Sn atom line was used, but overlap with a weak iron ion line prevented the calibration from passing through the origin. Nevertheless, the detection limit was estimated to be 0.01%. In another report, the distribution of H in electroplated coatings for steel was determined by GD-AES.[14] The results provide enough information to point to process changes and test procedures so that hydrogen embrittlement can be avoided.

Direct helium glow discharge mass spectrometry (GD-MS) was used by Itoh and co-workers to determine 15 analytes in steel.[15] The relative sensitivity factors were calculated from elements in a variety of steel reference materials. The concentration values obtained from various steel samples by GD-MS were in agreement with values obtained by X-ray fluorescence (XRF) spectrometry.

Coedo *et al.* determined both major and minor elements in ferro-titanium, ferro-niobium and ferro-vanadium by XRF spectrometry.[16] The RSD for Fe in pressed pellets varied from 0.17% to 0.22% for the three alloys. For samples prepared as fused beads the RSDs varied from 0.13% to 0.16%. Minor elements were determined with RSDs of below 3% for fused beads and below 5% for pressed pellets being obtained.

Secondary ion mass spectrometry (SIMS) continues to be reported to be a valuable tool for qualitative assessment of metal surfaces. SIMS was used to examine the depth profiles of N in plasma implanted stainless steel.[17] A more accurate measure of N was reported to be obtained by normalizing the N signal to the combined Fe, Cr and Ni signals. Implanted Ti was measured in stainless steel alloys and duralumin by SIMS and by Rutherford backscattering spectrometry (RBS).[18] In a paper by Rosner *et al.*, the spatial distribution of non-metallic impurities in steel was determined by 2- and 3-dimensional SIMS.[19] In another report, O penetration into Fe–Si–Mn alloys was studied by SIMS and XPS (X-ray photoelectron spectrometry).[20]

Merson and Evans have reported a solution method for ICP-AES that enables accurate (within ±1% relative) determinations of minor elements in steels.[21] Gold was used as an internal standard to correct for instrument drift and the iron and acid content of both samples and calibration solutions were closely matched. The method was reported as being ideally suited to the production of reference materials. In a paper written in Japanese, Cu was determined in dissolved steel by gas phase sample introduction when the sample was treated with citric acid.[22] A gas–liquid separator with a flowing argon stream was used to transport the unidentified copper gas phase compound to the ICP-AES instrument. Iron and other elements depressed the analyte signal but these were removed by solvent extraction with diethyl ether. A limit of detection of 1.5 ng mL^{-1} was reported.

Ammonia was used by Liu and Jiang as the reaction cell gas within a dynamic reaction cell ICP-MS to determine Si in steel.[23] The intensities of the interfering ions $^{12}C^{16}O^+$ and $^{14}N_2{}^+$ at the Si *m*/*z* 28 were reduced substantially for the dissolved sample. The signal to background ratio (SBR) was improved by more than one order of magnitude. The limit of detection was reported to be 2 $\mu g\ g^{-1}$ and accuracy was assessed using reference materials and was found to be within ±3%.

Flame atomic absorption spectrometry (FAAS) continues to be used for solution analysis with on-line pre-concentration and matrix separation. Cobalt was determined in steel by pre-concentration with 1-nitroso-2-naphthol adsorbed onto a C_{18} microcolumn in a flow injection manifold.[24] The acidified sample solution (0.1% nitric acid) was adjusted to pH 3 to pass through the column. The Co was eluted with ethanol (acidified to 1% nitric acid) into the nebulizer of the FAAS instrument. A precision of 1.6% RSD for 100 $\mu g\ L^{-1}$ was reported for ten replicates. A similar approach was used by Dadfarnia *et al.* for the determination of Cu in stainless steel, by using immobilized 1,5-diphenylcarbazone with flow injection FAAS.[25] A small volume of dilute hydrobromic acid was used for elution. The precision was reported to be 3.5% RSD for a 10 $\mu g\ L^{-1}$ solution.

1.2 Non-ferrous metals and alloys

Reports of LIBS being used for the analysis of non-ferrous metals showed a breadth of applications. There were two reports of LIBS being used for the analysis of archaeological metals and alloys.[26,27] These reports included qualitative, semi-quantitative, and quantitative analysis of a variety of materials. One paper indicated that LIBS demonstrated the potential for routine, rapid, on-site analysis.[26] Molten aluminium alloys were characterized by fibre optic probe LIBS in two reports from the same group.[28,29] The probe was 200 cm long and was inserted directly into the melt. Minor components, such Cr, Cu, Mg, Si and Zn, were determined, calibration being against solid standards. Iron was used as a reference element which was also ratiod to the major component, aluminium. An alternate hall-marking technique for jewellery using LIBS with partial least squares calibration was examined and compared with FAAS, ICP-AES and atomic scanning microscopy.[30] Calibration used 17 gold alloys and 8 silver alloys that included other elements normally found in jewellery. The analysis of gold and silver alloys by LIBS yielded results that were comparable to the official method. LIBS was also used to determine the layer thickness and composition of plated jewellery.[31] This was accomplished by monitoring the emission lines of elements as the piece was subjected to many laser shots and calculating the depth profile of the sample as the laser shots bore through the sample. The quantitative analysis of cobalt–chromium alloy wear particles from artificial knee joints using LIBS has been reported by Mokhbat and Hahn.[32] Particles ranged in size from 200 to 800 nm and emission signals could be correlated to masses for cobalt and chromium in individual particles.

Energy dispersive XRF (EDXRF) was used to analyze ancient copper coins[33] for Cu and trace elements (Pb, Sb, Sn and Zn). Silver and copper were determined in ancient silver coins by EDXRF.[34] The iron content of a special Zn–Fe coating on zinc–iron alloys has been determined by Hong and Kwon using XRF.[35] This coating was produced by annealing zinc coated steel, where iron and zinc inter-diffuse, forming a coating. The determination was accomplished by comparing the difference in probing depth of the Zn Kα and Zn Lα lines to differentiate between iron in the coating and iron in the alloy. The coating coverage was determined to an accuracy of ± 0.57 g m^{-2}.

The dissolution and passivation of a 70 : 30 cupronickel alloy in 0.5 M NaCl was studied using a variety of X-ray methods.[36] X-ray diffraction (XRD) was used to identify the compounds formed and X-ray photoelectron spectroscopy (XPS) studies examined the corrosion film composition covering the surface. XRF was used to determine the Cu and Ni content in corrosion film.

Using X-ray absorption near edge spectroscopy (XANES), Matsuo and co-workers showed that gold nanoparticles were formed from Au(III) complexes adsorbed onto titania and alumina without the addition of a specific reducing agent.[37] The technique was capable of obtaining spectra from particles of less than 1 nm in size.

A number of studies used several analytical methods to investigate or characterize a metal or alloy. Manasse and Mellini have used XRF, XRD and scanning electron microscopy with EDXRF to study slags from an ancient smelter site in Italy.[38] Hydrogen embrittlement of Sn–Al alloys in contact with water vapour was investigated by using XRF, XRD and SIMS.[39] It was found that the brittleness was caused by a failure of phase adhesion due to accumulation of hydrogen and the formation of oxidized layers on phase boundaries during contact of the alloy with water vapour. Evidence of metallic clusters of copper and silver nanoparticles in lustre coatings in ancient paintings were found by the use of XRD, SEM-EDXRF, electrothermal atomization-AAS (ETAAS), and inductively coupled plasma atomic emission spectrometry (ICP-AES).[40] Tinplate specimens used for food cans were characterized by using a wide variety of techniques including AAS, EDXRF and XPS.[41] Using this assortment of techniques, it was possible to quantify the Cr content in terms of "total Cr", metallic Cr and chromium oxide. One overview article, by Sudersanan, reviewed the role of analytical instrumentation for the characterization of high purity metals and other advanced materials used in the manufacture of electronics, solar energy conversion devices, superconductors, and shape memory alloys.[42]

Solid sample analysis continues to be examined by mass spectrometric techniques. The development of single shot LA-ICP-TOFMS (time of flight mass spectrometry) for the rapid identification of alloys was reported by Leach and Hieftje.[43] Good accuracy was reported for elements greater than 0.1%. Cluster analysis was used to classify alloys based on the concentrations of 15 elements. Validation was achieved using 18 standard materials and a 93% success rate was achieved for the identification using cluster analysis. It was reported that samples up to 500 mm in length and as low as one milligram in weight could be analyzed.

Sample preparation for the analysis of copper-based alloys by GD-MS was studied and a paper published in Japanese by Itoh *et al.*[44] The different methods were dry belt grinding (with alumina, corundum, and zirconia), specular grinding with alumina paste, and etching with nitric acid. The specular grinding method was deemed the most suitable because stable ion beam ratios were obtained in the shortest time. Chlorine was determined by GD-MS in Zr–2.5Nb alloys[45] using the ^{35}Cl isotope. Chlorine was first determined in a zirconium standard by a turbidity method and then used to set the relative sensitivity factor for GD-MS. The Cl concentrations determined in the Zr–Nb alloy by GD-MS were in agreement with values obtained by ion chromatography.

Work continues to be done with less common surface spectrometric techniques. Proton induced X-ray emission spectrometry (PIXE) is a non-destructive technique that was used by Enguita and co-workers to characterize the composition of ancient metallic threads and then to distinguish those made from homogeneous alloys from those made from a silver–copper alloy and coated with a thin gold layer.[46] PIXE was also used to study the elemental composition of old cast iron pots in an attempt to determine the origin of these artifacts.[47] The results of an inter-laboratory comparison of XPS data obtained with stainless steel have been presented.[48] The best results were obtained after removal of the chromium rich oxide layer on the sample surface. Concentration values determined for Cr, Fe and Ni agreed with the values obtained by EDXRF. Reports continue on the use of SIMS for the analysis of aluminium alloys,[49] ancient bronze materials[50] and tarnished silver.[51] McIntyre and co-workers used SIMS image depth profiles of a nickel alloy to determine the trace element distributions both within and outside of grain boundaries.[52]

The use of ICP-AES has been reported for a few solution applications. Several different iridium–aluminium alloys were analyzed quantitatively by fusing the sample with NaOH and Na_2O_2 and then dissolving it in water.[53] The fusion was done in a zirconium crucible and this fusion recipe minimized the amount of zirconium fused with the sample. ICP-AES was used in the forensic analysis of lead bullets.[54] Concentrations of seven elements (Ag, As, Bi, Cd, Cu, Sb and Sn) were determined to distinguish lead from different manufacturers. In another forensic based report, Suzuki *et al.* determined five trace elements in lead–tin solder by solution ICP-AES.[55] A 10 mg sample was dissolved in 1 mL HNO_3 followed by the addition of 1 mL HCl and 2 mL water and, upon dissolution, the volume was brought to 10 mL with water. Different solder types could be distinguished and accuracy was verified by using a reference material. Harmse and McCrindle used ICP-AES to determine Sb in lead–antimony alloys using Cd as an internal standard because it has a wavelength close to the selected antimony line and has a similar ionization potential.[56] Reference materials were used to verify accuracy. Day to day repeatability was reported to be $\pm 1.4\%$ (w/w) and a within day repeatability of $\pm 0.016\%$ was observed.

There have been a number of reports on isotopic composition and/or atomic weight measurements using ICP-MS in metals such as zinc,[57] samarium[58] and tin.[59]

Using a transversely heated graphite furnace and a sample boat, Dong and Krivan determined Si in titanium by solid sampling ETAAS.[60] Carbon powder and Pd–$Mg(NO_3)_2$ were used as modifiers. Aqueous calibration standards were used, by pipetting onto the residue of the previous sample. Amounts of up to 6 mg of sample could be handled by the method and a limit of detection of 30 ng g^{-1} was reported. Trace levels of Ag, Au, Cd and Pb in zinc samples were determined by atomic absorption spectrometry using matrix separation-pre-concentration with an Amberlite XAD-16 adsorption column.[61] The analytes were eluted by a solution of 1 M HCl and 0.3 M NaCl. Recoveries greater than 95% were reported. In another report, Cu(II) and Fe(III) were determined in zinc by selective adsorption on to Eporous AS-4 (an arsenic selective chelating resin) and measurement by FAAS.[62] The distribution coefficients of 8 metal ions on this chelating resin as a function of hydrochloric acid concentration were reported to be higher than the distribution coefficients of other chelating resins under the same batch conditions. Analyses of metals are summarized in Table 1.

2 Chemicals

2.1 Petroleum and petroleum products

2.1.1 Petroleum products. There has been an increase in papers related to petroleum product analysis ranging from trace metals in gasoline, ethanol and naphtha, to on-line analysis of exhaust gas and natural gas. Part per billion levels of trace elements in various process streams and products are undesirable since they can either foul up processes or create problems when present in the final fuel, contributing to engine deposit formation. For ethanol, which can be used as an octane boost, there is a strong possibility that the trace metal content will be part of the EU specification on the product.

Table 1 Summary of analyses of metals

Element	Matrix	Technique; atomization; analyte form[a]	Sample treatment/comments	Reference
As and Sb	Steels and copper	AES;Hy-MIP;L	Thiourea was used as a pre-reductant to form As(III) and Sb(III) prior to hydride generation. Thiourea and L-ascorbic acid were also used to reduce Fe(III) to Fe(II), which does not suppress the analytical signal. In copper, thiourea was effective in reducing interference from the matrix. High power nitrogen MIP used	63
B	Steels	MS;ICP;L	The sample was dissolved in *aqua regia* and a ^{10}B spike added for quantitation by isotope dilution. The pH was adjusted to above 10 to precipitate most matrix elements. The solution was centrifuged and the supernatant was put through a cation exchange to complete the matrix separation	64
B	Tantalum	MS;ICP;L	The sample was dissolved in HF and/or HNO_3, then loaded onto a strongly basic anion exchange column using 0.1 M HF as a carrier. Ta and B were strongly retained by the column material and B was eluted directly into the ICP-MS with 5 M HCl. The elution time was up to 300 s. The limit of determination (10σ) was reported to be 30 ng g^{-1}	65
Bi	Lead and cadmium	AAS;FI-F;L	Bi was retained and pre-concentrated on a microcolumn packed with 2-mercaptobenzothiazole modified silica gel at pH 3.0. Bi(III) was eluted with a mixture containing 3 M $HClO_4$, 0.5 M $NaClO_4$ and 0.2 M $NaNO_3$ and directly introduced into the nebulizer. The LOD was reported as being 0.010 µg mL^{-1} when a 0.30 µg mL^{-1} Bi(III) solution was pre-concentrated for 60 s	66
Cu	High purity iron	AAS;ETA;L	A chelating agent for Cu(II) was made by dissolving 50 mg of 8-quinolinol and 0.15 mL of Span-80 (non-ionic surfactant) in 5 mL of toluene. The solution was mixed with 1.5 mL HCl by ultrasonic agitation for 15 s. The resulting emulsion (25 mL) was added to the dissolved sample and mixed for 5 min. Cu was extracted into the aqueous phase and determined by ETAAS	67
P	Steels	MS;LA-ICP;S	Minimal sample preparation was required. A low pressure helium ICP was used	68
P	Tantalum	MS;ICP;L	The dissolved sample was loaded onto an anion-exchange column and P was eluted with an HF–HNO_3 solution. The eluted solution was treated with bismuth and ammonium hydroxide precipitating both phosphate and bismuth hydroxide. The precipitates were captured on a filter, washed with water, P dissolved by hydrochloric acid, and presented to the ICP-MS instrument. An on-line manifold was designed for the above sample preparation. P was determined as a molecular ion of $^{31}P^{16}O^+$ (*m/z* 47). The LOD was reported to be 1.3 ng mL^{-1} and RSD was 4.3% for 30 ng P mL^{-1}	69
Se	Nickel based alloys	MS;FI-Hy-ICP;L	The dissolved sample was treated with thiourea and citric acid to reduce interferences from transition metals in generating SeH_2 in a flow injection manifold. Methane gas was used in a dynamic reaction cell to reduce argon dimer interferences for $^{78}Se^+$ and $^{80}Se^+$. The LOD was observed to be between 3 and 7 ng g^{-1}	70
Various (6)	High purity iron	AES;ICP;L	Iron (1 g) was dissolved in 150 mL 20% HCl with heat. Upon cooling, a 10 mL solution of ascorbic acid and cupferron was added to precipitate the trace elements (Mo, Nb, Ta, Ti, V and Zr). The precipitate was filtered and dissolved in 10 mL HNO_3 and 10 mL $HClO_4$. After evaporating to dryness, the salts were dissolved in HNO_3 and analyzed. Ultrasonic nebulization was used. LOD was reported to be in the range 0.03 ng mL^{-1}(Ti) to 1.0 ng mL^{-1}(Ta)	71
Various (4)	Aluminium	MS;ICP;L	Bi, Cu, Pb and Zn were separated by taking 1 mL of the dissolved sample in dilute HCl and depositing it on a mercury plated glassy-carbon electrode (surface area 2 cm^2) at -1.30 V *versus* SCE for 90 min. The analytes were released into 1 mL 0.1 M HNO_3 at 0.1 V *versus* SCE for 1 min, then determined by ICP-MS. The limit of determination (10σ) was reported to be 0.35, 0.18, 0.05, and 0.03 µg g^{-1} for Zn, Cu, Pb, and Bi, respectively	72
Various (10)	Aluminium	MS;FI-ICP;L	A flow injection manifold was designed to separate the analytes from the dissolved matrix and present them to the ICP-MS instrument. A 50 mg sample was dissolved in 6 mL of a buffered solution (2.64% NaOH + 0.91% KCl; pH = 13.4). A 500 µl aliquot was injected into the manifold and through a micro-column packed with Metalfix Chelamin and Hyphan Cellulose. The trace elements were retained on the column and back eluted with 200 µl of a 3 + 1 mixture of 1 M HCl and 1 M HNO_3 directly into the ICP-MS instrument. LOD was reported to be in the ng g^{-1} range	73
Various (3)	Ag–In–Sn alloys	AES;ICP;L	Dissolution of the alloy with HNO_3–HF enabled Ag and Sn to be kept in solution	74
Various	Aluminium–silicon–magnesium alloys	SIMS;-;S	SIMS was used to investigate the 3 dimensional distribution of alloying elements and trace elements in modified alloys	75

Table 1 Summary of analyses of metals (*continued*)

Element	Matrix	Technique; atomization; analyte form[a]	Sample treatment/comments	Reference
Various (3)	Nickel alloys and copper	AAS;FI-Hy;L	Analytes (Bi, Se, and Te) needed to be separated from the dissolved sample prior to generating the hydrides. Lanthanum hydroxide co-precipitation at pH 10 was used for Bi and Se. Cupferron and a phosphate buffer were used to chelate and extract Te from copper. Linear ranges were reported to 15, 10, and 12 ng mL^{-1} for BiH_3, SeH_2 and TeH_2, respectively	76
Various (13)	Gallium	AES;ICP;L AAS;ETA;L	Gallium was dissolved in HNO_3 and precipitated as GaF_3 with the addition of HF. Centrifuging completed the separation and the supernatant was analyzed. LODs were at ng g^{-1} levels	77
Various (4)	Powdered metal sample	AES;ICP;L	A polyacrylacylaminothiourea chelating fibre was made from an acrylonitrile based fibre (nitrilon) and aminothiourea. Au(III) Pt(IV), Pd(IV), and Ir(IV) were pre-concentrated and separated from the dissolved matrix on the chelating fibre. An enrichment factor of 100 was achieved. RSDs of 0.7–3% were reported for 20 ng mL^{-1} of the analytes	78

[a] Hy indicates hydride and S, L, G and Sl signify solid, liquid, gaseous or slurry sample introduction, respectively.

Botto[79] stated that elements such as As, Hg, Na, P, Pb and V, when present in petroleum naphtha feeds, are harmful to the petrochemical process used for ethylene production and to certain catalytic processes used in refining. The trace element species of concern may be as volatile as the hydrocarbon matrix itself, making sample introduction and analysis by plasma spectrometry a major challenge. The heavy end of the petroleum barrel presents a different challenge, as this material can foul many devices used for sample introduction. This paper described the use of direct injection nebulization (DIN) for introducing a wide range of petroleum hydrocarbon types into the ICP-MS instrument. DIN-ICP-MS has been proved to be a sensitive and rapid analysis technique for the determination of trace elements in petroleum including those in volatile forms. Initial operational problems have been largely overcome and instrumental drift has been minimized through the use of internal standards. Accuracy has been verified by comparisons with other techniques and with spiked samples.

On-line Hg speciation in exhaust gas by using solid-phase chemical reduction has been reported by Tao and Miller.[80] Speciation of mercury in exhaust gas from combustion sources is important for both the design of equipment for mercury pollution control and incinerator operation control. A simple, portable atomic absorption spectrometer was described that can monitor, in real time, the mercury species present in stack gas. A $SnCl_2$-loaded reduction column was used to convert Hg compounds to Hg atoms, which were then detected by atomic absorption spectrometry. The adoption of solid-phase reduction of the molecular species simplified the instrument design and made analysis easier. Results presented in this paper demonstrate the potential of the proposed method for field application.

Since mercury can be present in pockets of concentrations rather than a steady equilibrium, it has been thought for some time that the determination of Hg in natural gas may not always give the true picture. The wrong impression of a gas well may be obtained by collecting a batch of samples and analysing back in the laboratory. This view has been supported by the paper by Rhyzov *et al.*,[81] who have evaluated on-line measurements of the Hg content in natural gases using a newly developed Zeeman atomic absorption spectrometer. The variation in concentration of the Hg ranges from 10 to 80% of the average mercury content in the gas; this has not been widely understood or verified previously.

2.1.2 Fuel. As stipulated above, trace metals in fuels, except in the case of additives, are usually undesirable and they normally occur in very low concentrations in gasoline, thus requiring sensitive techniques for their determination. Gasoline is notoriously difficult to spray directly into a plasma. A paper by Saint-Pierre and co-workers[82] described how this may be overcome by coupling ETV with ICP-MS. The problem related to the introduction of organic solvents into the plasma is minimized by this approach; furthermore, sample preparation as oil-in-water emulsions reduces problems related to gasoline analysis. In this work, a method for the determination of Cu, Mn, Ni and Sn in gasoline is proposed. Samples were prepared by forming a 10-fold diluted emulsion with a surfactant (Triton X-100), after treatment with concentrated HNO_3. The sample emulsion was pre-concentrated in the graphite tube by repeated pipetting and drying. External calibration was used with aqueous standards in a purified gasoline emulsion. Six samples from different gas stations were analyzed, and the analyte concentrations were found to be in the μg L^{-1} range or below. The limits of detection were 0.22, 0.02, 0.38 and 0.03 μg L^{-1} for Cu, Mn, Ni and Sn, respectively.

Two papers, from the same source,[83,84] discussed the analysis of ethanol by GFAAS. The second paper included the use of a permanent modifier (W–Rh) in addition to the use of the conventional mixture of $Pd(NO_3)_2$ + $Mg(NO_3)_2$ as the chemical modifier. The following elements were determined: Al, As, Cu, Fe, Mn and Ni. The first paper investigated the thermal behaviour of the analytes during the pyrolysis and atomization stages using the chemical modifiers and two concentrations (0.028 mol L^{-1} and 0.14 mol L^{-1}) of HNO_3. In the second paper the effects of treating the integrated platform of a transversely heated graphite atomizer (THGA) with tungsten followed by rhodium, forming a deposit containing 250 μg W and 200 μg Rh, were determined. In general, the introduction of the permanently modified platform improved not only the detection limits but also the lifetime of the platform by a factor of two.

The fate of methylcyclopentadienyl manganese tricarbonyl (MMT) in gasoline is still a topic under discussion. This is an organomanganese compound that is used as an octane enhancer for gasoline and other fuels. The widespread use of this compound has been suggested to be harmful to human health. Two papers carry out detailed investigations, one in a comprehensive review on how to determine it and the other in characterizing the engine deposits from fuel containing MMT. To assess its impact accurately, high sensitivity instrumentation for the determination of MMT and its derivatives is required. In the paper by Butcher,[85] a review of the three instrumental approaches taken by other workers for this analysis was made. The techniques included high-performance liquid chromatography (HPLC) coupled to flame laser-excited atomic fluorescence spectrometry (LEAFS) to evaluate the organomanganese compound responsible for organ damage in rats following subcutaneous injection of this compound. Gas chromatography (GC) coupled to an alternating current plasma (ACP) detector for the determination of MMT in gasoline and fuel samples was also described. Finally, the determination of MMT in water, gasoline, and urine by HPLC with diode laser atomic absorption spectrometry (DLAAS) was also discussed. The paper compared the analytical capabilities of these three approaches. The combustion chamber deposits from a 1996 GM3800 engine operating using a base fuel or the base fuel containing the organometallic anti-knock MMT were examined by various techniques to identify the morphology and the bulk chemical composition.[86] Glow-discharge mass spectrometry and XRD analyses were used to characterize the bulk chemical composition and also the crystalline structure of the deposits. In addition, X-ray photoemission and X-ray photoabsorption spectra for the deposits were compared with spectra obtained from a series of Mn compounds in an attempt to model and aid quantification of the constituents. Results reveal a mixture of Ca–sulfate, Mn–phosphate and Mn–oxide in the bulk of the deposits and a mixture of Mn–sulfate, Mn–phosphate and Mn–oxide on the surface of the deposits.

Various analytical techniques have been employed for the analysis of coal and coal fly ash, the principal technique being ETAAS. Here, both single element and multi-element analysis have been of interest. Reviewing the single element analysis first, Moreda-Pineiro *et al.*[87] used factorial designs to optimise different procedures of Sn hydride generation coupled with ETAAS from aqueous and acidified slurries of marine sediment, soil, coal fly ash and coal samples. A batch mode generation system and Ir-treated graphite tubes were used for the HG and atomisation, respectively. Eight variables, affecting the generation of the hydride (hydrochloric acid and sodium tetrahydroborate concentrations, particle size, acid volume and argon flow rate), the hydride trapping efficiency (trapping temperature and trapping time) and the atomisation efficiency (atomisation temperature) were studied and optimised. In addition, acid pre-treatment procedures assisted by ultrasonic energy were used for soil and coal matrices to obtain acidified slurries and acid leachates. The variables optimized in this part of the study were hydrochloric and nitric acid concentrations, exposure time to ultrasound, particle size and leaching solution volume. Various reference materials were analyzed to assess the accuracy of the analysis under the optimized conditions.

The conditions required to determine Cr in fly ash by slurry-sampling ETAAS have been reported by Baralkiewicz *et al.*[88] Stability tests for slurries have been carried out using Triton X-100 as a stabilizing agent. The procedure was validated by the analysis of SRM 1633b. The results of the determination of Cr by slurry sampling ETAAS in three real fly ash samples from Poland (Szczecin area) and Canada (Sydney, Nova Scotia area) were compared with the results of these samples analyzed by a wet digestion method. The detection limit was calculated to be 0.077 mg kg^{-1} and the precision of measurements for the slurry sampling method was 3.5–5.2% RSD for SRM 1633b.

Cal-Prieto *et al.*[89] studied graphite tube and platform deterioration, *via* the direct determination of Sb in solid samples. In this work several factors were considered to evaluate their influence on the tube ageing. The most important of the factors was found to be the nature and amount of sample matrix introduced into the atomiser, *i.e.* the concomitants. Scanning electron microscopy and XRD analysis were employed to assess the L'vov platform degradation, not only regarding its morphology but the chemical nature of the deposits observed on it. Three modes of sample handling were studied: aqueous solutions, acid extracts and slurries. Changes in the useful lifetime of the tube were studied when analysing Sb in different matrices (soils, sediments, coals, coal fly ashes and slag) and empirical solutions were presented to expand the lifetime of the tube. Coal revealed itself to be the most difficult matrix to deal with and several slurry methodologies were assayed. Included in these were introduction of an oxidative step, external ashing, enlargement of the temperature program and two extracting media.

Quadrupole ICP-MS equipped with a dynamic reaction cell has been used for the accurate determination of Cu in coal fly ash samples in the presence of excess titanium, using the reaction of Cu^+ ions with NH_3.[90] The method eliminated the effect of polyatomic isobaric interferences caused by the formation of $^{47}Ti^{16}O^+$, $^{49}Ti^{16}O^+$ and $^{47}Ti^{18}O^+$ on $^{63}Cu^+$ and $^{65}Cu^+$ by detecting Cu^+ as the product cluster ion $Cu(NH_3)_2{}^+$. Because of the interference effect exerted by $^{97}Mo^+$, $^{65}Cu(NH_3)_2{}^+$ was detected at *m/z* 99. The method was applied to the determination of Cu in coal fly ash reference materials. The precision between sample replicates was better than 2.0% and the results were in good agreement with the certified values. The power of reaction cell technology was clearly demonstrated in this application.

A LIBS technique has been applied successfully to detecting the C content in fly ash, char and pulverized coal under high-pressure and high-temperature conditions. This resulted in an automated LIBS unit being developed, which was applied to the monitoring of an actual power plant.[91]

Three papers[92–94] reported analyses concerned with fluidised bed combustors. The first reported the determination of alkali concentrations in a realistic industrial flue gas by an *in-situ* laser spectroscopic method entitled excimer laser induced fragmentation fluorescence (ELIF). This investigated the effect of bed temperatures, rate of fuel supply and addition of various compounds on the alkali concentration. The paper by Miller and co-workers[93] used ICP-MS and ICP-AES to determine analytes emitted from the co-combustion of coal with biomass and waste secondary fuels relevant to commercial fluidized bed combustors. A novel, bench-scale, suspension-firing reactor was used to establish a ranking of retention of elements in combustion ashes. It also investigated the effects of varying the burn conditions. In the third of the papers,[94] Cd speciation in biomass fly ash samples from fluidised bed combustion was reported. The fly ash particles were size separated using a centrifugal SPLITT fractionation cell. The fractionation was evaluated by environmental SEM, which also provided indications of the associations between Cd and other main elements on the particles through the use of XRF mapping.

Over the years many papers reviewed have concerned themselves with the pollution aspects of burning coal, usually looking at the trace metal impact, in particular As, Ge, Hg, *etc.* Bettinelli and co-workers[95] report on the determination of Br, Cl, F and I in coals using ICP-MS and ion chromatography (IC). During coal combustion in thermal power plants without pollution control equipment, these analytes present in coals are mainly volatilized as gaseous compounds. There are regulations governing the amount of halogens that can be emitted. It is because of this, as well as the necessity to maintain control of emissions from combustion plants, that it is important to monitor the concentration of halogens in fuels. The literature available for published data with regard to the amount of halogens in fossil fuels is limited, which emphasizes the analytical difficulties with regard to the determination of these analytes. In this paper, a pyrohydrolysis of the sample at 1100 °C, followed by the absorption of volatilized compounds in $Na_2CO_3/NaHCO_3$ solution, and the final instrumental analysis of Br, Cl and F with IC and Br and I with ICP-MS, has been adopted. The accuracy of the method, evaluated by analyzing some CRMs, was better than 95% for all analytes.

To conclude this section, two papers reviewed made use of solid sample analysis, one using pressed pellets and the other fusion using a number of lithium compounds. The potential of LA-ICP-MS was investigated for the inorganic characterization of different coal samples pressed into pellets.[96] Two different LA-sampling procedures were compared. For continuous sampling, three sites of the pellet were sampled for approximately 1 min, whereas for sequential sampling 15 sites were sampled for 2 s, respectively. The qualitative results of the two procedures were equivalent, but continuous sampling allowed faster analysis and better precision (RSD about 10%) than sequential sampling (RSD 10–20%). Different normalization procedures with internal and extrinsic standards were investigated and allowed the quantitative determination of Al, Ni, Ti, V and Zn, with measurement uncertainties below 10%, and of Fe, Si, and Sn with measurement uncertainties below 20%. The results were compared with those obtained using traditional acid digestion methods. The use of fusion sample preparation methods for the analysis of powder-form specimens by radiofrequency glow discharge optical emission spectroscopy (RF-GD-OES) has been evaluated for the test case of coal ash samples.[97] The development of an elemental analysis technique for chemically complex coal ashes presents a challenge in terms of having simple sample preparation, providing accurate results and minimizing analysis time. The adopted sample preparation procedure for the coal specimens involved a standard fusion methodology. It was found that coal ashes prepared as glass disks using a mixture of lithium compounds (not listed in the abstract) as the host matrix and analyzed using rf-GD-OES provide good plasma stability. The evaluation of discharge operating parameters and the assessment of approaches to quantitative analysis were also investigated. It is believed that the general methodology holds promise for rf-GD analysis of a range of inorganic solids in powder form.

2.1.3 Oils. The papers in this review period concentrated on multi-element determination of wear metals using various techniques, some of which would be deemed quite sophisticated for this type of analysis. This is illustrated by Bings who used LA-ICP-TOFMS[98] to determine metals in lubricating oils. This method offered the advantage of having a simplified sample preparation technique without recourse to sample decomposition or sample dilution with organic solvents, even though a relatively complex matrix was analyzed. Two different calibration strategies were investigated and showed good agreement: external calibration based on the use of different standard oils and aqueous solution-based calibration. The analysis of SRM 1634b showed good accuracy for all the elements investigated (Ag, Al, Co, Cr, Cu, Fe, Mg, Ni, Pb and Ti). Detection limits were in the range from 0.5 ng g^{-1} (for Pb) to 28 ng g^{-1} (for Cr) and the precision was typically around 6% RSD. Good agreement with results obtained using conventional ICP-TOFMS after sample decomposition for both fresh and used lubricating oil samples demonstrated that direct LA-ICP-TOFMS is a rapid and powerful tool for the analysis of trace and wear metals in lubricating oil.

Toujou and co-workers have used TOF-SIMS to evaluate the effect of wear metals from spindle and bearings on lubricant degradation.[99] From the findings, the authors concluded that the wear metals and operating conditions have substantial influences on oil degradation and that this methodology is a useful tool to judge lubricant quality.

Continuing on the unusual approach to used oil analysis, a paper by Yang and colleagues[100] described the development of a simple, particle size-independent spectrometric method for the multi-element determination of wear metals in used engine oil. A small aliquot (0.5 ml) of an acid-digested oil sample was spotted onto a G 18 solid phase extraction disk to form a uniform thin film. The dried disk was then analyzed directly by EDXRF. This sample preparation route provided a homogeneous and reproducible sample surface to the instrument, thus overcoming the typical problems associated with uneven particle size distribution and sedimentation. As a result, the method provided improved precision and accuracy compared with conventional methods using X-rays. One other advantage this offered is that the disk sample may be stored and re-analyzed or extracted at a later date. The limits of detection for Fe, Cu, Zn, Pb, and Cr are 5, 1, 4, 2, and 4 μg g^{-1}, respectively. Recoveries of these elements from spiked oil samples ranged from 92 to 110%. The analysis of two standard reference materials and a used oil sample produced results comparable to those found by ICP-AES.

There seems to be a general increase in the use of EDXRF in the oil industry. This is possibly because of the improvements made in the capabilities of such instruments in recent years. The use of polarized X-rays has increased the performance of this technology. The reduction of background noise decreases the limits of detection by up to a factor 10. Detection limits (3 sigma) of 1 mg kg^{-1} are achievable for Cl and S. Modern-day instrumentation enables the simultaneous multi-element determination of the elements from Mg to U. Automatic matrix detection enables the quantitative analysis of waste or used oils with unknown water content and the high performance of the technique is proved by several applications.[101]

EDXRF was used to measure the concentration of heavy metals in soils, sediment and solid wastes (sludge and scales) around one of the major crude-oil production terminals south-south-west of the Niger Delta in Nigeria. Fourteen elements (Ba, Br, Ca, Cu, Fe, K, Mn, Ni, Pb, Rb, Sr, Ti, Zn and Zr) were determined and it was found that very high enrichment factors were obtained for Sr, Zr, Pb, Ba and Fe in all the samples. In addition, Ca, K and Mn were found to be elevated in the solid waste samples. The high enrichment factors for heavy metals obtained in the soil and sediment samples show that there is a considerable heavy metal pollution, which could be correlated with the crude-oil production industry.[102]

Sanz-Segundo *et al.*[103] reported on the use of differential pulse anodic stripping voltammetry (DPASV) for the simultaneous determination of three metallic ions, Cu(II), Pb(II) and Zn(II), in used marine lubricating oils. The DPASV was employed as an alternative to other analytical techniques. Samples of spiked unused oils were used to study several experimental conditions and instrumental parameters, as well as the formation of Cu–Zn intermetallic compounds. FAAS was used as a reference technique, with the results and comparative data being included in the report.

Duyck *et al.*[104] described a method for the determination of trace elements in crude oil by ICP-MS after sample dissolution in toluene and subsequent ultrasonic nebulization (USN). Carbon build-up at the interface and ion lenses was minimized by optimization of the argon to oxygen ratio in the plasma and by the desolvating action of the USN. The analyte addition technique, combined with internal standardization (using ^{115}In), was the only calibration procedure capable of correcting properly for signal suppression. This signal suppression was observed especially in solutions with higher concentrations of asphaltenes. Analytical curves with good linearity ($r^2 > 0.99$) were obtained, yielding solution detection limits (3 sigma) of less than or equal to 0.1 μg L^{-1} for Ba, Cd, Co, La, Mo, Ni, V and Y and in the range of 0.1–1 μg L^{-1} for Ag, Al, Fe, P, Sn, Sr, Ti and Zn. Method validation was performed by analyzing two CRMs, where an accuracy of within 10% of the certified value was obtained. Asphaltenes were separated from the oil bulk of crude oil samples from the Potiguar Basin (Brazil) using precipitation in heptane. The heptane-soluble fraction (maltenes) was separated by elution chromatography into three sub-fractions: (1) saturated and low molecular mass (MM) aromatics; (2) aromatics and low MM polar compounds; and (3) high MM polar compounds (resins). Trace elements were determined in these fractions after dissolution in toluene, by USN-ICP-MS. Mass balance calculations showed a significant increase of most elements (10–30 times) in the asphaltenic fraction, and in minor proportions in fraction 3, compared with the crude oil samples. Comparison with microwave-assisted acid decomposition showed good agreement, validating the proposed methodology and emphasizing its applicability for routine analysis of crude oil and other toluene soluble petroleum products.

2.2 Organic chemicals and solvents

2.2.1 Chemicals. The use of organic chemicals to derivatize resins has been dropped from this year's review because it was thought that although many of the papers were interesting, they neither involved the analysis of an organic chemical nor did they offer any advances in knowledge of atomic spectroscopy. Even with this large section removed from the review, there has still been plenty of interest in the analysis and introduction of organic chemicals to atomic spectroscopic instrumentation.

The technique of *cloud point* pre-concentration has become extremely popular in this review period. A review of micelle mediated and cloud point extraction had been presented by Stalikas, who also gave an account of the fundamentals of micellar solutions and their solubilization capabilities.[105] Manzoori and co-workers have been great exponents of this technique, in that they have published four papers. In two papers, Cu[106] and Cd and Pb[107] were determined in hair samples. *O,O*-Diethyldithiophosphate was used as the hydrophobic ligand in both papers, but for the Cu determination Triton X-100 and for Cd and Pb Triton X-114 was used as the non-ionic surfactant. After phase separation at 40 °C and dilution of the surfactant rich phase, the analytes were determined using FAAS. The technique gave an enhancement factor of 22 and 43 for Cd and Pb, respectively, giving LODs of 0.62, 0.94 and 2.86 ng mL^{-1} for Cd, Cu and Pb, respectively. For Cu, the recovery was found to be in the range 97–101%. In another paper, Triton X-114 was used with 1-(2-pyridylazo)-2-naphthol (PAN) to pre-concentrate Co from urine samples prior to determination using FAAS.[108] The effect on the analytical signal of differing amounts of water in the methanolic surfactant solution was determined and was found to decrease markedly. The presence of 15 and 25% water decreased the signal by 30 and 52%, respectively. A 10 mL sample gave an enhancement factor of 115, yielding a LOD of 0.38 ng mL^{-1}. The final paper by this group determined Co and Ni in water samples, again with FAAS detection.[109] Polyethylene glycol–*p*-nonylphenyl ether (PONPE 7.5) and 1-nitroso-2-naphthol were used as the surfactant and hydrophobic ligand, yielding enhancement factors of 27 and 29 and LODs of 1.22 and 1.09 ng mL^{-1} for Co and Ni, respectively. The non-ionic surfactant PONPE 7.5 has been used by several other authors. Included in these are two papers by Ortega *et al.*, who determined Dy[110] and Gd[111] in urine using ICP-OES as the detection system. In both cases, the analyte was complexed with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (PADAP). After phase separation at 30 and 25 °C for Dy and Gd, respectively, the surfactant rich phase was retained at pH 9.2 on a micro-column packed with cotton. The analytes were then eluted using 4 M nitric acid at a flow rate of 1.5 mL min^{-1} directly into the nebulizer of the ICP-OES instrument. Enhancements of 50 (for Dy) and 20 (for Gd) were obtained, giving LODs of 30 and 40 ng L^{-1}, respectively. The Al content of parenteral solutions has been determined by Sombra and co-workers.[112] These authors also used PONPE 7.5 to extract the Al, giving a pre-concentration factor of 200. Using ICP-OES as the detection method, the LOD was 0.25 ng mL^{-1} and linearity was obtained up to at least 200 ng mL^{-1}. The same research group has also reported the determination of V in parenteral solutions.[113] On this occasion, the V was extracted as the V–PADAP complex at pH 3.7 into polyoxyethylene (5.0) nonylphenol (PONPE 5.0). The extracted surfactant rich phase (100 μL) was then mixed with ethanol (100 μL) and flow injected into an ICP-OES instrument for detection. An enrichment factor of 200 was achieved, giving a LOD of 16 ng L^{-1}. Precision at the 2 μg L^{-1} level was 2.3% RSD, and the calibration was linear to at least 5 μg L^{-1}. A cloud point method for the FAAS determination of free and organically complexed Cu species in natural waters has been presented.[114] The method was based on the neutralization of the electrostatic charge of the humate–metal complexes using a positively charged surfactant. The resulting complexes were then dissolved in the micelles of a non-ionic surfactant and were thus separated from the bulk aqueous phase. The free metal species were determined after complexation with a conventional chelating agent. The authors reported that the procedure was easy, rapid and free from interferences and enabled LODs of 8.5 and 0.9 ng mL^{-1} for bound and labile species to be obtained. The same authors also reported the speciation analysis of Fe^{II} and Fe^{III} using an on-line coupling of spectrophotometry and FAAS.[115] Both species were extracted as their APDC complex and then differentiation of the oxidation states was achieved by mathematical equations to overcome the interference of Fe^{III} in the spectrophotometric determination of Fe^{II}. The method was validated by analyzing the CRM IMEP-9, for which a recovery of 98.5% was obtained. Kulichenko *et al.* described the cloud point extraction of Cu using 1% non-ionic surfactant OP-10, 0.005 M capric acid and 0.01 M octylamine.[116]

Application of atomic spectroscopy in the *pharmaceutical* industry has shown a large increase of interest in this review period. Many of the papers are, however, simple applications and will only be dealt with briefly. A paper in Chinese described the determination of Bi in bismuth pectin, a drug used to protect the stomach mucous membrane.[117] The method of FI-HG-AAS was used, with parameters such as acidity of the sample solution and the reductant and the sodium hydroxide stabiliser concentrations optimised. The method was linear to 44 ng mL^{-1} and the LOD was 0.095 ng mL^{-1}. Lasztity and co-workers described a method by which Pd, Pt and Rh impurities were determined in pharmaceutical products.[118] Detection limits were 15, 2.8 and 2.5 ng g^{-1} for Pd in enalapril, Pt in calcium folinate and Rh in laevodopa, respectively. Breakdown products of NAMI-A, a Ru containing drug active against metastases, were determined by HPLC using a C_{18} column and a mobile phase of 0.5 mM sodium dodecylsulfate in 3% methanol at pH 2.5.[119] The UV traces were recorded and fractions of the eluate collected for off-line ETAAS measurement of Ru. The results indicated that all Ru containing compounds showed a peak in the chromatogram and that all Ru applied to the column was recovered quantitatively. Nuclear magnetic resonance identified one of the breakdown products as being the mono-hydroxy species of NAMI-A. The platinum anti-cancer drug ZD0473 was analyzed by HPLC-ICP-MS to determine its purity in oral and intra-venous dosing solutions.[120] In addition, Pt-containing metabolites in urine were also determined and the authors found that ^{14}C could be monitored in the carbon-14 labelled drug. The use of laser induced breakdown spectroscopy (LIBS) for the fast at-line assessment of the reliability of pharmaceutical manufacturing processes has been demonstrated.[121] The atomic line emission from an element present only in a particular component of the tablet, *e.g.*, P from the drug or Mg from the lubricant, enables the quantitative analysis of that component. The use of a carbon line as an internal standard was found to both improve the precision of the technique and to overcome a matrix effect. For drugs containing halogen atoms, the production of the plasma in a helium atmosphere increased sensitivity by a factor of 7–8. Different sample preparation methods have been compared for the analysis of active dry yeast.[122] Four different acid digestions, namely nitric, nitric–hydrochloric, nitric–sulfuric and nitric–perchloric were compared along with dry ashing using either magnesium nitrate or strontium chloride as ashing aids. Detection was by either FAAS (for Ca, Fe, Mg and Zn) or by AES (for K and Na). The authors then used a battery of chemometric processes to analyse the data obtained and concluded that Mg and Zn could be reliably determined by any one of the techniques. Since the amount of Mg added as the ashing aid would dwarf that found in the sample, this claim seems unlikely. However, for the analytes, the most reliable method was identified, and in all cases recovery was >95%. Coating thickness on tablets has been quantified in two papers. In one, the tablets were either acid digested or dry ashed and ICP-OES was used to determine Ti that was present in the coating.[123] The method was described as being accurate, precise and sensitive. In the other paper, LIBS was used as a rapid means of simultaneously determining the thickness and uniformity of an enteric coating on compressed tablets.[124] In this study, the core tablets contained large amounts of calcium, but the coating contained Mg, Si and Ti, all of which are excellent analytical targets for LIBS. The emission spectra of all four analytes were monitored simultaneously as the laser repeatedly interrogated the same spatial location. A profile of the spot was therefore obtained, with the Ca signal increasing and the Mg, Si and Ti signals decreasing as the laser sampled through the coating into the core tablet. By using different spots on the same tablet, an estimate of the uniformity of the coating thickness could be made. The technique could easily detect a change in coating application of less than 2% on a 100 mg tablet. The method was also very rapid, with 10 tablets analyzed in less than 15 min. Flores and co-workers have analyzed injectable drugs in two papers.[125,126] In the former paper, Sb^{III} and total Sb were determined by HG-AAS in drugs used for Leishmaniasis treatment. For Sb^{III}, citric acid (4% m/v), sodium tetrahydroborate (1% m/v) and a pre-reduction using 10% potassium iodide in 0.2% ascorbic acid, were used. For total Sb, sulfuric acid (0.5 M) and sodium tetrahydroborate (4% m/v) were used. Interference effects from As, Cu, Ni and Pb were assessed. The trivalent Sb corresponded to between 1.6 and 2.8% of the total Sb concentration and recovery was between 98.9 and 101.9%. The LOD was 1.5 ng absolute. In the other paper,[126] a similar approach was taken to determining total As in drugs containing high levels of Sb^V as *N*-methylglucamine antimonate. Sample was digested using *aqua regia* and then citric acid (10% m/v) was added. It was necessary to then leave the sample for 1 hour before the determination could be performed. No interference in As determination was observed in the presence of up to 1 mg of Sb^V, and the tolerance to Cu, Ni and Pb was again tested. Synchrotron radiation total reflectance X-ray fluorescence analysis (SR-TXRF) has been used to determine trace metals in drugs of abuse.[127] Sample solutions (1 µl) containing 10 µg of drug (either amphetamine, methamphetamine, heroin, cocaine or 3,4-methylenedioxymethamphetamine) were smeared over a silicon wafer for direct analysis. In addition, a leaflet of marijuana and a soft lump of opium were also analyzed. In these experiments, about 10 pg of contaminant elements could be determined. The authors analyzed the data obtained and concluded that the fingerprint of contaminants could be used to indicate the synthetic route. A paper in Chinese by Yi *et al.* described the nitric acid and hydrogen peroxide microwave digestion of ephedrine and the AAS determination of 12 analytes.[128] The parameters governing the digestion efficiency, *i.e.*, pressure, power, acids and time of digestion, were evaluated. The data obtained from the analysis of GBW 08501, a certified tea sample, were in good agreement with the certified values. The last paper in this section described the determination of Gd in biomedical samples by diode laser-based multi-step resonance ionization mass spectrometry (RIMS).[129] When the main Gd isotope of 158 was targeted, a LOD of 1.6 pg and a linear response over 6 orders of magnitude were obtained.

Atomic spectroscopy has also been used for the *indirect determination of drugs*. The content of 6-mercaptoprine (6-MP) in tablets was determined using a precipitation reaction with Pb.[130] The method of detection was FI-HG-AAS, which had a linear range of 0–52 ng mL^{-1} and a LOD of 0.195 ng Pb mL^{-1}. Recovery was 95.93–100.85%. Mefenamic acid in pharmaceutical preparations has also been determined using AAS.[131] The compound was reacted with copper amine sulfate and the complex formed extracted into chloroform. The Cu was then back-extracted into nitric acid and determined by FAAS. The method was linear between 30 and 241 mg L^{-1}. Zhang and co-workers have reported the indirect determination of ciprofloxacin by FI-FAAS.[132] The compound was reacted with Fe^{III} and the complex so-formed retained on a mini-column of cation exchange resin. Excess Fe^{III} was converted into anionic FeF_6^{3-} and was eluted from the column. The analyte was then reverse eluted to the nebulizer of the FAAS instrument using nitric acid. Using a reaction and adsorption time of 60 s, the calibration was linear over the range 5–100 mg L^{-1}, precision was 2.6% RSD and sample throughput was 30 per hour. The method was reportedly superior to HPLC methods because of its simplicity. Indirect methods have also been reported for the determination of several anti-malarial drugs[133] and for the anti-hypertensive agents ramipril and enalapril.[134]

The rest of the relevant papers for this section of the review are applications, although some are quite interesting. A review of FI methods for the analysis of different water types (excluding marine waters) for organic pollutants has been prepared by Dunec and co-workers.[135] The review also discussed the indirect determination of organic pollutants in water by FI-atomic spectroscopy techniques. Silylated organic compounds have been quantified using GC coupled with ICP-MS in a paper by Edler *et al.*.[136] The alcohols butanol, pentanol, hexanol and heptanol were silylated using *N*-methyl-*N*-trimethylsilyltrifluoroacetamide in pyridine and then analyzed directly. For an injection volume of 1 µL, a LOD of 100 nM was obtained. External and internal calibrations were found to have identical sensitivities, which simplified the analysis. Fourteen organochlorine, organophosphorus and pyrethrin pesticides have been determined by GC-AED.[137] The atomic emission detection enabled extremely selective chromatograms to be obtained, as opposed to a typical flame ionisation detector chromatogram, which may have very many peaks from un-related compounds. Liquid–liquid extraction with ethyl acetate yielded recoveries of between 76 and 113%. Dietary supplements have been analyzed for Se in two papers in this review period. In one,[138] a comparative study of ETAAS and HG-AAS detection for microwave digested samples was made. It was found that for HG-AAS, the presence of Cu in the sample decreased the Se signal intensity significantly. No interference effects were observed for the ETAAS detection. For this reason, the ETAAS method was chosen as the method most likely to give accurate results. The method was applied to assorted dietary supplements and the authors concluded that the Se content on the labels of the products were often inaccurate. In the second paper,[139] Se speciation in which selenite, selenate, selenocystine and selenomethionine species were separated using a Hamilton PRP X-100 anion exchange column prior to on-line detection using ICP-MS. The mobile phase used was 10 mM citrate (pH 5) in 2% methanol with a flow rate of 1.5 mL min^{-1}. Water extracts recovered only 15–50% of the total Se and therefore the authors used different solvents along with an enzymatic hydrolysis in an attempt to increase this value.

The analysis of *paint or artworks* has received considerable attention in this review period. Often, because the artwork must not be damaged, X-ray techniques are used. An example is the analysis of pigments from Spanish works of art using a portable EDXRF spectrometer.[140] One interesting paper has used a combination of laser ablation and XRF spectrometry.[141] The authors acknowledge that ideally non-invasive techniques are required, but when stratigraphic analysis of a paint is necessary to determine which pigments were used, it is necessary to sometimes cause minor damage. The authors used a flash lamp pumped Er:YAG laser (2.94 μm) at a repetition rate of 8 Hz in a Q-switched mode to ablate the sample and a state of the art portable XRF spectrometer with a Peltier cooled silicon drift detector as the detection system. The measurement technique is described and the first experimental results of samples composed of layers of different thickness and composition were presented. The authors concluded that this fully automated system offered the best choice of analysis in terms of minimal damage, ease of operation and speed of analysis.

2.2.2 Solvents. Fundamental studies of the effects of the introduction of organic solvents to plasma based atomic spectrometric techniques has shown an increase in interest in this review period. An interesting paper has been published by Gras *et al.*,[142] who used models to predict the droplet size distribution using a variety of different nebulizer types and solvents (including water, methanol, ethanol, 2-propanol and 1-butanol). The results predicted by the models were compared with those obtained experimentally using laser diffraction and the authors concluded that the overall droplet size distribution of pneumatically generated aerosols could be predicted with reasonable accuracy. In another interesting paper, the tolerance of high powered air and nitrogen MIPs, both generated using an Okamoto cavity at atmospheric pressure, to the introduction of an organic solvent was tested.[143] In addition, temperatures and electron number densities for the two plasmas were compared using a range of different operating conditions. The air MIP was found to have lower temperatures (by 300–400 K) but an electron number density an order of magnitude higher than the nitrogen MIP. It was discovered that the air MIP was also highly tolerant to direct organic solvent introduction.

The introduction of assorted solvents into a variety of different atomic spectrometric detectors has continued to be a very popular area of research. Many authors have used a simple solvent extraction to achieve a matrix elimination and/or a pre-concentration step. The trends in pre-concentration techniques prior to atomic spectrometric detection, including electrochemical, co-precipitation/precipitation, liquid–liquid and solid–liquid extractions have been reviewed by Pereira *et al.*[144] Cvetkovic *et al.*[145] determined Tl in wine by digesting the sample in nitric acid and hydrogen peroxide, reacting the Tl species with 0.5 M potassium iodide solution and then extracting the iodide complexes so formed into IBMK. Detection was by ETAAS, where tartaric acid, silver nitrate and ammonium tetrachloropalladate were compared as modifiers. The authors reported a 50-fold pre-concentration, enabling a LOD of 0.05 $\mu g\ L^{-1}$ to be achieved, with a precision at the 0.2–1 $\mu g\ L^{-1}$ level of between 6 and 12% RSD. A knotted reactor has been used during the determination of Cd in honey.[146] The analyte was retained on the knotted reactor as its complex with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) at pH 9.3. After pre-concentrating for 120 s, a sensitivity enhancement of 140 was achieved with a factor of 40 of this being attributable to the pre-concentration and a factor of 3.5 being associated with the introduction of the organic solvent to the FAAS instrument. The LOD was 0.5 $ng\ g^{-1}$, precision at the 5 $ng\ g^{-1}$ level was 3.5%RSD and the calibration was linear to at least 2000 $ng\ g^{-1}$. Ekberg and co-workers have described a method whereby Zr in both organic and aqueous phases could be determined accurately using ICP-MS using the same standards.[147] This was achieved by introducing the samples in a flowing stream of ethanol. The authors stated that the method was only successful if the organic and aqueous content in the carrier phase is kept below 10%. The authors said that the method could be applied to the measurement of the efficiency of solvent extractions or analyses such as fingerprinting of petroleum fluids. Several other simple applications using pre-concentration have been described. Cobalt seems to have been a popular analyte in this review period, with a further three research groups publishing methods. These included the retention of Co on a micro-column of 2-nitroso-1-naphthol immobilised on surfactant coated alumina, elution using ethanol and detection by FAAS,[148] retention on 1-nitroso-2-naphthol with ethanol elution and FAAS detection[24] and retention of the Co–8-hydroxyquinoline complex on Chromosorb 105 followed by ethanol elution and ETAAS detection.[149]

The introduction of dimethylformamide (DMF) to atomic spectrometric instrumentation has been reported in several papers in this review period. In one elegant method, trace metals (Co, Cu, Ni and Pb) were pre-concentrated from water samples by thermoresponsive precipitation of their APDC chelates into the water soluble polymer poly(*N*-isopropylacrylamide).[150] By mixing sample (100 mL, pH 3) with APDC (20 mg), 60 mg of the polymer and 850 mg of sodium nitrate, and then heating to 50 °C, the polymer precipitated into a gum- like substance that retained the metal chelates within it. This precipitate could then readily be dissolved in DMF, 5 μL aliquots of which were analyzed by tungsten filament ETV-ICP-MS. Using palladium as a modifier, the 100-fold pre-concentration yielded detection limits at the pg mL^{-1} to ng mL^{-1} levels. Precision and accuracy of the method were evaluated using a certified water sample. Two sets of workers have reported the use of the same adsorbent for the determination of trace analytes. Taher[151] used 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol, tetraphenylborate and microcrystalline naphthalene to retain Co from large volumes of aqueous samples. After filtration, the precipitate was dissolved in DMF and analyzed by FAAS. Pancras *et al.*[152] used exactly the same adsorbents but at varied pH ranges to determine Cu (pH 3–8), Fe (pH 3.8–7.5), Ni (pH 4.5–7.5) and Zn (pH 8.5–11). Again, precipitates were dissolved in DMF and analyzed using FAAS. In both cases, characteristic concentrations for the metals were at 20–120 ng mL^{-1} levels. Taher and Shamsi have also used 2-nitroso-1-naphthol-4-sulfonic acid (nitroso-S) and tetradecyldimethylbenzylammonium chloride (TDBA Cl) to adsorb Ni onto benzophenone.[153] Using the standard method of filtration and then dissolution using DMF, followed by FAAS detection, the characteristic concentration for the Ni was found to be 98 ng mL^{-1}. The method was applied to various alloys and biological samples.

Speciation techniques frequently require the use of an organic solvent. In this review period several such applications have been reported. Included in these is a paper by Wuilloud *et al.*, who pre-concentrated and speciated Cr^{III} and Cr^{VI} using Amberlite XAD-16 resin with determination using FI-FAAS.[154] Total Cr was determined by retention on the column as the Cr-4-(2-thiazolylazo)-resorcinol complex (Cr-TAR), whereas Cr^{VI} was determined using the same method but having masked Cr^{III} using 1,2-cyclohexanediaminetetra-acetic acid (CDTA). The Cr^{III} was determined by difference. The chromium complexes were removed from the column using ethanol. The authors reported a sensitivity enhancement of 250, with 50-fold arising from the pre-concentration and a further 5-fold from the introduction of the organic solvent. Using this method, a LOD of 20 ng L^{-1} was obtained with a precision ($n = 10$) at the 2 $\mu g\ L^{-1}$ level of 3.8% RSD. The method was found to be linear to 100 $\mu g\ L^{-1}$ and was applied to Cr speciation in water samples. A similar procedure has been reported by Tunceli and Turker,[155] who pre-concentrated Cr^{VI} as its diphenylcarbazone complex on Amberlite XAD-16 prior to elution with 0.05 M sulfuric acid in methanol for FAAS detection. Total Cr was determined by oxidation of Cr^{III} with potassium permanganate and Cr^{III} was calculated by difference. A pre-concentration factor of 25 was achieved yielding a LOD of 45 $\mu g\ L^{-1}$. Seven organotin and two organolead species have been determined by HPLC with electrospray interface to quartz-furnace AAS detection.[156] The vitreous body of the electrospray interface was heated externally to above the boiling point of the solvent mixture using conditions optimised by a full experimental design. The electrospray was reportedly capable of coping with a solvent flow rate in the range 50–1000 μL min^{-1}. The detection limits for tetramethyl and tetraethyltin were 140 and 155 ng mL^{-1}, respectively. These were found to be an order of magnitude lower than those obtained using a thermospray interface and were sufficiently low to determine the tributyltin content in the BCR 477 mussel tissue reference material. Glindemann and co-workers developed a multi-functionary interface to connect a capillary gas chromatograph and an ICP-MS instrument.[157] It was reportedly capable of analysing very high boiling point samples (up to C_{26} n-paraffin, which has a boiling point of 412 °C), using an interface temperature of only 140 °C. The design performs splitless large volume solvent injection to analyse both low and high boiling point analytes in one run. A clear explanation of how the interface operates was given, including a method of eliminating the solvent peak by reversing the flow through the transfer line, so that there was no risk of graphite deposition on the sampler cone. Detection limits of the propyl derivatives of numerous organotin species were in the range 68–250 fg absolute, and are at the pg L^{-1} range when 80 mL of water sample is extracted into 1 mL of solvent. Inorganic As speciation in natural waters using HG-AAS has been reported by Brana *et al.*[158] Both As^{III} and As^{V} were retained on an alumina micro-column, and then the As^{III} was eluted with British Anti-Lewisite (2,3-dimercapto-1-propanol) and As^{V} was eluted with 6 M hydrochloric acid. At 6 and 4 μg L^{-1}, the LODs for As^{III} and As^{V}, respectively, were already respectable, but the authors also claimed that pre-concentration could improve them by a factor of 100. As an application, the authors analyzed mineral and sea waters.

Mendiguchia and co-workers have described the use of *liquid membrane pre-concentration* for Cu in sea-water followed by FAAS detection.[159,160] The liquid membrane consisted of an organic solution containing di-(2-ethylhexyl)phosphoric acid (DEHPA) in kerosene. In one of the papers,[159] the pre-concentration system was optimised using a modified Simplex approach, which yielded an enrichment factor of 4.3. The reliability of the method was demonstrated by analysis of sea-water samples that had previously been analyzed using a well established technique.

Other interesting applications of organic solvent introduction to atomic spectroscopic detection systems have also been published. Skinner and Salin pre-concentrated Cd, Cu, Fe, Mn, Pb and Zn as their 8-hydroxyquinoline (8-HQ) metal chelates onto a C_{18} column, de-sorbed them with methanol and then collected the eluate on an inductively heated graphite direct sample insertion cup, prior to insertion into an ICP for AES detection.[161] The authors reported that the automated system managed to remove the organic solvent and much of the 8-HQ, so interferences in the plasma were minimised. Limits of detection were 8, 30, 60, 10, 9 and 40 ng L^{-1} for Cd, Cu, Fe, Mn, Pb and Zn, respectively, which, for an AES technique, are impressive. A homogeneous mixture of water–ethanol–IBMK solvents (1:14:10) has been used to introduce samples during the determination of Cr^{III} by FAAS.[162] The authors reported that the sensitivity of the determination was improved by more than a factor of two. An interesting paper by Ndung'u and co-workers compared an on-line chelation column using ICP-MS as a detection system with a conventional liquid–liquid extraction using 1-pyrrolidinedithiocarbamate–diethyldithiocarbamate and ETAAS detection for the determination of analytes in acidified estuarine waters.[163] Good correlation between the techniques was observed for Cd, Mn, Pb and Zn; but Co, Cu and Ni were found to give 10–20% lower concentrations using the chelating resin–ICP-MS technique. This was attributed directly to the interaction of the analytes with dissolved organic carbon. The problem was overcome by photolytic digestion of the samples prior to analysis.

2.3 Inorganic chemicals and acids

Last year saw an increase in the number of publications relating to multicollector ICP-MS for analysis of inorganic materials and this trend has continued into this review period. ICP-MS, in general, has featured strongly this year with the publication of several interesting papers, particularly in the areas of GC-ICP-MS and ICP-TOF-MS. Other analytical techniques have been cited less than in previous years, although some topics, such as the evaluation of permanent modifiers for graphite furnace AAS applications and the description of new methods of industrial relevance (soil remediation and analysis of landfill gases), have received considerable attention. On this latter subject, the fibre quality and phytoremediation potential of industrial hemp (*Cannabis sativa* L.) grown on land contaminated with heavy metals have been studied.[164] The dual use of hemp as a renewable resource for decontaminating heavy metal polluted soils and as a source of fibre for textiles and industrial yarn is potentially of considerable benefit to the environment. The focus of this study was the influence of heavy metals on the fibre quality, using flame AAS to perform the metals determination. Four different parts of the plant were examined, namely seeds, leaves, fibres and hurds. In each case, the concentration pattern found was Ni > Pb > Cd. However, heavy metal accumulation was found to vary widely between the different parts of the plant, with the highest levels being found in the leaves. In this trial, hemp showed a phytoremediation potential of 126 g Cd per hectare of vegetation. The fibre quality was tested by measuring the pure fibre content of the stems and the fibre properties after mechanical separation. Fibre from plants grown in polluted land was compared with those grown on un-polluted land, but since the un-polluted land was necessarily distant from the polluted land, the authors concluded that the observed differences in the fibre characteristics were only partially caused by heavy metal contamination.

On the subject of landfill gas measurement, a method for the analysis of malodorous sulfur gases and volatile organometalloid compounds in landfill gas emissions, using capillary gas chromatography with programmed temperature vaporization injection and atomic emission detection, has been reported by Junyapoon *et al.*[165] Volatile compounds containing analytes such as As, S and Sb within landfill gases are of concern as a source of toxic pollutants and unpleasant smells. Conventional analytical techniques for these compounds, such as ICP-MS and ICP-AES, are expensive and time consuming, so the authors developed a simpler technique based on programmed temperature vaporization injection (PTV) coupled to gas chromatography with atomic emission detection (GC-AED). With an adapted PTV injection system (using a combination of a ten-port and a six-port Valco valve), problems associated with AED discharge tube damage due to high carrier gas flow rate during sample loading were overcome. The gas samples generated from both a laboratory bio-waste digester and a domestic landfill site were characterized using these techniques. Sample gas was adsorbed onto a cooled sorbent trap containing Porapak Q, followed by rapid liberation onto a porous layer open tubular column (PLOT) using programmed thermal desorption. Arsenic and Sb were also detected in the landfill leachate collected from the same landfill site using HG-AAS. In this study, the efficiency of different traps was also compared.

Several papers exploring the use of *permanent modifiers* for graphite furnace AAS have been published this year. The use of zirconium–iridium coating as a permanent modifier for determination of Sn in stream sediment, oyster tissue and total diet slurries by ETAAS (using a transverse heated cuvette) has been described by Meeravali and Kumar.[166] Reference materials such as GBW07312 Stream Sediment, NIST SRM

1566a Oyster Tissue and NIST SRM 1548 Total Diet were used to validate the method. Slurries were prepared in a mixture of 1% v/v HNO_3, 2% v/v HCl and 0.2% Triton X-100 solution by using magnetic stirring and ultra-sonication. With the Zr–Ir-coated tube the characteristic mass obtained was 38 $\pm$ 2 pg, which was a near 5-fold improvement compared with using an uncoated tube. The tube lifetime using aqueous standards and slurries was nearly 500 atomization cycles. The Zr–Ir permanent chemical modifier was found to effectively reduce the interference effects from chloride, phosphate and silica, as nearly 90–100% recovery was obtained in the presence of 100 mg of the matrix. However, in the presence of 100 mg of sulfide, aluminium nitrate and sodium silicate, only 30–60% recovery was obtained, indicating that matrix interferences remained with these sample types.

The use of ruthenium as a permanent furnace modifier for the determination of As, Pb, Se and Sn in sediments by slurry sampling ETV-ICP-MS has also been reported by Dias and co-workers.[167] The samples were ground to a particle size of around 50 μm, then slurried with 5% (v/v) nitric and 1% (v/v) hydrofluoric acids in an ultrasonic bath. The slurry was homogenized with an argon flow in the autosampler cup, just before transfer to the graphite furnace. The tube was treated with ruthenium as a permanent modifier, and an optimized mass of 1 μg of NaCl was added as a physical carrier. The pyrolysis temperature was optimized at 800 °C and the vaporization temperature was set at 2300 °C. The effect of different acid concentrations in the slurry on the analyte signal intensities was also evaluated. The accuracy of the method was demonstrated by analysis of the NRCC certified reference sediments MESS-2, PACS-2 and HISS-1, the NIST materials SRM 2704 and SRM 1646a and a round robin test material, RS-4, using external calibration quantitation with aqueous standards prepared in the same medium as the slurries. The method gave low $\mu g\ g^{-1}$ detection limits for As, Pb, Se and Sn and acceptable measurement precision (from 1 to 12% RSD, $n = 5$). In a study using the furnace atomization plasma emission spectrometry (FAPES) technique, iridium has been tested as a permanent modifier for the determination of Cd and Pb in sediment and biological samples.[168] The iridium coating procedure, atomization conditions and FAPES parameters were optimized for the best analytical response and minimum background signal. Measurement precision of better than 3% RSD was achieved with the proposed method, with detection limits of $<5\ ng\ g^{-1}$ for each analyte of interest. The method accuracy was demonstrated by analysis of the MESS-3 and PACS-2 reference marine sediments and DOLT-2 and TORT-2 reference biological tissues. Matrix interference was compensated for by the use of standard additions calibration and good agreement was achieved between found and certified values.

As was mentioned earlier, ICP-MS applications have predominated in the inorganic chemicals and acids literature this year. As well as an increased number of MC-ICP-MS papers there have been multiple references to ICP-TOF-MS, collision/reaction cell ICP-MS and the growing hyphenated technique of GC-ICP-MS. Several other interesting articles regarding novel ICP-MS applications are also worthy of discussion.

Kishi and Kawabata have reported the use of quadrupole ICP-MS with a dynamic reaction cell (DRC) for analysis of semiconductor-grade hydrochloric acid.[169] The DRC, using ammonia as the reaction gas, eliminated the ClO^+ and $ClOH^+$ interferences obtained when analyzing HCl, thereby facilitating the determination of V and Cr in 20% HCl. For As and Se, oxygen was used as the reaction gas to generate AsO^+ and SeO^+ in the DRC, to separate As from the residual $ArCl^+$ interferences on masses 75 and 77. Limits of detection for V, Cr, As, and Se in 20% HCl of 2, 3, 2 and 8 $ng\ L^{-1}$, respectively, were achieved. Reaction cell ICP-MS technology has also been applied to the determination of ultra-trace metal contamination levels in high-purity (semiconductor grade) phosphoric and sulfuric acids.[170] The study compared the DRC approach with traditional ICP-MS background reduction techniques to compensate for phosphorus- and sulfur-based interferences. The results suggested that collision/reaction cell technology can reach the next generation of semiconductor purity levels for these chemicals.

The problem of measuring memory-prone elements accurately by ICP-MS has been addressed in a study evaluating the performance of the direct injection high efficiency nebulizer.[171] Both a direct injection high efficiency nebulizer (DIHEN) and a large-bore DIHEN (LB-DIHEN) were investigated for the determination of the memory prone elements B, Hg and I. The determination of these elements is difficult using conventional sample introduction systems incorporating spray chambers and/or desolvation devices, owing to the large surface area and long wash-out characteristics of these components. With the DIHEN or LB-DIHEN, use of a spray chamber is not required and the dead volume is reduced to $<10\ \mu L$, thereby reducing memory effects. In comparison with the crossflow nebulizer/spray chamber combination, wash-in and washout times were reduced to less than 10 s when a DIHEN or LB-DIHEN was used for B, Hg and I at a concentration of 100 $ng\ mL^{-1}$. The accuracy of the DIHEN-ICP-MS technique was evaluated by the analysis of the NIST SRM 2670 (Toxic Metals in Freeze-dried Urine) and NIST SRM 8414 (Bovine Muscle Powder). Further, the effectiveness of the DIHEN-ICP-MS technique was examined through the determination of Hg and I in an alternative remedy medicine and B in rodent liver samples as part of a pharmacokinetic screening study for B neutron capture therapy.

An interesting study by Guo *et al.* comparing chloride- and hydride-generation for the quantitation of Ge by headspace solid-phase micro-extraction-ICP-TOF-MS has been reported.[172] The conditions for generation of germanium chloride, including acid type and concentration, effect of sodium chloride and extraction time, were investigated. Detection limits of 20 and 92 $pg\ mL^{-1}$ and precisions of 18% ($n = 11$) and 9.7% ($n = 11$) were achieved for chloride and hydride generation, respectively, at a concentration of 10 $ng\ mL^{-1}$. The generated germanium chloride and hydride species identities were characterized and confirmed as $GeCl_4$ and GeH_4 by use of electron-impact ionization mass spectrometry. Chloride generation coupled with SPME sampling and ICP-TOF-MS detection resulted in a 2-fold sensitivity enhancement compared with GeH_4 and detection limits for continuous hydride generation were 20 times better than reported atomic fluorescence data. ICP-TOF-MS has also been used for the determination of Cd, Cr and Pb in six food-packaging materials (paper and paper board).[173] The samples (0.20–0.25 g) were digested in concentrated nitric acid in a high-pressure microwave oven at 180 °C for 15 min. Two different plasma conditions were applied in this study: semi-cool plasma conditions (760 W) for Cr and normal plasma conditions (1210 kW) for Cd and Pb. External calibration was used with Rh as the internal standard. Detection limits (3σ) in the digest of 0.01 $ng\ g^{-1}$ for ^{52}Cr, 0.03 $ng\ g^{-1}$ for ^{114}Cd and 0.02 $ng\ g^{-1}$ for ^{208}Pb, with measurement precisions for each analyte at the 10 $ng\ g^{-1}$ level (% RSD, $n = 6$) of better than 5%, were obtained. The chromium, cadmium and lead contents in the paper and paper board materials studied were in the range 0.25–0.64 $\mu g\ g^{-1}$ for Cr, not detected (nd) to 0.12 $\mu g\ g^{-1}$ for Cd and 0.28–0.99 $\mu g\ g^{-1}$ for Pb.

The use of multicollector ICP-MS for precise and accurate isotope ratio measurement has been steadily growing in recent years. For geologists, in particular, the technique holds several benefits over the traditional thermal ionisation mass spectrometry (TIMS) approach, in that less sample preparation is required for ICP-MS and the ICP source can be used to ionise volatile elements, such as Hg, which are not accessible to TIMS. The main disadvantages of using an ICP ion source as opposed to a thermal source are that the ICP is somewhat more 'noisy', so the ultimate isotope ratio precision may be degraded slightly compared with TIMS, and the mass discrimination observed with ICP-MS is larger, so requires larger correction factors to be applied which can affect the accuracy of ratio measurements. A study of the stable isotope natural abundances of Si using MC-ICP-MS has been performed by De la Rocha.[174] Widespread use of Si isotope ratio variations (expressed as δ ^{29}Si and δ ^{30}Si) as a geochemical and paleoceanographic tracer has been restricted, until now, by the hazardous nature of the analysis, which requires the use of a fluorinating gas to convert Si to silicon fluoride gas prior to measurement. Multicollector ICP-MS provides a safer means of silicon isotope analysis since this fluorination step is not required, although analysis of Si using ICP-MS in general is difficult because the Si background is high, long rinsing and sample introduction times are required and there are several interferences (principally COH^+, N_2^+, CO^+, $NO^+$and N_2H^+). Despite these obstacles, the measurement of δ ^{29}Si could be performed to a precision averaging ±0.1 parts per thousand in this study. The δ ^{30}Si, which cannot be measured directly because of the NO interference at mass 30, could be extrapolated from the theoretically derived and empirically verified relationship, $\delta\ ^{30}\mathrm{Si} = 1.93\ \delta\ ^{29}\mathrm{Si}$. Biological materials (sponge spicules and diatoms) measured using MC-ICP-MS gave δ ^{30}Si values that were in the range expected from the prior analysis of similar samples using the fluorination method.

A second study on the isotopic composition of silicon measured by multicollector plasma source mass spectrometry using a dry plasma approach has also appeared this year.[175] Precise Si isotopic fractionation in silica (quartz), opal (diatomite, sponges) and standards has been determined using MC-ICP-MS under dry plasma conditions, using a Cetac Aridus desolvating nebulization system. Variations in sample ^{28}Si/^{29}Si ratios were calculated as δ ^{29}Si units, which represented deviations in parts per thousand from the same ratio of the NBS28 standard measured using the standard-sample bracketing technique. The authors measured Mg isotopes for instrumental mass bias correction, applying the exponential law and external normalisation. The repeatability and internal precision of the δ ^{29}Si measurements of a 1 ppm Si solution in diluted HF–HCl was found to be better than $\pm0.1\%$ (±2 sigma). The accuracy of the method was demonstrated by cross analyses of an in-house standard with the laser fluorination-isotope ratio mass spectrometry (IRMS) technique. The use of this dry plasma methodology improved the sensitivity by >10 times compared with wet plasma MC-ICP-MS, and hence offers great potential for environmental, biogeochemical and geological sciences where improved Si isotope analysis opens up a range of new studies.

Comparison of a high resolution (HR) magnetic sector ICP-MS, quadrupole ICP-MS equipped with a hexapole collision cell (Hex-ICP-MS) and a multicollector ICP-MS system for the determination of the isotopic composition of Os samples has been reported.[176] All three methods gave good agreement for the Os isotopic abundance (which was in agreement with the literature values) while the ratio precision results reflected the performance expected for these 3 instrument types, namely that MC-ICP-MS > HR-ICP-MS > quadrupole ICP-MS. The ^{187}Os abundance in three highly enriched samples of unidentified, but assumed to be from Precambrian formation of Russian origin, varied between 98.93 and 99.53%. In addition, the ^{186}Os/^{192}Os, ^{188}Os/^{192}Os, ^{189}Os/^{192}Os and ^{190}Os/^{192}Os isotope ratios in all three enriched samples were close to the natural isotopic composition. The authors concluded that this may indicate radioactive decay of ^{187}Re to ^{187}Os in rhenium-rich osmium samples in which the original osmium with a low initial concentration was of natural isotopic composition.

Electrothermal vaporisation ICP-MS, although not a frequently used technique, has specific advantages for certain applications. The particular benefits of the technique have been highlighted in a paper discussing its use for the determination and speciation of trace elements in solid samples in a variety of real-life applications.[177] The authors looked at trace elements in industrial materials (including 3 different types of plastics (Carilon, polyethylene and poly(ethyleneterephthalate)) and photographic/thermographic materials) and various plant materials, animal tissues and sediment samples. The authors also used ETV-ICP-MS for Se speciation in proteins and Hg speciation in fish tissue. For the former work, separation of Se-containing proteins was accomplished using polyacrylamide gel electrophoresis (PAGE) followed by quantitation of the Se content in the protein spots using ETV-ICP-MS. The latter speciation study took advantage of the fact that the difference in volatilisation temperature of methylmercury and inorganic mercury allows these species to be separated from one another with respect to time, without the need for chromatographic or electrophoretic separation.

A novel article (written in Japanese) on the determination of halogens by low-pressure helium ICP-MS has also been reported this year.[178] The use of He offers improved performance over Ar-based ICP-MS for the halogen elements, since these elements have high ionization potentials and ionize more efficiently in He plasmas. In addition, He plasmas offer improved trace determination of iron, arsenic and selenium, since the ArO^+, $ArCl^+$ and Ar_2^+ interferences are not present. In this study, a 5 µl aliquot of an aqueous sample was placed on a looped tungsten filament and heated electrothermally at around 2500 °C. The resulting sample vapour was transported to the ICP in a stream of helium prior to detection of the analytes ^{79}Br, ^{35}Cl, ^{19}F and ^{127}I by a quadrupole mass analyzer. Detection limits of 23, 2.4, 0.13 and 0.05 ng mL^{-1} for F, Cl, Br and I, respectively, were achieved. The particular benefit of this procedure was the significant improvement in detectability for F, which was sufficient to allow its direct determination at low levels in water.

A number of articles have appeared this year on the growing subject of GC-ICP-MS. A cryo-sampling system together with a low temperature GC-ICP-MS method has been developed for the determination of phosphine (PH_3) for industrial hygiene purposes.[179] The effect of sampling temperature on the collection efficiency of PH_3 was investigated. Two trapping mechanisms were compared for temperature ranges from −190 to −160 °C and −110 to −35 °C. A cartridge filled with NaOH was used during the analytical desorption step to separate CO_2 from phosphine, providing phosphine recovery of better than 98% with precisions for peak area and retention times of better than 4% and 2% RSD, respectively. The use of a Nafion drying membrane before cryogenic trapping induced losses of PH_3 of about 15%. Sample conservation in a cryocontainer at −190 °C over a period of 15 days did not lead to significant losses of PH_3. For field experiments, air samples were collected in the fumigation room of a tobacco factory after fumigation and outside the room during fumigation, using both cryogenic sampling and standard filters impregnated with silver nitrate. The results showed that phosphine concentrations in the tobacco factory were below the limit values for occupational exposure to phosphine and also below the detection limit of the silver impregnated filter-ICP-AES method. The concentrations in ambient air were estimated to be about 1 ng m^{-3} and the detected concentrations in the vicinity of the fumigation room during the fumigation process were lower than 10 ng m^{-3}.

A method for the analysis of brominated flame retardants using fast gas chromatography with ICP-MS detection was the focus of an interesting article produced by Vonderheide and co-workers.[180] The term brominated flame retardants (BFRs) refers to a class of compounds added during the manufacture of some plastics to impede or suppress the combustion process by depriving the flames of oxygen. Polybrominated diphenyl ethers (PBDEs) represent a group of compounds used for this purpose and as a result of product emission and disposal, these structures have been found in both the environment and biota. In this work, ICP-MS coupled to gas chromatography (GC), in the form of fast gas chromatography, was explored to shorten the analysis times for the PBDEs. With ICP-MS detection, a run time of 10 min was established. A new commercially available interface was used that heated the entire device at 325 °C to maintain the resolution between the previously separated species. The introduction of helium increased the sensitivity, providing instrument detection limits at the low ppb level for all species examined. A precision of better than 7% was achieved for five manual injections. The authors found that more rigorous control of the interface temperature was required for analyzing species with more than six Br atoms per molecule. The method was successfully applied to the analysis of sewage sludge samples obtained from the Metropolitan Sewer, District of Greater Cincinnati, where the presence of three of the most abundant PBDEs was observed (BDE-47, BDE-99 and BDE-100).

Despite the considerable number of articles in which MC-ICP-MS has been used, TIMS articles continue to appear. One particular element which is beneficial to run using TIMS rather than ICP-MS is Li. Since the mass discrimination observed with this element using ICP-MS is very large (approximately 14% per u) compared with TIMS, a large correction must be made if ICP-MS is used. To this end, measurement of the isotopic composition of Li by TIMS has been reported.[181] The method was based upon thermal ionization of LiOH loaded onto a single SiO_2 coated Re filament. Using this method, stable emissions of Li^+ ion were achieved for an extended period of time. The proposed method was capable of analyzing the isotopic composition of trace quantities (40 ng) of Li in the presence of sodium with an uncertainty (two standard deviations on the ratio of the mean) of $\pm 0.000\,25$.

Aside from the large number of ICP-MS related applications reported this year, a couple of other publications regarding new applications of interest in the inorganic chemicals and acids field are worthy of discussion. A method has been developed for the determination of V in fertiliser samples, as an anionic ternary complex of V^V with 4-(2-pyridylazo)resorcinol (PAR) and hydrogen peroxide, after separation by capillary electrophoresis (CE), using a light-emitting diode detector.[182] The CE separation was conducted using acetate buffer at pH 6 as the background electrolyte, with a separation potential of -30 kV and injection time of 100 s. The V complex was detected photometrically at 568 nm by use of a light-emitting diode (LED), down to a detection limit of 19 ng mL^{-1}. The method was applied to the determination of V in fertilisers, following a clean-up of the digested fertiliser sample with Sep-Pak C-18 coated with tetrabutylammonium hydroxide to remove matrix ions, which otherwise caused electrophoretic de-stacking. Vanadium levels found in the fertiliser samples using the CE method were comparable to results obtained by HPLC and ICP-MS.

Finally, the application of a portable XRF instrument in the characterisation of As contamination associated with industrial buildings at a heritage arsenic works near Redruth, Cornwall, has been reported.[183] This study showed that contamination present on industrial buildings at the site had resulted from the absorption of arsenic by porous and semi-porous building materials that were in contact with As-rich flue gases. Results from an initial survey indicated that As is locked in these materials and is being gradually leached out by weathering processes. This weathering was found to lead to contamination of the adjacent building surfaces (averaging 1845 µg As g^{-1}), by a mechanism based on evaporation and transport of leach solutions in contact with air at the surface of the building materials. More extensive crystalline deposits were found under arches protected from dissolution and further dispersion by rain water. These deposits appeared to contain calcium sulfate (gypsum) associated with, on average, between 1.2 and 6.8% m/m As. The *in-situ* portable XRF instrument proved to be highly effective in locating sources of contamination at the site and in providing data that allowed hypotheses for the origin of this contamination to be formulated and tested in the field. The development of portable analytical instrumentation of this type offers many benefits (particularly speed), not only for geochemical applications but also for industrial chemical analysis 'at-line', so it can be anticipated to receive increased focus over the next few years.

2.4 Nuclear materials

The analysis of isotope ratios and abundance is still a growing topic in this section of the review. In two different papers, Becker has discussed the state of the art and progress in precise and accurate isotope ratio measurements by ICP-MS and LA-ICP-MS.[184,185] The former paper discussed many of the hardware devices and the techniques that have improved the accuracy of the measurement of isotope ratios. Included in here is the use of collision cell technology and multiple ion collector devices that can obtain a ratio with a precision of 0.002% RSD. The author went as far as to say that ICP-MS and LA-ICP-MS were increasingly replacing thermal ionization mass spectrometry (TIMS), which has been used for decades, as the method of choice for obtaining accurate isotope ratios. The latter paper was more applications based and concentrated mainly on a discussion of the many stable isotope methods currently available and their use in the study of global micronutrient deficiency. A similar sort of paper to the first has been presented by Balaram.[186] This author also gave an overview of ICP-MS and high resolution ICP-MS for the isotopic analysis of lanthanides, actinides and other elements. The advantages of LA-ICP-MS were also discussed, along with speciation applications using high-performance liquid chromatography (HPLC). The author also presented a discussion of the reasons why plasma-based techniques are superior to other techniques, such as TIMS and INAA, for the determination of these analytes in geological and nuclear materials. In another paper, Boulyga and co-workers determined $^{236}U/^{238}U$ isotope ratios in contaminated environmental samples using different ICP-MS instruments.[187] The ^{236}U isotope was used as a measure of spent U from nuclear fallout in soils from the Chernobyl nuclear power plant. The assortment of instruments used included a quadrupole ICP-MS both with and without a hexapole collision cell, a sector field ICP-MS and a multiple ion collector instrument. In addition, an USN was used and the sensitivity obtained with all three instrument types compared. Signals of between 12 and 18 GHz were obtained per ppm using ^{238}U. The absolute sensitivity for the sector field instrument, when used in conjunction with a direct injection high efficiency nebulizer (DIHEN), was 3600 counts fg^{-1}. The authors reported good agreement for the $^{236}U/^{238}U$ ratios when data from an inter-laboratory comparison were compared. Analysis of the upper 0–10 cm of soil indicated a spent U content of 2.4×10^{-9} to 8.1×10^{-7} g g^{-1}, depending mainly on the distance from the Chernobyl reactor. In another study, Boulyga and Becker undertook an isotopic analysis of U and Pu in contaminated environmental samples using a double focusing sector field ICP-MS instrument.[188] Using a low flow micro-concentric nebulizer and a membrane desolvation device, LODs of 0.2 pg L^{-1} (for ^{236}U in water) and 0.04 pg g^{-1} (for ^{239}Pu in soil) were obtained. The isotope ratios of $^{235}U/^{236}U$, $^{236}U/^{238}U$ and $^{240}Pu/^{239}Pu$ were also determined within a 30 km zone around the Chernobyl site. The authors noted a relationship between the $^{240}Pu/^{239}Pu$ ratio and the burn up of spent uranium. The same research group have also utilized LA-ICP-MS with isotope dilution for the determination of Am and Pu in moss samples.[189] Results were compared with those obtained using alpha spectrometry. In general, the Pu results were in good agreement, but the Am results were less so. This was attributed to the extremely low levels of Am present. Oliveira and Sarkis evaluated the reliability of ^{235}U/^{238}U isotope measurements using a quadrupole ICP-MS instrument and both certified and non-certified materials.[190] Their results indicated that a repeatability of 0.5% and a reproducibility of 0.27% could be achieved. Additionally, mass discrimination was found to be 0.03% per mass unit and the mean error of measurement obtained from six different CRMs was 0.77%.

Numerous other papers have been published that describe the use of techniques for isotope ratio measurement. Tamborini and co-workers described the use of SIMS for isotopic measurements in nuclear forensic applications.[191] Included in these applications were the age determination of Pu particles and the isotopic composition of O for geolocation assignment. For the ageing work, a relative sensitivity factor to correct for the difference in ionization efficiency between U and Pu was necessary. This was obtained by the analysis of standard materials with known ages. Using this correction factor, the ^{238}U/^{234}U and ^{240}Pu/^{236}U ratios were calculated, which enabled the dating of the material. Another paper that measured O isotopes, this time in uranium oxide micro-particles, has also been presented by the same group.[192] Again, SIMS was used in this nuclear forensic diagnostic role. Tests for matrix dependent discrimination effects on three different O isotope standards with substantially different matrix compositions were made and the results were checked by an inter-laboratory comparison. Results from the two laboratories involved were described as being in very good agreement, indicating that there was statistically indistinguishable instrumental mass discrimination. Many studies in this subject area have been presented by Japanese workers. Two papers by Sahoo *et al.* have described the use of TIMS in determining U isotope ratios. In one, ^{235}U/^{238}U was determined accurately in soil samples[193] and the isotopic compositions between the site at Chernobyl and at the JCO site in Japan were compared. The use of a wide aperture retardation potential (WARP) energy filter was found to improve the abundance sensitivity by an order of magnitude when compared with conventional TIMS. Reproducibility was stated as being better than 0.2% using two standard deviations. The other paper[194] detected ^{236}U and other U isotopes, again in samples affected by the JCO criticality incident. The chemical separation of the U was achieved by anion exchange and UTEVA extraction chromatography. Other papers in this area include ones by Yamamoto *et al.*,[195] Muramatsu and colleagues[196] and Tonouchi *et al.*[197] The isotopic composition and origin of Pu and U in soil samples collected in Kosovo has been studied by Danesi *et al.*[198] An assortment of techniques including alpha spectrometry, gamma spectrometry, ICP-MS and accelerator mass spectrometry (AMS) was used to determine the ratios. It was concluded that whenever the U content exceeded the normal environmental value (typically 2–3 mg kg^{-1}), the increase was due to depleted uranium contamination. Furthermore, it was possible to say that the depleted uranium came from a batch that had been irradiated and then reprocessed. Smith and co-workers used a LIBS instrument consisting of a laser induced plasma, a 2 m spectrometer and an electronically gated, intensified CCD detector to determine ^{239}Pu/^{240}Pu ratios.[199] The ^{239}Pu/^{240}Pu line shift of -0.355 cm^{-1} was clearly resolved in their system and the results obtained were in agreement with those obtained by TIMS and gamma spectrometry. It was concluded that the system should be capable of determining isotope ratios for all of the light actinides.

A paper by Taylor and co-workers claimed to be the first to describe the use of a multi-collector ICP-MS instrument for determining Pu ratios.[200] The main advantage of the technique is that it obviates the need to cycle a number of small ion beams through a single collector. Hence, the efficiency of the ion beam usage is increased. This, together with the elimination of the effects produced by ion beam instability, makes the technique ideal for the task of isotope ratio determination. Another more fundamental study has been produced by Magara and colleagues,[201] who elucidated the effects of alkali metals on the accuracy of isotope ratio measurements of U. The isotope ratios were measured using the isotopic reference materials NBS U-015 and U-350 in solutions containing various amounts of any one of K, Na and Rb. It was found that for the U-015 material, the ^{235}U/^{238}U ratio started to increase at 1 μg g^{-1} for K and Rb and at 10 μg g^{-1} for Na. For concentrations of 300 μg g^{-1}, the deviation from the certified ratio was found to be 1.9%, 0.8% and 2.5% for K, Na and Rb, respectively. An interesting environmental application has been published by Howe and co-workers, who employed the standard BCR three stage sequential extraction method to sediments from the vicinity of a uranium enrichment plant.[202] For preconcentration, the extracts were passed through a 2 cm column of AG1-X8 resin and the U eluted with 8 M nitric acid. The precision obtained for measurement of ^{238}U/^{235}U ratio in solutions containing 20 ng mL^{-1} of ^{238}U and 0.2 ng mL^{-1} of ^{235}U was 0.18%. Analysis of the sediments indicated that as the distance from the enrichment plant decreased, the overall U content increased and that the natural ratio of 137.9 decreased to less than 100, indicating contamination with ^{235}U. The three stage extraction also demonstrated that the U was either discharged from the plant in, or rapidly converted to, a relatively refractory form.

A number of simple applications have been published in this review period. Of these, some of the more interesting ones include several that have used on-line FI or chromatography to separate and/or pre-concentrate the analytes. Examples of these include papers by Kim *et al.*,[203] who determined ^{99}Tc using an automated FI system and TEVA resin to separate the analyte from Mo and Ru, and another by Lee and co-workers[204] who determined Mo, Pd, Rh, Ru, Te and Zr in spent pressurized water reactor fuels. In the former paper, a 3–5 hour analysis time was required per sample, but a LOD of 85 fg mL^{-1} was obtained. The latter paper described the microwave digestion of the undissolved materials containing the analytes followed by their separation from the transuranous elements by ion exchange and by di(2-ethylhexyl)phosphoric acid extraction chromatography. Another paper has also used TEVA resin, but on this occasion Np was the analyte.[205] In another paper, Evans *et al.* used a commercial polystyrene–divinylbenzene resin with a mobile phase of 1.5 M nitric acid and 0.1 mM 2,6-pyridinedicarboxylic acid to separate ^{238}U from ^{239}Pu.[206] Since the two analytes were separated physically, the system helped overcome the interference from uranium hydride on the signal of the Pu. The use of an USN enabled a LOD of 0.02 pg g^{-1} to be obtained and analysis of foods such as cabbage, milk and meat yielded results that agreed within 20% with published values. The use of a mixed bed of cation and anion exchange resins for the simultaneous separation and determination of Am, Cm, Np and U, as well as some lanthanides, has been described by Perna *et al.*[207] The chromatographic separation in terms of oxidation/reduction agents and mobile phase was optimized and the procedure was validated by the use of CRMs and by independent techniques. Detection limits were 0.25 ng mL^{-1} for lanthanides and 0.45 ng mL^{-1} for the actinides, whilst precision was better than 5% ($n = 7$). A robust and rapid procedure for determining ^{226}Ra that takes minutes rather than hours has been reported by Lariviere *et al.*[208] Using a combination of Sr*Spec and UTEVA cartridges, potential interferences were removed. The eluate containing the Ra was pre-concentrated further using a Ln cartridge, yielding an absolute LOD of 0.02 fg using less than 4 mg of sample or 25 mL of liquid sample. The same research group determined the same analyte in biological and uranium ore samples using collision cell ICP-MS.[209] Using the optimal collision cell gas mix of 7 mL min^{-1} helium and 4 mL min^{-1} hydrogen, a LOD of 1 fg was achieved.

Sediment samples from the Irish Sea have been analyzed for their Np content using dc-GDMS in a paper by Heras and co-workers.[210] After compacting the samples into pellets, the secondary cathode technique was used to promote their sputtering. A certified sediment was spiked with Np so that a matrix matched calibrant was obtained. Using 100 data points collected over a 300 ms integration time, an LOD of 80 pg g^{-1} was obtained. Results were in agreement with those obtained for ^{233}Pa using gamma spectrometry. Numerous techniques, including alpha spectrometry, ICP-MS and photon electron rejecting alpha liquid scintillation (PERALS), have been evaluated for the determination of ^{237}Np in a paper by Baglan and colleagues.[211] In addition to the instrumental methods of analysis, sample preparation techniques, including ion exchange, extraction chromatography and solvent extraction, were compared. The overall procedures were compared in terms of the concentration level capable of determination, time required for analysis and waste generation. Attogram quantities of ^{231}Pa in dissolved and particulate fractions of sea-water have been measured using isotope dilution TIMS in a paper by Shen *et al.*[212] The procedural blank was 16 ± 15 ag and, using a measurement time of $<$1 h, the quantity of Pa required to produce an uncertainty of $\pm$4–12% was 100–1000 ag. The sample size requirements were orders of magnitude less than traditional decay-counting techniques and significantly smaller than previously reported ICP-MS methods. The speciation of I in spent solvent from nuclear fuel reprocessing has been achieved using X-ray absorption near edge structure (XANES) spectroscopy, which is an element specific technique that is relatively independent of the sample medium.[213] The solvent (tri-butylphosphate and odourless kerosene) containing I at a concentration of 40 ppm was analyzed using XANES and the spectrum obtained compared with those obtained from eight reference compounds containing I at oxidation states of between -1 and $+7$. The authors concluded that the I was most probably present in the solvent as an organoiodide species, although the presence of molecular I, which has a very similar spectrum, could not be discounted. A paper by Mas *et al.* has reported the rigorous optimization of the instrumental parameters required for ^{99}Tc determination using a conventional ICP-MS instrument.[214] Using the partial variable control method and the 5-d Simplex method, LODs of 0.2 and 0.8 ppt were obtained, respectively, which represented a large improvement on that obtained by the instrumental automatic tune procedure (47 ppt). The authors also concluded that the formation of polyatomic interferences such as molybdenum hydride and refractory oxides were irrelevant to ^{99}Tc counting; but that isobaric interferences such as ^{99}Ru were potentially problematic. The sample preparation and quantitation of tritium by AMS has been reported.[215] The hydrogen of organic samples was converted to a solid, titanium hydride, which could be analyzed by AMS. The process by which this occurred was described in detail. The ^{3}H/^{1}H ratio of the titanium hydride is measured by AMS and normalized to standards whose ratios were determined using decay counting. Several sample types, including water, organic compounds and biological samples, were analyzed to validate the technique. Calibration spanned five orders of magnitude and samples smaller than 2 mg could be analyzed following addition of tritium-free hydrogen carrier.

Some papers have reported on the analysis of materials used in the nuclear industry. Papers by Junior and Sarkis[216] and by Dung *et al.*[217] have determined analytes in uranium compounds. In the former paper, ICP-MS was used to determine 24 analytes in uranium oxide fuel. Analysis of a set of CRMs indicated that 18 of the analytes could be determined accurately and with acceptable precision, whilst the remaining six could not. This was attributed to the effects of analyte signal suppression and spectral interference. The latter paper used a nitric acid dissolution of the samples followed by a matrix removal step in which the uranium was extracted into tributyl phosphate, and then AAS to determine the analytes (Cd, Fe, Mn, Mo, V and Zn). The Pb content of secondary coolants of a pressurized water reactor has been determined by ETAAS using a multi-injection technique.[218] By injecting nine × 90 µL aliquots with drying in between, it was possible to obtain a LOD of 0.012 ppb. The reference material NIST 1643c was used as a quality control measure. Sample throughput must surely have been very low to accommodate the drying of such a large sample volume in nine separate injections.

Atmospheric aerosols have been collected on polypropylene fibrous filters, which have subsequently undergone different ashing or microwave digestion protocols in an attempt to determine the effects of such parameters.[219] It was found, somewhat unsurprisingly, that for the dry ashing, parameters such as time, temperature and the properties of the element had an effect on the recovery. More volatile analytes were better suited to closed microwave digestion procedures. Analysis was by ICP-AES, although the use of a HPGe well detector led to greater sensitivity. In another paper, atmospheric particles were sampled from on site, near field and from Cactus Flats, a distance away from a waste isolation pilot plant, and then analyzed using a number of techniques.[220] Alpha spectrometry was used to determine ^{239}Pu and ^{240}Pu, and ICP-AES and -MS were used for other analytes. It was found that the Pu levels varied with the season, with the highest values being obtained in spring. It was noted, however, that the ^{239}Pu and ^{240}Pu activity concentrations were comparable over the three sites, indicating no contamination from the plant. In addition, it was found that the Pu tended to be associated with the particles of larger diameter ($>$10 µm).

Other typical environmental applications have been published. Kenna determined ^{237}Np as well as three isotopes of Pu by ICP-MS following a complete acid digestion procedure of the sediment samples.[221] Data from the analysis of standard reference materials and from the Ob river in Siberia, as well as data obtained from an inter-laboratory comparison, were presented and discussed. It was found that recoveries were 70 and 90% for Np and Pu, respectively, whilst precision was typically 1–5%; except for ^{241}Pu for which it was 10–15%. The LOD was 0.5 fg g^{-1} for all isotopes. A similar sort of paper has been presented by Chen and co-workers.[222] These workers used 10 g of sediment or up to 200 L of sea-water as their sample. Another paper that has analyzed sediments has been presented by Torgov *et al.*[223] These authors developed a procedure for determining Th and U isotopes from sediments from Lake Baikal. After sample decomposition, the Th and U were co-extracted with trioctylphosphine oxide, diluted with caprylic acid and then back-extracted prior to analysis by ICP-MS. The procedure was validated by the successful analysis of the reference material BIL-1, Lake Baikal bottom silt. A summary of analyses of chemicals can be found in Table 2.

3 Advanced materials

3.1 Polymeric materials and composites

There have been several reviews or overviews relating to subjects within this area in the review period. Kurmaev and co-workers produced a short review of the role of soft X-ray fluorescence in materials science that included applications involving conducting polymers and metal–polymer interfaces.[267] Karen *et al.* discussed the uses of TOF-SIMS for the characterization of advanced materials.[268] Both of these reviews are discussed in more detail in section 3.2. A more personal review has been produced by Vanhaecke and colleagues, who discussed the use of ETV-ICP-MS for the determination and speciation of trace elements in solid samples.[177] The review is illustrated with

Table 2 Summary of the analyses of chemicals

Element	Matrix	Technique; atomization; analyte form[a]	Sample treatment/comments	Reference
Petrol and petroleum products—				
As	Refinery streams	AAS;ETV;L	All the analytical parameters, *e.g.*, chemical modification, drying step, *etc*., were optimized based on the multivariate Doehlert design	224
Cu	Refinery waste water	AAS;F;L	FI spectrophotometric Cu determination using DDTC without solvent extraction. Resuilts compared with those from FAAS	225
Cu, Mn, Ni, Sn	Gasoline	ICP;ETV;L	Oil in water emulsions were prepared with Triton X-100 after pretreatment with nitric acid. These solutions were presented to the instrument and pre-concentrated in the graphite tube by repeated pipetting and drying	82
Pb, Sn	Gasoline	AAS;QT;L	HPLC separation of organo-Pb and -Sn species followed by heated electrospray coupling with quartz tube AAS	156
Na	Alcohol	AES;F;L	Inaccurate results normally obtained by direct analysis of alcohol fuels by flame photometry were overcome by use of standard additions. Here the use of an automatic flow-batch standard addition method is described	226
Various	Soils	AAS;F;L	Soils collected from areas of refined petroleum products handling in Lagos	227
Various	Petroleum well tubing adherence	XPS;-;S	The undesired material adhering to the internal surface of the tubing wall was identified and analyzed by XPS	228
Zr	Petroleum fluids	MS;ICP;L	Both aqueous and organic phases can be measured on the same calibration curve	147
Oils, fuels and crude oil fractions—				
Fe	Mineral and edible oil	AAS;ETV;-	Oil in water emulsion using Triton X-100 formed. No further sample pre-treatment necessary	229
Hg	Gas condensates	MS;ICP;L	Species selective determination of atomic Hg, non-polar di-alkylated Hg compounds, polar mono-alkylated species and inorganic Hg. GC-MS also used	230
V	Crude oil	AAS;F;L	V determined in burned and un-burned crude in an attempt to investigate its fate	231
Various	Used lubricating oil	TOF-MS;ICP;L	LA of the oil sample with no sample pre-treatment. Two different calibration strategies were compared	98
Various	Soils and sediments	XRF;-;S	EDXRF used to determine heavy metals around a major crude oil terminal	102
Various	Crude oil	AES;ICP;L	USN employed to remove the solvent from samples dissolved in toluene. Analyte addition and internal standardization require to overcome problems arising from asphaltenes	104
Various	Diesel exhaust particulates	PIXE;-;S	Samples collected on a polycarbonate membrane filter. Several elemental and ionic species were determined by PIXE and ion chromatography	232
Coal—				
Cd	Fly ash	AAS;F;L	Centrifugal SPLITT used to fractionate the particle size. Cd concentration, partition and speciation determined in each size fraction	94
Cr	Fly ash	AAS;ETV;Sl	Slurry sampling using Triton X-100 as a stabilizing agent	88
Sn	Coal fly ash	AAS;Hy;Sl	Various procedures for Sn HG were optimized using factorial designs. Details and results given. Ir treated tubes used to retain Sn hydride	87
Various	Fly ash	AES;ICP;L	A sequential extraction study of metals in fly ash was made. The focus was on water soluble, acid soluble, reducible and oxidizable fractions	233
Various	Coal and secondary fuels	AES;ICP;L MS;ICP;L	Trace elements in coal; and other fuels, *e.g.* biomass, determined	93
Various	Coal	XRF;-;S	XRD and XRF used to determine elements in mineral matter and Miocene coal	234
Inorganic chemicals and acids—				
Ag	Potassium thiocyanate in HCl	AAS;F;L	Dicyclohexano-18-crown-6 ether (in 1,2-dichloroethane) used to separate Ag^+ from 0.05 mol l^{-1} potassium thiocyanate solutions in 1 mol L^{-1} HCl, using complex formation followed by solvent extraction. Extracted complex back extracted with 3.0 mol L^{-1} potassium thiocyanate before flame AAS analysis	235
Al, Cd and Cu	Beer and beer ingredients	AAS;ETA;L	Liquid samples injected directly into the furnace. Solid samples introduced as slurries in H_2O_2, HNO_3 and $(NH_4)H_2PO_4$	236
As	Soils	AFS;FI-Hy;L	Samples sequentially extracted (water, KH_2PO_4, HCl then NaOH). Each extract then analyzed using flow injection HG-AFS. As^{III} and As^{V} determined	237
As and Hg	White beet sugar	AAS;Hy and CV;L	Samples dissolved before cold vapour generation AAS for Hg and hydride generation for As	238
As and Se	Industrial sulfur	AES; Hy-ICP; L	Sulfur digested with HNO_3/H_2O_2. As and Se converted to hydrides prior to simultaneous detection	239
As, Cu and Pb	Waste materials	MS and AES;ICP;L	Samples leached using a microwave extraction method then the leachate measured directly	240
As, Sb and Se	Graphite surfaces	SIMS	Samples analyzed directly	241
Au	Ore sample digests	AAS;FI-Hy;L	Flow injection vapour generation used to form volatile Au species that were then transported to the flame AAS detector	242

Table 2 Summary of the analyses of chemicals (*continued*)

Element	Matrix	Technique; atomization; analyte form[a]	Sample treatment/comments	Reference
B	High purity tantalum materials	MS;ICP;L	Samples dissolved with HF–HNO_3. On-line anion exchange matrix separation used to retain B, which was then eluted with 5 M HCl	65
Cd, Mn and Pb	Water samples	AAS; ETA; L	Analytes collected on an activated carbon microcolumn. Eluted using 2 M HNO_3 and analyzed off-line	243
Co	Water and table salt	AAS;F;L	Co extracted onto Chromosorb 105 resin on-line at pH 9 in NH_3 solution. Co eluted with 1 M HCl	244
Cr	Tannery effluents	AES;ICP;L	Cr^{III} separated by (i) precipitation as $Cr(OH)_3$ and (ii) cation exchange preconcentration. Cr^{VI} remaining in the samples then quantified	245
Cr	Tannery effluents	AAS;ETA;L	Samples analyzed directly. Procedure compared favourably to flame AAS and UV-vis spectrophotometric methods	246
Cr	Natural oak wood dust	MS;ICP;L	Samples dissolved in acid solution prior to direct analysis	247
Cr	Water samples	AES;ICP;L	$CaHPO_4$ powder added to collect Cr^{III}. Powder filtered, Cr^{VI} remaining in solution reduced to Cr^{III}—collected as before. $CaHPO_4$ samples dissolved in HCl, diluted and analyzed	248
Cr and Hg	Recycled paper	AAS;ETA and CV;L	For Hg, samples digested with HNO_3–H_2O_2 mixture before CV-AAS detection. Cr^{VI} extracted from the samples using NaOH before GF-AAS detection	249
Cu, Fe and Zn	White sugar samples	AAS;F;L	Samples dissolved in water and filtered. Analytes determined in the solution and the filtrate	250
Hg	Cigarette smoke	AAS;CV;G	Vapour phase Hg trapped on Au–Pt gauze before determination by two-stage amalgamation cold vapour AAS	251
Hg	Concentrated hydrochloric acid	MS;ICP;L	Hg (as an anionic chloride) collected on a column of cross linked chitosan. Method used to purify HCl. Hg removed with 1 M HCl–0.05 M thiourea	252
P	Fertilisers	AES;ICP;L	Total P, EDTA extractable P and water soluble P determined and results compared with those obtained using AOAC official method	253
Pb	High purity aluminium salts	AES;ICP;L	Pb complexed with APDC and extracted into MIBK. Extract digested with acid–H_2O_2 before analysis	254
Se	Vegetable digests and slurries	AAS;ETA;L	Samples digested with HNO_3. Six different matrix modifiers for Se measurement studied. $Pd(NO_3)_2$ was the most effective	255
Ti	Environmental materials	AES;ICP;L	Ti (as Ti^{IV}) complexed with dibenzo-18-crown-6 ether at pH 4 and extracted into 1,2-dichloromethane before analysis	256
Various	Industrial wastes	XRF	Lead smelting wastes analyzed directly using synchrotron induced XRF	257
Various	Industrial waste incineration fly ash	MS and AES;ICP;L	Samples leached with HNO_3 and *aqua regia* to study composition of compounds in the ash	258
Various (Rare Earth Elements)	High purity lanthanum oxide	HR-MS;ICP;L	Trace rare earth elements separated from the dissolved sample matrix using HPLC. Fractions collected from the column and measured	259
Various	Alumina	AES;ETV-ICP,S	Samples analyzed directly, using appropriate matrix modifiers	260
Various	Silver from waste X-ray photographic film	MS;ICP;L	Ag recovered from waste X-ray photographic film, using NaOH stripping procedure. Ag then dissolved, diluted and analyzed directly	261
Various (5)	Ammonium salts and industrial fertilisers	AAS;F;L	Analyte ions complexed with 1-nitroso-2-naphthol at pH 9 before solid phase extraction onto Diaion HP-20 resin. Extracted complex then eluted for analysis	262
Various (5)	Contaminated soil	MS;ICP;L	Samples leached using four leaching solutions. Efficiency of each compared against results of complete sample microwave digest	263
Various (6)	Domestic and industrial sludges	AAS;F;L	Different extraction procedures (acetic acid, EDTA, microwave) tested and compared	264
Various (8)	Alum	AAS;F;L	Analytes of interest chelate complexed and extracted from the alum material prior to analysis	265
Various (8)	Hazardous solid waste	AAS;F;L	Industrial waste material leachates measured before and after passing through calcium alginate beads (with/without humic acid added). Beads removed toxic heavy metals (by adsorption)	266

[a] Hy indicates hydride and S, L, G and Sl signify solid, liquid, gaseous or slurry sample introduction, respectively.

assorted examples from the authors' own laboratories and includes the analysis of several plastics, including Carilon, polyethylene, polyamide and poly(ethylene terephthalate).

Since many of the samples of this type are difficult to dissolve and/or digest, the majority of methods used to analyze them have involved techniques capable of analyzing the solid materials directly. Despite this, there have been two papers that have reported methods of dissolution. Eilola and Peramaki have modified a medium pressure, microwave digestion procedure used for biological samples so that it is capable of dissolving assorted polymers.[269] The digestion mixture comprised sulfuric and nitric acids, with hydrogen peroxide being present as an extra oxidant. Using ICP-OES as a means of detection, the method was validated by the successful determination of Cd in the reference material IRMM-VDA polyethylene, number 001-004. Other successful digestions were reported for 2-nitrobenzoic acid (2-NBA), 4-NBA and copper(II) phthalocyanine-3,4′,4″,4‴-tetrasulfonic acid tetrasodium salt; although digestion was incomplete for 3-NBA. In the other paper[219] polypropylene filters used for the collection of atmospheric aerosols were digested using an enclosed microwave system. Results were favourable when compared with those obtained from a dry ashing procedure, especially for volatile analytes. Detection was by ICP-OES.

As was stated previously, most methodologies have used techniques that analyze the solid material directly. Several examples have been produced. Included in these is the determination of Cu and Mg in polyethylene by suspension sampling FAAS (written in Chinese).[270] After crushing and sifting, the sample was suspended in an alcohol–Triton X-100 mix. The same mix was used to prepare the standards; whilst strontium was used as a releasing agent during the Mg determination and n-butyl alcohol was an enhancing agent. The method was described as being convenient, rapid and accurate. Trace amounts of Si have been determined in polyamides using an ETV-ICP-MS technique in a paper by Resano *et al.*[271] The effects of the vaporization temperature on the occurrence of interferences for all Si isotopes were evaluated, as was the presence of palladium as a chemical modifier. Optimum conditions were found to be a temperature of 2400 °C, use of ^{29}Si and with the addition of 1 μg of palladium. The authors demonstrated that successful analysis was possible using aqueous calibration, that there was a high sample throughput (20 minutes per sample) and that a low LOD of 0.3 $\mu g\ g^{-1}$ could be achieved.

X-ray fluorescence is a technique that is in common usage for this type of sample. Vazquez and co-workers used TXRF to obtain spectra from polymers with a mean molecular weight of 10^6 and then used chemometric tools, such as principal components analysis and cluster analysis, to visualize the differences in composition of the samples.[272] The polymers examined included aqueous solutions (1% m/m) of scleroglucan, polyacrylamide, polyoxyethylene oxide, glucomannan, 2,3,6-tri-*O*-ethylamylose and xhantan. A simple method of depth profiling ultra-trace impurities in polytetrafluoroethylene (PTFE) wares has been demonstrated by Tanaka and Takahashi, who employed surface scraping and acid vapour extraction followed by ICP-MS detection.[273] After scraping the surface of the PTFE with a silicon wafer, highly pure acid vapour was used to extract the surface and the extractant solution obtained was then analyzed by ETV-ICP-MS. Blank values for Al, Cr, Cu, Fe and Ni were 0.006, 0.004, 0.003, 0.005 and 0.002 ng, respectively. The method was capable of determining ng g^{-1} levels of impurities and was reportedly more effective than the acid-dipping method for the elimination of metal impurities.

The use of TOF-SIMS for the depth profiling of polymer solar cells for characterization purposes has been described by Bulle-Lieuwma *et al.*[274] Since depth profiling of polymer and polymer metal stacks is a relatively new field, the craters were thoroughly investigated by SEM, interferometry, surface profilometry and atomic force microscopy (AFM). It was found that there was a huge increase in crater roughness as the crater depth increased, resulting in a loss of depth resolution. Despite this, it was still possible to show that data concerning layer to layer diffusion and contaminants at buried interfaces could be extracted from the depth profiles. The use of laser induced plasma spectroscopy (LIPS) for routine on-line process analysis has been demonstrated by Fink and co-workers.[275] These authors used a system consisting of an echelle spectrograph, along with chemometric methods, for pattern recognition amongst recycled thermoplasts from consumer electronics. Using multivariate methods such as PCR and PLS and carbon as an internal standard, the authors obtained considerable improvements in selectivity and sensitivity, with LODs being at the ppm range. Analysis of low density polyethylene oxidation using ^{18}O and TOF-SIMS has been conducted by Moller *et al.*[276] By replacing the ^{16}O in the oxidation atmosphere with ^{18}O, it was possible to distinguish between the O already present and that introduced from the oxidation process. Another advantage was that the yield of O ions in TOF-SIMS is very high, giving good sensitivity. This ensured that the technique was ideally suited to following early stages of oxidative degradation. In another paper, Cruz and Zanin evaluated and identified degradative processes in post-consumer recycled high density polyethylene (HDPE).[277] Assorted techniques were used to study the process, including AAS, so that the catalytic residue in the HDPE could be identified so as to correlate it to the degradation process.

Several papers have used atomic spectroscopy as a means to characterise a new composite. The preparation and characterization of a composite material containing Fe in a cross-linked resin host based on styrene and divinylbenzene has been reported.[278] Using aqueous suspension polymerization to produce the materials, the effects of different types of porogen agent (toluene, toluene–n-heptane, or a toluene solution of polyphenylene oxide) on the bulk density, swelling and ferromagnetic properties were tested. In addition, AAS was used to determine the Fe content. It was found that the porogen agents used affected the Fe particle distribution on the bead surfaces. Other synthesis and characterization papers published in this review period include one by Song and co-workers, who discussed a CdSe–poly(4-vinylpyridine) quaternary ammonium nanocomposite[279] and another by Gupper *et al.* who used several techniques to characterize a polymer blend consisting of polyamide 6.6 (80%), PTFE (18%) and silicone oil (2%).[280] In the latter paper, FT-IR, SEM and EDXRF enabled the distribution and size of PTFE clusters in the polyamide matrix to be determined. The authors demonstrated that clusters of diameter 10–30 μm were distributed randomly throughout the matrix and that the silicone oil was present at the cluster–matrix interface. Samuel and co-workers produced a publication entitled "High styrene-rubber ionomers, an alternative to thermoplastic elastomers", in which the characterization of the products was realized by using techniques such as XRF, FT-IR, NMR and dynamic mechanical analysis.[281] The high styrene rubber ionomers were prepared by sulfonating styrene butadiene rubber in 1,2-dichloroethane using acetyl sulfate reagent, and then neutralizing with methanolic zinc acetate. The functionalization of PTFE surfaces by nitro- and bromophenyl diazonium tetrafluoroborate salts and the characterization of the products using cyclic voltammetry, XRF and TOF-SIMS has been described by Combellas *et al.*[282] The authors found that the nitro- and bromophenyl moieties were covalently linked to the material and could be removed only by abrasion. The characteristics of phosphates and transition metal complexes synthesized onto viscose rayon felt for flame retardancy have been discussed by Kim *et al.*[283] The metal complexes were synthesized onto the viscose rayon felt because the metals are known to have the effect of reducing the amount of smoke produced. All of the surface modifications were characterized by the use of techniques such as attenuated total reflection (ATR)-FT-IR and TOF-SIMS.

An on-line process monitoring system for the determination of F incorporation into polyethylene sheets has been described by Kasai *et al.*[284] The gaseous contents of a reaction chamber containing F, N and O, as well as the polyethylene sheet, were sampled *via* a peristaltic pump. After mixing with TISAB buffer, the F content was determined using an ion selective electrode. The monitored concentration of the F gas as a function of time coincided with the variation of the incorporated F in the polyethylene sheet, measured by XRF.

One interesting paper calculated the Rayleigh and Compton X-ray scattering cross sections for molecules, plastics, tissues and biological materials.[285] The scattering cross sections were calculated using Kα X-ray energies covering the angular region from 0 to 180 using non-relativistic, relativistic, relativistic modified and molecular form factors. The plastics investigated were bakelite, polycarbonate, nylon, lucite, polystyrene and polyethylene. The aim of the work was to develop a semi-analytical model that could be used for designing and optimizing an X-ray imaging system. Direct solids analysis has also been used for dental applications. Since the composites used in dentistry may be a source of elements that may cause adverse biological effects, it is necessary for them to be analyzed. In one paper PIXE, photon excited XRF and copper beam elastic recoil detection analysis (ERDA) were used during the analysis of composites used in restorative dentistry.[286] The techniques of PIXE and XRF were used to determine numerous (22) metallic analytes, whilst the ERDA was used to determine non-metals such as B, C, F, H, N and O, as well as some metals/metalloids, *e.g.* Al, Na and Si. In another dentistry orientated publication, Ghazi *et al.* reported the use of LA-sector field (SF)-ICP-MS to detect nano-leakage at the dentin adhesive interface.[287] Here, a study of the diffusion of silver nitrate into sub-micron voids beneath resin-bonded composite restorations was made. The authors determined ^{43}Ca as well as both Ag isotopes using a Nd:YAG laser operating at 266 (frequency quadrupled) and 213 nm (frequency quintupled) to ablate the sample. Precision for the analytes ranged from 2.8 to 7.1% RSD in the samples, but were somewhat better (1.8–2.5%) for the NIST 612 glass calibrant. The investigations revealed that there was considerable Ag penetration into the resin bonded dentin, with concentrations ranging between 35 000 and only a few 10s of mg kg^{-1}, depending on the depth. The authors concluded that the amount of Ag increased with the acid-etching time and that LA-SF-ICP-MS was a suitable technique for quantifying the amount of nano-leakage of bonded restorations.

3.2 Semiconductor and conducting materials

As always, this has proved to be a popular area of research. Several reviews/overviews of techniques that may be used during the analysis of such materials have been produced. Included in these is an overview discussing the role of the analytical technique for characterization of advanced and high purity materials.[42] The properties of many of these materials are affected by the concentrations of impurities, and therefore accurate analysis using techniques such as AAS, ETAAS, ICP-OES, ICP-MS, neutron activation analysis (NAA) and differential-pulse anodic stripping voltammetry (DPASV) can be essential. Other reviews have concentrated only on specific techniques. A short review of applications of soft X-ray fluorescence spectroscopy for the study of electronic structure and the chemical bonding of advanced materials has been presented by Kurmaev and co-workers.[267] The authors demonstrated that the technique was very efficient for characterising different materials such as transition metal compounds, layered superconductors, conducting polymers, metal–polymer interfaces and ion-implanted insulators. A paper by Misra and Mudher discussed the principle advantages of TXRF, namely the requirement of very little sample, high sensitivity and the ability to analyse surface and shallow layers up to a depth of a few nanometers, during the analysis of materials.[288] In particular, they discussed the analysis of a silicon wafer using TXRF. Recent developments of X-ray techniques covering both laboratory and synchrotron radiation (SR) applications to detect crystal imperfections and surface contamination in Czochralski-grown silicon wafers has been reviewed by Kawado.[289] Energy dispersive TXRF, SR-TXRF, wavelength dispersive XRF (WD-XRF) and WD-SR-TXRF were all discussed. The author concluded that the combined use of laboratory and SR experiments led to precise information about crystal imperfection and surface contamination in large diameter silicon wafers. Another review by Becker discussed the use of ICP-MS and LA-ICP-MS in materials science.[290] This review is discussed in more detail in Section 3.4 Ceramics and refractories. Karen *et al.* produced a paper entitled "TOF-SIMS characterization of industrial materials; from silicon wafer to polymer".[268] The authors discussed its use for the analysis of surface contamination and its extremely high sensitivity. In addition, the difficulty of interpreting the spectrum when real industrial samples with complicated surface compositions are to be analyzed was also discussed. The authors demonstrated the technique by investigating the factors that may influence the sensitivities of adsorbed species on a well-defined silicon surface and on organic polymers with different functional groups. Vapour phase decomposition-ICP-MS (VPD-ICP-MS) as a means of analysing semiconductor materials has been discussed by Ferrero and Posey.[291] The paper discussed the measures taken to improve the LODs by eliminating potential contaminants during the sample preparation procedure.

A *certified reference material* has been characterized using a multi-method approach.[292] Techniques such as Rutherford backscattering spectrometry (RBS), synchrotron XRF, instrumental neutron activation analysis (INAA) and ICP-isotope dilution–MS (ICP-ID-MS) were used to analyse a layer of Sb atoms implanted with an energy of 400 keV into a high purity silicon wafer at a nominal dose of 5×10^{16} atoms cm^{-2}. Excellent agreement between the different techniques was reported and the relative merits of each were discussed. The high precision measurements of very small sample spots enabled an estimate of the inhomogeneity to be determined. This was found to be better than 0.4%. The material was certified to have $4.81 \pm 0.06 \times 10^{16}$ atoms of Sb cm^{-2}.

A range of novel methods has been used to analyse semiconducting materials in this review period. Trace element accelerator mass spectrometry (TEAMS) is a combination of AMS, a technique that is commonly used to determine long-lived isotopes such as ^{10}B, ^{14}C, ^{36}Cl, *etc.*, at extremely low concentrations with SIMS, a technique that is used routinely to determine impurity levels in materials by depth profiling techniques. The use of TEAMS has been reported by McDaniel *et al.*[293] Molecular interferences are known to be problematic for SIMS analyses, but the molecular break-up characteristics of AMS were used in TEAMS to remove these. The combination of the techniques therefore appears to be an ideal solution. Impurities such as As, B, Cl, Co, Cr, Cu, F, Fe, Ge, Mg, Mo, N, Ni, P, Sb, Se, Sn and Zn were determined in a number of substrates, including gallium arsenide, gallium nitride, silicon, SiGe and $CoSi_2$. A new technique entitled low energy electron induced X-ray emission spectroscopy (LEXES) has been developed and a specific instrument called the shallow probe applied to the determination of doses of shallow dopants and film thicknesses.[294] The paper reported that the method can resolve depth at the nanometre range and that it had been applied to a wide variety of dopants implanted into silicon wafers, N quantification in oxynitride barriers as well as characterization of Sil-xGex structures. Results obtained from TOF-SIMS and TXRF analyses of trace metal contamination on silicon and gallium arsenide wafers have been correlated by Mowat and co-workers.[295] Close agreement between the techniques was observed. As an application, quantitative mapping of Cu and Zn on gallium arsenide using TOF-SIMS was demonstrated.

Two papers have discussed methods of decreasing interferences when analysing semiconductors and materials used to prepare semiconductors. Kawabata *et al.* demonstrated the use of a dynamic reaction cell fitted to a quadrupole ICP-MS instrument to overcome phosphorus and sulfur based interferences during the analysis of phosphoric and sulfuric acids.[170] The authors claimed that such technology could reach the sensitivity required to analyse future generations of such materials for impurities. In the other paper,[296] a hexapole collision cell using hydrogen as the reaction gas was used to overcome polyatomic interferences during the ICP-MS determination of trace analytes (Ag, Al, Co, Cr, Cu, Fe, Mn, Pb, Sr and Zn) from the surface of silicon wafers. The analytes were sampled by the use of 100 μL of a mixture of water, hydrogen peroxide and hydrofluoric acid. This paper demonstrated a number of techniques. The use of a direct injection high efficiency nebulizer (DIHEN) increased the sensitivity by a factor of between 2 and 9, depending on the analyte, when compared with a micro-nebulizer/spray chamber assembly. The precision obtained using the DIHEN was also reported to be greater than that using the conventional nebulizer/spray chamber assembly. In addition, the use of helium (rather than hydrogen) as the collision gas increased ion transmission efficiencies of analytes such as As, Ca, Cr, Fe and Se that are traditionally difficult to determine using a conventional quadrupole ICP-MS instrument, thereby improving their LODs. Two papers have described very different methodologies for determining Fe in indium phosphide. A method using a strongly basic anion exchange column on-line with ICP-MS detection has been described by Kozono and Haraguchi.[297] Sample solution was injected onto the column in a carrier stream of 9 M hydrochloric acid, which eluted the indium, but the Fe was retained on the column. Elution of the Fe to detection was carried out by using 0.3 M hydrochloric acid containing 1 ppb Co (as an internal standard). The LOD for Fe was 3 ng g^{-1}, whilst recoveries from 0.8, 2.4 and 8.0% indium solutions were close to 100%. The results from the analysis of an Fe doped indium phosphide wafer by this technique were in good agreement with those obtained by an ETAAS method. An alternative methodology has been reported by Taddia and co-workers.[298] These workers digested the Fe doped indium phosphide wafer using 1 + 1 hydrochloric acid, evaporated the sample to dryness, oxidised the Fe up to the +3 state using nitric acid, and dried the sample again before dissolving the residue in 0.01 M hydrochloric acid. The Fe was then complexed using 0.05 M acetylacetone in toluene. The complexes in the organic phase were then analyzed directly by ETAAS using an external organic standard calibration. The LOD was 0.03 μg g^{-1}. Analysis of real samples containing 0.2–0.7 μg Fe g^{-1} yielded precisions in the range 8–21% RSD. This group of workers has also reported the determination of B in silicon doped gallium arsenide.[299] Sample was digested using 1 + 1 *aqua regia* and, to prevent gallium interference during the ETAAS determination of B, a double extraction of chlorogallic acid in diethyl ether was performed. The graphite tubes were pre-treated with iridium and tungsten as permanent modifiers and a mixed modifier of nickel, strontium and citric acid was also used to improve instrumental performance. The authors reported a characteristic mass of 301 ± 47 pg and a LOD of 2.4 μg g^{-1}. The results of the method were compared with those obtained from a UV-vis spectrophotometric method and a simple ICP-OES determination of the digest.

As discussed previously, *depth profiling* is a task that SIMS is very capable of completing successfully. There have been a number of such applications, although many have appeared in journals that do not specialise in atomic spectroscopy. Hence, many of the applications give very few details of the atomic spectroscopy, other than the fact that it was used. As a consequence, these papers will not be discussed here. One paper that reported the results of a SIMS round-robin study of depth profiling of As implants in silicon is worth discussing, however.[300] Doses of between 3×10^{16} and 3×10^{14} ions cm^{-2} were implanted into the silicon, the latter providing a peak As concentration of 11 at.%. The use of ultra-low energy SIMS for depth profiling is a technique that is reportedly growing rapidly, especially in the semiconductor industry.[301] This report stated that the first challenge for the technique was to develop the equipment that was capable of obtaining high quality data with sufficient rapidity to be economically viable. A brief historical introduction was given along with a review of the instrumental developments. The author claimed that the current challenge is to obtain a good enough understanding of the experimental process to obtain accurate, interpretable data. The elementary requirements for this were also described. Numerous depth profiling techniques have been compared in a paper by Klockenkamper *et al.*[302] A silicon wafer implanted with Co ions at a dose of 10^{17} cm^{-2} was depth profiled using two variants of Monte Carlo simulation, X-ray photoelectron spectrometry (XPS), sputtered neutrals mass spectrometry (SNMS), grazing incidence XRF, RBS, and a newly developed method that used wet chemical etching and TXRF detection. The depth profiles were found to differ significantly and this was attributed to unsuitable calibration leading to high systematic errors. The wet chemical etch/TXRF and RBS techniques were, however, found to be in good agreement. According to Marcus *et al.*, radiofrequency glow discharge optical emission spectroscopy (RF-GD-OES) is a new depth profiling technique that is capable of elemental composition information on a wide variety of sample types.[303] In common with most depth profiling methods, the RF-GD plasma utilises an ion sputtering step to ablate the sample material in a layer by layer manner. However, it operates at elevated pressure (2–10 Torr) and has the inherent ability to sputter electrically insulating materials directly without any auxiliary means of charge compensation. Sputtering rates of 1 μm min^{-1} provide rapid analysis with depth resolving powers that are comparable to high vacuum sputtering methods. The authors demonstrated the use of the technique during the analysis of boron implanted silicon wafers, a barrier type alumina film and a porous type alumina film. It was concluded that the technique holds a great deal of promise for the thin films industry.

Several papers have used SIMS as a tool to analyse the purity of materials. An article by Tsukamoto *et al.* has discussed the present state and problems of SIMS from the viewpoint of characterization and has compared it with other analytical methods.[304] Godisov and co-workers have determined the purity of ^{28}Si layers grown by vapour phase epitaxy (VPE)[305] and of ^{28}Si and ^{30}Si grown by molecular beam epitaxy (MBE).[306] One of the more interesting applications of SIMS is a method of analysing insulating materials such as silicon nitride.[307] Such materials may prove problematic for SIMS analysis because they "charge up". In this paper the authors have embedded trenches formed by a FIB gallium beam. The trenches were then filled with platinum. These platinum filled trenches were capable of channelling away the charge, hence preventing the charging up and facilitating the SIMS analysis of the sample. The analytical protocols required to achieve good analytical precision during the determination of the dopant profile concentration of analytes such as As, B and P in silicon have been discussed by Chi and co-workers.[308] Factors such as analytical species, matrix ion species, energy bandpass and sample holder design were all discussed. The authors demonstrated that it was possible to distinguish As or P implant doses differing by 5%.

Characterization of a wide range of sample types is another task that SIMS can undertake, often in conjunction with other techniques. Many of the papers use the atomic spectroscopy as a tool, and therefore no huge amount of detail is gone into. However, a few highlights should be mentioned so that the reader can obtain a taste of the work that is being reported in the literature. Selected examples include the analysis of the composition of anodic and thermal oxides grown on indium phosphide and gallium arsenide,[309] where $^{16}O/^{17}O$ SIMS was used with Auger spectroscopy and XPS; characterization of hydrogen incorporation into the MOVPE growth of zinc selenide, zinc sulfide and ZnSSe epilayers on gallium arsenide;[310] and determining the transport properties of Mn doped GaAs grown on gallium arsenide substrate by molecular beam epitaxy.[311] In this latter paper, SIMS was used in conjunction with transmission electron microscopy (TEM) to demonstrate that the Mn dopants were abruptly confined. The purity of the trimethylindium (TMI) used for MOVPE grown indium phosphide has been measured using FT-NMR, ICP-OES and ICP-MS.[312] The impurity profiles in the TMI were compared with the electrical characterization of the grown indium phosphide layers in terms of electron mobility and carrier concentration, in order to establish a correlation. Other papers in the characterization and dopants area using SIMS include ones by Shamir *et al.*,[313] Porter *et al.*[314] and by As.[315] Another of the more interesting applications papers has been presented by Wei and co-workers, who used SIMS to determine impurities in GaNAs alloys grown by metalorganic chemical vapour deposition.[316] The N precursor was dimethylhydrazine and the Ga precursor was either triethylgallium or trimethylgallium. It was found that the product formed using the triethylgallium was of better quality and had fewer contaminants than that prepared from the trimethyl derivative.

Superconductors have been analyzed in two papers in this review period. Diffusion of ^{18}O in polycrystalline (Hg,Re)Ba_2-Ca_2Cu_3Ox ceramic superconductors at 450 °C has been measured using SIMS by Tsukui and co-workers.[317] The samples, which were made in two stages by solid state reaction of oxides and carbonates, followed by mercury incorporation by annealing at high temperature in a sealed tube containing the precursor and mercury oxide/mercury, were found by scanning electron microscopy (SEM) and SIMS not to be phase pure. The other paper[318] used XRF measurements to characterize superconductors of the $MA_2Ca_{n-1}Cu_nO_{2n+3}$ type.

3.3 Glasses

The analysis of glasses is again dominated by surface and direct solids analysis. This is common in modern manufacturing, archaeometric and forensics applications. The variety of techniques employed for the surface analysis of glasses was illustrated by a report on the characterization of silica composites containing Ag and Ag_2S nanoparticles.[319] These materials were produced by both sol–gel and ion implantation processes. The use of sequential implantation led to Ag–Ag_2S clusters. Advanced microscopic and X-ray analytical techniques, including XPS, X-ray excited Auger spectroscopy (XE-AES), SIMS and RBS, were complementary in providing compositional and microstructural information. This yielded valuable insights into the materials, the various production routes and allowed an analysis of the effects of synthesis parameters to be undertaken.

Laser induced breakdown spectroscopy (LIBS) is highly applicable to process control applications and has been the subject of a number of reports. The use of a fibre optic probe based LIBS system was described[320] and examples given of applications including real time elemental analysis of glass batches[321] and *in-situ* elemental analysis of glasses.[322] A similar application was reported for the process analysis of molten glasses used for the immobilization of high level nuclear waste.[323] The system was based around a plasma formed on the surface of the glass by the action of a frequency tripled Nd:YAG laser and an Echelle spectrometer that allowed the monitoring of emission between 200 and 780 nm. Calibration was obtained against 12 in-house reference glasses containing 27 elements. These reference glasses were produced on a laboratory scale, melted and held at 1200 °C during the calibration procedure. The calibration data was analyzed using a multivariate approach (PLSR). The calibrated instrument was then used to monitor the composition of molten glasses in a pilot plant. The results of these trials suggested that LIBS could be applied to highly radioactive glass melts.

An obvious requirement for investigation of archaeological specimens is that a non-destructive analysis technique is preferred. Such techniques include both PIXE and PIGE and the use of these techniques has been the subject of a number of reports. These include: glazes on Renaissance terracotta sculptures;[324] the characterization of the corrosion layer on soda glass artefacts to aid in dating and detection of fakes;[325] and medieval glasses from Ljubljana.[326]

The identification of glasses for *forensic purposes* continues to place high demands upon the reliability, accuracy and precision of analytical techniques such as ICP-AES and ICP-MS. These developments continue to provide an exemplary lesson in the validation of an analytical method. For example, the determination of the composition of glasses from automobile side windows using ICP-MS was investigated using a hierarchical sampling scheme to assess variances due to sampled population, sample dissolution, within sample heterogeneity and replicate measurements.[327] This provided a guide to the discriminating power of an individual element and, in conjunction with refractive index measurements, enabled an assessment of the potential of these techniques for forensic purposes. In another paper, the use of different comparison criteria was assessed in terms of the ability to discriminate between over 200 unrelated glass samples that had been analyzed for 10 elements.[328] A suitable statistical test was identified that resulted in no errors in terms of false association. The use of LA-ICP-MS for glass classification was reported.[329] The use of a linear discriminant data analysis procedure allowed the unambiguous identification of several common and pharmaceutical glasses based on the raw mass spectrum, *i.e.*, without calibration of the instrument response. For a summary of analyses of glasses see Table 3.

3.4 Ceramics and refractories

Several reviews or overviews of methods used during the analysis of ceramics and related materials have been published in this review period. X-ray fluorescence analysis of the raw materials for the glass and ceramic industries has been overviewed by Falcone *et al.*[335] The technique, which is described as being automatic, rapid, versatile, accurate, sensitive and easy to use for quantitative analysis, was described in detail from the preparation of the sample through to the treatment of results. The preparation of fusions in terms of sample to flux ratio *etc.*, the stability of the glass beads so-formed and the use of certified standards, inter-laboratory test materials and synthetic samples, were also discussed. The authors concluded that the results demonstrated that the validity of the analysis was satisfactory and that it conformed to the requirements of the glass and ceramics industries. The application of ICP-MS and LA-ICP-MS to materials science has been discussed by Becker.[290] The difficulty of calibration during LA-ICP-MS was addressed along with the potential hazards of polyatomic interferences. Methods of overcoming these interferences, *e.g.* by using sector field instrumentation or collision cell technology, were also discussed. The author also described new analytical developments and possible applications of ICP-MS and LA-ICP-MS in surface analysis for materials science. The problems associated with the dissolution of ceramic samples should not be under-estimated. An assessment of some of the current techniques has been made by Tsolakidou and co-workers.[339] These authors subjected 13 well characterized and very different samples to three different attacks, namely hydrofluoric–perchloric acids in open PTFE vessels, fusion with lithium metaborate and microwave digestion in PTFE bombs. The effectiveness of each procedure was evaluated in terms of its ability to dissolve the various mineralogical phases of the sample, of the number of elements that could be determined and of the time needed for the entire analysis to be completed.

Several simple applications have been described in the literature. In one paper,[340] a simple microwave assisted digestion in acid medium was proposed that enabled the ICP-OES determination of B and Li in ceramic frits. The method was reportedly more rapid than the traditional fusion method of sample preparation, enabled the determination of

Table 3 Summary of analyses of glasses

Element	Matrix	Technique; atomization; analyte form[a]	Sample treatment/comments	Reference
Ag, Na	Glass	XRF;-;S	Determination of concentration depth profiles	330
P, Si	Anti-reflection coatings on solar cells	SIMS	Depth profiled	331
Pb	Pb crystal glass.	SIMS, XPS and EPMA;-;S	Surface characterized before and after leaching with dilute aqueous ethanoic acid	332
Si	Silica glass	SIMS;-;S	Hydroxylation and dehydroxylation behaviour of silica fractures studied using temperature programmed SIMS	333
Various	SnO_2 coated glass	Secondary neutral mass spectrometry	Chemical depth profiles obtained before and after the glass was weathered	334
Various	Glass raw materials	XRF;-;S	Fusion with lithium tetraborate. Calibration *via* CRM and synthetic samples	335
Various	Bioactive glass	PIXE	Gel formed around implants characterized	336
Various	Float glass	SIMS	Glasses weathered. Depth profiling used to elucidate mechanisms for changes in surface composition	337
Various	Glass beads (16th Century)	μprobe XRF;synchrotron	Non-destructive chemical characterization to determine provenance and manufacturing location	338

[a]Hy indicates hydride and S, L, G and Sl signify solid, liquid, gaseous or slurry sample introduction, respectively.

both analytes simultaneously and was unaffected by different chemical composition of the frits. In another paper, micro-PIXE was used to develop standards for the microanalysis of ceramics by LA-ICP-MS.[341] The authors described how their LA-ICP-MS technique was capable of determining most elements whose concentration was greater than 100 ng g^{-1} and that matrix matched standards were necessary for accurate calibration. The aqueous degradation and chemical passivation of yttria–tetragonally stabilised zirconia (Y-TZP) has been studied using a number of techniques, with the goal of controlling the surface chemistry in aqueous suspension to promote dispersion and permit aqueous processing of Y–TZP powders.[342] Some powdered ceramic was placed in water at 25 °C and was analyzed by ICP-MS, while the surface and the bulk structure of the powder was analyzed by techniques such as XRD and NMR.

Numerous papers have been published describing the *preparation and characterization* of ceramics. Since many of the papers are published in specialist journals, details of the atomic spectroscopy in them are fairly scarce. Despite this, some of these papers are worth discussing. Shim and Lee described the synthesis of zirconia toughened alumina, titania toughened alumina and zirconia–titania toughened alumina by ultrasonic spray pyrolysis at various temperatures from starting salt solutions of various compositions.[343] The products were characterized using a variety of techniques including SEM, XRD, particle size analyser (PSA) and ICP-OES. The hydrothermal synthesis of doped lead zirconate titanate ceramic powders and the ICP-OES determination of dopant incorporation have been described by Texier *et al.*[344] The hydrothermal synthesis was reported to produce the homogeneous, fine and dis-agglomerated powders required whilst avoiding the drawbacks of compositional fluctuation and contamination of the milling process that are associated with the traditional solid state reactions. The materials were analyzed using ICP-OES in an attempt to determine the incorporation of the dopants that govern the ferroelectric and piezoelectric properties of the ceramic. The results were used to optimise the preparation process. Anti-ferroelectric lead lanthanum zirconate stannate titanate ceramic powders have been synthesised using a combined co-precipitation and solid state reaction.[345] The authors reported the use of XRF to analyse the stoichiometry of the calcined powders. It was found that the powders had the composition $Pb_{0.97}La_{0.02}(Zr_{0.65}Sn_{0.25}Ti_{0.10})O_3$. X-ray methods have also been used to characterize magnesium–carbonate co-substituted hydroxyapatites that do not decompose to tricalcium phosphate on sintering[346] and polycrystalline calcium strontium titanate powders.[347]

Leaching from ceramics has been addressed in two papers. In the first,[348] ceramic ware from the Solis Valley in Mexico was analyzed using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, which confirmed that Pb was present in the glaze as PbO. Then, after leaching for 1 min using 0.02 M citric acid, the leachates were analyzed by ICP-MS. It was found that concentrations of between 0.4 and 80.4 mg Pb L^{-1} were present, whereas control pottery made in the US leached only 0.1 mg Pb L^{-1}. Nitric acid extracts of teeth, soils and of the ceramics were analyzed for their $^{207}Pb/^{206}Pb$ isotope ratio in an attempt to demonstrate the use of isotope ratios for Pb source identification. The authors concluded that the Pb in the glazed ceramics posed a potential health risk. In the other paper, ions leached from dental ceramics during static *in-vitro* tests using Milli-Q water at 37 °C for 18 h and 4% acetic acid at 80 °C for 18 h were determined.[349] The ICP-OES analysis demonstrated that the major analytes leached were K and Na, and that the acetic acid extracts also contained large amounts of Al, Mg and Si and smaller amounts of Ca, Cr and Y. The authors concluded that none of the dental ceramics analyzed could be regarded as being inert.

Diffusion and depth profiling is an area of study where secondary ion mass spectrometry (SIMS) is generally regarded as being the analytical method of choice. This is because of its excellent depth resolution and because of its high sensitivity. There have been several studies in this area during this review period. Oxygen grain boundary diffusion in mullite ceramics has been measured using gas/solid exchange experiments, where the samples were placed in an ^{18}O rich atmosphere.[350] Following SIMS depth profiling, it was found that grain boundary diffusion coefficients were about 5 orders of magnitude higher than lattice diffusivities. A study of ^{18}O diffusion into $Hg_{0.75}Re_{0.25}Ba_2Ca_2Cu_3Ox$ super-conducting ceramic at 450 °C using SIMS depth profiling has been reported by Tsukui *et al.*[317] Similarly, Itoh and co-workers measured O diffusion in rare earth doped barium titanate.[351] These authors found that lanthanum and holmium doped systems had greatly reduced O diffusion compared with non-doped barium titanate. In addition, the authors reported that although the rate of O diffusion was dependent upon the amount of lanthanum dopant, the concentration of holmium was unrelated to the diffusion rate. The diffusion of Mg in fused silica platelets, annealed in 1 atm of flowing oxygen at 900 °C, has been found to be accelerated by the presence of Na, whilst Al was found to retard its progress.[352] The study was reported to yield valuable information for the understanding of the roles of various grain-boundary cations in the oxidation of silica forming ceramics. Diffusion of Mg in yttria (10%) stabilised zirconia (10YSZ) has also been studied.[353] A comparison of the diffusion coefficients through the bulk of the sample and through the grain boundaries was made across a temperature range of 1073–1273 K. It was found that the factor with which diffusion through the grain boundaries is enhanced when compared with the bulk sample decreased from 10^5 at 1073 K to 10^3 at 1273 K. Diffusion of B in polycrystalline hafnia films has been modelled by Liu.[354] Again, diffusion through the bulk sample and through the grain boundaries was compared. The author reported that the model predicted that B could penetrate through a 400 nm hafnia film through grain boundary diffusion, but not by bulk diffusion. Concentration profiles obtained using SIMS confirmed the predictions. Schmidt and co-workers presented a method based on high dose-ion implantation of stable tracers followed by SIMS depth profiling to estimate diffusivity in titanium based transition metal diborides and Si–B–C–N precursor ceramics.[355] The analytical basics, advantages and problems of the method were discussed and the authors demonstrated that it was possible to measure the temperature dependence of the diffusivities, especially for those ceramics that have a low diffusivity. Other applications of SIMS to the analysis of ceramics have included: a study of the defect structures in zinc oxide and transparent YAG ceramics,[356] in which cation and oxygen diffusion coefficients were measured; grain boundary chemistry and creep resistance of oxide ceramics;[357] and the analysis of the microstructure of fluorine doped barium titanate ceramics.[358] This latter paper described the preparation of the ceramic by calcination of the intimately mixed barium carbonate, barium fluoride and titanium dioxide. SIMS was then used to map the presence of the F. The authors demonstrated that F was distributed throughout the microstructure of the semiconducting sample but that it was enriched at grain boundaries and in the $BaTi_2O_5$ intergranular phase.

There has been a lot of interest in *historic pottery and ceramics* and many of these have used proton induced X-ray emission (PIXE) spectroscopy, even though the surface of some ancient ceramics can be very sensitive to particle beam irradiation, with brown stains being created by the bombardment.[359] The authors attributed this discoloration to atomic displacements in the material. The induced damage was quantified as a function of beam current, accumulated charge and sample temperature during irradiation. The damage recovery after irradiation was also studied. Fortunately, it was found that the discoloration slowly disappeared at room temperature, but could be very much accelerated at elevated temperatures. Analysis of ancient ceramics using PIXE and chemometric processing of the data has been used in three papers to identify the source of the ceramics. Kieft *et al.* analyzed ceramics from Tell Ahmar, North Syria, and from other places close by.[360] Using PIXE and cluster analysis of the data from the 12 most abundant elements, it was possible to identify which of the ceramic shards came from Tell Ahmar and which did not, even though the compositions were similar. In another example,[361] 50 pieces of pottery were collected from two domains with different types of ancient Sino-civilisation. Determination of the analytes Cr, Cu, Ni, Pb, Rb, Sr, Y, Zn and Zr, followed by multivariate statistical processing, enabled the authors to locate the place of origin of the shards. The final example analyzed white pigments from bronze-age Minoan pottery shards originating from Kommos, Palaikastro, Mochlos and Knossos.[362] The concentration of Mg from the Kommos samples were greatly elevated. One sample from Palakaistro also showed elevated Mg content, so the authors concluded that the technique could potentially be used to elucidate trade relations. The analysis of glazes on ancient pottery has also been reported in several papers. Examples include the analysis of green glazed ware from England and South Carolina,[363] the non-destructive analysis and appraisal of ancient Chinese porcelain, in which major, minor and trace elements were determined in the porcelain body, the white glaze and the blue glaze[364] and PIXE and micro-PIXE analysis of glazes from terracotta sculptures of the Italian renaissance.[324] This latter paper also discussed the problems related to the investigation of such heterogeneous materials and evaluated the experimental uncertainties. A number of techniques, including PIXE, XRF, XRD and a portable XRF used in the field, have been used to characterize Amarna blue pigment, painted on ancient Egyptian pottery.[365] The blue pigment was found to be enriched in Al, Ca, Cl, Co, Mn, Na, Ni, S and Zn. The XRD experiments indicated the presence of NaCl, $CaSO_4$ and $Co(M)Al_2O_4$.

A review entitled "pigment identification by spectroscopic means: an arts/science interface" has been presented by Clark.[366] Both molecular and elemental techniques were described, with emphasis on Raman microscopy and LIBS. These techniques were found to give excellent results in terms of reproducibility, sensitivity, non-destructiveness and immunity to interference from adjacent materials, whilst also enabling depth profiling to be undertaken. Identification of the pigment was noted to be critical if solutions to problems of restoration, conservation, dating and authentication are to be obtained. The use of the essentially non-destructive technique LIBS has been described in several other applications, including the semi-quantitative and quantitative analysis of multi-layered ceramics.[27] The semi-quantitative analysis determined the composition of the glaze, the lustre and the pigment decorations present on the surface; whilst taking into account the contribution to the signal arising from the ceramic layer beneath it. A bench-top LIBS instrument has been used for the analysis of pottery, jewellery and metal artifacts found from excavations in eastern Crete.[26] In the case of the ceramics, the pigments were identified, whilst for the jewellery and metal artifacts, the type of metal or metal alloy was determined. The authors concluded that the technique was suitable for performing routine, rapid, on-site analysis of archaeological objects. Characterization of pottery using LIBS and then using a database enabled Anzano and co-workers to use techniques such as linear and rank correlations to identify the samples.[367] The probability of correlation ranged from 0.8 to 1, with values of close to unity being obtained for most samples.

A variety of other simple applications have been described in the literature. Lead isotope ratios have been measured using a non-destructive technique in majolica shards from six 18th century presidios in northern New Spain.[368] The method used an EDTA extraction followed by ICP-MS determination. Chinese Yue ware, probably the oldest porcelain known, has been analyzed using non-destructive EDXRF.[369] After subjecting the results to multivariate statistical analysis, it was possible to differentiate compositional patterns between specimens from different production sites. A similar application has been described by Rieth.[370] This author used XRF to analyse Clemson Island (regarded as local products) and Owasco (regarded as foreign wares) objects in an attempt to determine the provenance. Unfortunately, no clear distinction could be made between the ceramic types and clay deposits. The author concluded that this may reflect the utilisation of similar resources. A new approach for archaeological ceramics analysis using TXRF has been described by Cariati *et al.*[371] The technique was reportedly more simple than traditional methods of analysis, *e.g.*, using AAS or AES, because it did not require a dissolution process. Instead, it enabled a homogeneous sample to be obtained by preparing a suspension of the ceramic, allowing the suspension to settle and then analysing the sedimented material. As a comparison, the ceramic was chemically digested and analyzed by ICP-OES, FAES and

ETAAS. Information on the provenance of the pottery was again obtained after treating the data from the atomic spectroscopy with chemometric techniques such as principal components analysis and hierarchical cluster analysis. Tsolakidou and Kilikoglou have also addressed the subject of provenance studies of ancient ceramics.[372] These authors used NAA, ICP-OES, ICP-MS and XRF to analyse the samples. Correlation coefficients of greater than 0.9 were achieved when data from the different techniques were compared. Multivariate statistical methods were also used in this application. A discussion of LA-ICP-MS for the analysis of archaeological materials has been made by Speakman and co-workers.[373] The authors state that the use of the technique has been increasing recently because of its minimal destructiveness. Characterization of obsidian, chert, pottery and painted and glazed surfaces was described. Ramos and co-workers have analyzed the enamel on medieval ceramic tiles using techniques such as XRF, AAS and electron probe microanalysis in an attempt to date them.[374] The authors concluded that the complementary nature of the spectroscopic techniques made it possible to evaluate the state of conservation, to establish measures to clean the tiles according to their nature and to date them. A similar paper by the same group analyzed tiles using XRF, XRD, thermal analysis and voltammetric methods.[375]

3.5 Catalysts

By far the largest area of interest in the analysis of catalysts is the *characterization of new products*. Unfortunately, many of these applications are published in specialist catalyst journals that discuss in detail the function of the catalyst, but merely mention that atomic spectroscopy (amongst other techniques) was used for the characterization. Hence, no experimental detail, sample preparation procedures, figures of merit, *etc.*, are given, and so there is little that can be discussed in this review. However, mention should be made of some of them, to give the reader an indication of the areas of interest in the catalyst industry. *Zeolites* have been used extensively in catalysis because of their microporous structure. However, according to Wang *et al.*, they have not yet been widely used in industrial heterogeneous catalysis because the limited diffusion rates influence the reaction rates adversely.[376] To overcome this problem, this group of authors modified the zeolite ZSM-5 with alkali solution, forming a microporous and mesoporous structure (MMM zeolite). This was then characterized by a battery of analytical techniques including XRD, XRF, XPS, SEM and nitrogen adsorption. The alkali was found to change the porosity and chemical composition of the zeolite and the extent to which this occurred was dependent upon the concentration of the alkali. The influence of a bentonite binder on the acid properties and performance of Pd/HZSM-5 and Pd/HM catalysts with different Si : Al ratios for the hydro-isomerization of n-butane has been studied.[377,378] The vapour phase synthesis of 3,5-dipropylpyridine using modified zeolite catalysts has been reported by Srinivas *et al.*[379] A high conversion ($>90\%$) and high yield ($>72\%$) were reported for a Pb-ZSM-5 catalyst. The modified catalyst was characterized using XRD, FT-IR, ICP-MS, temperature programmed de-sorption of ammonia and surface area measurements. Since the clay modifies the zeolite hydrogen transfer activity, the metal/acid site balance and the diffusion, the product selectivity is modified. Klingstedt and co-workers have prepared Pd–Y and Pd–Zr–Y zeolite catalysts by ion exchange of the parent ammonia–Y zeolite, thermally pre-treated Y zeolite and hydrothermally pre-treated Y zeolite.[380] The catalysts so formed were characterized using XRD, SEM-EDAX, nitrogen adsorption, XRF and DCP. Once characterized, the catalysts were used for the removal of polyaromatic hydrocarbons, carbon monoxide, methane and NO_x emissions. The Ga modified form of zeolites has been prepared using substitution reactions, ion exchange and physical mixing.[381] Using PQZSM-5 as a comparison, the catalysts were characterized using XRF, XPS, temperature programmed ammonia de-sorption and surface area measurement. The presence of the Ga was found to decrease the acidity of the catalyst, which enabled de-hydrogenation, alkylation and aromatization reactions to occur more easily. The oxidation capabilities of the zeolite BEA that had been isomorphously substituted with Mo, Ti or V has been reported by Niederer and Holderich.[382] The catalysts, that were characterized using techniques such as XRD, ICP-OES, NMR, ESR, DRIFT and nitrogen sorption, were active in olefin epoxidation; although they were inactive during the epoxidation of allylic alcohol. Leaching experiments indicated that the Ti variant did not leach whereas the Mo and V analogues did.

Numerous other catalyst types have been characterized. Included in these is chromium—incorporating mesoporous aluminophosphate and cubic Cr-MCM-48.[383] These catalysts have been found efficiently to catalyse the vapour phase oxidation of toluene by molecular oxygen. The mesoporous Cr-aluminophosphate was found to exhibit both acidic and redox properties, and hence oxidation as well as de-alkylation processes occurred, whereas the cubic silicate compound acted purely as a redox catalyst. Both catalyst types were characterized using UV-vis, ICP-OES and electron spin resonance (ESR). The isomerization of linoleic acid to conjugated linoleic acids over Ru/C and Ni/H-MCM-41 under mild reaction conditions (80–120 °C) has been reported by Bernas *et al.*[384] The catalysts were characterized using XRD, XRF, XPS, hydrogen temperature programmed de-sorption, DCP-AES and surface area techniques (BET). The isomerization reaction was enhanced by pre-activation of the catalyst under hydrogen. The preparation, catalytic properties and characterization of polymer-bound Schiff base ternary Co complexes have been reported by Wang and co-workers.[385] The preparation involved the polymer bound Schiff base, a cobalt salt and a second ligand such as 1,10 phenanthroline (Phen), 2,2′-bipyridyl (Bipyr) or 8 hydroxyquinoline (8HQ). The ternary complexes, which were capable of catalyzing the epoxidation of long chain linear olefins (*e.g.*, 1-octene or 1-decene), were characterized by IR and ICP-OES. Nanoparticulates of the noble metals Ir, Pd and Rh have been incorporated into the pores of MCM-41 to form catalysts active and selective during the hydrogenation of cyclic olefins such as cyclohexane, cyclooctene, cyclododecene and norbornene.[386] The catalysts so formed were characterized using XRD, ICP-OES, TEM and nitrogen sorption. The synthesis, characterization and study of magnetic and catalytic properties of dispersed Ni nanoparticulates on a mesoporous silica matrix have been reported by Carreno and co-workers.[387] Techniques such as TEM, NMR, SEM, FAAS and nitrogen sorption were used during the characterization. Other catalyst types that have been characterized include Ru–Mn bimetallic catalysts supported on high surface area silica,[388] different alkali metal promoters (K, Li and Na) in palladium chloride–copper chloride/activated carbon catalysts,[389] and titania modified SBA-15.[390] This latter example was active for the photo-degradation of 4-chlorophenol. Two different aluminium trifluorides (alpha and gamma AlF_3) of high surface area were prepared and characterized using IR, nitrogen sorption, XRD, XRF, SEM and temperature programmed de-sorption experiments.[391] The products were tested for the Cl/F exchange reaction of CCl_2F_2 (chlorofluorocarbon-12) and $CHClF_2$ (hydrogenated chlorofluorocarbon-22) in the gas phase. It was found that the alpha analogue was more active than the gamma, and this was attributed to the higher number of Lewis acid sites. Commercial silicas impregnated with a solution of $ZnBr_2$ have been characterized using SEM, adsorption/de-sorption porosimetry, EDAX, XRD and AAS.[392] The results indicated that $ZnBr_2$ is distributed evenly over the support regardless of its surface properties. The catalytic surface consists of $ZnBr_2$ and Zn^{II} sites. The catalyst was used for the isomerization of (+)-citronellal. Zircocene and niobocene catalysts have been supported on silica and on methylaluminoxane (MAO) modified silica.[393] The metal loading was determined by XRF and results indicated that a higher loading (0.42% and 1% for Nb and Zr, respectively) was achieved on the MAO-passivated silica. It was found that although the Nb-based catalyst showed no activity for the polymerization of ethylene, the Zr analogue had very high activity. A study by the same researchers characterized the compounds further using RBS, XPS and XRF.[394] Lee and Lee have reported a method whereby methane was partially oxidised to syngas over calcined Ni–Mg/Al layered double hydroxides.[395] On this occasion, the catalyst was characterized using, amongst other techniques, XRD, XRF, surface area analysis and CHNS analysis. The effects of the catalyst composition and the calcination temperature on the catalytic performance and extent of catalyst de-activation were investigated. It was found that the catalyst performance was related strongly to Ni particle size and the calcination temperature, with higher temperatures forming more active catalysts. Binary Al–Ni and ternary Al–Ni–Fe Raney nickel catalysts have been synthesised and characterized by Salmones and colleagues.[396] These authors used a two-step synthesis procedure involving mechanical metal alloying and alkaline aluminium leaching. This produced a fine nano-structured, slit-shaped material that was characterized using AAS, XRD, SEM and nitrogen physisorption. A new heterogeneous hybrid ruthenium catalyst, described as being an eco-friendly option for the production of polymers and organic intermediates, has been synthesised and then characterized using XRD, XRF, ICP-MS and both FT-Raman and solid state NMR.[397] The catalyst exhibited excellent stability, re-usability and leaching characteristics. Strobel and co-workers have produced two papers that have utilised LA-ICP-MS to analyse flame made platinum–alumina (that catalyses enantioselective hydrogenation)[398] and titania–silica (an epoxidation catalyst).[399] In the former paper, liquid precursors containing aluminium propoxide and platinum acetylacetonate dissolved in xylene–ethyl acetate were mixed in oxygen and combusted, forming nano-structured powders. These powders were collected and analyzed using TEM, hydrogen chemisorption, nitrogen adsorption, XRD and LA-ICP-MS. It was found that the Pt, although well dispersed, was confined to the alumina surface. It was reported that these flame spray pyrolysis catalysts showed a higher activity for the enantioselective hydrogenation of ethyl pyruvate than a standard commercial Pt–alumina catalyst. In the latter paper, silica and titania precursors were evaporated separately and then mixed prior to feeding into a hydrogen–air diffusion flame. Highly agglomerated nano-particles were formed, again with the Ti being confined to the surface.

Automobile catalysts have been studied extensively in this review period. Moldovan and co-workers have used LA-ICP-MS to determine the distribution of the platinum group elements (PGE) as well as the poisoning elements P, Pb, S and Zn in the surface of both gasoline and diesel automobile catalysts.[400] The technique of LA-ICP-MS was described as having both the sensitivity and the spatial resolution for the analysis. Both fresh catalysts and catalysts that had been aged over 80 000 km were analyzed. It was found that the concentration of the PGEs in the gasoline catalyst decreased at the front of the catalyst, whereas in the diesel type, the loss was more evenly distributed throughout the catalytic block. The distributions of the poisoning elements were less well defined. For the gasoline type, P, Pb and Zn were retained non-uniformly by the catalyst, whereas the same was true for only P and Zn in the diesel one. The authors hypothesised that this could indicate different ageing mechanisms between the two types of catalyst. Results that were not really in agreement with these findings have been obtained by Lucena *et al.* when they used laser induced plasma spectrometry (LIPS) to analyse fresh and used (80 000 km) diesel engine automobile converters.[401] These authors found that P and Zn poisoning elements were distributed along the full length of the catalyst after 80 000 km usage, and that the Pt was removed preferentially from the beginning of the converter, closest to the engine. In an extensive study, Moldovan and a plethora of co-workers elucidated the environmental risk of particulate and soluble PGEs released from gasoline and diesel engine catalytic converters.[402] Whole raw exhaust fumes from four different converters of three different types (Pt–Pd–Rh and Pd–Rh for gasoline and Pt for diesel) were examined during their useful lifetime (0–80 000 km). Samples were collected following the 91441 EUDC driving cycle for light duty vehicle testing, using a sampling device that could differentiate between the particulate and soluble fractions. Analyses were performed using both quadrupole and high resolution ICP-MS. The results showed that for fresh catalysts the release of PGE particulates through car exhaust fumes does not follow any particular trend, with a wide range (covering 1–2 orders of magnitude) for the content of noble metals emitted. Samples collected between 30 000 and 80 000 km presented a more homogeneous release for all catalysts studied. It was noted that for the gasoline catalysts, a decrease by one order of magnitude was observed when compared with the fresh catalyst, although this was not observed in the diesel catalyst. The fraction of soluble PGE (the environmentally important fraction because of the increased bio-availability) represented $<10\%$ of the total amount in fresh catalysts, but was substantially higher in used ones. This was especially so for Pd and Rh. A pre-concentration method has been developed that enabled the determination of Pd in complicated matrices using FAAS as a detection method.[403] A micro-column filled with polyamine Metalfix-Chelamine resin, a resin that is highly selective for Au, Pd and Pt, was used to retain the analytes prior to elution and detection. Using an injection volume of 4.7 mL, an enrichment factor of 20 was obtained, although the injection of larger volumes of sample could yield greater pre-concentration factors. The method was described as being sensitive (LOD $= 0.009$ mg L^{-1}), easy to operate and could be used for up to 60 times without any deterioration in performance. The applicability of the method was demonstrated by the determination of Pd in synthetic geological materials and in the pellet type used car catalyst reference material. A TXRF method of analysing three way catalysts for cars that does not require chemical manipulation of the sample and which has been described as being quick (30 min for sample preparation, 10 min for the analysis), precise (1–10% RSD) and simple, has been described by Fernandez-Ruiz *et al.*[404] The two catalytic monoliths contained in the cartridge were analyzed and the mass relationships between the detected elements and Si, a component of the cordierite ceramic substrate, were determined to follow the axial and radial profiles of the elements. Comparison of a fresh (0 km) and used catalyst (59 000 km) concerning the loss of active elements and retention of contaminating elements was made.

A review of xantphos based silica supported, selective and recyclable hydroformylation catalysts has been prepared by Van Leeuwen and co-workers.[405] Various catalysts were compared including SAPC, sol–gel-based catalysts, silica-anchored catalysts and modifications of silica-anchored catalysts. In all cases, leaching of Rh into the product was below the LOD of ICP-OES (1 ppm).

Several other papers have reported methods that have used atomic spectroscopy to try and elucidate mechanistic aspects of catalytic processes. The contaminants present in a three-way catalyst aged under real working conditions for approximately 30 000 km have been determined and reported by Larese *et al.*[406] These authors used techniques such as TXRF and SEM-energy dispersive X-ray analysis to determine both the presence and the distribution of contaminants such as Ca, Cd, Cr, Cu, Fe, Ni, P, Pb and Zn. The formation of $CePO_4$ was one of the mechanisms proposed that may interfere with the Ce^{3+}/Ce^{4+} redox pair, although poisoning with other elements such as Pb may also contribute. A study of the poisoning mechanism by sulfur dioxide on perovskite $La_{0.9}Sr_{0.1}CoO_3$ has been made by Wang and colleagues.[407] Techniques such as Auger, XPS and XRD indicated that the sulfur dioxide diffused into the perovskite layer forming $La_2(SO_4)_3$. After poisoning for a long time, the S within the catalytic layer was found to be homogeneous, indicating that a dynamic equilibrium was achieved between the poisoning reaction and the decomposition of the sulfates. Three catalysts for the electro-reduction of oxygen have been prepared by pyrolyzing between 400 and 1000 °C either iron acetate or iron porphyrin adsorbed on a synthetic carbon made from the pyrolysis of perylene tetracarboxylic dianhydride in a hydrogen–ammonia–argon atmosphere.[408] One catalyst (0.2% Fe loading) was prepared from the salt whilst two were prepared from the porphyrin (0.2 and 2% Fe loading). All three catalysts were analyzed using TOF-SIMS in order to correlate between the ions detected and the catalytic activity. It was found that in all the catalysts made, two different types of catalytic sites were identified. One site contained ions such as $FeN_4C_8^+$, whereas the other site contained ions such as $FeN_2C_4^+$. The abundance of the latter type of site occurred at a pyrolyzation temperature of between 700 and 900 °C, and constituted up to 80% of the sites for when the Fe salt is used to prepare the catalyst, dropping to about 50% for when the porphyrin was used. The $FeN_2C_4^+$ was found to be more electrocatalytically active than the $FeN_4C_8^+$ sites.

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