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Atomic Spectrometry Update: review of advances in the analysis of metals, chemicals and materials

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Abstract

The use of LIBS continues to increase and many studies have been undertaken attempting to ensure maximum accuracy. This was especially true in the ferrous and non-ferrous metals sections where the spectra produced from the materials can be very line rich. Several papers described different mathematical algorithms to facilitate data handling. These included sequential backward selection –

random forest, discriminant function analysis and genetic algorithms such as artificial neural networks. The use of such chemometric tools has also increased in sections including the analysis of cultural heritage samples, and the inorganic materials sections. In addition, it is still in common usage for dangerous samples, e.g. for explosives, nuclear materials etc. For the analysis of fuels, there is still a significant amount of wheel re-invention. Numerous papers are being published describing 'research', that are methods that have been in common usage in specialised fuels laboratories for some years. Sample preparation methods proved a popular area of research in this discipline. This is possibly a reflection of the necessity of analysing the different types of fuels now in common usage. The most recent pharmacopoeias are starting to describe the use of different atomic spectrometric techniques. There has therefore been an upsurge in the number of papers describing the analysis of pharmaceutical products. The lack of suitable reference materials for these and other organic-based sample types is problematic since method development has to rely largely on spike / recovery experiments. This review period has shown an increase in the number of papers using atomic spectrometry to elucidate mechanistic aspects of processes. This was especially true in the catalyst and electronic component sections. These studies frequently use several different techniques to obtain maximum information, e.g. oxidation state of the analytes, the surrounding chemical environment, bulk analysis etc.

Foreword

This is the latest review covering the topic of advances in the analysis of metals, chemicals and materials. It follows on from last year's review[1] and is part of the Atomic Spectrometry Updates series[2-6]. This year has seen several changes to the writing team, with John Marshall and Ian Whiteside retiring. We are very grateful for their years of service. We welcome Julia Waack and Rob Clough who have contributed to various sections.

1 Metals

The use of LIBS for the analysis of metals is gaining pace and several papers have discussed various aspects of this. Among the more common research topics is the use of mathematical algorithms to facilitate data interpretation. This is especially true for the ferrous metals since the spectra can be so complex.

1.1 Ferrous metals

A review containing 92 references by Dwivedi *et al.*[7] gave an overview of the *surface characterisation techniques used for corrosion studies of steels*. After a brief introduction, sections describing the methods of TOF-SIMS, XAS, PIXE, RBS, Auger electron microscopy, EPMA, NEXAFS, XPS microscopy, low energy electron diffraction, small angle neutron scattering and neutron reflectometry were presented. Comparison tables of capabilities, resolution (depth and lateral), advantages, disadvantages and information obtained by using them, were presented.

There is little doubt that the majority of novel applications of the analysis of ferrous metals have been achieved using LIBS. There have been two *reviews of varying aspects of LIBS analysis* of ferrous metals. One, compared LIBS with two of the other main techniques used to analyse metals, namely GD-OES and spark-OES[8] and the second reviewed the use of LIBS in molten metal processing[9]. The review by Bengtson[8], containing 47 references, was entitled "Laser induced breakdown spectroscopy compared with conventional plasma optical emission techniques for the analysis of metals – a review of applications and analytical performance". The review covered a brief history and the principles of all three of the techniques before moving on to comparing their relative attributes. Spark-OES is rapid and is easily automated. It also yields marginally better figures of merit than LIBS. The author concluded that for routine applications, a cost effective, fully automated LIBS system is not likely to be developed in the near future. However, when non-metallic inclusions in steel were analysed, the LIBS was easily superior. The spark-OES may ablate up to 100 times the amount of material compared with LIBS and therefore LIBS offers far better depth and spatial resolution. The advantage of GD-OES is that it is easier to use and is more robust than a LIBS system. Another important point to consider is that there are international standards for both spark and GD-OES methods. These have been developed over many years and, as such, LIBS still has a lot of catching up to do and is very unlikely to replace the conventional techniques in the foreseeable future. However, the author also concluded that LIBS is capable of on-line or near the line analysis, which the other techniques are not leading to cost benefits and potential application in both the scrap sorting market and on the production line with the analysis of molten steel. It is this last application which has been reviewed (with 56 references) by Hudson *et al.*[9]. This review gave the fundamentals of LIBS and presented an overview of current techniques used for the analysis of molten metals. Also discussed were possible future developments.

Numerous papers *used LIBS with various statistics / chemometrics* packages. Some of these facilitate the classification of steels, whereas others optimised the process of data handling. In LIBS analyses, the data from wavelengths of interest are often confounded by unwanted noise components. Therefore, spectral data matrix processing is critical for quantitative LIBS analysis. In one paper, Ruan *et al.*[10] determined P and S in steels using LIBS and then used sequential backward selection – random forest on the data. The authors first gave an overview of the chemometrics techniques and of their capabilities. Experimentally, the LIBS operating conditions were optimised and then nine different types of steel were analysed. These had already been analysed using ICP-OES and hence reference data existed for them. The data obtained from using the sequential backward selection-random forest approach, from random forest alone, from partial least squares calibration and from a univariate calibration approach were compared with the reference data. Average relative error values were very high in the case of the univariate calibration (11.1 – 19.8%), improved slightly for the partial least squares (9.2 – 14%), improved significantly by using the random forest alone (0.83 – 3.47%) and then had a further improvement using the combined approach (0.71 – 2.78%). It was concluded that the combined sequential background selection – random forest approach was a promising regression method for remote, real-time and *in situ* analysis that would facilitate both quality and process control in the steel industry. A paper by Ruiz *et al.*[11] discussed the at-line monitoring of continuous casting sequences of steel using discriminant function analysis and dual-pulse LIBS. These authors briefly discussed the LIBS instrument and then how discriminant function analysis works. Several related statistical outputs e.g. Mahalanobis distance, Wilks' lambda or chi squared were tested. Of these, the authors used Wilks' lambda because its values range between zero and one and may be used as a measure of the quality of the separation between two samples. The system was operated under as close to realistic conditions as possible i.e. at a temperature of 900ºC and from a distance of 7.6 m. It was capable of distinguishing between two stainless steels where the Cr content of nominally 17% differed by as little as 0.2%. Here, the Wilks' lambda changed from 1 to 0.75. For steels that differed markedly, the Wilk's lambda value changed from 1 to below 0.1. By monitoring the mould-powder contaminated oxide layer formed on the surface, it was also possible to determine the exact position in the production line where two steel grades, of very close elemental composition, started to change. An artificial neural network was used with LIBS by Li *et al.*[12] to enable quantitative determination of Cu and V in steel. A genetic algorithm was first employed to select the intensity ratio of the spectral lines of the target and matrix elements and these were then input to construct an analysis model based on the artificial neural network. The root mean square errors of prediction decreased from 0.0190 and 0.0201 for Cu and V, respectively when the genetic algorithm and artificial neural network were not used to 0.0040 and 0.0039% when they were. This represented an approximate reduction of 80%. It was concluded that use of the chemometric methods could aid the accuracy of analysis. Yi *et al.*[13, 14] proposed a novel method using a sparse low-rank matrix approximation *via* convex optimisation to facilitate the quantitative LIBS determination of Cr, Fe, Mn and Ni in 23 certified steel samples. Again, the theory behind the model was explained in detail, as was the experimental setup. A convex objective function was proposed that consisted of a data fidelity term and two parameterised penalty terms. The accuracy of the analysis was improved using a non-convex and non-separable penalty based on the Moreau envelope. The algorithm entitled 'alternating direction method of multipliers' was then applied to solve the optimisation problem. Analysis of the steels was undertaken applying both partial least squares and support vector machine regression models. The new low-rank matrix approximation scheme was shown to improve the performance of both regression methods.

A very complex paper by Porizka *et al.*[15] discussed the use of several *data normalization procedures for LIBS* data obtained from the analysis of steels, ores and aluminium alloys. Once pre-processed the data were then input to multivariate data analysis. Data from each sample type were split into two, with half the data being used as a training set and the other half used for testing purposes. Both principle component analysis (PCA) and soft independent modelling of class analogy (SIMCA), a chemometrics technique that utilises PCA output, were tested. Classical data pre-processing approaches such as mean centering and scaling were studied. The study demonstrated that selection of an appropriate normalization algorithm is troublesome since each sample type is composed of a different number of elements and corresponding elemental lines. For the analysis of steels, the best performance was obtained using classification of row-wise (applied on each spectrum individually) mean centered and raw data. Normalization to the total intensity of the spectrum also yielded good accuracy. The worst performance was obtained with data normalized to selected spectral line intensities. A comparison of strategies for multivariate regression models was also presented by Luna *et al.*[16], who applied them to the determination of Cr, Mn and Ni in 11 steel samples. This was another paper that discussed the theory of partial least squares regression, the selection of variables and the multivariate figures of merit. Data obtained were first smoothed using a second order polynomial and then transformed using a normal variate procedure. Then, two automatic variable selection algorithms (Variable Importance in Projection (VIP) and regression using interval in partial least squares (iPLS)) were employed as well as partial least squares regression alone. The relative standard error of prediction statistical method was used to assess the model's performance. The Wilcoxen signed rank test was used to compare the regression methods and demonstrated that there was no significant difference in performance. Similarly, the elliptical joint confidence region did not detect any systematic errors with any of the proposed methods.

Dominant factor-based partial least squares regression with spectral standardisation has been used by Afgan *et al.*[17] with a specially designed, handheld LIBS instrument to determine Cr, Mn, Ni and Si in 84 different certified steels. The theory of the chemometrics and a description of the instrument were presented. Both the accuracy and precision improved significantly when the dominant factor partial least squares regression was used with spectral standardisation compared with partial least squares alone. Average absolute measurement errors of 0.039, 0.013, 0.001 and 0.019 were obtained for Cr, Mn, Ni and Si, respectively. Precision was typically better than 5% RSD. The method also enabled the quantitative determination of C, which is difficult to achieve using partial least squares alone. Results had significantly lower error and better precision compared with those obtained using a commercial handheld XRF instrument. It was concluded that although there was still room for improvement for the determination of analytes at a concentration of < 0.1%, the method developed was still a significant improvement on previous studies that had used lasers with microjoule energy.

Two papers discussed the use of *calibration-free LIBS analysis* of steels[18] or stainless steels[19]. Both papers stressed the problem of self-absorption arising from iron and other major elements in the steels making it difficult to estimate plasma temperature and to construct a Boltzmann plot for each of the analytes. Both studies used an internal reference line to help overcome this problem. In one[19], the Stark broadening of the Fe(I) 381.584 nm line and the Saha-Boltzmann plots of this element were used to calculate electron number density and the plasma temperature, respectively. Wavelengths that exhibited self-absorption were eliminated in this study. The other paper[18] used an algorithm called ‘particle swarm optimisation’ to estimate the plasma temperature based on calculations from the Boltzmann plot. Fifteen certified alloy steel samples of known composition were analysed and the average relative errors were 4.4, 6.81 and 2.29% for Cr, Ni and Fe, respectively. It was concluded that the method demonstrated an improvement in accuracy over classical calibration-free LIBS and offered potential as an *in-situ* and real time method of analysis.

Two papers used *LIBS for depth-profiling purposes*[20, 21]. The first discussed the depth-profiling of type 116 stainless steel that had undergone corrosion in liquid lithium as part of the first wall of a fusion device. Analysis of the spectra identified Cr, Fe, Mn and Ni lines and variations of intensities from them was a measure of corrosion. The authors acknowledged that the determination of C would also have been useful. However, its content in this stainless steel was too low to be quantified. The second paper[21] discussed depth profiling of galvanoaluminium-nickel coatings on steel plates using both UV (266 nm) and visible (532 nm) LIBS, where both wavelengths originated from a Nd:YAG laser. A study of pulse energy (50 – 250 J cm^{-2}) on the signals was also undertaken whereas the pulse duration was kept constant at 4 ns. The elemental depth profiles were calculated and compared with those obtained using EDX of a section cut through the steel sheet. For Ni, the ablation rate was between 1 and 3.5 µm, depending on the fluence, for both wavelengths and the results obtained were in good agreement with a simple heat diffusion model. However, the results for Al deviated from this model significantly, with the ablation rate ranging from 2 to 4 µm for the 532 nm and from 4 to 8 µm at 266 nm, which was attributed to light-plasma coupling. A further depth-profiling paper was presented by Muniz *et al.*[22] who used a commercial glow discharge time of flight mass spectrometry (GD-TOF-MS) that has nanometer resolution and that is capable of determining most of the elements in the periodic table. The authors focussed the research on the determination of REE in corroded steels. Validation was achieved by the analysis of a homogeneous certified steel sample. Results (4 ± 1, 13 ± 1 and 5 ± 1 µg g^{-1} for La, Ce and Nd, respectively), were in reasonable agreement with certified values (6 ± 1, 14 ± 1 and 5 ± 1 µg g^{-1}). Results showed that REE contaminants did not penetrate deeper than 80 nm, even after soaking in 12 M nitric acid for a month.

Lednev *et al.*[23] described the use of a compact diode pumped Nd:YAG laser that was sufficiently small and light (400 g) to be *attached to a robotized arm for the remote analysis of low alloy steel* samples. Delivery of the laser energy through a fiber optic led to an improved fluence profile stability resulting in shallow and more reproducible craters. The plasmas formed were plane-shaped and dissipated twice as fast as plasmas formed when a laser was illuminated directly on the sample. The greater fluence of conventional LIBS provided a higher temperature plasma with 20-100 times greater emission intensity because of the greater mass of sample ablated and a higher electron number density. A comparison of linear range, LOD and the root mean square error between the fiber optic delivered and direct laser ablation was made for the analytes C, Cr, Mn and Si. The LOD were always better for the direct LIBS approach which also had greater linearity of calibration. However, since the plasma produced by the LA *via* the fiber optic was more stable and reproducible, the root mean square error was less. Conventional LIBS also enabled C to be determined (with a LOD of 55 ppm), which was not possible when the laser was sent through a fiber optic. This was attributed to the plasma produced using the latter being less intense.

The *increased sensitivity obtained using double pulse LIBS* has been exploited by Wang *et al.*[24] who used it to determine Cr, Cu and Mn in micro-alloy steel. Double pulse LIBS is where the sample is ablated and then a second laser beam re-excites the plume making it far hotter and hence increasing sensitivity. The signal enhancement was element dependent but typically ranged between 1.81 and 3.46. The enhancement was correlated with the excitation energy of individual wavelengths.

An *in situ LIBS analysis of the chemical composition of austenitic 14404 stainless steels during tungsten inert gas welding* was reported in a proof of principal study by Taparli *et al*.[25]. By monitoring the chemical composition of the weld pool, it is possible to govern the solidification behaviour and hence minimise defects. The LIBS system employed a Nd:YAG laser operating at 1064 nm, with a maximum energy of 200 mJ and with a repetition rate of 25 Hz. Both the shielding gas and the welding arc plasma have a significant effect (an increase in artificial intensity) of the Cr, Mn and Ni ion lines chosen. This artificial increase of intensity reached a maximum in the presence of the weld plume. This was true to the point that it was difficult to distinguish between welding plasma intensity from the laser induced plasma values. Mapping of the sample, post-weld, enabled distributions of the analytes to be determined. An accumulation of Mn was identified between the heat affected zone and the base material.

The *LIBS analysis of steel blooms* (the starting materials of seamless steel tubes) weighing two or three tons at the rolling mill was reported by Sturm *et al.*[26]. The scale at the surface could be removed and the sub-surface bulk sample could be analysed in < 50 s using the same laser. The LIBS process used a Q-switched diode pumped Nd:YAG laser operating at 1064 nm emitting pulses of 20 – 40 ns. A training set of 30 certified steels was used to calibrate the system and then 481 steel blooms were analysed for up to 14 analytes over several days. The relative mean square root error of prediction was 0.01 – 0.15% by mass when compared with the batch reference values. The LIBS analysis successfully distinguished 86% of the steel grades analysed. The remaining two had only minor compositional differences.

A *nuclear application* was presented by Xiao *et al.* who used LIBS to determine Cl indirectly in the surface of steel canisters used to store used nuclear fuel[27]. The presence of the Cl is known to play a role in the stress corrosion cracking of such materials and hence its determination is imperative. However, Cl demonstrates poor sensitivity in emission-based techniques because of its high excitation energy and also suffers from spectral overlap from some iron wavelengths. It is therefore necessary to determine a surrogate. The authors chose Na rather than the minor components of sea salt such as Mg or K because they are less sensitive during LIBS analyses. A Nd:YAG laser operating at 532 nm, with a fluence of 40 mJ and a duration of 10 ns was used; producing a crater that was reproducibly 200 µm in diameter. It was possible to determine 0.5 – 100 mg Cl m^{-2}. Monitoring the Na emission line at 589 nm yielded a LOD of 0.28 mg m^{-2} with a linear range extending to 20 mg m^{-2}. The linear range was limited by self-absorption effects.

Two papers by the same research group have used *a combination of LIBS and LIF* to increase the sensitivity of the determination of C[28] and of Cr and Ni[29] in steels. The sample was flushed with nitrogen and then a Nd:YAG laser operating at 532 nm and with a pulse duration of 6 ns and a repetition rate of 10 Hz was used to ablate the sample[28]. The C present in the steel then reacted with the N forming CN radicals. A Q-switched Nd:YAG laser was then used to pump a wavelength tunable laser that operated over the range 410 – 710 nm. This latter laser, operating at 421.60 nm, was used to excite the CN radicals making them fluoresce at 388.34 nm. The light emitted was transmitted through a fiber optic to a Czerny Turner spectrometer equipped with an intensified CCD. After careful optimisation of the parameters (inter-pulse delay, etc.), the system was used to analyse eight certified low alloy steel samples. Sensitivity was improved by two orders of magnitude compared with LIBS alone with a LOD of 0.039% and of 0.013 % being obtained when air and nitrogen were used as the flushing gas. A similar protocol was adopted in the second example[29] with the spectrometer being the same. On this occasion laser tunable over the range 225 – 2400 nm was used. The system was tested using 22 certified steel samples. Unfortunately, steel can be problematic for LIBS analyses because iron is a very wavelength rich element and these can interfere with the analyte wavelengths. Care had to be taken to ensure that Cr and Ni wavelengths were chosen that were not interfered with by the presence of large amounts of iron.

Spectral analysis of a laser weld plume is a relatively common practice. However, emission spectroscopy suffers from poor sensitivity. Simonds *et al.*[30] attempted to rectify this shortcoming by using laser induced fluorescence to probe the gas plume induced during fiber laser welding of 304L austenitic stainless steel. An optical parametric oscillator is capable of producing intense light that can be tunable to within 0.01 nm resolution, has a pulse duration of 5 ns and delivers 3.7 mJ per pulse. One of these devices was used with a Czerny-Turner spectrometer equipped with a CCD for the determination of Si. The Si was excited at 221.09 nm and then detected at 221.64 nm. The sensitivity was 10^4 times greater than emission spectroscopy and LOD was 0.04% Si, although this was dependent upon laser weld energy. Work in this area was to continue in an attempt to improve the sensitivity of other alloying elements, e.g. C, P and S.

1.2 Non-ferrous metals

The analysis of non-ferrous metals shows a similar trend to that observed for the analysis of ferrous metals, i.e. much of the more interesting work has been achieved using LIBS. This has often been in combination with a chemometric tool, e.g. artificial neural network, K nearest neighbour, support vector machine, etc. On-line use of LIBS has again featured heavily in the research.

Zhao *et al.*[31] reported *the use of LIBS on-line in a vacuum alloy production process* for the analysis of nickel-based alloys. A Nd:YAG laser operating at 1064 nm and an echelle spectrometer equipped with an intensified CCD were used in the system. The laser source, spectrometer and detector were all explained in detail. The spectrometer had to be temperature stabilised to yield maximum analytical precision. Monitoring of laser parameters such as pulse energy also aided precision. A further improvement in precision and accuracy was obtained by using a Ni internal standard. Calibration curves obtained through the analysis of six certified reference materials yielded correlation coefficients of 0.9559 and 0.9723 for Cr and Al, respectively; indicating that quantitative analysis was possible. Other elements, e.g. Co, Cu Mn, Mo, Nb, Si and Ti also had a correlation coefficient of greater than 0.9. The authors concluded that an improvement in precision was still necessary for the best performance.

Analysis of *aluminium-based alloys* has been described in four papers. In the first, Shakeel *et al.*[32] used calibration-free LIBS to analyse aluminium-silicon alloy. The plasma was formed by a Nd:YAG laser operating at 1064 nm and emission spectra were recorded after a 3.5 µs gate delay. Qualitative data were obtained showing the presence of numerous analytes (Al, Cu, Fe, Mg, Mn, Ni, Pb, Si, Sn, Ti and Zn). Once the background subtracted and self-absorption corrected emission spectra had been obtained, it was possible to calculate the plasma temperature (10,300 ± 300ºC) and to obtain quantitative data. Deviation from reference sample concentrations was no worse than 2.2%. The second paper, by Zhang *et al.*[33] used an intensity correction method as well as plasma position information to facilitate LIBS analysis of aluminium alloys. Severe signal fluctuations were obtained when the surface of the sample is not flat because the sampling depth of the laser and the position of the collection optics vary. An intensified CCD to monitor the plasma and to acquire positional information was used. A mathematical model that attempted to detect and then reduce fluctuations in the surface morphology of the sample was also constructed. Use of a combination of both of these for the analysis of five aluminium alloy samples improved the precision for several analytes (Cu, Fe, Mg, Mn and Si) from 31 – 39% to 4.63 – 7.64%. Correlation coefficients were impressive with the worst being 0.989 for the determination of Cu. Wavelet threshold de-noising for accuracy improvement in LIBS analysis of aluminium alloys was discussed by Xie *et al.*[34]. The paper discussed the theory of wavelet threshold in detail, especially the trade-off soft and hard threshold method. Using the algorithm and an internal standard aluminium line at 308.215 nm, the precision (RSD), root mean square error and linearity of the analytes Cu, Mg and Mn all improved significantly because of the elimination of white noise. An added bonus was that the algorithm took less computing time than many other methods. The fourth paper, by Aragon and Aguilera[35] discussed the use of CSigma LIBS for the analysis of aluminium alloys. CSigma LIBS is a variant of normal LIBS where the calibration scheme is very much simplified. It is calibrated using at least one standard sample, after which the system becomes characterised and other samples may be analysed. For a spectral line exhibiting self-absorption, growth curves are plots of the line intensity against the optical depth, with the latter being proportional to the concentration of the analyte. Advantages and disadvantages of the method were discussed as was the theory and mathematics behind it. The protocol was applied to the analysis of seven certified aluminium alloy samples with one being used for calibration and the other six for testing. Limits of detection for 10 analytes ranged from 1.4 µg g^{-1} for Ca and Mg to 9.7 µg g^{-1} for Cr. Precision varied depending on the concentration of the analyte with values being typically 8% for concentrations greater than 0.1% and increasing to 13% when the analyte was present at between 0.01 and 0.1%. Bias was between 8 and 21% away from accepted values, which was deemed acceptable.

It is established that the use of *double pulse LIBS leads to enhanced sensitivity* when compared with standard LIBS. A paper by Li *et al.*[36] reinforces this fact. A compact, field-portable double pulse LIBS spectrometer weighing only 10 kg was developed and then used for the analysis of assorted NIST standard aluminium alloys. The laser system produced a pulse duration of 16 ns with a fluence of 12 mJ per pulse and an inter-phase delay that is adjustable in 0.5 µs increments from a minimum of 0 s. A signal sensitivity enhancement of up to nine times was obtained compared with single pulse LIBS. An additional advantage is that the background emission was reduced by 70% leading to an overall improvement in LOD by an order of magnitude. Signal stability also improved by 128%, indicating the presence of a more robust system.

Depth-profiling is as common an area of study for non-ferrous metals as it is in ferrous ones. For depth profiling to occur, it is obviously necessary to ablate successive layers from the same spot. Therefore, both LIBS and GD-OES are two of the techniques that are commonly used. A proof of principle paper by Shaw *et al.*[37] used LIBS to determine the depth-profile of He implanted in polycrystalline tungsten. The He was implanted in the tungsten using an ion beam of 200 keV He^+ at 900°C with a fluence of 10^{23} m^{-2}. The experiment mimicked the conditions in plasma-facing components in a nuclear reactor. The LIBS system used a Q-switched, frequency doubled Nd:YAG laser, with an energy of 4-50 mJ per pulse, a repetition rate of between 1 and 20 Hz and a pulse duration of 4 ns. The operating conditions were optimised yielding values for pulse energy of 50 mJ and a gate delay of 0.5µs. Analysis of the crater after 100 shots indicateda depth of 9.23 µm and a width of 185 µm. However, the depth and width did not follow a linear trend with the number of shots; instead obeying a polynomial relationship. Interpolation of the polynomial showed a depth of 0.18 µm and width of 5.17 µm for a single laser shot. Experimentally measured values were 0.22 ± 0.13 µm depth and 9.01 ± 6.97 µm width per laser shot. The potential He wavelengths at 388.86 nm and 447.14 nm were identified. Although signal to noise ratios were not huge, it was possible to detect He during the depth profile with values obtained being in reasonable agreement with predicted ones. A second LIBS-based depth-profiling paper was presented by Cerrato *et al.*[38] who studied de-alloying of brass samples. These authors used a Q-switched, frequency doubled Nd:YAG laser with a pulse duration of 5 ns, an echelle spectrometer and an intensified CCD to obtain LIBS spectra. In the first instance the sample was chemically attacked using a 50:50 mix of 5% acetic acid and 3% hydrogen peroxide. The surface was then mapped (2-D mapping) using the LIBS setup in an attempt to locate areas of de-zincification. A total of 40 spots were ablated covering an area of 15.75 mm^2 and each spot then had 30 laser shots to obtain depth data. By repeating the analysis on a non-chemically attacked sample, the authors demonstrated that the depth of the layer of corrosion on the de-alloyed sample could be identified as being 75 – 90 µm. A paper by Suchonova *et al.*[39] used calibration-free LIBS to depth profile a LiSn alloy. The analysis was undertaken under low pressure in an argon atmosphere. Optimisation of the experimental parameters found an optimum gate delay and gate width of 300 ns. The electron number density and Saha-Boltzmann plots were used to calculate the concentrations present. A fourth depth-profiling paper was presented by Nowak[40] who used GD-OES to characterise four oxidised nickel-based superalloys (IN 792, PWA 1483, MCrAlY and Rene 80). The materials were oxidised by placing them in a thermobalance at 1050^{o}C for up to 50 hours. The heating rate was 90 K min^{-1} and the cooling rate was 10^{o}C min^{-1}. Nowak concluded that depth-profiling using GD-OES had several advantages over other techniques. These include a rapid rate of ablation but with decent resolution, the ability to determine most of the periodic table as opposed to SEM which struggles with analytes such as B and the ability to analyse oxide layers ranging in thickness from 2 – 120 µm whilst also being capable of analysing different oxide layers in multi-layered samples. The methodology was applied to used parts of gas turbines to prove that the technique is applicable to real samples as well as those prepared in the laboratory.

Two papers by Ahmed *et al.* discussed the use of *calibration-free LIBS* for the analysis of brass alloys[41] and for the analysis of different carats of gold[42]. In the first of these papers, the authors gave a decent explanation of the experimental setup and then provided a theoretical explanation of the different methods used to achieve calibration free-LIBS. This included the standard Boltzmann plot method and a modification of it entitled ‘internal reference self-absorption correction method’. For the latter, a step by step guide of how to calculate values was given. A certified brass alloy known to have a composition of 62% Cu and 38% Zn was used to validate the method. A TOF-SIMS method achieved these values, an EDX study obtained values of 61.75% and 32.25%, the standard calibration free LIBS method yielded data of 70% and 30% and the modified method 63.36% and 36.64%. In addition to greater accuracy, the modified method developed also had better precision, with values improving from 12% and 21% for Cu and Zn, respectively to 2% and 4%. In the second paper[42], the authors analysed five gold alloys with carats of 18, 19, 20, 22 and 24 meaning that their Au content is 75%, 79%, 85%, 93% and 99.99%, respectively. The calibration free LIBS system used a Nd:YAG laser operating in air and obtained spectra over the wavelength range 250 – 870 nm. Results obtained using both LIBS and TOF-SIMS were in excellent agreement with certified values. A third paper by the same research group discussed the analysis of copper-nickel alloys using a range of different LIBS methods, LA TOF-MS and EDX[43]. The paper discussed measuring the plasma temperature and the electron number density and went on to explain how these can be used to obtain data for the assorted LIBS types. Analysis of an alloy using the different techniques yielded data in reasonable agreement. Values of Cu and Ni were 69% and 31% using one line calibration free LIBS, 72% and 28% using self-calibration LIBS, 74% and 26% using calibration-free LIBS, 75% and 24.5% using EDX, 73% and 24.7% using XRF and 74% and 26% using LA-TOF-MS.

The use of *chemometrics with LIBS to sort different types of alloy* has been discussed in two papers[44, 45]. The paper by Aberkane *et al.*[44] used LIBS followed by either artificial neural networks, support vector machine or k nearest neighbour to sort six different zamak (zinc, aluminium and copper-containing) alloys. A brief description of the three chemometric methods was presented. The experimental setup included a Q-switched Nd:YAG laser operating at 1064 nm, an echelle spectrometer and a gated intensified CCD. The operating conditions were optimised prior to use to ensure optimal signal to noise ratio was obtained. All three chemometric methods were capable of classifying the different alloys successfully, but under very different circumstances. The support vector machine failed in identifying the alloy in the majority of cases when signal normalization was not undertaken, but improved to close to 100% success when normalization was used. The k nearest neighbour method was the most successful, with 100% correct classification being achieved. The artificial neural network had between 92 and 97.7% success rate in classifying the alloys. The other paper, by Campanella *et al.*[45] discussed the work involved in the European project entitled SHREDDERSORT, in which non-ferrous (especially aluminium) alloys used in the automotive industry, may easily be sorted once the car is scrapped. A mobile LIBS instrument was used that incorporated a Nd:YAG laser operating at 1064 nm and a fiber-optic spectrometer capable of wavelength detection between 200 and 430 nm with a resolution of 0.1 nm and between 415 and 900 nm with a resolution of 0.3 nm. Thirtynine samples, previously characterised using spark emission, were used in the test. Of these, 35 were used to to train the algorithm and four used as test samples.Three spots on each sample were picked at random for double pulse LIBS excitation. The data from 564 intensity values were then input to artificial neural network. The algorithm enabled a more robust, reproducible characterisation of the samples than simple emission line ratios. Despite this, it was still prone to occasional error with between 8 and 15% of samples wrongly characterised.

The analysis of *copper and its alloys* has been reported in two papers. Sample preparation by surface milling and microstructural defects can have a severe effect on the XRF analysis of copper-based alloys. Both problems lead to inaccuracy and poor precision. Gorewoda *et al.*[46] overcame these problems during the analysis of copper phosphide and copper / silver / phosphorus solders by using two different methods. In one, the alloy was re-melted under controlled conditions to obtain fine-grain samples. In the other, 1g of sample was dissolved with 0.2 g of strontium carbonate in 50:50 nitric acid, and then diluted to 100 mL. The strontium acted as an internal standard. An aliquot (50 µL) was then placed on a filter paper, dried and analysed. This therefore acted as a thin layer sample and, since the sample had been dissolved, micro-structural defects did not exist. Both methods led to an improvement in accuracy, with the root mean square error obtained for P decreasing from 1.24% in the original sample to 0.14% in the re-melted sample and to 0.08% in the thin layer sample. The second paper, by Phukphatthanachai *et al.*[47] described how previous studies had shown irreproducibility during the determination of S in copper and its alloys. They described a method that was traceable to SI in which the copper matrix was dissolved using ammonia, hence releasing the S, and then separated the matrix from the S by using a weak cation exchange resin. The S fraction was purified further using an anion exchange resin followed by a chelating resin. The S was finally determined using ID-ICP-MS. The method was very efficient with 99.999% of the copper matrix removed whilst keeping the S recovery above 80%. Low blank values (3 – 53 ng) enabled a LOD of 0.2 µg g^{-1}. Relative error values were calculated to be below 1%, which was deemed fit for purpose for both certification of reference materials and for assignment of reference values during inter-laboratory studies.

Sample introduction using electrothermal vaporization was described in two papers. In one[48], 23 analytes were determined in two certified electrolytic copper samples (ERM-EB074C and ERM-EB075C) using ETV-ICP-OES; a technique that gives a useful insight into the homogeneity of the sample. The data obtained using the method were compared with those obtained using a standard dissolution of the samples followed by ICP-MS or ICP-OES determination. The ETV-ICP-OES method demonstrated improved precision over the dissolution method for most analytes. In addition, the between unit (different chips of sample) uncertainties were also lower for ETV-ICP-OES than for the digestion method. Another paper to employ ETV-ICP-OES, this time for the determination of minor and trace elements (Al, Ca, Cu, Fe, Mn, Ni, Si and Zn) in magnesium alloys, was published by Scheffler *et al.*[49]. A mass of between 2 and 3.75 mg of the alloy AZ31 was weighed into a graphite boat without recourse to grinding, sieving or homogenization. The boat was then placed in an autosampler that transferred it automatically into the ETV device. Careful optimization of the temperature programme was conducted, leading to a pyrolysis step of 400°C for 20 s, cooling to 20°C for 15 seconds and then atomization at 2200°C for 30 s. To aid the volatilisation of the sample matrix, trifluoromethane was introduced at a flow rate of 8 mL min^{-1}. Argon flowing at a rate of 0.15 L min^{-1} transferred the atomised sample to the plasma and a support argon flow of 0.5 L min^{-1} ensured the plasma was "punched". Calibration was against differing weights (1–6 mg) of NIST 1648a urban particulate matter. The limits of quantification were estimated by using an empty graphite boat and assuming 3 mg of sample. The LOQ values ranged from 0.2 mg kg^{-1} for Cu up to 400 mg kg^{-1} for Ca. Results obtained using the method were compared with those obtained using conventional ICP-OES or ICP-MS following an acid dissolution method. According to the authors, results were in "reasonable agreement" with the reported values and with those from the dissolution. The big advantage of the proposed method was that of speed, with a sample being analysed in only 85 s.

1.3 Cultural heritage: metals

The majority of cultural heritage applications are summarised in Table 1. This is because they are interesting and are a significant proportion of the papers published. However, they often have limited novel information in them with regard to atomic spectrometry.

A paper by Heginbotham and Sole[50] *described a protocol for improved inter-laboratory reproducibility for the quantitative EDXRF analysis of heritage copper alloys*. The protocol, catchily named CHARMedPyMca, should facilitate collaboration and allow rigorous use of shared data and databases. It allows for the consistent and transparent application of a free to use, open source fundamental parameters software package (PyMca) that is independent of the instrumentation used. Calibration of the standardless PyMca data is against a set of certified reference materials designed specifically for use with heritage copper alloys (known as CHARM). A reproducibility study was undertaken in which the method was used on data obtained from eight different instruments of six different types. In comparison with a 2010 study, the data obtained was significantly improved in reproducibility and method sensitivity.

Table 1 Analytical applications for the analysis of cultural heritage samples.

Analyte	**Matrix**	**Technique; Atomization; presentation**	**Comments**	**Reference**
Various (16)	Gold finds from Bernstorf, Bavaria	MS; ICP; LA XRF; -; s	Eleven samples of gold analysed using LA-ICP-MS and synchrotron XRF. Different excitation and detection conditions for XRF were tested. Results obtained were in good agreement between the two techniques. Items were > 99.9% pure gold with main contaminants being Ag (20-200 µg g^{-1}) and Cu (1–10 µg g^{-1}).	51
Various	16th and 17th century gilded artefacts	XPS-; s TOF-SIMS	Paper describing multi-technique analysis of gilded objects and identifying manufacturing processes	52

			and corrosion products. Optical microscopy and XRD also used. Atomic spectrometric methods optimised to inflict minimal damage. Main degradation agents identified as being the soil constituents Cl, P and S.	
Various	Etruscan gold coins	p-XRF; -; s	Portable XRF instrument used in combination with the fundamental parameters method. Spectral data input to the self-organizing maps method so that classification of the coins was achieved. Four main classes were identified, with the quantity of Ag being the main discriminator. Information on the origin of the coins was obtained.	53
Various	Ancient copper artefacts	MS; ICP; LA	Novel portable LA system taken into field to analyse samples regardless of their size. The laser plume was either transferred directly to an ICP-MS instrument using a large capacity gas exchange device or was collected on a polycarbonate filter which was analysed later using LA-ICP-MS. The latter method agreed ± 30% with conventional LA-ICP-MS data. The LOD were at the µg g^{-1} level or lower. Further validation was achieved by independent analysis using GFAAS.	54
Various	Metal plaques and a statuette	MS; ICP; L MS; ICP; LA TIMS	A multi-technique study (also including SEM-EDS, optical microscopy and XRD) to authenticate materials. The TIMS	55

			was used to study Pb-210 / Pb-204 to date the artefacts and, after an acid dissolution of fragments, ID-ICP-MS determined numerous analytes. The LA-ICP-MS was used for composition and distribution studies. The Pb isotope ratios indicated that the samples were from approximately 1900 rather than 17th century and, hence, were not authentic.	
Various	Orichalcum ingots from the underwater archaeological site, Gela	MS; ICP; L OES, ICP; L	Small samples drilled from ingots acid digested and then analysed for major and minor analytes. Major chemometric study involving principle component analysis (PCA), cluster analysis, linear discriminant analysis and soft independent modelling of class analogy (SIMCA) undertaken. Three well-defined sets of ingots were identified. Insights into the manufacturing technology and providence were obtained.	56
Various	26 copper-based artefacts and fragments from Portugal	EDXRF; -; s	Combination of XRF with a Monte Carlo algorithm. All the samples had a layered structure of alloy substrate and a superficial layer of patina / soil encrustation. The method developed enabled analysis of the alloy without having to remove the overlying patina. The artefacts were high purity copper with approximately 3% As.	57

2 Organic chemicals and materials

2.1 Organic chemicals

Matrix matching remains a critical point for the analysis of organic compounds. Goncalves *et al.* showed that the use of external calibration in an aqueous matrix resulted in poor accuracy when detecting Cd, Cr, Cu, Ni and Pb in fusel oil utilising sequential microwave-induced plasma (MIP) OES [58]. Unsurprisingly matrix matched calibration, neat fusel oil or propanol solutions (5 or 50% v/v fusel oil), resulted in better accuracy as illustrated by spike studies. When using neat fusel oil standards, recoveries of 90-110% were obtained with excellent precision (RSD ≤2%) for all elements except Cd which showed higher variability (RSD 14%). Limits of detection were in the range 0.001-0.01 mg L^{-1} with LOQs ranging from 0.02 to 0.1 mg L^{-1}. Comparing the developed method to the common micro-emulsion extraction approach did not show a statistically significant difference (95% confidence) between the two methods. Sample preparation was therefore simplified significantly. An additional advantage was that the instrument utilises N_2 rather than the more expensive Ar used in ICP-OES analysis, hence giving a reduced analysis cost.

Advances in sample preparation techniques were reported for the detection of heavy metals in play dough and face and finger paints[59]. Multi-walled nanotubes and patent blue V sodium salt (a chelating agent) were utilised for a solid phase extraction approach to preconcentrate chelated Cd, Co, Cu, Mn, Ni and Pb. An extensive optimisation investigating the effect of pH, amount of patent blue V, sample volume, the eluent composition and its flow rate was performed. However, it was not clear if replicates were utilised. This would have been helpful to establish precision and detect potential statistically significant differences of the various conditions applied. Good correlations (R>0.997) were achieved, however, the concentration range was relatively narrow spanning over one order of magnitude (0.1-1 to 1-10 mg L^{-1} for the different metals). The LODs ranged from 0.21-7.71 µg L^{-1} for the different heavy metals. Applying the developed method to soil CRMs resulted in excellent recovery for all six metals investigated (92-105%). Cadmium, certified at 0.105 µg kg^{-1}, was below the method LOD. Spike studies performed in play dough and finger paint samples demonstrated good accuracy within these sample matrices with recoveries of ≥95%. Heavy metals were detected in the paints and play dough utilising the developed procedure. This highlights a potential route of heavy metal exposure to children.

A *direct Cl isotopic analysis* has been reported by Horst *et al. w*hich utilised a newly developed GC multi-collector ICP-MS method [60]. The GC outlet was connected to the MC-ICP-MS instrument *via* a heated transfer line (250ºC). Previously encountered isobaric interference caused by ^{36}ArH dimers could be minimized when utilising a dry plasma. Results were reported as δ^{37}Cl which expresses the difference of the ^{37}Cl to ^{35}Cl ratio obtained for the sample to that of methyl chloride. Good agreement between δ^{37}Cl values was obtained utilising this newly developed method. It was applied to both single compounds and analyte mixtures. The data obtained were compared with results obtained using a dual inlet gas source isotope ratio mass spectrometry (DI-IR-MS) method. An extensive method development was carried out for which the results obtained were available as supplementary data. The isotopic ratio was independent of the signal size when peaks of 3-27 V were considered. The method LOD was established as signal resulting in a precision of 0.1 mUr or better. This was achieved when injecting 2 nmol and 2.4 nmol of CH_3Cl and tetrachloroethane, respectively. Over a three-day period, the $\delta^{37}Cl$ values determined did not differ by more than 0.2 mUr. Further optimisation of this GC-MC-ICP-MS approach allowed the analysis of GC compatible samples with a boiling point of up to 350ºC [61]. To achieve this, the sample gas was preheated in the GC oven avoiding sample condensation. Furthermore, a transfer line (1/16 inch stainless steel tube) was introduced and the position of the silica capillary connecting the GC and ICP-MS system adjusted to end in the hottest zone within the transfer line. These modifications combined with the introduction of 10^{12} Ω resistors improved the LOD to 250 pmol Cl with a precision of ≤0.1 mUr. The authors investigated the performance of the method, in terms of linearity, accuracy, and precision, for analytes with a varying range of boiling points. This illustrated the broad applicability of the optimised method. In addition, the method was applied to both single compounds as well as sample mixtures which resemble real life situations more closely. The results showed good agreement within ± 0.2 mUr with no carry over effects detected.

A different approach to *Cl determination* was taken by Lesniewski *et al.* [62] who described a plasma assisted reaction chemical ionization (PARCI) MS method which operated at atmospheric pressure at both sides of the plasma. Optimum conditions were reported at carrier gas flows of 2.2 L min^{-1} which, as pointed out by the authors, was nearly twice as high compared with other methods. Utilising a dual spray chamber system allowed the separate introduction of sample and ionisation reagent. To enhance Cl^- formation Na, as easily ionisable element, was introduced to the system increasing the sensitivity by a factor of 1.7. It was pointed out that methanol was also shown to have a positive effect on sensitivity, but the developed method did not allow to decouple and elucidate the combined effect of Na and MeOH on Cl sensitivity. The developed detection system was shown to be compatible with liquid chromatography as, once optimised, only minimal distortion of the chromatographic peak was observed. The LODs for ^{37}Cl and ^{35}Cl were 6.79 and 11.2 ng mL^{-1}, respectively. Unfortunately, a large background of 170 ng mL^{-1} was reported. The authors suggested that Cl contamination was responsible for this and hope that further optimisation will reduce this significantly to enable lower LODs to be obtained.

A *coupled HPLC-ICP-AES approach was utilised to identify polyoxometalates* in reaction mixtures [63]. The main challenge was the compatibility of the HPLC effluent with the plasma as solutions containing >70% acetonitrile extinguished the plasma. The introduction of a micro-column as well as the introduction of deionised water *via* a polyethylene joint to reduce the organic load enabled this issue to be overcome. Both Mo and V in HPLC fractions were quantified utilising an external calibration and the results agreed well with those obtained using ^{51}V NMR analysis. This qualitative approach shows good promise for the analysis of polyoxometalates in reaction mixtures. However further method validation in terms of accuracy, precision, linearity, sensitivity and limits of detection is required if quantitative analysis is to be achieved.

2.2 Fuels and Lubricants

The number of papers in this area increased this year with more contributions related to crude oils and alternative fuels possibly reflecting the industry, oil price and environmental concerns. There is a large contribution from China particularly on the subject of coal analysis. There is still considerable 're-inventing of the wheel' with a number of standard laboratory methods featuring prominently. Authors and reviewers should make themselves familiar with published standard laboratory methods (EI, ASTM etc.) which may not be covered in many literature reviews. Actual laboratory practice in the industry still appears be several years ahead of that being currently published in academic journals and authors would be wise to seek out collaborative partners in industry in the field they wish to study. Industry analysts can be hard to find via conventional academic routes however these people are well worth seeking out and have a wealth of experience in their own fields.

2.2.1 Petroleum Products – Gasoline, Diesel, Gasohol and exhaust particulates.

Only two papers were of note in this section this year. The first by Garcia *et al.*[64] described a method for the determination of *As, Hg and Se in gasoline and petroleum derived products*. This method uses a nebulizer system consisting of three nebulizer units with a cyclonic spray chamber to produce in-chamber chemical vapour generation followed by ICP-OES detection. The sample was introduced *via* one nebuliser with the other two nebulising $NaBH_4$ and HCl. System optimisation was undertaken using multivariate analysis of the $NaBH_4$ and HCl concentrations and the total liquid flow. Detection limits achieved for As Hg and Se were 25, 13 and 140 $\mu g\ kg^{-1}$ respectively. The samples chosen for evaluation unfortunately had analyte levels below the method detection limit therefore evaluation was undertaken using samples spiked with commercial standards. These spike recoveries were in the range 96-113%. Historically determination of these elements in gasoline and other petroleum distillates has proved problematic using nebulisers and spray chambers due to species volatility. It would be desirable to see this method validated with naturally occurring As, Hg and Se species which do occur in some gasolines and distillates rather than spikes to ensure this method is fit for purpose.

The second paper by Dalla Nora *et al.*[65] described a method for the *digestion of diesel fuel by microwave induced combustion and trace element determination using ICP-MS*. The diesel samples were directly weighed onto quartz wool, allowed to stand for 2 hours in a laminar air flow and then wrapped in polyethylene film prior to microwave induced combustion on a quartz holder using filter papers and NH_4NO_3. After combustion the quartz holder was placed in a quartz vessel with 6ml of 14.4 mol L^{-1} nitric acid, sealed and pressurised with oxygen and a microwave digestion step performed. The resultant solution was diluted with water prior to analysis. Limits of quantitation of 0.1, 0.2, 0.1, 0.7, 0.1, 1.6, 4.0 and 0.1μg g^{-1} for Cd, Co, Cr, Cu, Mn, Ni, Pb and V, respectively were achieved. The standard reference material SRM NIST 1084a (wear metals in lubricating oil) was used to evaluate the method with no statistical difference being found between the results and the certified values for Cr, Ni, Pb and V.

2.2.2 Coal, peat and other solid fuels.

All of this year's contributions come from China. The first by Zhang *et al.*[66] described a *distance correction method for improving the accuracy of online particle coal X-ray fluorescence analysis*. The accuracy of online XRF measurements is affected by many factors including the distance from the XRF analyser. This paper describes the use of a laser rangefinder to measure the distance from the sample to the XRF spectrometer. A correction equation was derived based on distance and XRF intensity. When this correction equation was used the % deviation for the known Fe concentration of 0.59% in raw coal reduced from 0.68 without correction to -0.02 with correction.

Three papers looked at different aspects of coal analysis using LIBS. Yao *et al.*[67] investigated *optimizing the binder percentage to reduce matrix effects for the LIBS determination of C in coal*. The calorific value of coal affects the price and this can be estimated from the carbon content. Although LIBS can be used to measure the carbon content, the measurement accuracy is affected by matrix effects caused by non-linear laser-material interactions during ablation, plasma formation and vaporisation. This paper described the use of pellets with KBr as a binder to reduce these matrix effects. Pellets with varying KBr percentages were prepared for nine samples of coal. The difference of the excitation temperature between the nine different coal samples was minimised and 60% KBr binder was found to be the optimum concentration. This binder percentage produced an RSD value of plasma temperature of 4.26%. A multivariate calibration model using Si and K from the binder as internal standards was used to construct a calibration for coal C content using LIBS.

Qian *et al.*[68] looked at the *on-line measurement of elemental composition of coal using LIBS*. Laser wavelengths of 355, 532 and 1064 nm were investigated looking at plasma time evolution and spectral line intensities for the different elements. Energy threshold was also tested to verify how it varied with the different laser wavelengths. It was shown that a higher intensity and energy threshold can be achieved using 532 nm indicating it is good choice for coal LIBS testing.

The last paper in this section by Zhang *et al.*[69] looked *at proximate analysis of coal using LIBS*. The diverse species of coal in China cause a 'matrix effect' and the accuracy of LIBS in this application needs to be improved. This work looked at both the spectral pre-treatment methodology and the calibration model for the conversion of laser induced coal plasma spectra to optimise the coal proximate analysis results. Compared with the traditional methodology single or multiple-peak Lorentzian spectral fitting for spectral line intensity calculations reduced the mean RSD from 12.1% to 9.7%. By combining the single or multiple-peak Lorentzian spectral fitting method with particle swarm optimization and support vector machine regression modelling the average absolute errors of predicted proximate analysis results were 1.37% for coal with an ash content of 16%, 1.77% for coal with an ash content of 30% or more, 0.65% for coal with a calorific value of 9 MJ kg^{-1}, 1.09% for coal with volatile matter of 20% or less, and 1.02% for coal with volatile matter of 20% or more.

2.2.3 Oils – crude oil lubricants

Two review papers were of note in this section. The first by Maryutina Yeo *et al.*[70], containing 149 references, looked at *present day methods for the determination of trace elements in oil and its fractions*. This review is a little simplistic but covers all the techniques in current usage and would be a good place to start for someone entering the field. The paragraphs on ICP-MS however somewhat underplay a technique which has been widely used in industrial petrochemical laboratories for many years. The second review by Bajia *et al.*[71], containing 48 references, looked at *the determination of S content in petroleum products*. Again, this is a good place to start for a researcher entering the field looking for an overview of the subject and covers total S measurements as well as S species.

Li *et al.*[72] looked at the *effects of surfactant and La on the determination of Fe in crude oils using MIP-AES*. This analysis can suffer from poor sensitivity and poor matrix tolerance. The results show that non-ionic surfactant has an inhibiting effect on the Fe signal while cationic surfactant and lanthanum chloride have a sensitizing effect. A concentration of La^{3+} of 0.5 mg mL^{-1} reduced the matrix problems from Ca, Co, Cu, Mn, Mg, Na, Ni and Zn and the iron intensity increased 2.4 times. The detection limit also decreased from 0.0275 mg L^{-1} to 0.0085 mg L^{-1}. The method was applied to the determination of Fe in crude oil samples and the measured results agreed with those obtained using FAAS.

Another paper using MIP-AES was submitted by Poirier *et al.*[73]. This paper compared *preparation methods for the determination of metals in petroleum residues and analysis by MIP-AES and ICP-OES*. A wet ashing technique using sulphuric, hydrochloric and nitric acids was compared with direct xylene dilution and the MIP-AES performance was compared with that of ICP-OES. The techniques and preparation methods compared well for the determination of Ni and V with the MIP-AES producing detection limits of 2.93µg kg^{-1} for Ni and 5.23µg kg^{-1} for V. The MP-AES analysis also yielded recoveries of 100.91% for Ni and 102.52% for V for CRM NIST 1643C. The determination of Fe by direct dilution however did not compare well with that for the wet ashing technique with recoveries around the 50% mark. This was thought to be possibly due to the Fe being present in these samples as micro-particles which are not transferred to the plasma using direct dilution.

Xiu *et al.*[74] looked at the *detection of trace wear elements in engine oil using indirect ablation LIBS*. A rapid and effective approach for oil performance analysis was proposed using the indirect ablation of oil films on metallic substrates. In this analysis the substrate was ablated taking with it the oil film on its surface. A universal calibration curve was established with coefficients better than 0.99 being achieved for Fe, Mg and Ni. The analysis of samples showed good agreement between measured and known values.

A number of papers used speciation techniques to look at crude oils or their components. Vetere *et al.*[75] produced an interesting paper on *qualitative and quantitative determination of S compounds in crude oil using LC-ICP-MS-MS*. Sulphur is a hot topic within the industry as sweet low S crude reservoirs are being depleted necessitating the use of higher S sour crude oils. Regulation for low S in transportation fuel with limits of 10ppm in the EU and US mean hydrosulfurisation is used in refineries to remove sulphur, however some species withstand the process. These species are mostly condensed thiophenic compounds. Using HPLC employing ligand exchange chromatography on a Pd coated stationary chromatographic phase allowed thioethers, 1-ring thiophenes and condensed thiophines to be determined separately within one method. Sulphur quantification was performed using ICP-MS-MS with O_2 as a reaction gas and measuring the S as $^{32}S^{16}O$ at mass 48. Comparison of direct loop analysis and LC fractionation gave a S recovery figure of 95.8%.

Another novel paper was presented by Nelson *et al.*[76] who looked at the *characterisation of dissolved metals and metallic nanoparticles in asphaltene solutions by single particle ICP-MS*. Metals in refineries can poison catalysts, induce corrosion and accumulate in processing units and if they pass into fuel products they can damage engines. Metals accumulate in heavy fractions particularly asphaltenes. This paper looks at Fe, Mo, Ni and V in asphaltenes using single particle ICP-MS. The recently developed single particle technique uses the signal flash induced by a nanoparticle in the plasma over the continuous signal from the dissolved elemental contribution. This allows elemental information to be collected as well as the size of the particle to be ascertained as the size is proportional to the intensity of the signal flash. This allows particle size distribution data for nanoparticles of each element to be produced as well as dissolved concentrations. The study of three asphaltene samples from different origins indicates that Ni and V are entirely dissolved however in contrast it was found that Fe and Mo are forming part of nanoparticles.

Gascon *et al.*[77] looked at *size distribution of Ni, S and V compounds in crude oils and fractions by gel permeation chromatography (GPC)-ICP-HRMS*. Four crude oils were analysed using three styrene-divinylbenzene gel permeation columns connected in series and coupled with a high resolution ICP-MS instrument operated at a resolution of 4000 to resolve interferences from the analytes. Masses used were ^{66}Ni, ^{32}S and ^{51}V. The results show trimodal distributions of V, Ni, and S compounds in the crude oils and residues. The V and Ni compounds are present in both-resins and asphaltenes. Trimodal distributions are apparent in the resins but not in the asphaltenes. In the resins, compounds with a medium molecular weight were expected, however high molecular weight compounds were observed indicating that nano-aggregates or large molecules exist in both the asphaltenes and resins. Low-molecular weight compounds are present in the resins but do not represent more-than 22% of V and Ni present in crude oil. These compounds appear to have molecular weights similar to simple metalloporphyrins.

2.2.4 Alternative fuels.

The number of papers in this section has increased compared with previous years. This possibly indicates more interest in these samples because of environmental concerns and diversification of fuel types.

Three papers describing *sample preparation methods* were of interest. The first by Lima *et al.*[78] described a method for the determination of Cu and Pb in biodiesel and oil samples using a fairly complex combination of dispersive liquid-liquid micro-extraction and emulsion breaking with the analysis being performed using GFAAS. The method produced detection limits of 0.23 and 0.24 µg L^{-1} for Cu and Pb respectively. Analysis of spiked SRM NIST 2772 B100 biodiesel gave recoveries of 87-113% for Cu and 99-107% for Pb. This does however seem a rather cumbersome method when alternative and simpler standard methods are available for both metals in this matrix. Antunes *et al.*[79] described a method for the determination of Al, Cr, Cu, Fe and Zn in biodiesel using a microemulsion preparation method and FAAS detection. This method was described as safer and ‘greener’ than conventional direct analysis methods. For the microemulsion 1.7g of biodiesel and 1100µL of 1.4 mol L^{-1} nitric acid were made to 10mL with *n*-propanol and this was then analysed directly. Limits of detection were 1.7, 0.9, 0.1, 0.3, 0.07mg L^{-1} for Al, Cr, Cu, Fe and Zn, respectively and spike recoveries of 93-102% were achieved. Sanchez *et al.*[80]described a method for aerosol extraction for the determination of Ca, K, Mg and Na in biodiesel with subsequent analysis using *ICP-OES*. The method used a nebuliser and peristaltic pump to nebulise dilute nitric acid above the biodiesel sample in a vial. The aerosol passes through the diesel, extracting metals and collects at the bottom of the vial, it is then extracted and analysed using ICP-OES. This method has an improved extraction efficiency compared with standard liquid/liquid extraction methods. However, it is somewhat complicated compared with existing methods and would be of limited use in a high throughput industrial laboratory. Limits of detection achieved were 0.05-0.06 mg kg^{-1} for all four elements. Back to back measurements for four fuel samples compared the aerosol technique with acid digestion. A t-test was applied and this showed no significant statistical difference in data obtained between the aerosol technique and acid digestion.

Almeida *et al.*[81] proposed a method for the *determination of Cu Fe and Pb in ethanol fuel samples using high resolution continuum source electrothermal AAS using sequential and simultaneous strategies*. After preparation the sample was injected onto the graphite tube with platform and the instrument was set at 217.0005 nm for the determination of Pb. The first measurement was performed at an atomisation temperature of 1400 ˚C after which the tube was cooled. The wavelength was then changed to secondary absorption lines of 216.5090 nm and 216.4550 nm for the determination of Cu and Fe and the atomisation temperature raised to 2400 ˚C. This allowed the determination of all three elements from one injection. Detection limits of 3.06µg kg^{-1} for Cu, 136.0 µg kg^{-1} for Fe and 0.94 µg kg^{-1} for Pb were achieved. Seven samples were spiked with the three elements and recoveries achieved were between 84% and 113%. This may be a useful technique for laboratories without ICP-MS instrumentation which is more commonly used for the determination of these elements in this sample type.

An interesting method was proposed by Zhu *et al.*[82] for the *measurement of Ca, K, Mg, Na, P and S in biodiesel fuel after xylene dilution and ICP-MS-MS analysis* using the mass shift capability of this instrumentation to determine P as PO at mass 47 and S as SO at mass 48. Calcium was determined using hydrogen in the reaction cell to remove the Ar isobaric interference at mass 40. Xylene dilution is fairly standard for these sample types however an internal standard is normally used to correct for instrument drift, matrix effects, viscosity and sample evaporation, however no internal standard was mentioned in this paper. This could be because many of the organic standard solutions contain sulphonates, which would make the determination of S impossible, but sulphur-free standards do exist for many common internal standard elements. Detection limits of 0.0006, 0.003, 0.00009, 0.003, 0.00007 and 0.015 mg kg^{-1} were achieved by this method for Ca, K, Mg, Na, P and S, respectively.

A paper by Cachia *et al.*[83], concerned the determination of *trace elements in gas* and described a high pressure rig for the sampling and collection of trace elements from high pressure gas samples. The rig is designed for use ‘in the field’ for transportation networks. Trapping is attained by bubbling the gas at 6 or 50 bar through three consecutive traps containing 1% $KMnO_4$ for Hg or 10% HNO_3 for Al, As, Ba, Cu, Se, Sn and Zn. The gas flow rate was 20 L min^{-1}. Sampling for Hg lasted 1 day producing a sample volume of 40 Nm^3. Sampling for the other metals lasted 5 days and produced sample volumes of 140 Nm^3. The final solutions were analysed using ICP-MS with Rh as an internal standard. Using this method 96% of the metals were trapped with more than 90% being found in the first trap demonstrating the efficacy of the traps. Quantitation limits for this analysis were 0.39, 0.006, 0.04, 0.22, 0.1, 0.004 and 0.17 ng Nm^{-3} for Al, As, Ba, Cu, Se, Sn and Zn respectively. Gas is predicted to be increasingly used in the future for transportation as well as heating and cooking consequently this sort of analysis will probably become more important in the next few years.

The last paper in this section by Rahman and Hopke[84] assessed *preparation methods of wood pellet samples* prior to analysis using ICP-MS. Wood pellets are used extensively throughout the world to produce energy. Combustion of contaminated wood pellets containing waste wood such as painted wood or pressure treated wood poses potential environmental problems because of the elemental content of the emitted particulate matter. Sample homogeneity and sampling were discussed as was the grinding of the pellets prior to digestion. A microwave assisted direct acid digestion technique was compared with an ashing and microwave acid digestion technique. The NIST standard reference material SRM 1571 Orchard Leaves was used to evaluate the two approaches and produced good agreement between the digestion methods for As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, V and Zn. The optimised methods were then applied to the analysis of 30 pellet samples, with both methods producing RSD values below 1%. With wood pellets being increasingly used more widely as a 'green' alternative, analysis of this material type will no doubt increase in the future.

2.4 Pharmaceutical applications

A lot of research has been published in the field of pharmaceuticals and the methods developed have started to become incorporated in the European and American pharmacopoeia. A *review summarising the emerging techniques utilised to establish physical-mechanical properties of tablets* was published by Dave *et al.* [85]. This was an extensive review containing 125 references comparing advantages and disadvantages in terms of cost and ease of use of more traditional techniques with those of newer acoustic and thermal-based approaches. These newer techniques are currently used mainly to support results obtained using the traditional methods. However, the authors point out that, given further optimisation of the instrumentation and software available, these techniques show great potential. It was emphasised that more detailed studies focusing on individual applications are necessary to further optimise these techniques. A second review focused mainly on the detection of counterfeit and identification of drugs [86]. The authors utilised 83 references which included, amongst others, XRF, XRD and ICP-MS-based approaches.

Due to the complex matrices encountered in pharmaceutical preparations *efficient analyte extraction as well as preconcentration* remains a vital step. An approach to optimise sample preparation for the determination of trace Pd utilised glutaraldehyde cross-linked magnetic chitosan nanoparticles [87]. Optimum extraction conditions were reported when 20 mg of the nanoparticles were added to sample solutions containing 50 µg Pd L^{-1} at pH 3 and allowing the samples to interact for 5 min. Optimal desorption was achieved using 1 mol L^{-1} thiourea. Despite this great effort in optimisation, the actual data obtained were not given. It would have been helpful to have either tabulated results or graphs in the form of, for example, supplementary data. In addition, the work would have benefited from a more detailed experimental section. In particular more detail with regards to the assessment of interferences and the performed spike studies in active pharmaceutical ingredients would have been useful. Nonetheless, applying this procedure to a soil and a sediment CRM showed excellent recovery of 96.9-97.4%, although this is hardly representative of a pharmaceutical substance. It is, however, possibly the best the authors could do given that more relevant materials do not exist. The linear range reported was 5-500 µg Pd L^{-1} ($R^2 = 0.9989$) for which a LOD of 2.8 µg Pd L^{-1} was achieved. Inter-day and intra-day precision were excellent with RSD values of 2% (n=6) and 3.3% (n=3), respectively.

New *guidelines issued by US pharmacopoeia and European pharmacopoeia with regards to elemental impurities of active pharmaceutical ingredients* continue to drive method development within the pharmaceutical industry. To fulfil these guidelines an ICP-MS method for the detection of 12 elements in active pharmaceutical ingredients was developed by Chahrour *et al.*[88]. The use of aqueous solutions containing 5% HCl (v/v), 0.1% acetic acid (v/v) and 0.076% thiourea (w/v) eliminated the need for a time-consuming digestion step. In addition, Os recovery was below 30% when microwave digestion utilising various acid mixtures was employed. However, it was not clear if replicates were used for the investigation which would have enabled an assessment of extraction precision. Similarly, spike studies performed in different sample types showed excellent recovery (94-109%), but the precision was not reported for the optimisation experiments. The MS analysis was performed utilising both He mode and high energy He MS mode for which good linearity was obtained (R>0.99). Reported LODs ranged from 0.0005 to 0.3277 ng mL^{-1} and 0.0007-0.1993 ng mL^{-1} for He and high energy He mode, respectively. The high energy He mode was run at a flow rate of 10 mL min^{-1}, which was twice the rate compared with the normal He mode. This resulted in improved LODs for As, Cr, Mo, Ni and Pd, whereas increased limits were reported for Cd, Cu, Hg, Ir, Pt, Ru and V. Analysts will need to decide for individual cases if the LOD improvement for certain elements seen in high energy mode justifies the additional use of helium. Alternatively, the He mode might be more appropriate when for Cd, Cu, Hg, Ir, Pt, Ru and V are the main elements of interest. Overall accuracy and repeatability were determined for all 12 elements (n=7). Excellent results were obtained with mean spike recovery of 100 ± 5 % and reproducibility better than 5% in both helium and high energy helium mode (1 or 1.5J). In addition, analysis on a different day, performed by a second analyst, gave rise to values that varied by less than 20% which was within the requirements of the USP.

An alternative approach for drug analysis was employed by Tiwari *et al.* who *utilised LIBS in combination with principal component analysis (PCA) and partial least square regression (PLSR) analysis* [89]. A LIBS spectrum of five different voglibose ($C_{10}H_{21}No_7$) tablets was obtained and the ratio of H to C determined. Utilising principal components 1 and 2 allowed classification of 96% and 98% of the samples, when the analysis was performed in air and argon, respectively. The PLSR analysis was applied to relate LIBS spectra to H/C ratios. The method performance was promising showing an R^2 of 0.9452 and 0.8819 for validated and predicted values, respectively when analysed in air, respectively.

When analysed in argon, the correlation coefficient for validated and predicated ratios were 0.9584 and 0.8506, respectively. This approach could also prove useful for the detection of counterfeit drugs.

In contrast to traditional calibration methods, suitability of a new standard dilution method was investigated in three different pharmaceutical preparations[90]. For this approach two standard solutions were prepared per sample. The first one consisted of the sample and standard solutions with an internal standard (1:1), whereas the second solution contained the sample and blank solution (1:1). Solution 1 was introduced into the MIP-OES system and the analyte signal monitored until it stabilised. At that point the second solution was added to the initial vial containing solution 1 and the drop of the analyte signal evaluated. The concentration of the actual sample remained unaffected by this addition. The calibration was obtained by plotting the ratio of analytical signal over the internal standard (y-axis) versus the inverse internal standard concentration. Better precision was achieved (2.5-8%) compared with results obtained utilising external calibration, a standard addition method and internal standardisation approaches. For these results the %RSD varied from 5 to 32.5%. The LODs obtained for the standard dilution approach were higher compared with all three other calibration methods. A sequential MIP-OES method using varying nebuliser flows and plasma positions for the determination of Al, Cr, Co, Cu, Fe Mn, Ni, and Zn had been applied for these. For the standard dilution nebuliser flow and plasma position were constant for all 8 elements which explains the slightly higher LOD values. Nonetheless, the excellent accuracy and precision observed highlight the great potential of this approach.

2.5 Cosmetic products

A sample *drop flow micro-extraction* was employed by Ahmadi-Jouibari *et al.* for the detection of Cd in three different cosmetic products [91]. For this purpose microwave digests were spiked with the chelating agent ammonium pyrrolidinedithiocarbamate (APDC). This sample solution was introduced to carbon tetrachloride *via* a syringe needle extracting the Cd-APDC complexes into the organic solvent which was consequently analysed using GFAAS. The authors performed an extensive optimisation investigation considering a large number of aspects throughout the overall analytical process. This included the type and volume of extraction solvent, flow rate, pH etc. However, not all the data obtained for these experiments has been made available which, for example in the form of supplementary data, would have been beneficial. The method was linear for Cd concentrations of 0.005-0.050 µg kg^{-1} and achieved a LOD of 0.002 µg kg^{-1}. Repeatability and reproducibility were excellent (RSD <5%). The authors acknowledged the lack of a suitable CRM for Cd in cosmetic products. Therefore, a soil CRM (NIST 1571) was utilised to assess the method's accuracy, resulting in excellent recovery of 94.2%. In addition, spike studies were performed in all three matrices resulting in relative recoveries ranging from

91.0 to 108.8%. Applying the developed procedure to lipstick, eye shadow and hair dye samples the authors detected Cd concentrations ranging from 3.22 to 68.25 µg kg^{-1}.

Petrova *et al.*[92] *preconcentrated Au from cosmetic products using a solid phase extraction procedure* that utilised N-Benzyloxycarbonyl-L-Methionine modified silica gel. Subsequent determination of the Au was achieved using ICP-OES. Optimal results were obtained by applying the following conditions: Au sorption in 0.1 mol L^{-1}HCl, a contact time of 30 min and the use of 1 mL of 0.7 mol L^{-1}thiourea in 2 mol L^{-1}HCl for the elution of the Au. Accuracy of the method was assessed through spiking studies as no suitable CRM material was available. Excellent recoveries were achieved (90-103%). The LOQ for this method was 0.1 µg g^{-1} in a cream matrix (RSD <11%). Comparing the results obtained with those obtained using ICP-MS, performed in an external lab, indicated no statistically significant differences between the two methods (95 % confidence limit). This method could potentially allow laboratories without the more expensive ICP-MS instrumentation to achieve similar LOQs. Alternatively, those laboratories that do have an ICP-MS instrument could use the technique to decrease the LOD significantly.

Microwave digestion remains a crucial sample preparation tool for the detection of elemental impurities in various matrices. The effect of different acid mixtures utilised during microwave digestion prior to the ICP-MS determination of Cd and Pb in lipstick was investigated by Mesko *et al.*[93]. For this purpose the suitability of acid mixtures containing HF, HCl and HNO_3 was evaluated. Even though total solubilisation after digestion was only observed when mixtures containing HNO_3 and HF were utilised, the Cd and Pb concentrations obtained did not show statistically significant differences compared with results obtained for a HNO_3 / HCl mixture (6 to 0.5). In addition, because of the safety implications of HF and higher Pb LODs reported when HF was utilised, the authors concluded that the HNO_3 and HCl mixture was the most suitable digestion aid. The digestion procedure developed enabled LODs of 3 and 77 ng g^{-1} for Cd and Pb, respectively. Owing to the lack of available reference materials, spike experiments were performed which showed excellent recovery for both Cd and Pb (95 and 103%), respectively. However, it was not clear if replicate samples were analysed which would have been helpful to assess precision. The developed procedure (n=3) enabled the detection of Pb and Cd in two out of seven lipstick samples at concentrations ranging from 271 to 2250 ng g^{-1}and from 7 to 31 ng g^{-1} for Pb and Cd, respectively.

2.6 Polymers and composites

A *review entitled* "*Improvements in the direct analysis of advanced materials using ICP-based measurement techniques*" that covered the analysis of polymers as well as semiconductors, electronic components, high purity metals and ceramics was presented by Limbeck *et al.*[94]. The drawbacks of traditional nebulisation methods, e.g. spatial information lost, potential contamination or analyte loss, the time associated with bringing the sample into solution, etc. were all discussed. Methods of analysing the samples directly (e.g. LA and ETV), were discussed in far more detail. The review contained 121 references and described how such methods often lead to improved sensitivity. In the case of LA, it also provides spatial data and depth-profiling information for bulk, trace and ultra-trace analytes; depending on whether ICP-OES or ICP-MS is used as detection method. Sections on capturing short duration transient signals using ICP-MS and ICP-OES were presented and Tables of applications were given to aid the reader. Also covered was LA in liquid followed by slurry introduction to the ICP instruments. Problems associated with the solid sampling methods and potential future directions were discussed.

It is known that *microplastics in the environment* can act as sinks and preconcentrate trace metal contaminants as well as organic pollutants. A series of papers by Turner discussed the analysis of plastics found on beaches in the South West of England. In one[95], a portable XRF instrument operating in low-density mode and capable of small spot analysis was used to analyse 924 samples of microplastic for Br, Cd and Pb. Among these samples were pre-production pellets and irregularly-shaped fragments from other sources, e.g. fishing nets. A minority of samples contained Cd or Pb at a significant level (6.9 and 7.5% of the total number, respectively), but those that did contain the analytes often had very high concentrations (~ 100 mg kg^{-1}). The samples containing high concentrations were usually coloured red or yellow. There was correlation between Cr and Pb and between Cd and S. This was attributed to the presence of lead chromate and cadmium sulphoselenide. The Br was found in approximately 10% of samples and was often present at massive concentration e.g. 13,000 mg kg^{-1}. An interesting twist to the paper was the ICP-MS analysis of solutions that mimicked the gut of a seabird. After soaking some of the pellets in this solution, analysis demonstrated that up to 50 mg Pb kg^{-1} and 8 mg Cd kg^{-1} were present; concentrations far exceeding those that would be found in the natural diet. A similar paper by Turner described the use of FTIR to identify the type of plastic and portable XRF for the determination of Br, Cd, Cr and Se[96]. Again, simulated gut solution extracts were analysed using ICP-MS. Although the gut solution extractable fractions were relatively low (0.2 – 0.4% for Cd, Cr and Pb), the extractable Br was much higher (7%). Since the total concentrations were exceptionally high (2420, 1460, 909, 3770 and 240 mg kg^{-1} for Br, Cd, Cr, Pb and Se, respectively) the extractable concentrations were still appreciable. A third paper compared total concentrations of Br, Cd, Cr, Cu, Fe, Pb and Zn in plastics determined using portable XRF with the data obtained using ICP-MS following a sulfuric acid digestion[97]. Agreement between the methods was reasonable, with values typically being within 20% of each other. The advantage of the portable XRF method was speed, with up to 35 samples of microplastic being analysed per hour.

Four papers have used *LIBS and chemometrics techniques for polymer identification* and sorting. This is because of the advantages LIBS has (e.g. simultaneous multi-element determination, free from sample preparation, rapid and possible real-time analysis, is unaffected by colour and inflicts limited damage on the sample) over many of the other analytical techniques. Shameem *et al.*[98] used a hybrid LIBS-Raman system to obtain analytical data and these were then inserted to PCA and

Mahalanobis distance to enable categorization of the polymers. The two analytical techniques complemented each other in that the LIBS gave elemental data for all plastics, including the coloured ones, whereas the Raman spectroscopy gave molecular information - especially for the transparent polymers. Combination of the techniques enabled 100% discrimination of the polymer samples. A paper by Costa *et al.*[99] used LIBS to determine C, C_2 (Swan Band), H, N and O in several different polymer types, including acrylonitrile-butadiene-styrene, polystyrene, polyethylene, polypropylene and polyamide derived from e-waste. The LIBS operating conditions (laser energy, spot size and delay time) were optimised using Doehlert design. Using the intensity at each of the emission lines and their ratios, the data was input to the chemometric packages PCA, k nearest neighbour (KNN) and soft independent modelling of class analogy (SIMCA). Initial work using PCA enabled distinction between most of the polymer types, but not polystyrene and acrylonitrile-butadiene-styrene. The data set comprised 477 samples of which 277 were for calibration and the rest for validation. Using KNN, 98% of the polymers tested could be identified, whereas for SIMCA this number dropped slightly to 92%. The third paper (in Chinese) was by Sun *et al.*[100] who described the use of LIBS and the supervised learning model Support Vector Machine to identify different types of coloured polymers. Again, the LIBS operating conditions were optimised and these authors also picked non-metallic emission lines for the identification. The use of non-metallic emission lines reduced the training time required for Support Vector Machine. Initially, 100 spectra from 20 different plastics were analysed of which 50 were used as a training set and 50 as validation. The method developed was then used to analyse 1000 test spectra, of which 99.6% were correctly identified. A fourth paper (also in Chinese) used an optimised in-house built spectrometer to analyse 2200 sample points prior to using Partial Least Squares to analyse the spectral data[101]. Again, recognition was close to 100 % for the 11 plastics analysed.

Another paper used *X-ray absorption Spectroscopy (XAS) combined with chemometric packages to identify polymers*. Wang *et al.*[102] used XAS because it has the capability of penetrating opaque plastics and because of its stability. Fifteen kinds of plastics were selected as specimens and the spectra acquired using a cadmium telluride detector were processed using PCA. Following PCA analysis, the Back Propagation Neural Network algorithm was used on the processed data. Using this combined approach, a recognition rate of 96.95% was achieved. This rate was sufficiently high for the authors to claim that the method could be used at plastic waste sorting and re-cycling sites and that, potentially, XAS could be used to classify other types of substance.

The *detection of halides in polymers* has been a popular area of research in this review period. Those applications that have more novelty with the atomic spectrometric detection will be discussed here. Included in this number is a paper by Kojima *et al.*[103] who determined Cl in polymeric materials using ETV-ICP-AES. The samples were moulded into thin films and weighed into small sample cuvettes. An ethanolic solution of potassium hydroxide that acted as a matrix modifier was then added and the cuvette warmed on a hotplate to ensure that the sample was spread over the bottom of the cuvette. The cuvette was then placed in a tungsten boat furnace and the temperature raised gradually until 1800 °C, when the Cl evaporated as KCl into the ICP instrument for quantification at 134.724 nm. Calibration was achieved using aqueous standards. A LOD of 1.5 µg g^{-1} of Cl was achieved when a sample mass of 2 mg was used. By preparing a large number of cuvettes prior to analysis, a total of approximately 20 samples could be analysed per hour. The method was validated using several CRMs, including ERM-EC680k, ERM-EC681k, ERM-EC681 and ERM-EC680; all of which are polyethylene samples. Ohata and Wada[104] compared the sample pre-treatment methods of combustion / absorbent mixture and microwave digestion prior to ID-ICP-MS determination of Cl in plastics. The methods of combustion / absorbent collection and the microwave digestion were described in full along with where in the procedure the spike of ^{37}Cl was added. The instrument used was a triple quad with a reaction gas of hydrogen. This facilitated the determination of Cl since polyatomic interferences such as $^{16}O^{18}O^{1}H$ and $^{36}Ar^{1}H$ on ^{35}Cl and ^{37}Cl, respectively were removed. The microwave digestion method was flawed because of a large Cl signal arising from the blank. This led to poor signal to background ratios (SBR) and poor isotope ratio measurements. The combustion / absorbent method did not suffer from such problems because the absorbent solution (0.1 % hydrogen peroxide) contained very little Cl. The method developed was again validated using BCR 680 and BCR 681. De Gois *et al.*[105] compared two methods for the direct determination of Br in plastics. One technique was LA-ICP-MS and the other high resolution solid sampling continuum source graphite furnace molecular absorption spectrometry. The former method was calibrated using a single CRM and using an internal standard of C. Helium as the carrier gas improved sensitivity and the dry plasma led to fewer polyatomic interferences. The latter method relied on the use of a permanent modifier (a solution of Zr repeatedly injected into the atomiser), a matrix modifier of Pd injected on top of the samples and calibration using aqueous standards. Since the Br absorption lines are in the vacuum UV region, the authors relied on molecular absorption, monitoring CaBr. In general, analysis of the certified reference materials ERM-EC681, ERM-EC680, PE H11A, ERM-EC591, BAM-H010 and PE-L-11A led to reasonable agreement between the techniques and with certified values. For LA-ICP-MS analysis, the Br value obtained for ERM-EC591 was half the certified value and the PE-L-11A was used for calibration. The LOD obtained were 100 and 10 µg g^{-1} for LA-ICP-MS and the molecular absorption technique, respectively. Despite the large difference in LOD, it was concluded that both methods were fit for purpose.

High purity polyimide samples were analysed for Cr, Cu, Mn, Na and Ni using *solid sampling GFAAS* by Santos *et al.*[106]. The temperature programs were optimised to ensure maximal sensitivity and minimal interference and a matrix modifier of Pd was required only for Mn determination. Again, calibration was achieved using aqueous standards. The zeeman background correction employed could be switched from a low strength (high analytical sensitivity) to high strength (low sensitivity), thus enabling extension of the linear part of the calibration curve. Precision ranged from 3 to 20%, depending on concentration and analyte and LOD in the high sensitivity mode were: 7, 25, 1.7, 17 and 0.12 ng g^{-1}

for Cr, Cu, Mn, Na and Ni, respectively. Although no CRM was analysed, the method was validated by alternative techniques, namely NAA and, following a high pressure acid digestion, ICP-OES and ICP-MS. Results for polyimide powders were very similar for all methods.

Digestion of polymeric materials can lead to the potential losses through volatilisation of some trace elements. Iop *et al.*[107] developed a *microwave digestion procedure with simultaneous UV photolysis* for the determination of Br, Cd, Cr, Hg, Pb and Sb in polymeric waste electrical and electronic equipment (WEEE). Polymer (200 mg) was weighed into a digestion vessel and then mixtures of both nitric and hydrochloric acids, at differing concentrations, were used to obtain maximal extraction efficiency for the analytes, whilst losing as little of the Br as possible. The optimal conditions were 0.5 mol L^{-1} nitric, 0.5 mol L^{-1} hydrochloric and 5.3 mol L^{-1} hydrogen peroxide, used in conjunction with the photolysis. Detection was by ICP-MS with the Hg being introduced using a home-made HG apparatus. Analysis of the CRMs ERM 680k and ERM 681k yielded data in good agreement with certified values for all elements except Cr which was only 20 – 25% of the certified value.

Speciation analysis using HPLC-ICP-MS has been achieved for the determination of different oxidation states of analytes. In one example, Sb species in spirits stored in polyethylene terephthalate bottles was discussed by Carneado *et al.*[108]. Both Sb^{III} and Sb^{V} in the spirits were identified, but the authors also found that the dominant species was an unknown compound. Using an orbitrap-based LC-MS instrument, they tentatively identified this as an acetaldehyde-bisulphite pyruvate Sb complex. However, mass balance calculations demonstrated that the sum of the species could be as low as 41% of the total Sb determined using pneumatic nebulisation ICP-MS. Maintaining the spirits at 60°C led to significantly higher concentrations of Sb being leached out of the plastic than the legal limit. Interestingly, when maintained at this elevated temperature for a week, the "unknown" species decreased in concentration and Sb^{V} and Sb^{III} became the predominant species. In another example the determination of As^{III} and As^{V}, Sb^{III} and Sb^{V} and Cr^{VI} in mineral water stored in different type (glass and polyethylene terephthalate) and different colour (light and dark green, light and dark blue, pink and transparent) bottles was described[109]. Samples were filtered and then, in most cases, analysed directly although some required dilution. Species were separated within eight minutes on an anion exchange PRP X-100 column using a gradient 3 mM sodium EDTA and 36 mM ammonium nitrate mobile phase and the ions detected using ICP-MS with oxygen as a reaction gas. A comparison of calibration strategies was undertaken resulting in a two point standard addition being chosen as being optimal. Limits of detection ranged from 0.038 µg L^{-1} for Sb^{V} to 0.098 µg L^{-1} for Cr^{VI} and spike recoveries for 0.5 µg L^{-1} ranged between 84 and 117%, depending on the analyte. There was significant variation though, with precision for the spiking experiments being typically 20% for each analyte. In general, higher concentrations of As species were found in water from glass bottles whereas Sb^{V} was found in water stored in polyethylene bottles. No Sb^{III} was found in any sample. The Cr^{VI} was found only in bottles coloured green be they glass or plastic.

Leaching of analytes from food packaging into food simulants has been another popular area of research. The majority of these applications, although interesting, do not really use a novel method of atomic spectroscopy and will not be discussed further. One exception to this was a paper by Hetzer *et al.*[110] who used AF4-ICP-MS and single particle ICP-MS to characterise and monitor nanoparticles of silver leaching from packaging materials into water, 10% ethanol and 3% acetic acid. Total Ag content in the films was determined using a microwave digestion followed by ICP-MS analysis. Similarly, the amount of Ag leached into the simulants over two hours at 70°C and for 10 days at 40°C was also determined using classical ICP-MS. For single particle ICP-MS, the nanoparticle mean size was determined to be 21.6 ± 2.3 nm. This was marginally higher than the value determined using SEM, but was considered to be in reasonable agreement; especially considering some of the nanoparticles were below the particle sizing LOD of the ICP-MS. The AF4 was of particular use when separating ionic from nanoparticulate Ag. The paper gave a good explanation why this was the case. The authors then exploited this advantage by coupling AS4 with single particle ICP-MS. With the signal produced by ionic Ag effectively removed, the determination of size and concentration of the particulate Ag was facilitated.

The majority of applications that determine analytes in food packaging materials use some sort of ICP, because most *X-ray based techniques need a minimum thickness of sample to yield reliable data*. This has been addressed in a paper by Goodlaxson *et al.*[111] who described the development of a correction factor equation that enables accurate determination of Sb in up to 94% of the samples tested. The result was that a rapid, accurate and cost-effective screening method was developed.

Arnquist *et al.*[112] developed a *dry ashing protocol* that enabled Th and U to be determined in high radiopurity polymers. The polymers were weighed in ultra-low background, electroformed copper crucibles and then ashed for 14 hours at 800°C in the presence of air flowing at 4 L min^{-1} in a quartz tube furnace. The ashed sample and oxidised copper crucible were then dissolved in 8M nitric acid which was then placed on a pre-cleaned AG 1X4 resin bed. Much of the copper matrix was then eluted with a 600 µL aliquot of 8 M nitric acid. The Th and U were then eluted in 1.8mL of 2% nitric acid ready for analysis using ID-ICP-MS. Recovery of the analytes from the column was tested using isotopic tracers and was 80% for Th-229 and 90% for U-233. Detection limits were impressively low, being approximately 1 pg g^{-1} for a 100 mg sample size, but could be lower if larger sample mass was used. Sample types analysed included Max-Prene 955 (a non-fluorinated biomedical polymer) in the form of both a powder and as a solid bar, polyvinylidene fluoride in the form of pellets and powder and polyethylene.

2.7 Cultural heritage: Paintings and manuscripts

Since *XRF techniques are largely non-destructive, they remain the most dominantly used techniques* for the analysis of paintings. A recent review by Cotte *et al.*(with 69 references) in this field focused on the status of a specific instrument, the ID21 X-ray and IR microscopy beamline as well as discussing recent applications in the field of cultural heritage [113]. This high energy electron accelerator provides four end stations and is commonly utilised for 2D micro XRF (µXRF) and single point micro X-ray absorption near edge structure (µXANES) analysis. Improvement and updates to software and hardware have been made. Moreover, sample preparation techniques such as AgCl resin embedding and cryo-sectioning can be performed. A second review reported developments for the analysis of historical paintings [114]. This extensive work (197 references) summarised the developments with regards to both instrumentation and software for UV/VIS, IR and XRF spectrometry. The authors pointed out that researchers tended to focus on the optimisation of individual applications rather than instrumental advances. In the field of XRF this was mainly related to the limited primary beam intensity to minimise radiation damage and associated health risk. In addition, the X-ray optic (polychromatic radiation) themselves have not seen major advances. Therefore, the authors were not expecting significant development in the field of macro-XRF. It was pointed out that, due to the vast amount of data created, data storage and handling has become a more dominant focus. Similarly, statistical methods have been very helpful to cluster spectral data in an attempt to evaluate large volumes of data more easily.

A *mobile XRF spectrometer, enabling on site micro and macro XRF analysis*, has been developed by Romano *et al.*[115]. Previous limitations of slow scanning times when using X-ray tubes with pinholes have already been overcome by employing the use of poly-capillaries. However, the evaluation of spectra has been performed offline. By combining a poly-capillary X-ray tube with two simultaneous operating silicon drift detectors, real-time elemental mapping at even scan times of up to 100 mm s^{-1} was achieved. Detection limits of 20 ppm and 120 ppm were achieved for various elements (atomic numbers 25-40) and K, respectively. A combined macro- and micro-XRF approach was developed by Sciutto *et al.* for the analysis of painted surfaces [116]. For this purpose, larger areas were initially scanned using macro-XRF (~33 mm s^{-1}) to obtain an overview of the sample. Areas of greater interest, where a number of different elements were identified during the first scan, were consequently analysed using micro-XRF (8.25 mm s^{-1}) to achieve better signal to noise ratios and therefore lower the limit of detection. This, in combination with an off-line spectrum fitting algorithm, enabled the additional detection of Au, which had not been seen during the initial low-resolution scan.

The *combination of multiple analytical techniques* has also helped to gain new information. Pouyet *et al.* found a hidden text from the 6th century in the binding material of a 16th century manuscript[117]. The writing on the parchment had been removed by either scraping or washing, and hence was invisible or, at best, blurred. Analysis of the parchment showed it had been treated with Ca, lines had been ruled onto it using a Pb-based ink or pen and some of the writing had been done using an Fe gall ink. The authors fused the obtained low resolution XRF image cube to a manually selected visible hyperspectral image cube and a transformation matrix, representing a pixel by pixel union, was calculated. By then calculating cosine similarities the correlation between low and high resolution was learned. This deconvolution and machine learning approach enabled de-blurring of images and identification of the previously hidden text.

A *laser ablation system coupled directly to a quadrupole ICP-MS instrument* for the detection of trace elements in paintings was developed by Marin and Garcia[118]. In addition, a camera was incorporated to enable real-time observation of the ablation. In contrast to most analyses performed on cultural and heritage objects this is a destructive technique, however the damage caused was minute. It was used as a complimentary technique to the non-destructive SEM and FTIR techniques performed previously. The destructive nature proved useful as it enabled the elemental composition analysis of different paint layers. Therefore, this approach allowed the differentiation between original areas on the painting and those that had been altered. Analysts need to carefully assess if that additional information gain justifies the damaging of these minute areas for each individual case.

Table 2 Recent applications of atomic spectrometry in organic samples.

Analytes	**Matrix**	**Technique**	**Comment**	**Reference**
Multiple	Paper (Stamp)	EDXRF	Determination of ink composition on Ottoman stamps.	119
Ca, Cu, Fe, K, Pb	Painting	macro-XRF	Determination of elemental contributors in pigments.	120
Al, As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Tl, V, Zn	E-cigarette (liquid and vapor)	ICP-MS	Vapor created with smoke machine. The analytes Cd Co, Cr and Sb detected in some of the e-vapours. All LOQ <20 µg L^{-1} except for Zn < 200 µg L^{-1} in the liquid. For the smoke produced As, Cd, Cr, Pb, Sb, and Tl LOQ <2.1 pg mL^{-1}puff.	121
Pb	Incense	GFAAS	Pb determination in incense rod yielded a calibration with regression R^2 = 0.99995. The absolute LOD was 5.6 pg (RSD = 4.3%). Mass balance investigation suggested that	122

			up to 80% Pb was released into the air.	
$^{87}Sr/^{86}Sr$	Illicit heroin	ICP-MS	Microwave digestion of samples and $^{87}Sr/^{86}Sr$ isotopic ratio analysis to determine country of origin of illicit heroin.	123
Ag, Al, Ar, As, Au, B, Ba, Br, Ca, Ce, Cl, Cr, Cs, Cu, Ge, Hf, Hg, In, Li, Mg, Mo, Ni, Pb, Pd, Pt, S, Se, Si, Sn, Ti, V, W, Zn	Automotive Paint	SS-ETV-ICP-OES	Electrothermal vaporization ICP-OES combined with PCA to identify manufacturers and production year of cars using paint samples.	124
C, Ca, H, K, Mg, N, Na, O, Ti	Fire debris	LIBS	Depth-profiling of fire debris to establish if accelerant could have been used.	125

Table 3 Applications of atomic spectrometry to pharmaceutical samples

Analyte	**Matrix**	**Technique**	**Comments**	**Reference**
Cr	Pharmaceutical formulation	HR-CS-GF AAS	Direct analysis of solids, LOD 2.9 µg kg^{-1}. Excellent agreement of direct analysis compared with conventional digestion approach (95% confidence). Concentration in samples: 0.05 - 1.92 mg kg^{-1}.	126
Sb	Solid and liquid Pharmaceutical formulations	HR-CS GF AAS	Assessment of Sb in pharmaceutical preparations, their containers and also the potential of leaching from containers as affected by temperature and time.	127
Al, Ca, Cr, Fe, K, Li, Mg, Mn, Mo, Na, Si, Sr, Zn	Pharmaceutical formulation (solid)	LIBS	Calibration free compositional analysis of multivitamin tablets. Magnesium used as reference material.	128
Cd	Cosmetics	GFAAS	A sample drop flow microextraction procedure was utilised for Cd determination of microwave digested lipstick, Eye shadow and hair dyes. Reproducibility and repeatability were better than 5%. Reported LOD for Cd 0.002 µg kg^{-1}.	91

Various	Pharmaceutical formulation (solid) but also explosives	LIBS in combination with Raman	Multiple Raman/LIBS spectra obtained at same sample spot to improve signal to noise ratios. Also applicable to detection of explosives stored in non-transparent containers due to depth profiling.	129

3 Inorganic chemicals and materials

In a continuation of the previous review period, papers detailing the development, or interesting application, of atomic spectrometry have been grouped into the following topic areas; Catalysts, Building Materials, Fertilizers and Inorganic materials. Additionally, this review period has seen a return of interesting papers in the field of forensic analysis.

3.1 Inorganic chemicals

The quantification of trace analytes in high salt containing samples by ICP-OES can be troublesome and often requires significant dilution or costly accessories. Swearingen *et al.*[130] discussed the optimisation of a commercially available instrument for the determination of Sr, V and Y in 5 M sodium chloride solutions, achieving detection limits of 1, 4 and 4 ng L^{-1} respectively. It was noted that salt build up on the injector was not prevented, but could be minimised with careful adjustment of the nebuliser and auxiliary gas flows. The paper also discussed optimisation of the same instrument for organic analysis and would serve as a useful guide for those starting out in the field. Arnquist and Hoppe described an ICP-QQQ-MS protocol for the quick and ultrasensitive determination of K in sodium iodide powders/crystals to be used in potential dark matter detection[131]. When working at extremely low levels, background contamination is an obvious issue and all studies were performed in a class 10,000 cleanroom and a thorough cleaning procedure was used for all labware. Achieving ultralow background signal for potassium analysis by ICP-MS is notoriously difficult because of interferences from the Ar plasma gas. However, it was shown that operating at cool plasma conditions (600-800W) can remove much of the *m/*z 39 background associated with $^{38}ArH^+$, whilst still providing sufficient energy to ionize K. Remaining $^{38}ArH^+$ background and potential water gas cluster ions were removed using 10% NH_3/90% He reaction gas in the collision cell. Fully optimised, they were able to achieve an instrument detection limit of 11 parts-per-quadrillion (11 fg kg^{-1}) in pure water. This translated to a sub ng kg^{-1} detection limit in the solid sample when diluted and calibrated by the method of standard addition. Boron was separated from a high salt solution using Amberlite IRA 743 resin as a means of analyte enrichment and matrix removal[132]. Sodium ions, undesirably absorbed on the resin, were removed using a 3 M NH_3 wash prior to eluting B with 10 mL 0.1 M HCl for determination using TIMS.

Spike recoveries were within 106% and a detection limit of 0.02 mol.L^{-1} was achieved. This simple sample preparation could also be useful for other detection techniques.

Given the difficulties analysing salt materials by plasma-based techniques the direct determination of metals in the solid samples is understandably desirable and a number of papers were published discussing LIBS for such use. Williams *et al.*[133] discussed the use of LIBS for the measurement of Ce and Gd in solidified lithium chloride-potassium chloride salt from the pyroprocessing of used nuclear fuel. Molten samples were drawn into a pyrex tube under vacuum and allowed to solidify. These were then measured simultaneously using LIBS and ICP-MS. Data from the latter were used to develop a LIBS calibration model. The Ce 551.1 nm and Gd 564.2 nm lines were used for analysis resulting in detection limits of 0.099 and 0.027 wt%, respectively. Maji *et al.* studied the feasibility of LIBS for the quantification of five lanthanides in lithium fluoride – potassium chloride salt[134]. Two interference free emission lines were identified for each element, each show linearity over 0.3 – 5 wt% and good correlation with synthetically spiked samples. The performance of solid analysis using LIBS, LA-ICP-OES and LA-ICP-MS for the determination of S in edible salt was compared with aqueous ICP-OES following sample dissolution[135]. The laser-based techniques did not suffer from loss of S, which was observed in aqueous ICP-OES because of the formation of volatile species and precipitates upon dilution in water. LIBS and LA-ICP-OES showed good accuracy for the detection of S in a range of reference samples, whilst LA-ICP-MS was found to suffer from the known isobaric and polyatomic interferences at *m/z* 32. Additionally, LIBS was able to show correlation between S and oxygen, thus elucidating chemical information about the presence of S^{2-} or SO_4^{2-}, which can be associated with the salts origin.

The determination of ultra-trace impurities in high purity materials can be troublesome due to lack of sensitivity or spectral and non-spectral interferences caused by the bulk material matrix. Selective analyte separation and pre-concentration is often used to overcome these issues. Wada *et al.*[136] discussed a process for the determination of 12 trace contaminants in high purity cadmium using ICP-MS and ICP-SFMS, following matrix separation employing an anion exchange resin. Samples were dissolved in HNO_3 on a hotplate, evaporated to dryness and the residue dissolved in dilute HCl. This was then passed over AG MP-1M anion resin bed to remove Cd from solution. The resulting supernatant was concentrated by evaporation and analysed using both ICP-MS and ICP-SFMC. Unsurprisingly, ICP-SFMS was found to offer lower detection limits, down to 0.82 ng kg^{-1} for In. Full method and instrument optimisation was discussed. Eskina *et al.*[137] demonstrated the application of sorption preconcentration of Co, Cr, Cu, Fe, Mn and Ni on 1-hydroxy-2-(perhydro-1,3,5-ditazin)-5-yl-ethane from high purity niobium digests. Samples of high purity niobium oxide were first digested with 1:1 HF:HNO_3 in an autoclave and the resulting solutions diluted with 2% HCl. Sorbent was then added to the sample, mixed with sonication for 40 minutes, filtered and the recovered sorbent digested with HNO_3. Analytes in the resulting solution were determined using HR-CS-GFAAS. Spike recoveries of

93-100% were achieved for all analytes with spiked concentrations ranging from 0.001 – 0.145 µg mL^{-1}.

Often marketed as having negligible matrix effects, TXRF is gaining popularity. However, this is often not true for real samples. Regadio *et al.*[138] explored the effect of sample preparation and choice of internal standard as a means of reducing matrix effects when measuring high salt matrices using TXRF. Samples with a varied $CaCl_2$ matrix were spiked with 20 metals at concentrations ranging from 3 to 50 mg L^{-1} and the recoveries assessed. In samples of low matrix content good recoveries were observed regardless of the internal standard selected. However, samples with a higher matrix content required careful selection of internal standard at a concentration close to that of the unknown. Additionally, samples required dilution in a Triton X-100 solution to aid homogenous dispersion of sample across the sample disk. Without this recoveries of most of the 20 analytes were neither accurate nor precise.

The setup and optimisation of a miniaturised Liquid Cathode Glow Discharge Atomic Emission Spectrometer (LCGD-AES) and its applicability for the determination of Ca, K, Mg and Na in salt mine samples was reported by Yu *et al.*[139]. The glow discharge was produced between a needle-like Pt anode and the sample (as cathode) overflowing from a quartz capillary. The stability of the LCGD and effects of operation parameters, such as discharge voltage, solution flow rate, supporting electrolyte, solution pH, and interfering substance on emission intensity were investigated in detail. Once optimised, LOD of 0.390, 0.054, 0.048 and 0.032 mg L^{-1}, for K, Ca, Na and Mg, respectively were achieved. Results were in good agreement with those determined using ICP-OES. The authors hope that, with further development, the instrument can be used in the field for on-site, real-time monitoring.

3.2 Fertilizer

Interest in the combination of LIBS and chemometric data analysis for sample classification is rapidly growing in multiple fields, and the analysis of fertilizers is no exception to this. Both single- and double pulsed LIBS in association with PCA was demonstrated to distinguish and classify a wide range of phosphate fertilisers from varying sources[140]. Samples were pressed to pellets for analysis and chemometric models prepared by comparison to metals determined previously using ICP-OES. An improvement for the calibration of a LIBS system for the quantification of P using multi-variant nonlinear regression was discussed[141]. The intensity of atomic spectral lines 255.3 and 844.6 nm for P and O, respectively, was measured for 14 samples of known concentration. The proposed regression method improved the correlation coefficient of the LIBS predicted concentration with reference concentration from 0.83, achieved using a linear system, to 0.98. A novel preparation and calibration method was developed by Andrade *et al.*[142] for the determination of macronutrients in suspension fertilizers using LIBS. Samples were mixed with 10% polyvinyl alcohol (PVA) and dried at 50 °C on a glass disk. This resulted in a solid polymer film with the immobilized liquid sample. This approach overcame the drawbacks, such as splashing and short plasma lifetimes, caused by the interaction of the laser with liquid samples. The method allowed calibration with aqueous standards using the C signal from PVA as an internal standard to correct for variability and signal fluctuations. The method was applied to the analysis of eight commercially available suspension fertilizers with excellent agreement with results obtained using the AOAC Official Method 2006.3 for digestion and ICP-MS detection.

The optimisation of a *single vessel microwave digestion procedure* for the determination of 13 elements in mineral fertilizer by ICP-OES was comprehensively evaluated by Fioroto *et al.* at the Instituto de Química, Sao Paulo[143], The recovery values from the reference material SRM 695 was systematically tested for a total of 12 different acid mixtures containing nitric, hydrochloric, orthophosphoric, hydrofluoric or boric acids. An optimised procedure consisting of 3 mL HNO_3 + 0.5 mL HF + 0.2 g H_3BO_3 + 2.5 mL H_2O was proposed and showed good recovery for all analytes.

3.3 Forensic samples

Elemental mapping is commonly limited to small localised areas, narrowing its forensic use to applications such as fingerprints, recovered gunshot residue (GSR) etc. However, Langstraat *et al.*[144] investigated the use of large object macro XRF scanners, that are used extensively to study historic artworks, for the imaging of forensic traces on entire pieces of clothing. Using a Bruker M6 instrument with Rh-target micro focus tube and capillary optics at a working distance of 1 cm they were able to map an area 80 x 60 cm with a resolution of 500 µm. This was successfully applied for the identification and mapping of a range of human biological traces on large fabrics on the basis of elemental markers, for example Fe, Cl and K for blood. Additionally, the depth penetration of XRF was able to easily detect and map gunshot residue (GSR) hidden under blood stains. Lopez-Lopez *et al.*[145] explored the potential of elemental mapping using LIBS for the visualisation of GSR patterns. A sticky plastic film was used to collect residues from around the bullet holes of cloth targets shot at varying distance. The film not only preserved the spatial arrangement of the GSR, but also provided a flat surface analysis for mounting on a motorised X-Y stage. The LIBS spectra were collected over an array of spots evenly spaced 800µm apart, covering a total area 130 x 165 mm^2 (31,050 individual spectra). The areas under the lines for Pb (283.3 nm), Sb (259.8 nm) and Ba (455.4 nm) were used to construct the maps, which showed distinct patterns at varying distance. The proposed method is thought to offer a number of advantages over the established colour test, such as limited sample preparation and element specificity leading to a reduction in the possibility of a false positive. The use of LIBS as a screening tool for lead free GSR prior to confirmation by SEM-EDX was suggested by Fambro *et al.*[146]. Their study showed that LIBS was able to detect the fingerprint of Ba, Al, Si, K and trace of Ti, Fe and S typically found in lead free GSR. Whilst some sample was inevitably lost during analysis, they were able to show that sufficient amounts were preserved to allow further confirmation by SEM-EDX.

Calcium ammonium nitrate, a widely available fertilizer, is a frequently used precursor for the production of homemade explosives. High resolution multi-collector ICP-MS was used to determine concentrations of 64 elements as a means of developing signatures for producer discrimination[147]. A total of 96 samples were dissolved in water to produce water soluble and water-insoluble portions; the latter was further digested with HNO_3. Sample solutions were first screened using elemental mode analysis, with only the central Faraday cup, in order to adjust ICP-MS parameters. For quantitative analysis, a scan rate of 1000 ms/amu and a dwell time of 2000 ms were used. Mass scale calibration was performed using aqueous standards. A partial least squares model from the data was able to successfully discriminate the production factory of 73% of the test specimens. The direct measurement of explosive materials involves some obvious potential risk; some of which could potential be overcome using stand-off LIBS systems. Kalam *et al*. discussed the use of one such system for the identification of explosives at a distance of 8.5 meters using 50 fs laser pulses[148]. Although atomic emissions were detected, the study focused on molecular information for identification. A conventional LIBS system equipped with a 1064 nm Q-switched Nd:YAG laser was used to determine the Al content of aluminised plastic-bonded explosives (PBX)[149]. The intensity ratio of AlO molecular emission and Al atomic emission was used for quantification to reduce the influence of experimental parameters such as sample to lens distance, laser power and sample matrix effects and a linear calibration curve was prepared using PBX samples with known Al content. However, it was noted that the method was only applicable for PBX within the specified class range and specimens with different particle sizes and/or additional binders will give various plasma chemistries and thus require different calibration curves.

The forensic analysis of glass is a subject tackled by Van Es *et al.*[150] who assessed a likelihood ratio approach for the evaluation of LA-ICP-MS evidence. The evaluation of whether or not two samples are similar often involves the t-test or some other rudimentary statistical check. This does not take into account the rarity of a glass sample and can lead to error. The authors therefore described a two-level model that helps discriminate between same and different source materials. The LA-ICP-MS method was based on the ASTM method E2927-13, which determines 18 analytes in glass, of which the ^{29}Si was used as an internal standard. A total of 979 glass particles were tested of which 659 were used to train the two-layer model and the rest were used as test samples. The mathematical model appeared to give a robust method of discrimination with a 0.3% error rate being obtained when glasses of the same source were classed as being different and a 0.2% error rate when glasses from different sources were classed as being the same.

3.4 Catalysts

A number of papers discussed the coupling of electrochemical flow cells (EFC) with atomic spectroscopic techniques to investigate electrode stability. This combination allows real time monitoring of catalyst dissolution under working conditions and extended electrochemical stress tests.

The stability of carbon supported palladium and bulk polycrystalline-palladium electrodes for the catalysed oxygen reduction reaction under acid conditions was investigated using EFC-ICP-MS [151]. Cyclic Voltammetry was performed under varying scan rates and upper potential limits whilst monitoring Pd concentrations in the electrolyte. Three peaks were observed in the scan cycle, one anodic and two cathodic. The anodic dissolution was believed to be Pd^{2+} dissolution proceeding in parallel with surface oxidation. Cathodic peaks were thought to be the dissolution of Pd^{2+} following reduction of Pd^{2+} and Pd^{4+} surface oxides. However, further work would be needed to fully confirm this mechanism. A similar study was performed for iridium based oxygen evolution reaction catalysts by Jovanovič *et al.*[152]. Again both anodic and cathodic dissolution was observed with a larger number of oxidation and reduction processes seen. Quasi *in situ* XAS analysis was conducted to confirm their Ir surface oxidation and reduction dissolution pathway hypothesis. The combined EFC-ICP-MS technique was also used to demonstrate the stability of indium tin oxide supported platinum nanoparticles as a catalyst for the oxygen reduction reaction[153]. A standardised ECF-ICP-OES procedure for the benchmarking of oxygen evolution reaction catalysts was described by Spanos *et al.*[154]. In addition to coupling an ECF to the ICP-OES instrument, an oxygen sensor was also included on the cell eluent line. This allowed the continuous monitoring of activity allowing differentiation of activity losses through deactivation and catalyst dissolution.

The optimisation of ETV-ICP-MS for the determination of Gd, La, Tb, Tm, Yb and Y in spent catalysts, following dispersive liquid-liquid microextraction was reported by Ramos and Borges[155]. The effects of digestion, extraction and vaporisation parameters were investigated using a multivariate approach. Analytes were chelated with 8-hydroxyquinoline and extracted into CH_3Cl following initial microwave assisted digestion with HNO_3, HCl and H_2O_2. A palladium modifier was used to aid vaporisation and improve transport efficiency to the ICP-MS. Detection limits ranging from 0.08 ng g^{-1} (Tm) to 150 ng g^{-1} (La) were achieved with good agreement between determined and certified values for a number of geological and catalyst materials.

Samples containing high levels of sulphur can lead to rapid decrease in the lifetime of the reduction catalysts used during the automated determination of mercury by thermal combustion in accordance to EPA Method 7473. Many automated instruments contain a transition metal oxide reduction catalyst (often Mn_3O_4) that is susceptible to sulphur poisoning. McLagan *et al.*[156] proposed the addition of sodium carbonate to all samples and as a catalyst pre-bed as a simple adaption to prolong lifetime. Sulphur dioxide generated during sample combustion rapidly reacts with sodium carbonate to form sodium sulphite and or sodium sulphate, preventing contact with the catalyst. The group validated the method with multiple replicates of NIST 2685c reference material and a sulphur impregnated carbon loaded with Hg. Recoveries were 100 ± 3% for both material, whilst lifetime was extended 10 x compared with an unaltered system. This simple adaption could lead to significant savings for a high volume laboratory.

The imaging of catalysts and other functional materials under reaction conditions has advanced significantly in recent years, largely benefitting from increased access to synchrotron facilities. Sheppard *et al.*[157] used complimentary data from µXRF-CT, µXRD-CT and STXM-CT to understand the activation and reactivity of Cu/ZnO/Al2O3 ZSM-5 core shell catalyst for the one-step conversion of synthesis gas to dimethyl ether. *In situ* measurements were made using a 0.4mm quartz capillary reactor at the I18 beam line at the Diamond Light Source. Optimised conditions allowed 3D µXRF imaging with a 2 x 2 µm resolution. The spatially resolved studies uncovered the presence of metastable Cu_2O during reduction, and a significant increase in the presence of mixed Cu oxidation states under model reaction conditions. This indicated the possible role of Cu_2O in methanol by-product synthesis. A similar *in situ* characterisation study, investigating activation of cobalt based Fischer-Tropsch catalysts, was undertaken at the same beamline by Beale *et al.*[158]. The migration of cations from cathode electrocatalysts into the membrane electrode assembly was long believed to be a cause of proton exchange membrane fuel cell (PEMFC) performance loss. However, it had never been observed directly. Cai *et al.*[159] utilised the sub-micron spatial resolution capability of synchrotron µXRF and a purpose built test cell to monitor Co cation migration in electrodes under operating conditions. The paper described the set up and operation for *operando* monitoring under varying conditions, noting the performance of such tests was strongly impacted by the membrane electrode assembly.

Quantitative elemental imaging of a model Pd/Al_2O_3 *egg shell catalyst was achieved using LIBS*[160]. The LIBS system was configured with a motorized X, Y, Z platform to allow the 2 dimensional scanning of a prepared catalyst. The highly focussed laser allowed measurements with a spatial resolution as low as 15 µm, controlled mainly by the speed of the stage. The advantages of LIBS imaging, over established techniques such as LA-ICP-MS, EPMA and µXRF, are speed of analysis and potentially low limits of detection. However, a lack of reference materials leads to prior analysis of samples using the aforementioned techniques that can be calibrated independently using pure materials.

Balerna *et al.*[161] *used EXAFS to investigate local atomic structural differences* between Cu nanoparticles formed on poly-4-vinylpyridine and carbon supports, and how these affected their catalytic activity in Huisgen azide-alkyne cycloaddition reactions. Measurements were performed using the K absorption edges at the Italian GILDA beamline of the ESRF, Grenoble. All spectra were collected at liquid nitrogen temperature using a high purity Ge detector coupled with an X-Ray pulse digital analyser. Structural characterisation was performed considering both XANES and EXAFS data, drawing comparisons with metallic Cu, CuO and Cu_2O reference foils. Whilst Cu nanoparticles were formed on both supports, Cu(I) was prevalent in the Cu/PVPy sample, whereas in the Cu/C sample, they were as the Cu(II) oxidised state. The former was active and re-usable whereas the analogous carbon-based system was almost inactive. The activation of precursor-dependent Pd nanoparticles on two inorganic supports was comprehensively followed using in situ XAS[162]. Catalyst pellets were prepared from either $Pd(NO_3)_2$, $PdCl_2$ or $Pd(OAc)_2$ precursors supported on γ-Al_2O_3 or activated carbon and loaded into a multipurpose reaction cell. Results indicated that the thermal stability of the metal precursor plays an important role in the size and speciation of the formed Pd nanoparticles after the activation process.

3.5 Building Materials

An overview of case studies where portable XRF, in combination with portable Raman and IR, has been used for in situ investigation in archaeometry was presented[163]. Among the applications discussed, XRF was able to identify two types of mortar, found at the archaeological site of Scifi, Italy, to be from distinct chronological phases, dating back to the 3rd and 5th Century. The use of ICP-MS for the determination of REEs in mortar specimens collected from a range of areas around the Castle of Sagunto, Spain, was reported[164]. Samples were digested in 1.8 mL of aqua regia in glass sample tubes over a water bath. A total of 31 elements were determined including major elements, trace elements and REEs. The data were processed using PCA to highlight any differences among the mortars belonging to different buildings and construction periods. The compositional analysis and mapping capabilities of LIBS were exploited for the study of ancient Roman mortars[165]. Four thousand LIBS spectra were acquired from an area of 10 mm^2, with a 50 µm lateral resolution. Elements of interest (Al, C, Ca, Fe, H, K, Mg, Mn, Na, O, Si and Ti) were detected and mapped to understand aggregate and binder compositions. Garcia-Florentino *et al.* demonstrated the use of a µ-EDXRF instrument for the sequential mapping and bulk characterisation of historic mortars[166]. A range of 15 Portland cement certified reference materials were milled to <250 µm, mixed with wax and pressed into a pellet for calibration of 12 elements. The analysis of mortar samples, prepared in the same way, showed good correlation with results determined using established WDXRF methods for pressed pellet analysis. However, it is unclear why mapping of ground and pressed samples would be useful, or the situation in which an analyst would choose to do this over the established methods. The same authors also described the use of EDXRF for the analysis of aqueous and acid extracts from ancient building materials, such as mortar[167]. Water-soluble extracts were obtained by mixing 0.1 g sample with 100 mL of distilled water with sonication. The acid extracts of the materials were obtained after a microwave digestion of 0.5 g of sample using aqua regia as described in EPA 3051A. The liquid extracts were then deposited on special sample retainers made of an external PET ring which holds a polyester film in where an adsorbent cellulose filter was fixed. Preparation of the sample in this way resulted in significantly reduced matrix effects and allowed calibration using multi-element stock solutions. It was proposed that this method could serve as a faster means of analysis compared with ICP-OES and ICP-MS whilst obtaining comparable analytical quality.

3.6 Ceramics and refractories

The majority of the interesting applications of the analysis of ceramics have been in the area of cultural heritage. Here, the samples are usually analysed in such a way as to cause minimal or no damage, so

LA, XRF and LIBS are the more common techniques. Many ceramics are very difficult to dissolve and so lengthy, sometimes hazardous digestion protocols are often used. Techniques that enable analysis of solid samples directly, e.g. LA, ETV, XRF etc. are therefore popular during the analysis of industrial ceramics.

3.6.1 Industrial ceramics

A *review into the direct analysis of advanced materials*, including ceramics, using ICP-based techniques was presented by Limbeck *et al.*[94]. The review (containing 121 references) covered ETV and LA sample introduction and ICP-OES and ICP-MS detection systems. The authors pointed out the obvious advantages of analysing solids directly. These include the analytes not being diluted as they are with dissolution / digestion protocols, lack of sample manipulation means less chance of contamination or of loss of volatiles / insoluble precipitates and the opportunity to gain spatial data. In the case of LA sampling, the spatial data can be extended to the third dimension, i.e. depth-profiling. Sections in the review included the measurement and processing of short transient signals for both ICP-OES and ICP-MS and then the bulk of the review covered applications. The material was often presented in easy to understand tables with column headings including the detection system, the LOD, the analytes, the amount of sample used and typical precision values. Also covered in the ETV section was the analysis of slurries, an often overlooked method of solid sample analysis. The LA sections included LA in liquid and depth-profiling of layered structures.

Laser ablation in liquid is a method that is useful for transforming hard to dissolve solid materials into microparticulate forms that are soluble. A paper by Machida *et al.*[168] discussed the analysis of certified silicon carbide powders NMIJ 8001a and 8002a and JCRM R021, JCRM R022 and JCRM R023 using the technique. Comparison was made with data obtained using conventional LA-ICP-MS analysis as well those obtained using acid digestion followed by nebulisation ICP-MS. For conventional LA-ICP-MS, the particles produced by ablation were passed through a cascade impactor and only the smallest particles (< 1 µm) were introduced to the ICP-MS instrument. This was to avoid elemental fractionation that is observed in larger particulates. The acid digestion procedure used only 1 mg of sample which was digested at high pressure and temperature using a mixture of nitric, hydrofluoric and sulfuric acids. The digest was then evaporated to dryness before the residue was taken up in dilute nitric acid ready for analysis. For the LA in liquid sampling, the surface of the sample was first cleaned in acid and then it was placed in water. Laser ablation rasters at 100 µm intervals were then performed and the particulate produced became suspended in the water. These were then pipetted into a pressure vessel and acid digested using the same procedure as for the silicon carbide powder. The amount digested was calculated by weighing the sample before and after ablation. The agreement of the results from the different preparation methods was very variable. For instance, in one silicon carbide sample, determined Al was 518 ± 16 µg g^{-1} using conventional LA-ICP-MS (with calibration using

NMIJ standards), 460 ± 35 µg g^{-1} using LA in liquid-ICP-MS and 261 ± 6 µg g^{-1} using acid dissolution. The latter two techniques were both calibrated against liquid standards. Detection limits for LA in liquid ranged between 0.04 and 0.4 µg g^{-1}, which were approximately an order of magnitude superior to conventional LA-ICP-MS.

3.6.2 Cultural heritage ceramics

A *portable hybrid spectrometer capable of LIBS and diffuse reflectance spectrometry* was described by Siozos *et al.*[169], who applied it to the analysis of inorganic pigments on objects of cultural heritage, including ceramics. The paper gave technical details as well as schematic diagrams of the design and discussed its operation in depth. The LIBS spectrometer was capable of obtaining spectra over the wavelength range 250 – 660 nm, whereas the diffuse reflectance obtained data over 380 – 950 nm. The complementary information obtained enabled distinction between paints even if they had similar chemical composition or colour.

The majority of the applications of the analysis of cultural heritage are given in Table 4. As usual, the majority of them use non-destructive techniques of analysis or, at worst, minimally destructive e.g. LA-ICP-MS or LIBS. Priority in the discussion has been given to those papers that provide some novelty during either the analysis or the handling of the data produced. Basic papers that simply report data and then make conclusions, no matter how interesting, have been omitted.

Table 4 Applications of atomic spectrometry to the analysis of cultural heritage ceramics

Analytes	**Matrix**	**Technique; Atomization; presentation**	**Comments**	**Reference**
Various (16)	Pre-colonial pottery from three sites in Brazil	XRF; -; s PIXE	Computed radiography and optical microscopy used in addition to XRF and PIXE. The multivariate statistical analysis tools of PCA and hierarchical cluster analysis were used to separate and correlate different groups of samples.	[170]

			Two distinct sub-groups were identified as being manufactured from different types of clay.	
Various	Chinese Mise-type wares	EDXRF; - s	Both ceramic body and glazes of ceramics from different dynasties and from different kilns around Shanglin Lake, China were analysed using EDXRF. Analysis of data using PCA identified that the porcelain bodies from the kilns were virtually identical for both time periods, indicating continuity of firing technology and raw materials. However, the glazes were different. The MnO_2 and ZrO_2 content could be used to discriminate between samples from the two kilns and time periods.	[171]
Various (9)	Proto-porcelain unearthed from Yejiashan Cemetery,	OES; ICP; LA SEM, XRD	Twenty seven bodies and 23 glazes of proto-porcelain were analysed. All bodies were characterised by high silicon and low aluminium. Glazes	[172]

	Suizhou , China		were typical high temperature calcium glazes with relatively high Mn and P content. Data were analysed using PCA. The combined analysis and chemometric approach enabled information on firing temperature, provenance and glaze technology to be obtained.	
Various (22)	Porcelain from Imperial Palace of Qing Dynasty, China	OES; ICP; LA XANES μ-XRD	The LA-ICP-OES was used to confirm the chemical composition of the paints on the ceramics and identified significant As concentrations. The NIST CRMs 610 and 612 were used for calibration / validation. The XANES and μ-XRF were used to give information on the chemical state of the As compounds used. The XANES identified it as As^{V} and the μ-XRF confirmed this as likely being the compound AsO_4^{3-}.	173

Various	Limoges painted enamels	p-XRF; -; s MS; ICP; LA	Portable XRF used for non-invasive analysis of materials and LA-ICP-MS was used on four tiny micro-samples (< 1 mm^2) taken from the bulk samples. A comparison of line and point LA-ICP-MS was undertaken, with results being in excellent agreement. Similarly, results from p-XRF were in reasonable agreement with those obtained using LA-ICP-MS. The presence of Pt in a foil repair was identified.	174
Various	Celadon from the Ming dynasty	MS; ICP; LA	A comparison of Zhejiang Longquan celadon with its imitation from Dapu kiln in Guangdong. Despite outward appearances being very similar, data showed large differences in composition of ceramic body composition. The glazes from the two sites had very different	175

			Ce and REE content. Easy distinction between the two materials was therefore possible.	
Various	Late bronze age Cypriot ceramics from Hatay, Turkey	XRF; -; s MS; ICP; L	Samples were powdered with mortar and pestle and then fused into a glass disc ready for WDXRF analysis. Powdered sample were acid digested using nitric and hydrofluoric acids prior to ICP-MS analysis. One of the few papers that reported significant damage being inflicted, albeit to small masses of sample. Binary plots indicated that White Slip Ware and monochrome ware was imported to Turkey from different areas of Cyprus.	176
Various (Ca, Fe and Mg)	Roman archaeological ceramics	LIBS, AAS; F; L	Quantitative LIBS analysis of five ceramics undertaken. Ample (0.5 mg) was taken and pulverised with zinc as an internal standard to improve accuracy and	177

			precision. The pulverised and homogenised sample was then mixed with potassium bromide to minimise matrix effects. Results were compared with those obtained using FAAS and were in good agreement. The LIBS analysis was only quasi-non-destructive in this example.	
Various (13)	Ceramics from Buddhist sites in India	PIXE; -; s INAA	Sample was pulverised and then 300 mg mixed with graphite powder and pressed to form a pellet prior to PIXE analysis. Reference materials IAEA SL-1 and IAEA SL-3 used for method validation. Results also compared with those obtained using INAA. Good agreement obtained. Cluster analysis of data identified two groups of samples. Similar grouping had previously been identified by archaeologists using	178

			physical characteristics.	
Various (26)	Archaeological ceramics and CRMs	WDXRF; -; s	Sample (1.5g) was taken from shards, pulverised and then fused into glass beads. Major, minor and trace analytes determined in the glass bead. Forty three CRMs / RMs of varying compositions including soils, sediments, rocks and ceramics were used for calibration. Performance in terms of precision, accuracy, LOD and repeatability were tested. The aim was to set up a methodology that is comparable with others, e.g. NAA,	179
Various	Archaeological ceramics from Brazil	p-XRF; -; s computed microtomography	Non-destructive portable XRF used to analyse chemical components of four ceramics from two archaeological sites. Computed microtomography used to obtain structural information. The XRF data were analysed using PCA with Varimax rotation	180

			which identified the samples as coming from three separate groups. These same groups were also identified using the computed microtomography through the ceramic matrix, inclusions / temper values effects on density.	
Various	Chinese red and white porcelain	EDXRF; - s μ-XRF XRD	Corning glass standards used for calibration of EDXRF instrument. Detection limit for most analytes was 0.02% and the diameter of the beam was 1 mm. The synchrotron μ-XRF was used to view the spatial distribution of the analytes. The spot size was 5 x 50 μm^2 and the instrument was used in mapping mode; i.e. 6000 data points over 5 mm x 4 mm area. Analytical data provided information on painting techniques.	181
Various (16)	13th and 14th century Fine-paste ware	EDXRF; -; s XANES	Twenty sherds from five archaeological sites from three	182

	from South East Asia		different areas analysed for eight trace and eight major analytes. No sample preparation was required. The XANES identified the proportion of α-Fe_2O_3 and γ-Fe_2O_3 in the samples. Cluster analysis with Ward's method was used to treat the analytical data and identified three distinct groups, enabling conclusions about provenance and a trade route to be made.	
Various (15)	Chinese blue and white porcelain	p-XRF; -; s Fiber optic reflectance spectroscopy	Portable XRF used to determine composition of 23 blue and white porcelain sherds. Ternary plots used to visualise data. Corning A glass used to validate data, with results compared with other workers' using LA-ICP-MS.	183
Various	Pottery from grave goods from Luxor	PGAA, Neutron tomography, radiography	Prompt gamma activation analysis (PGAA) and the other techniques used to non-destructively map composition in 3-D. A	184

brief summary of what the techniques can do was given. This was the first study of this type on these grave goods.

3.7 Glasses

3.7.1 Industrial glass applications

Forensic science is an area of analytical chemistry where it is highly desirable to avoid destruction of the sample. Therefore, applications of atomic spectrometry often involve the use of non- or minimally-destructive methods, e.g. XRF, LIBS or LA. It is this latter technique that has been the focus of a study by van Es *et al.*[150]. This paper is discussed in more detail in section 3.3.

The use *of LA-ICP-MS for the analysis of glasses* has been discussed in two other papers. In one,[185] a double focusing single collector ICP-MS instrument was used to evaluate Pb isotopic measurements in silicate glasses to determine whether or not it could be an alternative to multiple collector instruments. The instrument employs fast-scanning ion deflectors to place a series of flat-topped isotopic peaks sequentially into a single counting detector at a fixed accelerating voltage and magnetic field strength. A large range of certified glass samples were used for the tests. Peak tailing, background correction, correction for instrumental mass bias, spot size effect and matrix interference effects were all tested and discussed. Results indicated that at very small spot sizes (25 µm), the Pb ratios in NIST 610 were anomalously low. This could be because the material is not homogeneous at the microscopic level or because there is a non-spectral interference on the Pb isotope ratios. Since a minimum sample mass of 250 mg is recommended for analysis of NIST 610, it is likely that inhomogeneity would play a part. Similarly, higher than expected ratios were observed for NIST 612 and some iron-rich reference materials. This was attributed to potential differences in ablation behaviour because of the composition of the materials compared with the NIST 610 bracketing standard. In general, results for many of the ratios were more precise than those reported in other papers that had used a different type of single collector instrument, although they were typically far more sensitive. An improvement in the sensitivity of the instrument described was thought likely to lead to further improvements in precision. Performance compared with a multi-collector instrument was broadly similar although measurement of ^{20x}Pb/^{204}Pb when total Pb was > 5 ppm was better for the multi-collector. The second paper[186] described a Matlab-based data mining system, which is capable of extracting LA-ICP-MS data with no user input. They applied this software to their own database of approximately 5700 analyses of 10 glass and carbonate reference materials collected over five years for

14 analytes. The relative importance of systematic analytical bias and possible error in reported values through a mass-specific breakdown of the analytes, was examined. Even when very different LA conditions were used it was possible to obtain comparable data and specific recommendations could be made of how to improve data quality. Such recommendations may include use of a diatomic gas, the effect of differential inter-glass fractionation factors and even the choice of the transport tubing material. It was thought that the system would be of particular use during inter-laboratory comparisons because similar data sets from other LA-ICP-MS systems could be produced rapidly.

Two *X-ray based papers* are worthy of note. In one by Marks *et al.*[187] the Br, Cl, F and I content of several reference glasses (NIST 610, NIST 612, BHVO-2G, BIR-1G, BCR-2G, GSD-1G and GSE-1G) were determined using various techniques including TXRF, ion chromatography following a pyrohydrolysis treatment, instrumental NAA, EPMA and LA-ICP-MS. For most of the samples, agreement between the techniques was within 15% for a range of concentrations covering 20 – 300 µg g^{-1} for F, 70 – 1220 µg g^{-1} for Cl, 0.2 – 285 µg g^{-1} for Br and 9 – 3560 ng g^{-1} for I. However, for the silica rich NIST glasses, agreement was worse. The paper by Zhang *et al.*[188] described the determination of Br in minerals and glasses using EPMA and compared the data with those obtained using microbeam synchrotron XRF. The presence of aluminium in the sample can cause severe interferences when determining Br using EPMA. The authors developed a method through which the interference enhancement of the Br L-beta peak by the Al K-alpha peak can be expressed as a linear function of the aluminium oxide content of the sample. This was done by analysing Br-free, Al-containing materials. Signal enhancement (sensitivity increase) of the Br was obtained through the use of high beam currents and long measurement times. Results obtained from the two techniques were in agreement and LOD for the EPMA method was between 100 and 300 µg g^{-1}.

3.7.2 Cultural Heritage

In common with all other cultural heritage sample types, e.g. ceramics, paintings etc. the analysis of glasses requires minimal damage to be inflicted on the sample. The majority of the papers discussed have therefore used techniques that are minimally damaging, e.g. LA-ICP-MS or LIBS or inflict no damage, e.g. XRF. The majority of the papers discussed in this section are purely application-based and have therefore been summarised in Table 5. Those discussed have either itemised how calibration was achieved, discussed quality control measures or have introduced the analytical data to a chemometrics package in an attempt to maximise the amount of information gleaned.

Table 5 Applications of atomic spectrometry to the analysis of glass

Analyte	Sample Matrix	Technique; atomization; presentation	Comments	Reference
Various (9)	Bulgarian late antique and medieval archaeological glass	TXRF; -; s	Samples were analysed as slurries in Triton X114. The CRM BAM-S005 Type A (a soda-lime glass) was used to validate the method. Precision was typically better than 10% RSD.	189
Various	Colourants in 2977 pieces of late prehistoric glass	XRF; -; s MS; ICP; L TIMS	Portable XRF used to determine major elements. The REE were determined following an acid digestion of 1 mg of sample. High resolution ICP-MS was used to determine Pb isotope ratios and TIMS used for Sr isotope ratios. The XRF data were validated using BAM-S005 and by comparison with ICP-MS data for some samples.	190
Various	Pyrotechnological objects from Greece	OES; LIBS; s	Glass materials as well as ceramic and metal objects analysed using a portable LIBS instrument. The instrument was capable of being operated anywhere where a desk and electricity was sited and was capable of obtaining accurate preliminary data.	191
Various (>50)	Fragments of medieval glass from Ciudad de Vascos (Spain)	MS; ICP; LA	Analysis of 141 fragments identified three classes, depending on the fluxing agent used. The material NIST 612 was used to	192

			validate measurements, with precision being typically 5% RSD and accuracy for the majority of elements being within 5 – 10% of certified values.	
Various	Ingots, raw glass chunks and glass wastes from vessels from fifth century from palatine Hill (Rome)	MS; ICP; LA SEM, EMPA, XRD	Numerous analytical techniques used to characterise 20 glass fragments. Three origins identified: Levantine, Egypt and North African.	193
Various	Wine bottles from 17th to 19th centuries.	MS; ICP; LA PIXE	Major and minor elements determined using PIXE and trace and REE analytes determined using LA-ICP-MS. Data analysed using PCA to identify four classes of glass. These classes were tentatively identified as coming from Bristol in the UK, two classes from Belgium and the fourth from France.	194
Various	Hellenistic glass vessels	MS; ICP; LA EPMS SEM-EDX	Calibration achieved using NIST 610 whereas quality control was maintained using NIST 612. A laser operating at 193 nm with a fluence of 2.8 J cm^{-2} was used creating a crater of 70 µm diameter.	195

Various	Glass beads from the Kongo Kingdom	p-XRF; -; s FT-IR, GC-MS	Portable EDXRF instrument and several other analytical techniques used to characterise beads. The analytes As, Cu, Fe and Zn (k lines) and Pb (L line) were determined using XRF. Analytical XRF data used to construct bi-plots and also inserted to PCA. The PCA was performed with oblique matrix rotation.	196
Various	Stratified glass eye beads from China	p-XRF; -; s µ-Raman, Optical coherence tomography	Portable instrument used to analyse samples dating from 475 BC to 221 BC. The chemical composition seemed to indicate a European origin. In addition, two different types of colourant / opacifier were identified. These contained Co, Mg, Cu and Fe as well as Sb.	197

3.8 Nuclear materials

The testing of materials used in fusion reactors remains a popular topic in the analysis of nuclear materials, with LIBS the most commonly applied technique. A second popular topic is the analysis of radionuclides of importance to decommissioning and monitoring of waste storage/disposal facilities. In this area, ICP-MS procedures are the most common, with prior purification of the radionuclide of interest commonly achieved using online separation techniques. The importance of accurate isotope ratio measurements for source attribution remains an important topic, with the majority of publications focusing on actinide elements. Additional topics include the development of rapid sample preparation and measurement procedures for emergency response scenarios, and measurement of ageing or damaged reactor components. Rapid measurement with limited or no sample preparation is a common theme across all topics mentioned, with the benefits mentioned including higher sample throughput, reduced dose and labour time for the analyst, and for working in harsh environments.

3.8.1 Fusion materials

The characterisation of materials used or proposed for use in fusion reactors is a popular area of research. The dominant analytical technique is LİBS, including *in situ* and *ex situ* approaches. The retention of hydrogen isotopes and subsequent impact on material behaviour during reactor operation is a common topic, as is the modification of materials to prevent damage. *A review of the applications of LIBS in fusion technology* was prepared by Li *et al.*[198]. The paper focused on applications that could shorten operational lifetime, namely wall erosion, material transport and fuel retention.

Several papers outlined the *advantages of in situ measurement using LIBS for fusion materials*. Hu *et al.*[199] noted that this technique can monitor the lifetime of plasma facing components without the need to remove materials between plasma discharges. A combination of LIBS with laser-induced ablation spectroscopy (LIAS) was used for *in situ* laser-based diagnostics of fuel retention on the first wall after different conditioning methods. There was no need to remove the tiles between and during plasma discharges. A separate study applied a similar approach to *in situ* diagnostics of the chemical composition of the first wall in the EAST Tokamak [200]. The experimental approach focused on the dynamics of optical emission of plasma-facing materials, such as W, Mo and graphite, which had not previously been investigated in a laser produced plasma under vacuum. The key results were determining plasma and ion lifetimes, as well as the order of expansion velocities for different species in a multi-component system, which were related to plasma sheath acceleration and mass effect.

Hu *et al.*[201] used *in situ* LIBS to investigate fuel retention and impurity deposition in a Tokamak. The technique was used to identify deuterium, tritium and elemental impurities, as well as to obtain qualitative results including elemental depth profiles and deposition layer thickness. Fantoni *et al.*[202] presented the improved sensitivity of double pulse LIBS compared with single pulse LIBS for *in situ* measurement of deuterium deposition in surface layers of Mo coated with a mixed W-Al layer. The double pulse technique offered lower limits of detection and improved ability to detect trace level contamination.

Despite the advantages of in situ LIBS, *ex situ measurement remains a popular technique*. A study by Li *et al*. looked at the analysis of limiter graphite tiles exposed to He and H plasmas [203]. Depth profiles showed higher H content and retention depth in zones dominated by deposition compared with those dominated by erosion due to C-H co-deposition formation. This study was the first to apply a pico-second pulsed laser, and the results were in agreement with those obtained using EDX and cross-section SEM images. Kim *et al.*[204] detected various impurity elements including Fe, Cr and Ni on the divertor tile surface. Consecutive laser pulses were used to generate information on depth profiling, determined by the change in spectra. It seems likely that *in situ* LIBS will become increasingly popular, given that it is better suited to measurement during reactor operation, when removal of materials is relatively destructive and time consuming.

Understanding the *sorption behaviour of hydrogen isotopes on materials* is a key area. Deuterium retention was studied in Cu-Zr alloy by Nguyen *et al.*[205] using cylindrical specimens from 1-5 mm thickness. Analysis using SIMS showed the desorption rate of deuterium was inversely proportional to the sample thickness increment, and proportional to the loading temperature. Desorption was observed from 400°C, with complete retrieval after dynamic pumping at 800°C for 15 minutes. Thermal desorption spectroscopy showed two types of trapping energy in CuZr alloy, estimated at 62 and 79 kJ/mol. Hodgson *et al.*[206] also applied SIMS when investigating the role of multiple reactor operating conditions on deuterium absorption on flow channel inserts made of SiC in two fusion reactor operation designs. Deuterium absorption is associated with silicon-deuterium bonding, and absorption was shown to be linearly dependent on ionising dose and gas pressure, but not on dose rate, with more complex behaviour measured with irradiation temperature.

Modifying materials to improve resistance to degradation during reactor operation to extend operational lifetime, is also an important consideration. Liu *et al.* demonstrated that LIBS could be used to monitor the cleaning process of tungsten and molybdenum tiles used as first wall materials in a fusion reactor [207]. The optimised setup showed that cleaning of the lithium/deuterium co-deposited layer was effective under He gas, with a higher lithium removal in tungsten tiles, compared with a slightly higher deuterium removal in molybdenum tiles.

Studies *not using LIBS commonly use a range of analytical techniques*. Tsavalas *et al.*[208] measured the erosion and migration of beryllium in marker tiles, given their use in plasma facing components at the JET Tokamak. The focus was on the deposition of carbon plasma impurities on the beryllium surface, with analysis carried out using SEM, XRD, XRF and nuclear reaction analysis. The carbon content was low on the tile surface, but elevated in grooves of castellation sides, and higher still in the wider gaps between tiles. Several elements (Cr, Fe, Mn, Ni, O and Ti) were detected in all samples exposed to plasma. The impact of an alumina coating for preventing corrosion on Pb-17Li eutectic after heating at 550°C for 1000 hours was investigated by Gazquez *et al.* using SIMS, SEM and EDX[209]. The corrosion on coated tiles was considered to be insignificant, whilst uncoated materials suffered with damage and/or loss of material. The coating was therefore considered effective under the conditions tested.

de Castro *et al.*[210] studied the use of liquid lithium combined with tungsten on the first wall of magnetic fusion reactors as a method to *improve H-mode plasma confinement and heat handling capabilities*. Laser induced desorption mass spectrometry (LID-QMS) was used for quantifying deuterium retention on W-Li films, based on the concern that tritium retention could represent a safety risk. Several other techniques including SIMS and FAAS were used for characterisation of the films. The results showed negligible deuterium uptake over the conditions tested, with a deuterium/lithium atom ratio of <0.1 % at 400°C on a 100 nm thick thin film. The results suggested this material could potentially be used in real reactors. Several techniques were applied by Modi *et al.*[211] to the measurement of lithium titanate and lithium aluminate, which were proposed as tritium breeding blanket materials in deuterium-tritium fusion reactors. Neutron activation analysis was used to determine trace-element concentrations from long-lived nuclides, and PIGE was used to quantify Li, Ti and Al concentrations.

3.8.2 Nuclear forensics

The accurate measurement of isotopic ratios is a key topic for identifying the source of nuclear contamination, and is a much more powerful tool than obtaining the activity concentration alone. Measurement of actinide elements (particularly U and Pu isotopes) is most common, either following chemical separation, or through direct measurement techniques.

As with fusion materials, *the potential of LIBS* was the focus of some studies. Bhatt *et al.*[212] combined LIBS with chemometrics for rapid and direct measurement of concealed and limited size nuclear materials. A detection limit of 76 µg g^{-1} was established for U in cellulose, and several 'weak' and 'resonant' lines were identified for uranium spectra. Multivariate calibration models were developed using these lines to predict the concentration in CRMs, with a relative error prediction of 4.32% and 9.75% for weak and resonant lines, respectively. The method developed also grouped samples into their mineral mine of origin, demonstrating the potential for using this technique for source attribution. Uranium isotopic analysis using LIBS combined with laser ablation molecular isotopic spectrometry was the focus of a study by Mao *et al.*[213]. Along with computer simulation of acquired spectra, an optimal precision of 0.42 % was achieved when simulations were based on a combination of molecular bands and atomic lines.

The *separation and measurement of individual particles* is a common application for identifying the source of nuclear material. Lee *et al.*[214] used TIMS with a continuous heating method to measure U and Pu isotopic ratios in 0.6-3.3 mm particles without pre-treatment. The values obtained were in good agreement with certified values within the range of error, however, the authors highlighted that the sensitivity was not sufficient for measurement of low abundance ^{234}U and ^{236}U in smaller particles. In another paper, Yomogida *et al.*[215] combined micro-Raman spectroscopy and SIMS to assess the chemical states and isotope ratios, respectively of uranium particles. Each particle was initially identified using SEM combined with EDX, with the intention of using the method developed to identify the origin and history of each particle. Faure and Dalger[216] combined the sensitivity and imaging capabilities of SIMS to measure ^{235}U at 10-97 % abundance in a range of CRMs, with an abundance accuracy of <0.5 %.

Manard *et al.*[217] used a combination of I*CP-MS and LIBS to characterise uranium particles*, which were doped at various concentrations up to 2 % in a 50:50 Ni:Fe mixture. A 50 minute analytical time was required to cover a 5 mm^2 area, with a measurement uncertainty within 10 % for U isotopic composition. Ono *et al.* [218] studied the physical characteristics of particles emitted from the Fukushima Nuclear Power Plant. The particles were separated from soil and measured using XRD, XRF and XANES analysis. The physical characteristics and composition of some crystalline materials led to the conclusion that the particles were released into the atmosphere from reactor 1, and showed that chemical composition was an alternative to radioactive isotope ratios for determining the contamination source.

A further application of nuclear forensics is *determining the source and history of materials with limited information*. Rim *et al.* [219] used a range of techniques to determine that two Pu foils with limited production information had most likely been used as targets for experiments such as cross-section measurements. Among other techniques, XRF, gamma spectrometry and trace elemental analysis were combined with available reactor and historical information to provide information on the grade, most recent purification date and likely production site. Barybin *et al.*[220] investigated the composition of uranium-erbium fuel before and after irradiation using SIMS. Post burn-up analysis measured an 11-fold decrease in ^{167}Er concentration compared with the initial value, whilst ^{168}Er concentration increased. Similarly, the ^{235}U concentration decreased 6-fold, with an increase in ^{236}U.

A common theme for a number of forensic studies is the *comparison between solution-based mass spectrometry (commonly ICP-MS) and direct measurement (such as LA-ICP-MS or SIMS)*. The previously mentioned study by Faure and Dalger[216] highlighted the advantage of SIMS over ICP-MS and TIMS for ageing individual particles in a mixture of nuclear materials. Other studies directly compared different measurement approaches. Reading *et al.*[221] developed a fusion bead procedure (9 parts $MgSiO_3$ with 1 part sample) for the production of homogenous, flux-free glass beads from various materials that were then measured using LA-ICP-MS. Data obtained for the rare earth elements were in good agreement with those from solution ICP-MS, and these elements were highlighted as a particular advantage for forensics studies. Spano *et al.*[222] also demonstrated agreement between solution and LA-ICP-MS for trace element measurement of several uranium ore concentrate and uraninite samples. This was carried out to show the potential to use such samples for source attribution. The variation in elemental abundance was slightly higher using LA-ICP-MS, whilst solution MC-ICP-MS was used for uranium isotopic measurements.

The *importance of standards used and measurement method are also highlighted for nuclear forensic studies*. Jakopic *et al.*[223] used IDMS for high accuracy measurement of actinides, by adding large sized droplet spikes of enriched ^{235}U and ^{239}Pu. Results were presented of external verification measurements by the European Commission and International Atomic Energy Agency. Ruas *et al.* determined the quantity of high purity uranium by gravimetry after calcination[224]. Expanded uncertainties were lower than 0.2 %, verified using a reference uranium nitrate solution, with an additional advantage that the technique is not related to a chemical standard.

3.8.3 Rapid measurement for emergency response

Whilst rapid measurement is a common theme for all nuclear material applications, it is something mentioned in all studies relating to measurement following a nuclear incident. As well as developing methods for these applications, the preparation of testing materials relevant to nuclear incidents e.g. post-detonation glass, is also a key area.

Wang *et al.*[225] developed a procedure combining *extraction chromatography* separation (UTEVA and DGA resins) with ICP-MS measurement for rapid determination of actinides in water samples. Simultaneous measurement of U, Th, Pu and Am was achieved with a total procedural time of 8 hours, and the accuracy of the technique was validated using IAEA-443 seawater reference material. Maxwell *et al.*[226] focused on rapid Pu measurement in steel samples following a radiological emergency. A preparation time of 6-8 hours was required for digestion, extraction chromatography separation, followed by measurement using either alpha spectrometry or ICP-MS.

The *complete and rapid digestion of complex sample matrices is key for achieving high analyte recovery* prior to further sample preparation and measurement. Hubley *et al.*[227] developed a rapid dissolution procedure (<3 h) of reference materials using ammonium bifluoride prior to ICP-MS measurement. The results were evaluated with regards to use in post-detonation nuclear forensics. Elemental recoveries in geological reference materials were 80-120 %, compared with 90-100 % for all tracers other than iodine for two NIST materials spiked with radiotracers. The dissolution technique was effective for materials with various silica content. The study by Reading *et al.*[221] described previously outlined that the speed of the fusion technique developed for dissolution of solid materials into glass beads (~10 minutes preparation time) was beneficial to investigation of seized or suspect nuclear material.

The *development of appropriate materials relevant to emergency response applications is key to ensuring procedures developed can be appropriately tested*. Campbell *et al.*[228] developed a U-doped urban glass matrix material to simulate nuclear explosive debris. The capability of LA-ICP-MS was demonstrated for uranium isotopic ratio measurements, whilst SEM and XPS were used for surface and cross section morphology and major element composition, respectively. Bonamici *et al.*[229] showed that measurement of stable heavy elements (including Sr, Zr, Ba, Sm, Lu, U and Th) could be used as a proxy for radionuclides for measurement of complex post-detonation materials. Both EPMA and SIMS measurements showed that the determination of stable elements could offer some insight into the formation of debris and how materials were fixed into the debris. This therefore yielded valuable information of chemical fractionations and physical mixing.

Weisz *et al.*[230] studied the *mechanisms and conditions by which materials including soil behave following a near surface nuclear explosion*, and subsequent incorporation into glassy fallout material. Two fallout glasses that had agglomerated and fused were measured using nano-SIMS, which revealed higher uranium enrichment ($^{235}U/^{238}U$ >7.5) in 8 of 11 interface layers. These layers were also enriched in Fe and Ca bearing species (50 % relative to average concentrations), and depleted in Ti and Al-bearing species by approximately 20 %. The results suggested unexpected vaporisation/condensation behaviour, or an anthropogenic origin of the enriched species.

3.8.4 Contamination of nuclear fuel materials

The presence and behaviour of impurities that can adversely affect the performance of fuel components is a common topic. This is usually focused on impacts over long timescales. A range of analytical techniques are used, rather than other applications where one technique is dominant. The behaviour of zirconium alloys was a common theme. Pathak and Sengupta[231] developed a method using chemical separation prior to ICP-AES analysis to measure multiple trace metal constituents in Zr-Nb alloy. The method was validated using a synthetic sample, with all 31 contaminants measured at the 1 mg L^{-1} level with a precision of <5 % RSD.

A paper by Kashkarov *et al.*[232] identified the issue of *hydrogen accumulation in zirconium alloys* over long time periods, followed by mechanical degradation, hydride and stress corrosion cracking. Titanium nitride (TiN) implanted Zr-Nb alloy was investigated as a method for reducing hydrogen absorption, with samples analysed using XRD, SEM and GD-OES. Following hydrogenation, it was shown that TiN films and Ti implantation reduced the H absorption rate of the alloy, with the most effective results achieved using denser films. Tupin *et al.*[233] also determined H diffusion in corroded zirconium alloys, focusing on the measurement of oxides under simulated water conditions using isotopic tracers and SIMS. Results showed a H-permeable external oxide film and an inner protective film. Thermal desorption spectroscopy analyses revealed hydrogen interaction sites in two oxide sub-layers. The change in behaviour in zirconium over time in dissolved irradiated fuel was determined using a combination of TIMS and ICP-MS by Baghdadi *et al.*[234]. Uncertainties lower than 3 % were achieved for real nuclear samples, with ICP-MS using a lutetium tracer to perform a relative analysis.

Several papers used *LIBS for the analysis of fuel materials*. Ruas *et al.*[235] presented the online monitoring capabilities of LIBS for measuring Zr in solution, in relation to fuel debris composition at the Fukushima Nuclear Power Plant. A detection limit of 4 mg L^{-1} was achieved when combined with ultra-thin liquid jet sampling, making the technique a promising option for analysing complex zirconium mixtures. A paper by Lissenden *et al.*[236] developed robotic delivery of LIBS in combination with electromagnetic acoustic transducers for the monitoring of spent fuel canisters in environments with limited space, high temperature and radiation. Measurement of Cl using LIBS was used to detect chloride-bearing salts on canisters, which can lead to stress corrosion cracking, particularly in marine environments. Williams and Phongikaroon developed a procedure for LIBS measurement of molten salt electrolyte formed during pyrochemical separation of used nuclear fuel[237]. The LIBS system was optimised with regards to laser energy and gas pressure, and showed an advantage over static surface measurements that suffer from poor reproducibility and homogeneity.

3.8.5 Nuclear decommissioning

The global trend towards decommissioning of nuclear sites is reflected in the high number of publications on measurement of radionuclides of importance to decommissioning and longer term waste storage and disposal. ICP-MS is the most commonly used technique, often preceded by offline or online chemical separation of the radionuclide(s) of interest. The role of *ICP-MS for nuclear decommissioning and waste characterisation was critically reviewed* by Croudace *et al.*[238]. The review contained 312 references and presented Tables of data for easy reference. Sections were included for individual isotopes and for instrument type.

Advances in ICP-MS instrumentation and chemical separation capabilities are increasing the number of radionuclides that can be measured using this combination of techniques. The long-lived fission product ^{93}Zr was measured by Osvath *et al.*[239] in nuclear power plant waste by ICP-MS following extraction chromatography separation. The mass overlap from ^{93}Nb was corrected using a Monte Carlo activation model to calculate the ^{93}Zr/natural Zr mass ratio expected. In order to reach measurement uncertainties of <10 %, a decontamination factor of 10^3 was required. Petrov *et al.*[240] focused on online separation using ICP-MS equipped with a collision-reaction cell as a rapid alternative to offline chemical separation for measurement of ^{93}Zr in a standardised solution. Using a combination of NH_3 and H_2 to separate ^{93}Zr from interfering ^{93}Mo and ^{93}Nb, a decontamination factor of >10^4 was achieved for both interferences. A separate study by Garcia Miranda *et al.*[241] employed the same approach, using O_2 to separate ^{151}Sm from overlapping ^{151}Eu through formation of ^{151}Sm^{16}O to enable measurement in graphite. A one order of magnitude decontamination factor was achieved, which was sufficient to reach the ^{151}Sm waste criteria exemption level.

The separation and measurement of individual lanthanides relevant to decommissioning is a challenging topic that several papers addressed. Coupling online separation to mass spectrometry measurement is preferable to offline separation. Van Hoecke *et al.*[242] applied high performance ion chromatography to isolate five lanthanides prior to mass spectrometric determination. A cation exchange column and gradient elution with alpha-HIBA was used for separation, which was also focused on the removal of contamination from activation and fission products. An alternative online separation approach using isotachophoresis coupled with MC-ICP-MS was used by Vio *et al.*[243] for the determination of isotopes of several lanthanides (Eu, Gd, Nd and Sm). A single analysis of 20 ng of each element returned a reproducibility of <0.4 %, whilst online correction of mass bias using sample standard bracketing was possible, due to the use of a nebulisation interface that could inject isotopic reference standards.

The high sample throughput and improved sensitivity of ICP-MS means it is increasingly being used for measurement of relatively short lived radionuclides, including the *high yield fission product and decommissioning radionuclide* ^{90}*Sr*. Kolacinska *et al.*[244] combined ICP-MS with sequential injection analysis to obtain a purified ^{90}Sr sample. A method detection limit of 2.9 fg mL^{-1} was achieved for 1 L samples, and the optimised procedure was applied to spiked river water, reference water samples, and reactor coolant samples. Takagi *et al.*[245] described the determination of ^{90}Sr using ICP-MS following Cascade pre-concentration and separation. The Cascade setup was based on solid phase extraction, achieving a detection limit of 0.06 fg L^{-1}.

Separation of radionuclides prior to measurement using *bespoke chemical separation setups rather than commercial systems* is also an area of interest. Measurement of long-lived ^{107}Pd by Yomogida *et al.*[246] was considered as an approach to assess the long term safety of high level waste repositories. A non-contact separation technique using laser-induced photoreduction was employed, which would minimise radioactive contamination and worker exposure. The method was optimised using a simulated high level waste solution, with a Pd recovery of 59 %, and removal of approximately 99 % of contaminants. Gao *et al.*[247] investigated the capabilities of a chip-based microfluidic platform for ion exchange and extraction chromatography separation of impurities in various U and Pu materials. Compared with traditional techniques, the solution volume reduction was 90 % or higher, with quantitative recovery of 28 elemental impurities. Chips based on PTFE, PVC and polypropylene showed the highest compatibility of the nine materials tested.

Other mass spectrometric techniques are less frequently used compared with ICP-MS for the determination of long-lived radionuclides. Vivo Vilches *et al.*[248] used AMS to measure ^{41}Ca. Mixing of CaF_2 with Ag was used to generate a source material with a stable current and to reduce interference from overlapping ^{41}K, which was also corrected for through measurement of ^{39}K. The setup was capable of measuring ^{41}Ca/^{40}Ca ratios higher than 4×10^{-11}, with the results showing good correlation with a second AMS facility. Comte *et al*.[249] applied SIMS in combination with radiochemical measurements to study the dispersion of ^{36}Cl in contaminated graphite. Combining techniques helped to explain dispersion, which enabled measurement over a range of timescales. Another highly sensitive mass spectrometric technique, RIMS, was applied to the determination of ^{99}Tc in a soil sample by Schonberg *et al*.[250]. Very low level measurement of 1.5×10^{9} atoms per gram of dried material was achieved, with ^{97}Tc measured as a tracer. Additionally,^{98}Tc was detected as a contaminant, which was the first time all three isotopes have been detected using RIMS. The enhanced sensitivity of RIMS and AMS is at the expense of lower analytical flexibility, higher instrument cost and lower commercial availability compared with ICP-MS.

3.9 Electronic materials

This has been a popular area of research, but many of the papers are routine and bring no novelty to the area of atomic spectroscopy. Therefore, they will not be discussed in this review.

A review of the analysis of advanced materials, including electronic materials, using ICP-based techniques was presented by Limbeck *et al.*[94]. This review was discussed in detail in section 3.6.1.

3.9.1 Wafers, thin films and multilayer materials

There are several topics of interest in this area including in data analysis techniques for XRF analyses and the use of gas cluster ion beams for surface analysis. The need for results that are reproducible between laboratories has also been approached in this review period.

A *review of depth profile analysis using glow discharge spectrometry*, containing 103 references, was presented by Lobo *et al.*[251]. The review covered both GD-MS and GD-OES and gave details of commercial instrumentation, methods used for quantification and recent applications. The GD-MS methods of quantification are based on ion beam ratio or relative sensitivity factors; the latter of which requires the use of CRMs for calibration. For many sample types, no CRMs exist and this is therefore a major drawback. An alternative method of quantification, entitled absolute sensitivity values, was also discussed.

There is a need for certified reference materials or at least some reassurance that *results produced for a sample in one laboratory are similar to those obtained in another laboratory* for the same sample. The results of two inter-laboratory tests were reported by Kim *et al.*[252, 253]. In the first example, copper indium gallium selenide films were sent to seven National Metrology Institutes and one other institutes for the measurement of the molar ratios of Cu, Ga, In and Se ratios. A film with mole fractions of these analytes that had been certified using ID-ICP-MS and that is traceable to SI (Système International) was supplied to the institutes. A total number counting method was recommended to determine the signal intensities of the analytes in depth-profile studies using SIMS, XPS, and Auger electron spectroscopy. The molar fractions of each analyte were determined using non-destructive XRF and EPMA. The average values for the degree of equivalence uncertainty (a measure used during inter-laboratory comparisons to quantify the similarity between data from different laboratories) were 0.0093, 0.0123, 0.0047 and 0.028 mol/mol for Cu, In, Ga and Se, respectively. These values were significantly lower than that of Fe in an iron-nickel alloy film when that sample was analysed in a previous comparison. The second paper reported the results of a round-robin measurement of the layer thickness of multilayer films using SIMS depth-profiling[253]. Seven laboratories from five countries were involved in the test. Two types of material were used during this test: a silicon germanium alloy ($Si_{52.4}Ge_{47.6}$) reference film was used to determine the relative sensitivity factors for the Si and Ge and a Si/Ge multilayer reference film was used to determine the relative sputtering rates of the different Si and Ge layers. The raw SIMS depth profiles of the Si/Ge multi-layer films were converted to compositional depth profiles using the relative sensitivity factors of Si and Ge derived from the reference SiGe film. The expanded uncertainties for the Si and Ge in a multilayer sample with similar layer thickness to the reference sample were 0.76 and 1.17 nm for Si and Ge, respectively. However, for a film that had a layer thickness less than the reference material, the expanded uncertainties increased to 1.04 and 1.59 nm.

A s*oftware package designed to facilitate data interpretation* from the analysis of multilayers was reported in a paper by Brigidi and Pepponi[254]. The package was called Grazing Incidence Material analysis with Python (GIMPy). The software combined the fundamental parameter approach of XRF spectrometry with the electrical field calculation in stratified media which delivers the total reflected intensity measured using XRR. The code was able to simulate the angular dependence of fluorescence in the grazing incidence format and was also capable of simulating XRF spectra by implementing a physical model for the response of the detector. Secondary fluorescence and the cascade effect were accounted for during this simulation. Also accounted for were effects originating from deviations from ideal conditions. These include non-monochromatic excitation, beam divergence, beam size and shape, the area of the sample inspected and the solid angle of detection. The overall result was package that was capable of quantifying XRF data by direct fitting of the spectrum from a sample model without the need for an intensity extraction.

Two papers have discussed *the analysis of silicon*, with one using ICP-OES[255] and the other high resolution continuum source ETAAS[256]. In the former paper, samples of p-type semiconductor pure silicon with particle size < 2 mm was digested in a microwave oven using 16 mL of a mixture of 8.5 M hydrofluoric acid and 1.35 M nitric acid. An optimised step-wise programme was used for digestion. The authors noted the mass of sample plus acid at the beginning of the digestion and at the end to monitor loss through volatilisation. This digestion method was significantly quicker than the traditional method that involves the removal of silicon through volatilization. However, great care had to be exercised during the analysis to avoid spectral overlap of analyte lines with those from silicon. Calibration was achieved in two ways: matrix matching and multiple standard additions. Much of the paper was descriptions of the algorithms required to obtain accurate data and the statistical tests used. Method validation was achieved through the analysis of the reference materials IPT134, IPT135 and NIST 57b. The determination of 12 analytes (Al, B, Ca, Cr, Cu, Fe. Mg, Mn, Ni, P, Ti and Zr) yielded data in good agreement with certified values. For the wavelengths used, LOD ranged from 0.03 µg $g^{-1}$for Mn up to 1.52 µg g^{-1} for Ca. The other paper discussed the use of solid-sampling ETAAS using a continuum source instrument for the determination of Co, Fe and Ni in high purity (solar grade and electronic grade) silicon[256]. The samples were also analysed using line source FAAS following a microwave-assisted acid digestion. A paired t-test demonstrated there was no difference between the two sets of data. For a sample containing 7.80 mg kg^{-1} Co, 36.2 mg kg^{-1} Fe and 228.5 mg kg^{-1} Ni, precision values (n=12) were 6.4%, 6.1% and 1.0% for Co, Fe and Ni, respectively. Spike -recovery experiments of a high purity silicon sample yielded recoveries of 94.3 – 97.1% for Co, 86.7 – 109% for Fe and 88.4 – 98.9% for Ni.

Gubal *et al.*[257] compared the analytical performance of two different kinds of discharge cells, namely a Grimm and a hollow cathode, where the quantification method was emission spectrometry. Both semiconducting (silicon, silicon carbide and gallium nitride) and non-conducting (quartz and alumina) samples were analysed. A detailed description of the two cell types was given. The Grimm cell was operated in continuous RF mode, whereas the hollow cathode cell was operated in both the continuous RF and the pulsed DC modes. A comparison of OES signal intensities was made between the different cells and different modes using the same power and pressure conditions. When operated in continuous RF mode the hollow cathode cell gave at least as good a signal intensity as the Grimm cell. The hollow cathode cell had an especial advantage with thick dielectric samples because, unlike the Grimm cell, the signal intensity was independent of sample thickness. When operated in the pulsed DC mode, signal intensities obtained using the hollow cathode cell were several orders of magnitude higher than the Grimm cell. This was particularly true for dielectric samples.

Gas cluster ion beams are at the forefront of ion beam technology for surface analysis. Holzer *et al.*[258] used a large O_2 cluster to record depth profiles of alkali metal ions within thin silica layers. The gas cluster gave a similar erosion rate to the commonly used O_2^+ ion but, because of its high sputter yield, the beam current was a factor of 50 lower. This resulted in a significantly lower number of excess charges at the silica surface and hence, a reduced electric field is obtained within the remaining dielectric layer. This helped prevent the migration of the alkali metal ions that is commonly observed during depth profile measurements using TOF-SIMS in dual beam mode. The use of the gas cluster reduced the migration of K^+ and Na^+ to a negligible amount, thereby facilitating artefact-free depth-profiling with high sensitivity and low power. By switching between the sputter beam from O_2^+ to gas cluster O_2 and back it was possible to investigate the migration process in detail. The K^+ was transported through the SiO_2 layer only within the proceeding sputter front. However, Na^+ migrated through the unaffected SiO_2 layer towards the adjacent Si / SiO_2 interface.

The use of *LIBS for the analysis of thin films* has been reported in four papers. Davari *et al.*[259] reported the use of calibration-free LIBs for the analysis of silicon oxide thin films of varying thickness grown on silicon wafers under different temperatures in a moisture-free environment. The crater produced by LIBS was analysed using AFM. In reality, the expression calibration-free is somewhat mis-leading. The authors actually used an internal calibration that involved normalization of the analyte densities with the bulk matrix densities. The species densities of O (analyte) and Si (bulk) were measured from the emission intensities under the same plasma conditions to give an O to Si ratio. Results obtained using LIBS were compared with those from ellipsometry, SEM, AFM and profilometry. The detection limit with respect to depth for the LIBS was 10.5 ± 1.4 nm. Femtosecond

LIBS was used by Ahamer *et al.*[260] to obtain high spatial resolution elemental images of copper thin films on glass and yttrium barium copper oxide thin films. The LIBS system comprised a Ti:sapphire laser producing light with a wavelength of 800 nm, a beta barium chloride crystal that doubled the frequency to 400 nm, some optics designed to block stray light and non-paraxial beams and then to focus the light onto the sample. Light emitted went *via* a fibre optic to an echelle spectrometer and an intensified CCD. The diffraction images of the echelle spectrometer were binned to reduce the read-out time for the detector and to increase the stability of the emission signals. A raster across the sample surface using a single pulse of the laser gave an elemental two-dimensional map. The crater size was dependent on the thickness of the film. Emission efficiency, defined as intensity produced at a Cu atomic wavelength per ablated volume, decreased rapidly when films were thicker than the optical penetration depth. Spatial resolution in the yttrium barium copper oxide films was approximately 6 µm which, according to the authors, was among the best values reported for LIBS imaging. Unfortunately, the emission spectra from the yttrium barium copper oxide films were very complex. Quantification was only achievable if one element at a time was determined. The authors hypothesised that use of a more rapid detector system, e.g. a Paschen-Runge spectrometer and of more efficient collection optics would lead to better spatial resolution and a reduction in the measurement time. A new LIBS technique designed to measure the thickness of films that are thinner than the ablation rate was presented by Nishijima *et al.*[261]. This technique is called spatially offset double pulse LIBS. The work continued from a previous study and so unfortunately, the setup was described only briefly. It utilized a calibration curve formed by the signal intensity from reference thin films of known depth. Calibration curves were successfully made for W thin films and for Cr, Fe and Ni in a mixed material film. The last LIBS application to be discussed was by Xiu *et al.*[262] who reported the qualitative and quantitative determination of Sn doped in titanium oxide nanometer films.

Table 6 Applications of atomic spectrometry to the analysis of semiconductor materials

Analyte	Matrix	Technique	Comments	Ref
Various	Titanium nitride and titanium aluminium nitride coatings. Pure copper and iron films	OES; GD; s	Instrument modified to include a dedicated IR spectrometer placed on the zero order of the first one. An interferometer was also coupled with the spectrometer. By using the surface of the sample near the crater as a reference surface, the crater depth could be determined simultaneously with the collection of analytical data. Comparison of the results from the interferometer with those from a mechanical profilometer agreed to within 2% relative mean square error.	263
O and Si	Electro-deposited SiO_x films grown on copper	OES; GD; s XPS; -; s SIMS	Films depth-profiled using XPS, SIMS and GD-OES. The Si and O were uniformly distributed across the film.	264
Cr and Fe	Iron / chromium multilayers of between 1 and 15 Angstrom thickness.	XRR Angle resolved EXAFS	Depth resolved method developed combining XRR data (of element concentration profile) with those from angle resolved EXAFS. A mathematical algorithm was derived that deconvolves the depth-dependent problems associated with scattering and absorption.	265
In and Sn	Indium tin oxide films on polyethylene-terephthalate	Laser excited atomic fluorescence (LEAF)	A two-pulse LEAF method with laser operating at 193 nm was used to obtain depth-profile information. Laser fluence and gating and time delays were all optimised. Detection limits were	266

			0.1% and 0.43% for Sn and In, respectively. Craters were examined using SEM. Negligible damage was inflicted.	
Various	Atomic layer deposited metal and oxide nano-scaled films	XRF; - ; s	Insulating oxides, e.g. alumina, hafnia and zirconia, semiconducting oxides, e.g. titanium dioxide and zinc oxide and platinum metal film analysed. Film thickness measured and compared with predicted thickness based on atomic layer deposition growth rate calculations. Results were in good agreement.	267
O and Ta	European standard BCR 261T, 30 nm thick tantalum pentoxide film on tantalum foil.	XPS; -; s	Ion beam of Ar^+ and cluster ion beam of Ar_{1000}^+ used to etch the reference material at different energies. The crater was analysed using XPS. The preferential sputtering of O was less when Ar_{1000}^+ was used at 6 keV compared with Ar^+ being used at either 500 eV or 3 keV. The Ar^+ ion beam gave a steady state O/Ta ratio as a function of depth, whereas the Ar_{1000}^+ gave a gradual decrease. However, the etch rate and depth resolution were better for the Ar^+.	268
Co and Zn	Cobalt doped polyvinylidene fluoride – zinc oxide thin films	XPS XANES EXAFS	Nanocrystalline zinc oxide doped with cobalt as the compound $Co_xZn_{1-x}O$ was added to polyvinylidene fluoride producing a flexible composite film. Atomic spectrometric techniques used to determine the valence states (XPS and XANES) and of the local	269

			structures surrounding the Co and Zn (EXAFS). Results confirmed the substitution of Zn sites by Co ions in the zinc oxide lattice.	
Co, Cr, Cu, Fe, Ni, Si	Cu/NiCu layers with thickness of tens of nanometers	TOF-MS; GD; s	Pulsed GD-TOF-MS used for measurements. Problems associated with saturation of the detector by major elements overcome by using the afterglow region for all elements except Cu, which used the plateau region. An alternative was to use the afterglow region for all elements, but to monitor ArCu signal rather than Cu. Thickness and composition measurements were in agreement with expected values.	270
Ga and Zn	Transparent conducting zinc oxide thin films	XRR GIXRF	Combination of XRR and GIXRF used simultaneously to measure thickness of layers, roughness of the surface, density and elemental profile of samples pre- and post-annealing. Regarded as a non-destructive technique. The combination of XRR and GIXRF can distinguish between elements of very close atomic number.	271
Ge and Si	Silicon germanide ($Si_{1-x}Ge_x$) thin films	SIMS; -s XPS	For XPS measurements, analysis of a reference film using a conventional method, average intensity method and total number counting method was used to determine the intensity-to-composition conversion. For SIMS, use of an oxygen ion beam	272

caused matrix effects. A Cs ion beam was therefore preferred. Data obtained using XPS and SIMS were comparable. The measurement uncertainty on the XPS data were highly improved when average intensity or total number counting were used.

3.9.2 Solar cell materials

The use of *LIBS for characterization of solar cell materials / quantum dots* has been discussed by Both Banerjee *et al.*[273] and by Skarkova *et al.*[274]. In the former paper, femtosecond LIBS was used to characterize organic photovoltaic devices. These comprised a top electrode (aluminium, magnesium or molybdenum), an organic layer, a bottom electrode (indium tin oxide), a silicon nitride barrier layer and substrate layer. These layers varied in depth between 115 and 250 nm. The LIBS measurements were undertaken using a 40 fs titanium: sapphire laser operated at a very low pulse energy (7 µJ) and at 800 nm. This was to ensure that sufficient resolution was achieved for the thinner layers when the laser was used repeatedly to ablate the same spot. Clear differentiation between the layers was achieved. The paper by Skarkova *et al.*[274] reported the use of LIBS for the two-dimensional mapping of cadmium telluride quantum dots that had been injected as an aqueous suspension onto filter paper. The effects of pH and the presence of copper on the LIBS signal were investigated. The LIBS data were compared with those obtained using fluorescence microscopy. The latter technique showed signs of signal quenching. This, with the fact that LIBS is easily automated and has simple instrumentation, led the authors to conclude that LIBS offered a fast alternative to other techniques.

Copper-indium-gallium-selenide quantum dots capable of harvesting light over a 1000 nm range were prepared and used to construct solar cells[275]. Numerous techniques including ICP-OES, XRD, XPS and ultraviolet photoelectron spectroscopy were used to characterise the product and to elucidate how the Ga was alloyed into the copper indium selenide host.

3.9.3 Electronic equipment and devices

The analysis of *lithium ion batteries* is an extremely popular area of research. In many cases, the work entails a simple change of material for either the anode or the cathode, but in other cases mechanistic aspects of the process are elucidated using atomic spectrometric techniques. Other papers discuss the analysis of specific components of the batteries.

Two *reviews pertinent to the analysis of lithium ion batteries* have been published during this review period. The first, by Alemu and Wang[276] discussed (with 102 references) the use of *in-situ* electrochemical synchrotron radiation, i.e. the use of techniques such as XAS, XRD and transmission X-ray microscopy, for their analysis. These techniques are especially useful for the detection of oxidation state changes, crystallographic transformations and characterization of the solid electrolyte interphase. This means that intercalation and de-intercalation can be studied which would give insights into the fundamental reactions occurring within the battery. The second review (with 179 references) was entitled "elemental analysis of lithium ion batteries" and was prepared by Nowak and Winter[277]. The authors explained that although lithium ion batteries have been around for 25 years and are the first choice for portable electronic devices, they are prone to aging, i.e. the cell constituents degrade. This means that their calendar life (their physical age) and their cycle life (how heavily it is used) can be affected. The authors reviewed the composition and structure of the batteries and then went on to explain why analysis is necessary. The later sections discussed analytical applications, e.g. analysis using XANES, TXRF, XAS, ICP-OES and ICP-MS and the determination of Li distribution in the cell.

As well as the review, the same research group produced a paper in the same area[278]. Evertz *et al.* used pulsed GD-MS and matrix-matched standards for the *quantification of elemental lithium ion battery degradation products* deposited on carbonaceous negative electrodes. The standards were prepared by mixing graphite powder with the ternary mixture of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (otherwise known as NCM 111). This was then coated on a copper foil as a current collector. Homogeneity of the mixture was determined using SEM-EDX and, following a microwave assisted digestion, ICP-OES was used to validate the bulk homogeneity of electrode sheets. The GD-MS calibration was linear for Li between 1 and 28 mg g^{-1}, with a LOD of 80 µg g^{-1}. The contents of the other analytes were between 3 and 77 mg g^{-1} in the samples with LOD ranging from 260 and 393 µg g^{-1}. These relatively poor LOD values were attributed to four different factors; namely: the high resolution required to overcome polyatomic interferences, the roughness of the surface, the low power (8 W) of the discharge and the low excitation yield of the carbon matrix. Quantification relied on the matrix-matched relative sensitivity factors of the standards compared with the samples. Another paper, again by the same research group[279] used LA-ICP-MS and ICP-OES to quantify Li in the solid electrolyte interface as a measure of age degradation of the battery cell. Matrix-matched, solid state standards were used for quantification. The LA-ICP-MS data from the standards were compared with those obtained using ICP-OES following a microwave assisted digestion. The method was then applied to graphite electrodes aged to determine Li loss from the interface using depth-profiling LA-ICP-MS. The authors applied defined charging voltages to the electrodes and this set up an initial lithiation process with target intercalation compounds formed to include LiC_{30}, LiC_{18}, LiC_{12} and LiC_6. The graphite electrode was then discharged completely, which should remove the Li from the lattice. By taking the amount of Li present that originated from the lithium hexafluorophosphate electrolyte, it is possible to subtract the amount of Li in the solid electrolyte interphase.

Hirose *et al.*[280] used *XAFS to determine the oxidation state of Si* during the charging / discharging cycle of carbon-coated silicon oxide high capacity negative electrode material. During the charging, the Si^{4+}absorbed the Li forming predominantly Li_4SiO_4 although some other lower valence state lithium silicates were also formed; with Si and Si^{2+} forming at the beginning of the charging process. Low valence state oxides, e.g. Si^{+} and Si^{2+} formed during the middle of the charging process. The fully charged battery contained all of the valence states. During the discharge phase, the Li was released mainly from the composites with a Si^{2+} valence state. A minority was released from Li_4SiO_4 at a higher voltage forming Si-O.

Depth-profiling of nanometer thin layers using a *newly constructed instrument employing laser desorption and laser post-ionization time of flight mass spectrometry* (LD-LPI-TOF-MS) was described by Yin *et al.*[281]. Extremely low ablation rates were achieved (0.026 nm per pulse) for a series of nickel-coated samples. Multi-element information from each layer and substrate was gleaned enabling the impurities to be determined and thereby improving quality control during sample preparation. The ability to measure layer thickness was also obtained. The authors concluded that it had the potential to become a versatile tool for depth-profiling studies.

3.10 Nanostructures

As might be expected, given the increasing use of NPs in commercial products, the number of papers covering the preparation, characterisation, properties and detection of engineered nanomaterials continues to grow. There are four *review papers* to report on this year. The first of these, a tutorial review with 88 cited references, covers the current trends in atomic mass spectrometry for the speciation and imaging of metal based nanomaterials[282]. The areas covered include the isolation and separation of ionic and NP fractions of an element by CPE, SPE, SEC and hydrodynamic chromatography (HDC), FFF and single particle (sNP) ICP-MS. Most of the examples given cover either Ag or Au NPs. Imaging techniques reported include µXRF, µXANES, µPIXE and LA-ICP-MS whilst the sample matrices covered include waters, sludge, serum, plasma, blood, cells, tissues and embryos. The authors concluded that the use of a range of complementary analytical techniques, including molecular MS, will be required in individual studies to fully understand the value and fate of metallic NPs in the environment. In a wider review on MS imaging, which mainly covers molecular MS techniques, there is a section covering SIMS (120 references)[283]. The review gives a brief theoretical introduction to SIMS and then describes various applications, including the detection of NPs in cells, and the authors conclude that the use of SIMS capable of producing ‘nano’ ion beams, possibly in conjunction with FT-ICR-MS, will soon find powerful uses in the materials sciences.

Another review was concerned with FFF and the ‘nanoworld’(143 references)[284]. The review gives a history of FFF, a theoretical introduction to the different forms this technique can take and the various detectors used. The applications section concentrates on the detection of nanomaterials in foods, biomaterials and environmental samples. There is also a detailed section on calibration in flow FFF, often termed AF4, for particle size measurements. The authors concluded that due to the ability to maintain species information the technique should be more widely used but use is limited due to the lack of availability of FFF in research laboratories. The final review covered here (86 references) covers sNP-ICP-MS as a potential tool for performing bioassays[285]. It gives an overview of the capabilities of sNP-ICP-MS, instrumental limitations, heterogenous, homogenous and single molecule assays. The authors concluded that although the complex sample preparation required is still a major challenge to sNP analysis and bioassays the technique has promising potential for the development of multiplex immunoassays, DNA hybridization assays, and other biomolecule assays at the single molecule level.

There is a growing use of *single nanoparticle (sNP) ICP-MS to determine NP size and number concentration* in a wide variety of sample types. A key component of sNP-ICP-MS is the use of a calibration approach using ionic standards of the NPs of interest. Workers at NIST have conducted a systematic assessment of the accuracy, precision and robustness of this approach using RM 8017, a recently available PVDP coated Ag NP material[286]. Data for the study was collected using a Q-ICP-MS instrument in time resolved analysis mode, with data acquisition for 180 s and a dwell time of 10 ms. The nanoparticle types were Ag and Au with solution of 1.7 x 10^4 particles mL^{-1} being used which gave at least 400 particle events for each run. Sample flow rate was quantified gravimetrically and was independent of the sample matrix. The transport efficiency was determined *via* both the particle size and frequency methods and data processing was performed using a previously validated spreadsheet. The stability of suspensions of AgNPs was also investigated. Ionic calibrants for ICP-MS signal response determinations should be prepared in 2% HNO_3, with other diluents causing a signal suppression that was not observed when Ag NPs were aspirated in a variety of solution matrices. The experimental data also suggested that there was a significant difference between the calculated transport efficiencies using the particle size and frequency methods. The size-based method produced the more robust and reliable results, within 3% and 10% of reference values for size and number concentration, respectively. Finally, the results of the stability study suggest that samples should be stored at the highest possible concentration and at the lowest possible temperature above freezing point of the sample matrix and that the time lapse between sample dilution and measurement is minimised. The same research group also compared hydrodynamic and size-exclusion chromatography (HDC and SEC respectively) approaches, both coupled with an ICP-MS instrument, for the characterisation of Au NPs[287]. For the HDC approach two 7.5 x 400 mm PS-1 columns, packed with 15 µm non-porous particles were used. For SEC, two MCX SEC columns were used that had dimensions of 8 x 300 mm and with 10^6 and 10^3 Å nominal pore sizes with 10 µm diameter sulfonated styrene/divinyl benzene copolymer particles. The mobile phase in each case was 0.5 mmol L^{-1} Na_2HPO_4, 0.05% Triton X–100, 0.013% SDS and 0.05% formaldehyde at pH 7.5 in water. Indium (0.1 ng g^{-1}) was also added to the mobile phase for use as an internal standard. For SEC, the use of the above mobile and stationary phase combination allowed quantitative recovery of NPs to be achieved, including for a ternary blend of particle sizes, which is rarely the case for SEC and the results obtained compared favourably with those from the HDC-ICP-MS analysis. A superior chromatographic resolution was also obtained for SEC over HDC. The authors concluded that once molar mass detectors, e.g. DLS, are able to be coupled with SEC this should allow for the fully quantitative characterisation of NP molar mass, size, shape and chemistry continuously across the chromatograms.

The effect of *quadrupole settling time and the duration of a measurement cycle* when no data is recorded, on the accuracy of sNP-ICP-MS particle size measurements was investigated[288]. In this work the sample transport efficiency was measured by collection of the aspirated solution onto silica gel placed at the torch injector exit. This is in contrast to the usual approach of measuring the uptake to and waste flows from the spray chamber and determining the mass transported to the plasma by difference. The direct measurement approach reported in this work gave a transport efficiency of 6.3 ± 0.3%, which was in statistical agreement (Student's *t*-test) with those obtained by using the frequency method and a Au NP standard, 6.2 ± 0.1%. The settling time of the Q-ICP-MS used was large, 26 ± 5 ms, which, in conjunction with a dwell time of 5 ms, resulted in data only being acquired for 19% of the 60 s TRA time. Correcting the transport efficiency by the actual time spent acquiring data resulted in particle size measurements for Au NPs in statistical agreement with those obtained using TEM. If the correction factor was not applied the results obtained were 80% higher than those obtained by TEM. For users of instrumentation with much shorter settling times, e.g. single digit ns, then this approach may not be necessary but the need for it should be evaluated. It may also prove advantageous if multi-isotope data is acquired in a single TRA for the detection of bi- or multi-elemental NPs.

This year the most reported on *NPs are those containing Ag*, presumably because of their use as a biocide in a wide range of products. A study has been undertaken to compare five different particle sizing techniques, TEM, dynamic light scattering (DLS), sNP-ICP-MS, AF4-ICP-MS and AF4 multi-angle laser light scattering (MALS) with citrate or PEG stabilised Ag NPs as the target analyte[289]. The TEM size data, provided by the Ag NP producers (20,60 and 100 nm diameter), were taken as the reference values. The paper gives a detailed description of the methodologies used with each instrument and contains a good discussion on calibration strategies and the stability of the Ag NPs in the different sample matrices used. For the particle size measurements DLS always gave the highest mean value for a sample whilst AF4-MALS always gave the lowest mean value and all values for each technique were in statistical agreement with the particle size values obtained by TEM analysis. The authors concluded that whilst sNP-ICP-MS was a ‘very attractive’ method it can suffer from higher particle size LOD values, due to electronic background or the presence of ionic Ag in samples, and that bias can occur when the calibration standard and sample matrix differs. It is also concluded that, for more complex samples than the model ones used, more than one technique should be used to give accurate and reliable particle size measurements. The density of Ag NPs has been determined by two different methods, sNP-ICP-MS and centrifugal FFF (CeFFF) in conjunction with TEM measurements[290]. The density measurements by each technique, of Ag NPs of nominal diameters of 30, 60, 75 and 100 nm, were all in agreement within uncertainty limits, with a difference range of between 0 and 19%. It was also found that the NP density was 18 – 24% lower than that for solid metallic Ag indicating the level of porosity of the Ag NPs.

Three papers have been published *investigating the effects of instrumental parameters, gas flows and dwell times, for the measurement of Ag and Au NPs by sNP-ICP-MS*. Modern ICP-MS instrumentation often comes equipped with additional mass flow controllers to allow gas/aerosol phase sample dilution post nebulisation. A study was undertaken to investigate this and also the effect of plasma sampling depth[291]. The paper gives a detailed discussion on the role of sampling depth on particle residency time in the plasma, and hence ionisation efficiency, and the need for optimisation of this parameter. Typically, sampling depth is optimised, along with a number of other instrumental settings *via* an autotune routine, with the aim of minimising an oxide:element ratio and maximising sensitivity to give robust plasma conditions which is inevitably a compromise situation. This work reports that reducing the sampling depth, by about half from that derived by the autotune routine, increased the sensitivity for Ag and AU NPs by a factor of two without compromising signal stability or repeatability. This improvement in sensitivity, and in this case signal to noise, reduced the size limit LOD values for NPs by 26% for Ag and 32% for Au from those obtained under ‘robust’ autotune derived plasma conditions. An increase in the peak width in the NP histograms was also observed, which would normally decrease the size resolution obtainable, but this was compensated for by the sensitivity increase to such an extent that the NP size resolution obtainable actually increased. For the aerosol dilution mode it was found that, as the nebuliser gas flow needed to be proportionally decreased as the aerosol dilution flow was increased such that the overall gas flow was constant, the nebulisation efficiency was degraded to the extent that a strong signal loss was observed. This led the authors to conclude that careful optimisation of sampling depth would be beneficial but that aerosol dilution would not be beneficial with the instrumental set up used. The same research group also investigated sNP-ICP-MS, in both ‘normal’ (6 ms dwell time) and ‘high temporal resolution’ (20 μs dwell time) modes, for determining the structure and composition of spherical bi-metallic NPs containing differing proportions of Ag and Au[292]. It was found that the molar ratio of Ag:Au could be determined with good accuracy and precision with normal resolution sNP-ICP-MS analysis whilst combining this data with high resolution data acquisition allowed the differentiation between homogenous alloy NPs and core-shell structured NPs, and which element comprised the core or shell. The authors emphasise that this is only possible if the density of the core-shell NPs, which is often lower than bulk alloy NPs of the same elements, is known. It was also found that the width of the signal peak linearly correlates with the diameter of spherical nanoparticles and that the width of signal peaks for same-size NPs was always significantly larger for Au than for Ag. The same research group also reported on the dimensional characterisation of gold nanorods using the same 'normal' and 'high resolution approach'[293]. For this work hemispherically capped cylindrical particles, with an aspect ratio range of 1.5 to 4.5, were synthesised and characterised using UV-Vis spectroscopy, TEM and DLS based methods. A comparison of NP signals and time profiles for spherical and rod-shaped NPs allowed a) the volume of the particles to be assessed by conventional sp-ICP-MS measurements using a joint, linear calibration plot; and b) the aspect ratio to be calculated based on the shape of signal time profiles and transit times for equal-volume spherical and rod shaped NPs. The authors also caution that, since the similarity of nanoparticles in any batch is always limited, characteristic values for the dimensions of the most abundant particles only can be expected.

Three papers from the same research group report on the *use of CE-sNP-ICP-MS for the separation and detection of Ag or Au NPs*. In the first application a short dwell time of 5 µs was used to overcome the probability that, due to the increase in the number of particles entering the plasma from the narrow peak widths obtainable with CE, particle co-incidence can occur[294]. A polyimide-coated fused-silica capillary (75 µm i.d. x 375 µm o.d.), coupled to a self-aspirating microflow nebuliser mounted in a low volume spray chamber, was used to separate the Ag NPs. The CE system was operated at voltages from 10 to 25 kV with either hydrodynamic injection at 50 mbar for 3 s without polarity switching or for 10 to 150 s in reversed electrode polarity stacking mode. Under optimal conditions, 110 s injection time at 50 mbar and 20 kV and a running buffer of 60 mmol L^{-1} SDS, 10 mmol L^{-1} and 10 µg L^{-1} Cs and Ag NPs of 20, 40 and 60 nm diameter could be separated with LOD values of between 0.48 and 0.71 µg L^{-1} depending on the particle size. In the second paper [295] two component mixtures, of 40 nm diameter AgNPs coated with either polyethylene glycol and citrate and 60 nm diameter AgNPs coated with either polyvinylpirrolidone or citrate, were successfully separated. The migration order matched that of the theoretical migration order. The same analytical methodology was also used to separate and quantify Au NPs[296]. The paper contains a good section on the theory and data treatment required to extract particle size distributions, particle number concentrations and the analytical figures of merit from the resultant electropherograms and also on the current limitations of the technique. Finally, the presence of the dissolved form of the target NP, often termed the 'ionic' fraction, in samples will increase the particle size detection limit due to noise in the elevated baseline of the time resolved data. One strategy to overcome this ionic background is ultrafiltration, which was applied to a mixture of ionic and NP Ag[297].

It is *unusual to find an electrospray device being coupled with an ICP-MS instrument* but this is reported in two papers report this year. In the first of these a differential mobility analyser (DiMA) was also included in the instrumental set up to give an ES-DiMA-ICP-MS combination[298]. As air was used as the ES carrier gas a gas exchange device was inserted between the ES-DiMA and the ICP-MS instrument. This allowed the colloidal stability, drug loading and drug release of polyethylene glycol (PEG) stabilised cisplatin complexed Au NPs to be assessed. The relative molar mass of PEG had no significant influence on Pt^{II} uptake or release performance, while PEGylation substantially improved the colloidal stability of the conjugate. Notably, the Pt^{II} release over 10 days (examined at 0.5 Pt^{II} nm^{-2} drug loading) remained constant for non-PEGylated, 1K-PEGylated, and 5K-PEGylated conjugates. In the second paper on this topic[299] a 50:50 $Ar:O_2$ mixture, flowing at 1.0 L min^{-1}, was used as the carrier gas obviating the need for the gas exchange device mentioned previously. The outlet of the ES device was split 50:50 to the ICP-MS instrument and a scanning mobility particle sizer (SMPS). Nanoparticles of $MgSO_4$, $NH_4H_2PO_4$, and $Al_2(SO4)_3$, of 0.5% m:v with respect to either Mg, P or Al, were respectively produced *in situ* in the ES device from salt solutions and analysed by ES-ICP-MS and ES-SMPS. The concentrations and flow rate used meant that approximately 500,000 NPs were introduced to the ICP every ms. It is not clear from the paper why this work was undertaken, or what might be achieved by it use unless it is for the production of NPs, for which with Mg over 94% were in the 3 to 23 nm size range, *via* the ES device.

The *accurate determination of low concentrations Si by ICP-MS* can be difficult because of C and N based polyatomic interferences. However, the advent of tandem ICP-MS/MS instruments offers a solution by either reacting the interference away from the analyte (on-mass mode) or reacting the analyte away from interference (mass-shift approach). Researchers in Belgium and Spain have evaluated both approaches to characterise SiO_2 NPs using a variety of collision/reaction gases, namely He, H_2 (both for on-mass and mass-shift), O_2, NH_3 and CH_3F. For the mass-shift mode, CH_3F was the optimal reaction gas, producing SiF^+ in the reaction cell and m/z 47 monitored. However, H_2, which reacted with the polyatomic species allowing interference free measurements at m/z 28, was the preferred gas for on-mass mode. A detailed discussion of the method development, modes of operation of the ICP-MS/MS instrument, sNP-ICP-MS analysis and the reaction pathways is given and is recommended reading for those new to this technique. The recovery (mass concentration based) was 90% or greater for NPs of 100, 200 300 and 400 nm diameter in both on-mass and mass-shift modes and the data compared favourably with those obtained using TEM. Measurements of 80 nm diameter particles were hampered by the dissolved Si background signal (20 ng L^{-1}) unless a deconvolution approach was used to process the data. For readers of Japanese, the development and use of a high performance triple-tube concentric nebulizer fitted to a low volume spray chamber, for sNP-ICP-MS analysis of Pt NPs was described[300]. It had originally been designed to introduce cells to the plasma.

Commercial usage of *TiO_2 NPs* includes as a pigment in foodstuffs, paints and coatings, textiles and, due to their UV light resistant/absorbant properties, in photocatalytic sensors, pharmaceuticals and cosmetics. In one study the amount of TiO_2 NPs and total Ti leached from commercially available textiles: table placemats, wet wipes, microfiber cloths, and two types of baby bodysuits was reported[301]. An HF/HNO_3 microwave assisted extraction procedure, with quantification using ICP-MS, was used to determine the total Ti content, which ranged between 2.6 to 1500 µg kg^{-1} with the larger mass fractions being detected in synthetic textiles. For the leaching experiments 400 cm^2 of textile was suspended in deionised water, sonicated for 15 minutes and then shaken for 24 hours at 150 rpm with the aim of mimicking the physical process of wearing or washing of textiles. This was followed by a further 15 minutes of sonication of the leachate prior to analysis using sNP-ICP-MS. The leachate was also digested with the HF/HNO_3 microwave assisted extraction procedure and the total Ti content determined using ICP-MS. The amount of TiO_2 NPs released from the textiles ranged between 8 and 80%, defined as the amount detectable by sNP-ICP-MS:total Ti by microwave assisted extraction ICP-MS, with the higher values obtained for the synthetic textiles. A method was described for the detection of TiO_2 NPs in waters[302]. As the aim was to allow both the dissolved and added NP content to be quantified using sNP-ICP-MS the effect of dwell time on the accuracy of the results was investigated. For particle size and number concentrations of TiO_2 NPs in water, no differences in 'recoveries' were observed for dwell times of 3, 5 and 10 ms. The latter value of 10 ms was chosen for the sNP-ICP-MS analysis as the data for the dissolved fraction was considered more reliable. High purity water was spiked with either the rutile of anatase forms of TiO_2 NPs, at 0.03 and 0.3 ng mL^{-1} and 0.6 and 0.35 ng mL^{-1} respectively, and 'ionic' Ti at 0.5 and 0.05 ng mL^{-1}. Recoveries ranged between 83 and 100% for the NPS and 91 and 126% for the 'ionic' Ti. Subsequently, TiO_2 NPs were spiked into river water samples, which had a natural Ti content of 0.5 ng mL^{-1}, at concentrations 0.01 (anatase) and 0.03 (rutile) ng mL^{-1} and NP recoveries were 104 and 138% respectively. High resolution Scanning Auger Electron Spectroscopy and TOF-SIMS were used to investigate the structure and elemental composition variation in both a bulk sample of TiO_2 nanotubes (NTs) and a single tube[303]. The TiO_2 NT array was grown by anodic oxidation of Ti foil in a fluorine-containing ethylene glycol electrolyte. It was found that the studied anodic TiO_2 NTs had a layered structure with sharp interfaces. The differences in Auger electron spectroscopy depth profiling results of a single tube with the focused primary electron beam (point analysis) and over an area of 75 µm in diameter of a nanotube array with the defocused primary electron beam are discussed. Depth profiling by TOF-SIMS was carried out over approximately the same size of a nanotube array to determine possible ionic fragments in the structure.

Most of the papers covered in this section feature plasma source or X-ray-based instrumentation. However, this year there are *reports on the use of GFAAS for the analysis of NPs* as well. Following on from previous work on Ag NPs characterisation using continuum source GFAAS a research group in Ulm have applied the methodology for the characterisation of Au NPs[304]. The technique uses time resolved data to calculate to factors, the 'atomisation delay' and the 'atomisation rate'. The former increases as the analyte mass in a sample increases, due to reduced heat transfer in the atomisation tube, whilst the latter could be described as the number of atoms that are atomised per second. These two values are calculated using monodisperse suspensions of NPs at different sizes and linear regression. A detailed discussion of the instrumental process and data processing is given in the paper. The method was applied to the analysis of multimodal suspensions of Au NPs. The ability to resolve particle sizes of 2 and 5 nm in diameter was achieved as was the distinction between ionic Au and the 2 nm Au NPs. Workers in Thailand also reported the use of GFAAS for the sizing of Au and Ag NPs[305]. Again, a detailed discussion of the procedures used was given. The size results obtained by GFAAS were comparable to those from analysis using FFF-UV-VIS spectroscopy and in agreement, within uncertainty limits, with those obtained using TEM. Sample throughput was 20 per hour and particles as small as 10 nm in diameter were successfully detected.

The synthesis and *characterisation of Selenium NPs* was reported this year[306]. The Se NPs were synthesised by exposing different *Lactobacillus* strains to Na_2SeO_3 (25 mg L^{-1} Se) in a nutrient broth for 24 hours at 37 °C and subsequently extracted with sonication, centrifugation and filtration. The average size obtained, which was between 176 and 130 nm in diameter, depended on the *Lactobacillus* species involved with *L. reuteri* proving to be the most suitable species. This was because of its tolerance of higher Se concentrations and production of a greater number of Se NPs. A comparison of DLS and AF4 data suggested that some agglomeration of the Se NPs occurred when the latter technique was used. Finally in this section on NPs two papers describe the techniques used to characterise quantum dots. In the first of these[307] colloidal Mn^{2+}-doped ZnS quantum dots (QDs) were synthesised, surface modified with dihydrolipoic acid (DHLA) ligands to produce nanocrystals with a strong phosphorescent-type emission and improved aqueous stability, and characterised using a range of techniques including XRD, ICP-MS and AF4-ICP-MS. The data from the latter analyses allowed the calculation of the DHLA surface ligand density of the QDs which the authors describe as a critical parameter for the further use of the QDs as luminescent markers for *in vitro*, *in vivo*, or quantitative bio-sensing applications. The authors also concluded that the described methodology could be extended to the comprehensive characterisation of other types of inorganic NPs with different core compositions and surface modifications. The second paper on QDs details the synthesis of the QDs and the role that attaching the DHLA ligand has in removing side nanoparticulated populations generated during a simple one-pot synthesis[308].

Table 7 shows other applications of nanomaterial characterisation presented in the literature during the time period covered by this ASU.

Table 7 Applications of nanomaterial characterisation

Analyte	Technique	Comments	Reference
PtRu NPs	*in situ* XPS, TOF-SIMS	Characterisation of the formation of PtRu nanoparticles, deposited by evaporation onto pyrolytic graphite	[309]
Co-implanted ZnO nanowires	XANES, XRF	High-temperature ion implantation with subsequent thermal annealing was found to be an effective approach to achieve the strongest optical activation of Co ions.	[310]
Au NPs	Grazing incidence-XRF	Estimation of Au NP size found to be in good agreement with AFM measurements.	[311]
AlSiO$_2$, Al-polystyrene, Cr	SIMS, GI-SAXS	Preparation and characterization of inorganic and organic/inorganic as potential reference structures for 3D analytical techniques	[312]
Ag, NiO NPs	XPS, ICP-OES	Production and characterisation of Ag and NiO NPs for use as catalysts or nanosensors.	[313]
TiO$_2$ NPs	XPS, XRD	Study on the effects of ablation energy on the structure and properties if TiO$_2$ NPs.	[314]
Fe$_2$O$_3$ NPs	XPS, XRD	In-house fabricated micro-plasma system used to produce Fe$_2$O$_3$ NPs at atmospheric pressure. Ferrocene used as starting material and decomposition pathways discussed.	[315]

organo-Fe_3O_4-palygorskite NPs	XRF, XRD.	Preparation and characterisation of polystyrene coated magnetic NPs for use as oil adsorbants. Approximately 98% of oil in synthetic oily water samples was removed.	[316]
$CoPt_3$ NPs	SAXS, XAFS, XANES	Extensive surface purification resulted in leaching of Co from synthesised $CoPt_3$ NPs. This transformed them into $CoPt_3$/Pt core/shell structures which led to enhanced catalytic activity.	[317]
Ag NPs	XAFS, SAXS, XRF	Elucidation of a reaction pathway, proposed to be a Galvanic exchange process, for the conversion of citrate-capped Ag NPs to AgAu nanocages.	[318]
PtCu NPs supported on γ-Fe_2O_3 NPs.	ICP-OES, XRD, XAS	Investigation into the radiochemical synthesis of NPs. Increasing the amount of Cu in solution increased the amount of Cu in the synthesised NPs.	[319]
TiO_2 nanotubes enriched with Ag nanograins	XPS, ICP-MS	Estimation of the immunological activity of the nanotubes. Fibroblast adhesion to the surface of the nanotubes was observed and the anti-biofilm activity, against S. aureus reference strain was described as desirable.	[320], [321]
$CoFe_2O_4$-TiO2 Hybrid NPS	XRD, XRF, XPS, ICP-AES	Synthesis of the NPs achieved using an oil-in-water microemulsion reaction method.	[322]
AgNP coated yttria-	XPS, GI-XRD, ICP-AES	Synthesis and characterisation of anti-bacterial NPs. An accelerated aging test in artificial saliva	[323]

stabilised zirconia		showed that less than 1% of the Ag in the NPs was solubilised.	
Ag NPs in commercial products	sNP-ICP-MS, ICP-MS	Commercial anti-bacterial products were tested for their antibacterial activity and NP content. Only two of the six products tested exhibited anti-bacterial activity.	[324]
Pt/SiO_2 NPs	spICP-MS, SEM-EDS, TEM, XPS and ICP-MS	Comparison of techniques for particle characterisation. Results for sNP-ICP-MS and TEM in agreement with those from SEM-EDS. However, XPS and solution mode ICP-MS strongly overestimated the NP concentration.	[325]
Al^0, Al_2O_3 and TiO_2 NPs	TEM, SAXS, XRD ion beam microscopy and sNP-ICP-MS	Characterisation of NPs prior to use for ecotoxicity experiments. Passivation of the surface of Al^0 NPs was observed. Advantages and disadvantages of the techniques used were discussed. Paper can be seen as a practical guide to particle characterisation techniques.	[326]
Al, Al_2O_3	SAXS, TEM, SIMS, sNP-ICP-MS	Bioaccessibility estimations of Al from NPs using artificial saliva, gastric and intestinal fluids. Minimal dissolution of the NPs was observed.	[327]

Glossary of terms

2D	Two dimensional
3D	Three dimensional
AAS	Atomic absorption spectrometry
AES	Auger electron spectrometry
AFFF	Asymmetric field flow fractionation
AF4	Asymmetric flow-field flow fractionation
AFS	Atomic fluorescence spectrometry
AFM	Atomic force microscopy
AMS	Accelerator mass spectrometry
APM	Atom probe microscopy
APT	Atom probe tomography
ASTM	American Society for Testing of Materials
ATR	Attenuated total reflection
BCR	Community Bureau of Reference
CCD	Charge coupled device
CE	Capillary electrophoresis
CRM	Certified reference material
CPFAAS	Collinear photofragmentation atomic absorption spectrometry
CS	Continuum source
CT	Computerised tomography
CV	Cold vapour
CXRF	Coincidence X-ray fluorescence
DA	Discriminant analysis
DLS	Dynamic light scattering
DLTV	Diode laser thermal vaporisation
DRC	dynamic reaction cell
DSC	Differential scanning calorimetry
EBS	elastic back scattering spectroscopy
EDAX	Energy dispersive X-ray analysis
EDS	Energy dispersive spectrometry
EDTA	Ethylenediamine tetraacetic acid
EDXRD	Energy dispersive X-ray diffraction
EDXRF	Energy dispersive X-ray fluorescence
EPMA	Electron probe microanalysis
ERDA	Elastic recoil detection analysis
ESI-MS	Electrospray ionisation mass spectrometry
ETAAS	Electrothermal atomic absorption spectrometry
ETV	Electrothermal vaporisation
EXAFS	Extended X-ray absorption fine structure
FAAS	Flame atomic absorption spectrometry
FFF	Field flow fractionation
FI	Flow injection
FI-CVG	Flow injection chemical vapour generation
FTIR	Fourier transform infrared
FWHM	Full width at half maximum
GA-XRD	Grazing incidence X-ray diffraction
GC	Gas chromatography
GD-MS	Glow discharge mass spectrometry
GD-OES	Glow discharge optical emission spectrometry
GI-SAXS	Grazing incidence small angle X-ray scattering
GI-XRD	Grazing incidence X-ray diffraction
GI-XRF	Grazing incidence X-ray fluorescence
HG	Hydride generation
HPLC	High performance liquid chromatography
HR-CS-AAS	High resolution continuum source atomic absorption spectrometry

hTISIS	Heated torch integrated sample introduction system
IAEA	International Atomic Energy Agency
IBA	ion beam analysis
ICP	Inductively coupled plasma
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
ICP-QMS	Inductively coupled plasma quadrupole mass spectrometry
ICP-TOF-MS	Inductively coupled plasma time-of-flight mass spectrometry
ID	Isotope dilution
IL-DLLME	Ionic liquid-dispersive liquid-liquid microextraction
IP	Institute of Petroleum
IRMS	Isotope ration mass spectrometry
ISO	International Organisation for Standardisation
LA	Laser ablation
LASIL	Laser ablation of sample in liquid
LC	Liquid chromatography
LEIS	Low energy ion scattering
LIBS	Laser induced breakdown spectrometry
LIF	Laser induced fluorescence
LIPS	Laser induced plasma spectroscopy
LOD	Limit of detection
LOQ	Limit of quantification
LTE	Local thermal equilibrium
MALDI-TOF	Matrix-assisted laser desorption ionisation time-of-flight
MC	Multicollector
MEIS	Medium energy light scattering
MHCD	Micro hollow glow discharge
MIP	Microwave induced plasma
MIP-AES	Microwave plasma atomic emission spectrometry
MS	Mass spectrometry
MCR-ALS	Multi curve resolution-alternating least squares
MWTN	Microwave thermal nebuliser
NAA	Neutron activation analysis
NAAR	Neutron activation autoradiography
Nd:YAG	Neodymium doped-yttrium aluminium garnet
Nd:YLF	Neodymium doped-yttrium lithium fluoride
ND	Neutron diffraction
NIST	National Institute of Standards and Technology
NMR	Nuclear magnetic resonance
NRA	Nuclear reaction analysis
OES	Optical emission spectrometry
PARCI	Plasma assisted reaction chemical ionisation
PCA	Principal components analysis
PDA	Phase-Doppler anemometry
PGAA	Prompt gamma neutron activation analysis
PGM	Platinum group metals
PIGE	Particle induced gamma ray emission
PIXE	Particle-induced X-ray emission
PSDA	Particle size distribution analysis
PLS	Partial least squares
PLS-DA	Partial least squares discriminant analysis
ppb	Parts per billion
ppm	Parts per million
PVG	Photochemical vapour generation
RBS	Rutherford backscattering spectrometry

RDA	Regularised discriminant analysis
REE	Rare earth elements
rf	Radiofrequency
RIMS	Resonance ionisation mass spectrometry
RSD	Relative standard deviation
SEM	Scanning electron microscopy
SEM-EDS	Scanning electron microscopy-energy dispersive spectrometry
SF	Sector field
SIFT-MS	Selected ion flow tube mass spectrometry
SIMCA	Soft independent modelling of class analogy
SIMS	Secondary ion mass spectrometry
SP	Single particle
SR	Synchrotron radiation
SRM	Standard reference material
SRS	Synchrotron radiation source
SXRF	Synchrotron X-ray fluorescence
STXM	Scanning transmission X-ray microscopy
TE	Trace element
TEM	Transmission electron microscopy
TGA	Thermogravimetic analysis
TIMS	Thermal ionisation mass spectrometry
TLC	Thin layer chromatography
TPR	Temperature programmed reduction
TXRF	Total reflection X-ray fluorescence
UOP	Universal Oil Products standards
USGS	United States Geological Survey
UV-VIS	Ultraviolet-visible
VOC	Volatile organic carbon
VUV	Vacuum ultraviolet
WDXRF	Wavelength dispersive X-ray fluorescence
WC-AES	Tungsten coil atomic emission spectrometry
XAFS	X-ray absorption fine structure spectrometry
XANES	X-ray absorption near-edge structure
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
XRPD	X-ray powder diffraction
XRR	X-ray reflectometry

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