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Atomic spectrometry update: review of advances in the analysis of metals, chemicals and materials

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This update covers the literature published between June 2020 and May 2021 and is the latest part of a series of annual reviews. It is designed to provide the reader with an overview of the current state of the art with respect to the atomic spectrometric analysis of various metals, chemicals and materials. It is not designed to be a comprehensive review of all papers that have used an atomic spectrometric technique. Instead, it includes only those papers that have some novelty through making an advance in either knowledge or the application of atomic spectrometry. Also included, especially for forensic-based applications, for recycling applications and for cultural heritage samples, are those papers that have treated the analytical data produced with chemometric packages to provide invaluable information on provenance or to aid identification. Other research has focussed on calibration strategies for LIBS analyses and improving the resolution of depth and lateral profiling to facilitate the elucidation of mechanistic aspects of electronic components. An additional topic of interest includes the identification of oxidation states and neighbouring atoms using

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techniques such as XPS and XANES, again attempting to elucidate mechanisms for electronic components or to elicit speciation data.

1 Introduction

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]

The ever-expanding repertoire of LIBS analysis has continued in this review period. Its on-line/*in situ*/standoff abilities continues to make it an attractive proposition in many areas. Research in the metals industry has used it for several years, but it has been plagued by the fact that calibration can be problematic. Methods to improve the accuracy of calibration have continued and many different models have been produced. In this review period, this has been especially true for non-ferrous metals, where it may be used during manufacture or during the re-cycling of scrap. It has also found use for sorting different polymers during re-cycling, estimating the calorific values of coal, and use in the cultural heritage sector. The standoff ability of LIBS has also found significant use for nuclear applications. The drive to expand the number of radionuclides measurable to contribute to safe, cost-effective decommissioning continues. To this end, several reports of new techniques were developed. The analysis of fuels has continued to be of great interest, although, somewhat surprisingly, the analysis of alternative fuels has received less attraction during this review period. The analysis of cultural heritage artifacts has also received huge interest. Since these samples are precious, the majority of these applications use non-destructive or minimally destructive methods of analysis. Therefore X-ray-based techniques, LIBS or laser ablation sample introduction feature heavily. Often, these are used in combination with one or more chemometric techniques to try and elucidate manufacturing processes, provenance *etc.* Similar strategies are often adopted for the forensic analysis of materials, where sample destruction should be avoided and chemometric methods may aid classification/identification. The analysis of electronic components, wafers, thin films and solar cells often makes use of surface analysis tools such as SIMS, TOF-SIMS and assorted X-ray-based techniques. Some of the X-ray techniques, *e.g.* XPS and XANES give information on the chemical surroundings or speciation of the analyte whereas others give bulk surface concentrations. Other techniques may be used for depth-profiling studies, *e.g.* LA, LIBS or SIMS. The requirement for better resolution (both lateral and depth) is driving the research for depth profiling/surface analysis techniques. The analysis of nanostructures has also matured, with fundamental studies of nanoparticle sizing being fewer in number than previous years. Instead, a large number of reviews have covered varying aspects of nanostructure analysis. Other papers have concentrated on improving figures of merit and validating existing procedures. The number of application-based papers for nanomaterials has increased markedly. This indicative of

the methodology developed and reported over the last few years reaching maturity.

1.1 Reviews of instrumental techniques

A brief section has been provided in this year's review because several review pieces have been published that cover numerous topic areas. It was therefore deemed sensible to cover these in this one section rather than writing about them all in four or five different sections. Other, more focused reviews, are given in the relevant individual sections.

The majority of the *review papers covering general industrial applications have discussed the use of laser induced breakdown spectrometry (LIBS).* The use of LIBS has certainly increased significantly over the last five years. This is because of its ability for rapid and cheap analysis as well as its potential for on-line use at manufacturing plants. It is certainly a money saver for industry if their product can be analysed as it is made rather than collecting a sub-sample and then having it analysed off-line in a laboratory. Alterations to the product recipe can be made in real-time, saving time and expense. The stand-off ability of LIBS also offers numerous advantages where dangerous or unpleasant conditions occur. Examples include the nuclear industry where the use of LIBS enables analysis of components from a safe distance for the operators. Similarly, it may prevent the need for a reactor shutdown so that sample can be collected for laboratory analysis. The standoff analysis of potential explosive devices also has clear beneficial health implications. Despite its many obvious advantages, LIBS does have a couple of drawbacks. It is not completely sample non-destructive, but its main drawback is that it can be very difficult to use quantitatively. This is because the sensitivity of analysis can be affected by numerous parameters, *e.g.* the matrix, temperature, pressure, the atmospheric medium, *etc.* Numerous research papers have been published over the years describing assorted different calibration strategies. These have been summarised in a review with 93 references presented by Costa *et al.*[7] It covered methods such as matrix matched calibration, internal standardization, standard additions, multi-energy calibration, one-point gravimetric standard addition, one point multi-line calibration, slope ratio calibration, two point calibration transfer, single sample calibration, multiple linear regression, principal component regression (PGR), partial least squares and artificial neural network. Examples of each were given and the advantages, disadvantages and limitations of each discussed. A review by Zhang *et al.* (with 70 references) covered the use of machine learning algorithms as a method for overcoming calibration problems and for gleaning the maximum amount of information from the data.[8] Other review papers covering LIBS were prepared by Guo *et al.*[9] which contained 210 references and covered developments in the application of LIBS in recent years and another by Senesi *et al.* who discussed field portable LIBS, giving a historical review, current status and future prospects (118 references).[10] In the latter review, two types of instrument were compared: hand-held instruments and those that are modular and joined by an umbilical. The performance of both was also compared with

portable XRF. The industrial applications of LIBS were reviewed (with 190 references) by Legnaioli *et al.*[11] The subject areas covered in particular were applications in the steel and coal industries. Also covered was LIBS applications in the re-cycling industry, *e.g.* of plastics for recycling. A further review, of remote analysis LIBS, was presented by Li *et al.*[12] The review covered 123 references and concentrated on methods of signal enhancement, its use in a variety of fields and some of the problems encountered. A review of methods and applications of LIBS containing 230 references was published by Shah *et al.*[13] In one section, the sensitivity, speed of analysis, accuracy and sample preparation methodology were compared with other techniques. A second part focussed on the instrumentation used and the third part on quantitative and qualitative analysis. Different analysis parameters and their effects as well as the fields of application were also discussed. A final review of LIBS analysis covering its use for mapping studies of samples was prepared by Limbeck *et al.*[14] This review cited 188 references and covered sample types such as cultural heritage samples, thin films, catalysts, biological materials and concrete. The review was split into instrumentation types (different lasers, spectrometers, collection optics *etc.*), sub-sections for assorted chemometric data handling methods and calibration. Overall, it is a good read for a novice just starting in the area.

The related technique of *laser ablation assisted spark induced breakdown spectrometry* (LA-SIBS) and its applications was reviewed (with 42 references) by Zhou *et al.*[15] This methodology also needs no sample preparation and hence, is quick and likely to gain in popularity. The fundamentals were described in the review, which also covered applications – especially those involving conducting materials.

Synchrotron-based X-ray techniques are known to have several advantages over some techniques because they have a high intensity, monochromatic and collimated beam. The use of techniques such as small/wide angle X-ray scattering (SAXS and WAXS), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), grazing incidence X-ray diffraction (GI-XRD) and different methods of X-ray imaging were reviewed (with 131 references) by Rahimabadi *et al.*[16] Each technique was discussed in its own sub-section with both theory and applications being present.

2 Metals

2.1 Ferrous metals

This has been an even more active area of research that in previous years. There has, however, been a change of emphasis. In previous years, a lot of the research was based on the calibration of laser induced breakdown spectrometry (LIBS) or on methods to minimise interferences during LIBS analysis. This review period still has a high number of LIBS-based applications, but these are more application-based and include several papers describing other techniques used. It should be noted that those applications describing the analysis of cultural heritage samples can now be found in Section 5.

One of the advantages of LIBS is that it can be portable and can hence be taken to the field or production site. This helps speed of the analysis since samples do not have to be returned to a laboratory. There have therefore been several *applications reported of the LIBS analysis of steel at the production line*. An example of this was a paper entitled "feasibility investigation for on-line elemental monitoring of iron and steel manufacturing processes using LIBS", published by Wang *et al.*[17] The paper studied the effects of different sample temperatures, lens to target distance and the angle of analysis. The Q-switched Nd:YAG laser operating conditions and the spectrometer used were discussed in detail with the aid of a schematic diagram and the method validated by the use of numerous standard steel samples. The sample temperature effects were studied by undertaking analysis at room temperature, 300, 500 and 700 °C. The emission intensity increased with increasing temperature. This was attributed to lower laser energy being required for sample ablation and vaporization meaning that more can be used for plasma evolution processes to enhance the plasma emission intensity. Similarly, the ablation and vaporization of sample also increased causing the increase of plasma emission intensity. Consequently, the emission intensity of measured spectra at higher sample temperature is higher than that at lower sample temperature. This study therefore indicated that calibration of the LIBS system was sample temperature dependent. Although this finding is not completely unexpected, it does highlight the potential pitfalls of simply using an instrument and assuming correct answers will be produced. Lens to target distance was varied between 3.5 and 4.1 m, with 3.9 providing highest intensity. Spectra obtained using different sample angles of 0°, 15°, 30° and 75° were obtained with results indicating that an increased sample angle (meaning the sample surface was far away from the vertical direction of laser beam), led to the signal intensity decreasing. A 3D profile measurement system was also described in the paper. A paper by Zeng *et al.* described the production of a prototype instrument capable of the rapid on-line analysis of steels through the use of a mobile fiber optic LIBS system.[18] A schematic of the prototype instrument was provided to aid the reader. Numerous standard steel samples were used for calibration purposes, including the six carbon steels (GBW01211–GBW01216), seven standard samples of microalloy steel (GSB 03-2453-2008-1 to GSB 03-2453-2008-7) and 11 samples of low alloy steel purchased from NIST. A polynomial fitting was required to obtain the best calibration functions for the analytes Cr, Cu, Mn, Mo, Ni and V, since linear fitting led, in some cases, to poor regression coefficients (with 0.861 for Cu being the poorest). Once polynomial fitting was used, regression coefficients of the calibration curves improved to greater than 0.99. Average absolute errors of Cr, Cu, Mn, Mo, Ni and V were 0.440, 0.003, 0.039, 0.07, 0.033 and 0.057 wt%, respectively. Their average relative errors fluctuated from 2.9% to 15.7%. The instrument provided LOD at the mg kg^{-1} level, with the best being 31 (for Cr) and worst being 290 (for Mo). As mentioned previously, the production of instruments capable of working on-line or in-line provide a huge benefit in terms of time- and cost-saving since samples do not have to be returned to the laboratory for analysis. Once they are reliable and easy to use, even relatively untrained workers may use them successfully.

An application was reported by Lednev *et al.* in which LIBS was used *on-line to detect defective laser welding*.[19] A description of the system was provided along with schematic diagrams and a photograph. Briefly, the diode pumped pulsed solid state Nd:YAG laser (1064 nm, 5 ns, 130 mJ per pulse, 10 Hz, $M^2 = 90$) beam was focused by quartz lens ($F = 280$ mm) through a pierced aluminium mirror at a 45° angle to the sample surface. Analysis of the melt pool enabled both atomic and ionic lines for major components (Cr, Fe or Ni) to be compared as well as lines for alloying elements (Mn, Si). The spectral region from 275 to 290 nm enabled this to be undertaken. If the melt pool becomes too hot, then this results in a defective weld. By measuring the intensity of the atomic Fe 278.81 nm and ionic Fe 274.67 nm iron lines signals as well as their ratio, it was possible to use hypothesis testing by paired sample *t*-test to identify defects. Two other sensing procedures were attempted. These were: thermal emission spectroscopy of the welding melt pool induced by a continuous wave laser (passive sensing) and LIBS analysis of a solidified hot weld. Both of these methods failed to detect defects. Another paper to use LIBS for the analysis of welds was presented by Taparli *et al.* who used it for the *in situ* chemical composition analysis of tungsten inert gas (TIG) austenitic stainless steel welds.[20] These authors used a similar setup to that of Lednev *et al.*, but employed an analysis angle of 20° rather than 45°. The Mn signal was enhanced during the welding process. This was attributed to Mn vapour forming over the weld pool and then on-cooling, it re-condenses and forms a layer on the surface of the weld. As well as the on-line LIBS, the authors also used LIBS to study the effects of differing welding currents, finding that local increases in Mn and Ni concentration occurred at higher current. Again, this was attributed to higher Mn concentrations entering the vapour phase, later to re-condense on the surface. The advantages of these systems is that they can detect faults in real time, enabling corrective action to be undertaken and hence decreasing the number of failures.

Another paper that discussed LIBS measurements was presented by Petersson *et al.* who used the technique for the *rapid analysis of steel slag*.[21] The experimental setup was described in detail and entailed a YAG laser operating at 10 Hz and with a pulse energy of 300 mJ at a wavelength of 1064 nm. Also incorporated into the experimental setup was a spherical aluminium mirror in a near-colinear configuration to collect the light emitted, a CCD detector and a rotating sample holder to ensure that data could be averaged from a sufficiently high number of laser shots covering a large area of sample. This last attribute was necessary because of the inhomogeneous nature of the slag samples. Averaging of several hundred laser pulses was required to obtain a good overall estimate of bulk composition. A large number of samples were also analysed using XRF and the concentration data from these helped calibration of the LIBS system. Samples analysed using XRF were also used for a comparison of data between the two techniques, with good agreement being obtained. Despite the large number of laser shots used, precision for the LIBS system was still 2–4 times worse than that from XRF. However, it was concluded that they were still adequate for on-line or near the line applications and,

with further optimization, could potentially be improved. These authors also indicated that slag at 1200 °C gave a very different LIBS intensity response to that from cold slag. Further work was required to develop "transfer functions" from room temperature calibrations to those at elevated temperature.

The concept of *transfer learning that enables LIBS calibration obtained at room temperature to be transferred to analysis at elevated temperature* was also addressed by Chang *et al.*[22] Spectral data of calibration samples obtained at room temperature (12 CRMs) and spectral data of uncalibrated samples (8 samples) at high temperature were transferred to a high dimensional feature space using kernel function mapping. One in this space a model is trained and established. Results for Cr indicated that the use of the feature-based transfer learning method decreased the mean relative error from 32.31% to only 6.08%.

A paper by Lednev *et al.* investigated the feasibility of using on-line LIBS for *the analysis of compositionally graded alloy parts during their fabrication*.[23] Chromium bronze and stainless steel 410 powders were deposited using laser cladding, forming a metal part with a compositional gradient. The LIBS measurements were undertaken on the melt pool, the finished material as well as the powder starter materials. Results produced from the melt pool and the finished product were comparable because of a homogeneous mixture of analytes being present. However, very poor precision degraded the data from the start powders to the extent where it was concluded that the LIBS analysis could not be performed reliably. Despite this, the transition zone between two pure components was quantified using LIBS for the first time and so the experiment could be regarded as a success.

Some papers have used *chemometrics approaches to aid either the calibration of LIBS analysis of steels or to distinguish between different steel grades in a scrapyard*. The determination of C in steels can be problematic because the C line at 193.09 nm is in the vacuum UV region and light emission is easily absorbed, leading to a huge drop in sensitivity. Another C line (at 247.856 nm) is interfered with by Fe lines. Zhang *et al.* employed the chemometric method of least absolute shrinkage and selection operator for spectral feature selection in combination with back-propagation neural networks to correlate LIBS spectra with C concentration without explicitly measuring C spectral lines.[24] This machine learning approach succeeded by first using 12 certified materials with a C content ranging from 0.013 to 3.73% and with a widely varying concentration of other metals to help train the calibration model. A further three CRMs were used to validate the method developed. The multivariate chemometrics approach was summarised nicely in a flow chart. Once optimized, the method had a LOD of 0.0366% and produced regression coefficients of 0.9999. Poggialini *et al.* used multiple artificial neural networks (ANN) to greatly improve the precision and accuracy of a commercial hand-held LIBS instrument.[25] The ANN algorithm links a set of inputs (the spectral intensities of some lines in the LIBS spectrum) to a set of outputs (the concentration of the elements of interest) through a non-linear relation that can be determined by minimizing the deviation between the predicted and nominal

outputs on a set of known samples. The relation obtained between inputs and outputs is then used for obtaining the outputs associated with unknown samples from the measured inputs. Several ANN were prepared including: one for the major elements and one for minor elements. The performance with the calibration built into the instrument were compared in terms of linearity of calibration and relative mean standard error (RMSE). Performance with and without the ANN were comparable for standards/known samples, but the ANN assisted calibrations were significantly improved for unknown samples, with RMSE improving from 1.83 to 0.70% for Cr and from 2.98 to 0.62% for Ni. Kashiwakura and Wagatsuma developed a method using a LIBS system made in-house followed by partial least squares regression (PLSR) for the rapid determination of components of austenitic stainless steels.[26] Eight CRMs of the JSM M 200 series (materials 21–28) were used to train the model for the analytes Cr, Mo, Nb, Ni and Ti. Spectral data could be obtained very rapidly (approx. 13 s), but more than 10 minutes was required for the calculation of regressions when all the relevant wavelengths were utilised. However, the calculation time could be reduced if single wavelengths that had higher excitation levels were chosen for each analyte. The method was applied to the analysis of five stainless steel types: SUS304, SUS310, SUS316, SUS321 and SUS347. The range of recovery rates were 94.3–111% and precision was better than 10% RSD. Another paper that determined C in both solid and molten steels was presented by Cui *et al.*[27] These workers employed a UV long-short double pulse LIBS system that they both discussed in detail and provided a schematic diagram of. Six CRMs were used for calibration at room temperature and then one of them was heated to 1800 °C. Spectra were taken at three different periods after the melting process. After 0.5 min, a clear C peak was observable at 193.091 nm. However, this peak diminished significantly after 12 min and had disappeared completely after 15 min. This is a well known effect in the steel industry and is termed the carbon escape phenomenon. The influence of the presence of oxygen was studied and had a significant effect on the presence of C, with much of it boiling off as carbon dioxide. It was concluded that this was unavoidable in molten steel. In a second paper by the same research group, sample temperature effects were compared for both single pulse LIBS and colinear long-short double pulse LIBS.[28] The authors used the emission intensity ratio of Mn 404.136 nm/Fe 402.187 nm and the Fe 402.187 nm/Fe 400.524 nm for the comparison. The effect of the delay time between pulses was also studied. As would be expected, a temperature rise from 20 to 700 °C had a very adverse effect on accuracy of analysis when single pulse LIBS was used. This effect was very much diminished in the long-short pulse version. This was attributed to it maintaining a higher plasma temperature and for longer. An attempt to correct for plasma temperature using Fe 402.187 nm/ Fe 400.524 nm resulted in a marginal improvement in precision from 22.56 to 21.86% RSD for the single pulse LIBS. However, the long-short double pulse LIBS provided a much improved precision of 6.46% anyway, which improved further to 1.78% once plasma temperature had been corrected for. Improvements to calibration are obviously welcome since it betters the

chance of obtaining accurate data. These papers therefore add to the increasing volume of literature that will enable more accurate data to be provided by instruments in the future.

Several other papers reporting the LIBS analysis of steels have been reported. In one, by Cai *et al.* a portable LIBS instrument built in-house was used *to study the aging of the heat resistant steel T91*.[29] The chemometric tools of wavelet threshold de-noising followed by multiple scattering correction were used to clean up the data. Then, both support vector machine (SVM) and *k*-fold support vector machine-recursive feature elimination (K-SVM-RFE) were used on the data from slices of pipe that had undergone different levels of aging to establish the model. This was then applied to artificial samples. The performance of the wavelet threshold de-noising and multiple scattering correction on the performance of the model were studied. Once optimized, the process was capable of determining the age of the material with an accuracy of 85.17%. Although clearly not perfect, it does give a very good indication of how old and hence, how likely to fail, a steel is.

Electrical steel (steels containing between 1.1 and 4% Si) is used for things such as electric motors, transformers, generators and high frequency convertors. It requires analysis to ensure that the correct grade is used for the right job. Silicon is known to be problematic to detect using LIBS because of self-absorption and matrix effects. A combination of *LIBS and laser induced molecular fluorescence was used by Zhang et al. to measure Si as the molecule SiO*.[30] The paper showed a convenient schematic of the experimental setup, which comprised two lasers one of which (a Nd:YAG operating at 1064 nm; pulse duration: 6 ns; beam diameter: 5 mm; repetition rate: 10 Hz; pulse energy: 60 mJ) was used to ablate the sample and the second (OPOTek, VIBRANT™ HE 355 LD; wavelength range: 225–2400 nm; pulse duration: 10 ns; operating at 10 Hz and 1 mJ) was used for SiO molecular excitation. An XYZ translation stage, collection optics and a Czerny–Turner spectrometer equipped with an intensified CCD were also part of the setup. Seven certified materials (GSB 03-2453-2008-1 to GSB 03-2453-2008-7, with Si contents of between 0.021 and 1.370%) were used as the samples. The atomic Si 288.16 nm line was interfered with by the ionic Fe 288.08 nm line at a low silicon content. This obviously greatly limited the analytical accuracy and sensitivity of LIBS for silicon in steels. Two types of molecular excitations were therefore evaluated: vibrational ground state excitation and vibrational excited state excitation. Both showed a huge improvement in Si detection capacity, with the excited state excitation (with detection of SiO at 248.68 nm) showing the best results of all. For that, regressions (R^2) were 0.988, the LOD was 187 μg g^{-1} and the root-mean-square error of cross-validation (RMSECV) was 0.046%. The method is therefore a significant advance on other LIBS methods.

The *rapid analysis of the content and size of aluminium inclusions in middle alloy steels* using LIBS was reported by Wang *et al.*[31] The instrument comprised a Q-switched Nd:YAG laser operating at 1064 nm, a laser beam shaping system and a vacuum Paschen–Runge spectrometer. A total of 15 reference materials were analysed including GBW01238, GBW01241, GBW01242, and GBW (E) 010224, which are all certified for total

Al and acid soluble Al, were analysed. One laser pulse per spot was used for the analysis, with the excited region being 10 mm × 10 mm, and the distance between the centres of two adjacent spots being 250 μm. A total of 1681 sets of intensity data were obtained for each analysis. Several series of mathematical functions were derived enabling a relationship between intensity of light emitted and the particle size to be deduced. Results obtained using the method developed were compared with those obtained using SEM-EDS. According to the authors, general agreement was obtained, but there was still room for improvement. However, the inclusion content and particle sizes can be analysed simultaneously using LIBS, which therefore, offers a simple sample preparation and rapid analysis.

Wang *et al.* used *LIBS employing a picosecond laser to analyse molybdenum–copper stainless steels containing Fe* within the range 40–70%.[32] The micro-LIBS experimental setup mainly consisted of a combination of a laser, a timing trigger, an energy attenuator, a camera and two integrated spectrometers. One spectrometer had a wavelength range of 244–360 nm and the other 382–469 nm. The setup was shown in a schematic diagram. The inter relationship between the different parts of the unit were described. When the laser power was 0.044 W, a crater with an inner diameter of approximately 3 μm was achieved. After background correction of the spectra, a quadratic function was used to correlate the intensity and concentration of each of the eight analytes (Al, Cr, Cu, Mn, Nb, Ni, Ti and V). Regression coefficients of better than 0.99 were obtained for Al, Cu, Nb, Ni and V, whereas correlations for the other analytes were better than 0.95. Detection limits varied significantly, with Ti providing the lowest at 0.04%, despite the fact it produced the worst regression. The highest LOD (1.77%) was for Ni.

A commercial hand-held LIBS instrument was used by Senesi *et al.* to *determine C, Mn, P, Si and Ti in pig iron* from blast furnaces in the steel industry.[33] Data obtained from the instrument underwent a three-stage pre-treatment. These steps were: employing a standard normal variate procedure, applying a Savitzky–Golay smoothing procedure and then cutting the spectra into fragments to cover only the ranges required for the analytes. Once these steps had been performed, both univariate and multivariate (partial least square) calibration and validation protocols were tested. The predictive capability of each calibration model was evaluated by calculating the Pearson's correlation coefficient (R), root mean square error (RMSE), and mean absolute prediction error (MAPE) and LODs, whereas the leave one out cross validation (LOO-CV) method was used to perform external validation. Correlation between LIBS and XRF data were plotted. The multivariate approach was significantly better than the univariate with R^2 values of 0.93–0.99. These were particularly good for Si and Ti (both 0.99) compared with the univariate approach (0.95 and 0.85, respectively). In addition, the MAPE values improved from 18.04 and 19.4% to 14.07 and 11.61%, respectively.

Techniques other than LIBS have also been used to analyse ferrous materials. An example by Hu *et al.* used *glow discharge-mass spectrometry (GD-MS) to determine metal impurities in iron–nickel-based superalloys*.[34] High resolution of the mass spectrometer was required to overcome some polyatomic interferences. The GD-MS operating conditions, in terms of argon flow rate and discharge current, were also optimized. Relative sensitivity factors of the calibrations of 12 analytes were determined and then applied to the analysis of the CRM IARM Ni909-18. Results were in good agreement with certified values. In addition, results obtained using alternative techniques, namely ICP-OES and ICP-MS following acid dissolution procedures, were also compared with those from GD-MS. Semiquantitative data were also obtained for some analytes. The agreement between semiquantitative GD-MS and ICP data was less impressive, with data for some analytes agreeing reasonably well whereas others differing by a factor of three. Despite this, the direct analysis of a solid sample is attractive because it is quicker (and therefore cheaper) and uses no corrosive substances.

Two publications by Kuptsov *et al.* discussed the optimization of operational parameters[35] and the analysis of steels[36] using a *two-jet arc plasmatron using spark ablation*. The technique uses much higher power than an ICP (15 kW) and is used to analyse powdered solid samples directly, without recourse to dissolution procedures. The principle of operation is based on the action of a spark discharge created between the surface of a conductive sample and a tungsten electrode. The solid aerosol formed as a result of exposure is transported by a flow of argon to the excitation source. Parameters optimized in the first of these papers included the operating conditions of the plasma torch (argon gas flow rate, angle between plasma jests and torch height), the sparking time, discharge frequency and pulse duration.[35] The samples used throughout the study were a high purity copper and standard reference samples GSO 130 alloyed structural steel. Under optimal conditions, detection limits varied significantly between different analytes and were 10^{-5}% for Mn and V, 10^{-4}% for Cr and Cu, and 10^{-3}% for Mo and Si. The second paper applied the technique to the analysis of steel samples including the reference materials UG-5K and UG-7K.[36] Agreement with certified values was very good. However, it was noticeable that precision was relatively poor. As an example, the experimental Cu result in UG-5K was 0.53 ± 0.06% ($n = 4$) compared with the certified value of 0.490 ± 0.003%.

A 3D-printed electrochemical flow cell coupled with ICP-OES was used by Klaes *et al.* to *characterise hot-dip zinc/zinc alloy coated steel*.[37] Samples were cut into 3 × 10 cm rectangles, cleaned with acetone and lint-free cloth to remove the anti-corrosion oil coating and then subjected to analysis. Sample was dissolved in 20% hydrochloric acid, a qualitative electrochemical measurement potential is measured against a Ag/AgCl reference electrode was made to identify the elements present and then the resulting solution transported to the ICP-OES instrument for fully quantitative analysis. Results were compared with those obtained using GD-OES and were in reasonable agreement. Linearity, repeatability and reproducibility were all tested. Repeatability of ten measurements was variable, with the Fe content ranging from 0.23–0.27%, the Al between 0.46 and 0.49% and the Zn being most variable, ranging from 42.75 to 50.13 g m^2. Reproducibility of 20 different

values determined on three different days yielded similar, but slightly more variable results.

2.2 Non-ferrous metals

Many of the overall themes for the analysis of non-ferrous materials are the same as for the ferrous ones, although the sample types are more diverse. Strangely, there are still a large number of papers reporting methods for LIBS calibration. The number of these were significantly diminished in the Ferrous section during this review period. Several papers discussed the use of chemometric methods to aid the calibration, assist with classification or undertake data pre-treatment or reduction. The use of chemometrics is still a very popular area of research for several reasons. Data reduction is required because LIBS can produce an enormous amount of data. Reducing this to the relevant wavelengths facilitates calculations and enables it to be accomplished with a more basic computer. Calibration is very dependent on matrix, temperature and pressure. For on-line analysis, chemometrics may be used to calculate correction factors or isolate data that are least affected by changes in operating conditions. The biggest advantage of LIBS over more traditional atomic spectrometric methods is that it (as well as portable XRF) may be used in the field. This has a particular advantage in the recycling of scrap, since different alloys may be identified rapidly, minimising the potential of cross-contamination and, in some cases, facilitating an estimate of worth to a customer. Portable LIBS instruments are available commercially. If the calibration models can be improved, then the accuracy of these instruments may be improved.

2.2.1 Copper and copper-based alloys. A few papers in the Ferrous section discussed the influence of temperature of the target sample on LIBS analyses. This theme has continued in the Non-ferrous section, with a contribution by Shao *et al.* determining the effects of *temperatures between 25 and 200 °C on the LIBS analysis of a brass* sample.[38] The LIBS system employed a Ti:sapphire laser operating at 800 nm with a pulse duration of 50 fs. Using laser energies of both 0.3 and 0.5 mJ, a linear increase in Cu signal at 521.82 nm was observed with increasing temperature, with the 0.5 mJ producing a greater emission intensity. A study of the electron number density and temperature was undertaken using the Boltzmann equation and Stark broadening. As the temperature of the sample increased, the electron temperature increased whereas the electron density decreased. It was concluded that an increased target temperature leads to improved resolution and sensitivity of femtosecond LIBS.

A two jet arc plasma with spark sampling and calibration was discussed at length in the Ferrous section.[35,36] A related paper, by Kuptsov *et al.*, discussed its use for the analysis of dissolved solutions of brass samples.[39] Operating conditions were optimized and the effect of the concentration of matrix elements on the signal to background ratio of the analytes was determined. Calibration was achieved through the use of standard solutions and the coefficients of relative sensitivity factors. Analysis of reference materials MCH-7 yielded results within 15% of certified values. This was thought to be fit for purpose.

Relative sensitivity factors for elements in a copper matrix were also studied by Zhang *et al.* who compared continuous direct current glow discharge mass spectrometry and micro-second pulsed GD-MS for the analysis.[40] High purity copper powders (99.999%) were spiked with a solution containing 72 analytes and the relative sensitivity factors obtained using a high resolution double-focusing sector-field GD-MS instrument equipped with a Grimm-type fast-flow dc source. The precision was comparable to that of data obtained using ICP-MS and ICP-OES following a dissolution procedure. The GD-MS method therefore offered the clear advantages of time-saving and of not requiring the use of corrosive chemicals and the associated fume extraction. The technique had a limited linear range, with a regression of 0.9993 when additions of 1, 5 and 10 mg kg^{-1} were used, but this reduced to 0.9177 when the calibration was extended to 50 and 100 mg kg^{-1}. Recovery of 10 mg kg^{-1} spikes ranged between 80 and 120%. Comparison of relative sensitivity factors obtained using the two modes of GD-MS indicated that those for the pulsed mode were between 2 and 40% lower. Repeatability was, however, better for the pulsed mode, with a value of <10% being obtained compared with <15% for the continuous mode. The method was validated through the analysis of the certified reference materials M-376a, ERM-EB375 and SRM-1117. Results were mixed, with the pulsed mode providing better accuracy for some analytes (*e.g.* Al, As, Cd, Mn, P and Zn) and the continuous mode providing better accuracy for others (*e.g.* Bi, Pb and Si).

Collinear long-short double pulse LIBS was described previously in the Ferrous section. Cui *et al.* discussed its use for the underwater analysis of copper materials in two papers.[41,42] Underwater analysis obviously has huge benefits in the field of archaeology where *in situ* measurements can prevent the expense of raising articles to the surface only to find that it is not made of the material expected. Water is known to have quenching problems though and so operating conditions tend to be quite different to normal analyses. Both papers provided a schematic diagram of the setup. The first of the papers found that the plasma formed underwater had a cold shell with a very low emission intensity and a hot core with much greater emission intensity.[41] The early-stage plasma formed produced continuum emission from the hot core and this was absorbed by the Cu atoms in the colder plasma edge, causing Fraunhofer-type absorption at both 324.754 nm and 327.396 nm. An inter-pulse delay of 10 ns provided an absorption at 324.754 nm with a precision of 1.5% RSD, which increased to 5.3% RSD when the inter-pulse delay was increased to 30 ns. Precision at 327.396 nm was 2.7% and 3.3% for 10 and 30 ns inter-pulse delays, respectively. The reason for poorer precision at higher inter-pulse delay was that the amount of absorption decreased. Underwater LIBS can suffer from light transmission losses back through the fibre optic to the detector. This, when added to the quenching effect by the water has a deleterious effect on the sensitivity. The experiments undertaken in these experiments help optimise signal so that some of the losses can be minimised.

An interesting application was reported by Bonin *et al.* who reported the ICP-MS detection of *Ra at the attogram levels in*

copper samples.[43] After acid dissolution of the copper matrix, the Ra was retained on an AG50W-X8 BV column. A 5 mL bed volume had to be used to retain all of the Ra and to allow the copper matrix to be removed. Sample was flushed onto the column which was then rinsed with dilute hydrochloric acid to remove the copper. A further rinse with an ammonium EDTA solution completed the copper removal process. The Ra was then eluted with a solution of the ammonium salt of nitrilotriacetic acid. Using a sample volume of between 200 and 500 mL and an elution volume of 10 mL, significant preconcentration factors were achieved. The figures of merit of the method were conveniently tabulated and showed that an excellent instrumental LOD of 2 mBq L^{-1} (53 fg L^{-1}) was obtained. When 100 g of copper was dissolved, the method LOD was 0.3 μBq g^{-1} (equating to 9 ag g^{-1}). Recovery was 100 ± 3%. The chromatographic separation was fairly rapid, enabling a sample to be prepared in 20 minutes. The rate limiting step was the acid dissolution, which took over three hours per sample.

2.2.2 Aluminium and aluminium-based alloys. Two papers by Wang *et al.* discussed the use of *high repetition rate LA-spark induced breakdown spectrometry (LA-SIBS) for the analysis of aluminium alloys.*[44,45] One reported a one point calibration strategy, in which the results of a certified alloy were used to construct a model and then data from unknown samples were input to the model so that concentrations can be calculated.[45] The paper discussed the theory behind calibration-free LIBS and then how this was modified to make the one point calibration model. The model was trained using one certified aluminium alloy and then tested on four others. Experimental results were in reasonable agreement with certified values, with averaged relative errors being: 0.065%, 19.45%, 11.97%, 13.03%, 9.77% and 7.81% for Al, Cr, Cu, Mg, Mn and Zn, respectively. The authors concluded that the method was a convenient, rapid and reliable way of determining both major and minor elements in the samples. The advantages of the system over LIBS systems include its fast speed of spectral data collection, cost-effectiveness and its low continuum background. The other paper used particle swarm optimization to narrow down the full dataset to those parts that give most reliable results and then combined this with extreme learning machine.[44] The theory of these two techniques is beyond the scope of this text. However, particle swarm optimization is a stochastic global optimization algorithm based on swarm intelligence and extreme learning machine is a signal hidden layer feed-forward network with fast learning speed and high learning accuracy. Both statistical techniques were described in full in the paper and a schematic of the experimental setup was also given. During the experiment, 11 alloys were used, seven of which were used for calibration and the remaining four for prediction. All samples had previously been analysed using either AAS or XRF. The data obtained for the four predictive samples were compared with these reference data. In addition, other models were also compared. These were: a univariate approach, support vector machine and extreme learning machine without the particle swarm optimization. In all cases (all four samples and for Cr, Cu and Mg), the particle swarm

optimization combined with extreme learning machine provided results in closest agreement with those obtained using XRF. Using the combined method, correlation coefficients for calibration were greater than 0.997 and the root mean square error of prediction was 0.0045%, 0.0095% and 0.0138% for Cr, Cu and Mg, respectively.

Machine learning applied to LIBS data from aluminium alloys has been reported in other papers.[46,47] The paper by Dai *et al.* identified different aluminium alloys (060, 6061, 5052, 2024, and 7075) with the prospect of re-cycling them from scrap.[47] The authors first used PCA to help with the identification and then followed this by least squares support vector machine to classify five different aluminium alloys. The results were compared with those obtained from data analysis using support vector machine alone. As is the norm for this type of paper, a training set of spectra was required from samples of known composition and this was used to develop the model. Other samples of known composition are then used to verify the accuracy of the model before it can be used on unknown samples. Both classification methods performed well, with the support vector machine alone classifying 98.3% of samples correctly and the PCA – least squares support vector machine 100%. The results for the support vector machine showed that of the 60 spectra of the test set, one 7075 aluminium alloy spectrum was misclassified as 5052, with the remaining 59 spectra being predicted correctly. Therefore, the prediction accuracy of 7075 is 91.67%, and the prediction accuracy rate of the other four aluminium alloys was 100%. It is known that LIBS spectra can vary through changes in laser fluence. Yue *et al.* used machine learning to correct for this efficiently.[46] These authors deliberately changed the fluence of the Nd:YAG laser used between 7.9 and 71.1 mJ and collected the LIBS spectra from aluminium alloys, with Mg being the analyte. Comparison of the data obtained using the proposed method was made with other methods, *e.g.* through correction for crater volume, electron number density and plasma temperature and a classical univariate correction method (normalising with laser pulse energy and total spectral intensity). The authors noted that improvements over no correction were made for the crater volume, electron number density and plasma temperature method. However, they pointed out that measurement of crater volume is not always easy and can be time-consuming, especially for an industrial application. The machine learning method, however, first used the back propagation neural network to train and validate the model. This led to an average precision of 6.3% RSD being achieved for the test samples; a significant improvement over the other methods. This could potentially allow it to be used in an on-line industrial setting.

A paper by Wang *et al.* described a feature selection method called *recursive feature elimination (RFE) and combined that with ridge regression* and then applied this combination to data obtained from the LIBS analysis of aluminium alloys.[48] The paper described the model in full mathematical detail. This method uses a base model for multi-round training. After each round of training, several features of weight coefficients are removed, and the next round of training is based on a new feature subset. The RFE method recursively reduces the size of feature subsets

by sequential backward selection. This greatly reduces the randomness of spectral lines. In this paper, the ridge regression is used as the basic model of RFE to solve the quantitative problem. The ridge regression model is used to fit the calibration set data, and the regression coefficients are recorded. The spectral features are sorted according to the absolute value of the regression coefficients. The lowest ranking spectral feature is deleted from the feature set in each cycle. Once the weakest of the data had been removed, the remaining subset was input to a partial least squares regression model (PLS). The analytes determined were Cu, Fe, Mg, Mn, Si and Zn. Comparison was made between partial least squares regression using the full data set, a genetic algorithm partial least squares model and the proposed model. The calibration results of the analytes and root mean square error of prediction were improved significantly using the proposed model.

Sorting of different aluminium alloys using LIBS was a subject tackled by Fugane *et al.*, who attempted the sorting through the determination of seven analytes (Cr, Cu, Fe, Mg, Mn, Si and Zn).[49] After careful optimization of the gate delay (500 ns) and gate width (50 μs) to ensure optimal signal to background ratio, calibration curves were prepared using certified aluminium alloys containing different concentrations of the analytes. Several commercial alloys (A1050, A1100, A2017, A2024, A5052, A5083 and A6061) were then analysed using the system. Overall, the method was deemed successful, although several could not be classified into the alloy type. This though was not a failing of the LIBS system. Instead, it stemmed from the different alloys having extremely similar chemical fingerprints. To prove their point, the authors used a dissolution method followed by ICP-OES and had similar results. It was noted that the LIBS analysis was rapid and could be undertaken on-line, whereas the ICP-OES analysis could not and required a sample dissolution procedure, making it far slower.

A second paper by Fugane *et al.* used LIBS for the rapid *detection and characterization of inclusions in re-cycled aluminium materials.*[50] The Nd:YAG laser system, optics, detection system and motorized X,Y,Z sample plate were all discussed in detail. Again, the gate delay and gate width were optimized prior to analysis. The inclusions contained significant amounts of Fe and Si. The number of inclusions was estimated by analysing the surface of the 4 mm × 5 mm sample and then, assuming homogeneity throughout the sample, the number of inclusions on the surface was extrapolated to the number in the whole sample. Lateral resolution of the LIBS system was restricted by the size of the ablated crater and was approximately 100 μm. Analysis of the entire surface took approximately 40 minutes to complete. The authors did specify that this time could be reduced significantly if spectrum analysis was automated using a high-performance computer. The LIBS system was clearly well-suited to such an analysis, since a standard procedure would require the dissolution of the sample which would also probably dissolve the inclusion.

2.2.3 Nickel and nickel-based alloys. An interesting application was reported by Kugler *et al.* who described the *analysis of fine and ultra-fine particles of Inconel 718 formed during laser cladding of materials.*[51] The particles formed during the process

were passed through a cascade impactor, which separated them according to nine different size categories, ranging from 0.07 μm to 17.9 μm when a flow rate of 16.7 L min^{-1} was used. The particles collected at each stage were analysed using TXRF so that an identification of the bulk components could be made. Analysis of the original material confirmed that Inconel 718 contains ~52% Ni, 20% Cr and 18% Fe, with much smaller concentrations of Mn, Mo, Nb and Ti also being identified. The particles formed during the process were mainly in the <100 nm fractions and had a very different composition; with 47% Cr, 26% Ni, 18% Fe and almost 10% Mn being found. A XANES study of the oxidation states of the four main analytes in the particles was then undertaken. This identified that Cr, Fe and Mn all demonstrated significant oxidation compared with the original sample, but that the Ni remained in its metallic form. Fortunately, there was no evidence that Cr^{VI} had been formed as this would have had significant health implications for the workers. The work was therefore a good example of where atomic spectrometry can be used not just to determine the composition of samples, but also to use the information to assess toxicity.

The *on-line monitoring of nickel alloy smelting processes* was discussed by Li *et al.* who described an iterative multi-energy calibration (IMEC) method for LIBS analysis.[52] This process is an advancement of the commonly used multi-energy calibration method. The IMEC method is a two-stage process. The first is the preparation of a standard. This is undertaken in the same furnace, under the same conditions and should have as close to the same composition as the samples to be formed as possible. A portion of this is sent away for analysis to confirm the composition. The second stage is to use this standard during the LIBS analysis along with a quantitative analysis algorithm. This algorithm was discussed in detail in the paper. The performance of the methodology was compared with that of an internal standardisation method during the analysis of 13 batches of sample. Average values of both the root mean square error (RMSE) and the RSD were improved by a factor of approximately two.

2.2.4 Other non-ferrous materials. Numerous sample types fit into this category. A paper by Lednev *et al.* described the *in situ* LIBS measurements during laser welding of *superalloys.*[53] This paper was extremely similar to one discussed in the Ferrous section and so will not be discussed further here. The reader is directed to that section for a more in-depth discussion. Another paper reporting the analysis of superalloys was presented by Li *et al.* who used both μ-XRF and LIBS for the surface and depth-resolved analysis of the composite powders, respectively.[54] The nickel-containing superalloy had a mean particle size of 100 μm and 42 g was mixed in a ball mixer with cobalt (8 g) that had a mean particle size of <5 μm. Steel balls (100 g, 7 mm diameter) were used for the mixing which occurred at 200 rpm, since higher speeds led to adsorption of the powders to the mixing balls or vessel. Mixing times of 0.5, 2, 4, 8, 12 and 24 hours were used and the resulting powder from each (10 g) was pressed at 900 MPa into a disk suitable for μ-XRF and LIBS analysis. The crater depth arising from LIBS analysis was determined using a three-dimensional optical profilometer. The

analysis of the bulk material was achieved using ICP-OES. Analytical data from μ-XRF showed that the concentration of Co increased rapidly between 0.5 and 4 hours, but then stabilised to a value of approximately 62%. Precision improved from nearly 14% RSD after four hours to approximately 4% RSD after 24 h. The optical profilometry indicated that, at the surface, a single LIBS laser shot produced a crater of depth 0.5 μm. This value increased with increasing numbers of laser shots. Overall, the samples taken after 24 h were homogeneous, but the Co content was less than that expected from the ingredients added. It was concluded that the very fine particulate Co powder was adsorbed to the steel balls and vessel to a greater extent than the larger superalloy particles.

A paper by Medvedev *et al.* described the *ICP-MS and ETV-ICP-MS determination of trace analytes* in high-purity tungsten[55] and molybdenum.[56] For ICP-MS analysis, sample (0.3 g with 99.999% purity) was dissolved and the resulting solution analysed directly. A total of 54 analytes were determined with LOD ranging from 0.4 to 3000 ng g^{-1}. Unfortunately, there was quite a sizeable matrix effect for many of the analytes, with their signal dropping by up to 90% when the tungsten reached 3 g L^{-1}. The worst affected analytes were those with a mass of between 40 and 130 a.m.u. A bigger dilution of sample (*e.g.* a tungsten concentration of <700 mg L^{-1}) went some way to overcoming this problem, but led to many analytes being diluted to below their LOD. Subsequent ICP-MS analyses were undertaken with a tungsten concentration of 700 mg L^{-1}. The operating conditions for ETV-ICP-MS had to be optimized. Factors considered were the plasma power, ETV temperature program, the transfer gas flow rate and the ion lens settings. The sample was introduced as a 5000 mg L^{-1} tungsten solution, *i.e.* far more concentrated than for pneumatic nebulisation. A total of 26 analytes were chosen. Their LOD ranged from 1 to 200 ng g^{-1}, representing improvements of between 3 and 70 compared with nebulisation. Method validation for the ETV-ICP-MS was achieved through comparison with ICP-MS and ETAAS data and through spike/recovery experiments. The ETV-ICP-MS method could use a lesser dilution, thereby improving LOD whilst not suffering the problems associated with viscosity affecting nebulisation efficiency and signal suppression.

The same research group has also undertaken the *analysis of high-purity cadmium*.[57] A novel method of vacuum preconcentration with matrix volatilization was described. Briefly, 1.5 g of sample was placed in a quartz cup that was placed in a vacuum distillation device. This was then heated to 390 °C. When the first sign of melting occurred, a tiny bleed of filtered air was admitted so that an oxide layer formed on the surface. Vacuum distillation then occurred for a period of 3 hours, leaving a thin film of cadmium oxide rich in impurities in the quartz container and the cadmium coated elsewhere. The cadmium oxide film containing the analytes was then dissolved in nitric acid and diluted to 3 mL for ICP-MS analysis or to 5 mL for ICP-OES analysis. The LOD for 41 analytes ranged from 0.002 to 10 ng g^{-1} for ICP-MS and from 0.1 to 40 ng g^{-1} for 43 analytes using ICP-OES. Method validation was through spike/recovery experiments and through comparison of data obtained using the two instrumental techniques. The detection limits obtained

were therefore very impressive. However, at three hours per sample, the method was clearly quite slow.

Quantitative analysis of zirconium alloys using borate fusion and WDXRF analysis of the glasses formed was described by Sieber *et al.*[58] The alloys were prepared for analysis through the formation of lathe turnings that were 0.5–2 mm wide and 2–10 mm long. Approximately 0.5 g of these "chips" were weighed into 10 mL of water. Then, hydrofluoric acid (1 mL) was added very slowly (20 min) to minimise splashing. Then, 5 mL aliquots of the solution were placed in a clean platinum crucible and dried at 107 °C. Further aliquots were added and dried until the residue from the whole solution was present. The lithium borate flux was added and the mixture fused using a complex temperature program (provided in the paper). Overall, the zirconium and 17 analytes were diluted by a factor of 16. The methodology was applied to the analysis of assorted zirconium alloy reference materials, including SRM 360 c, 360 b and the discontinued materials Zr alloy SRM: 360, 360a, 1210, 1211, 1212a, 1213, 1214, 1215, 1234, 1235, 1236, 1237, 1238 and 1239. Results from the procedure were in sufficiently good agreement with those obtained using ICP-MS for the method to be deemed successful for many analytes. There were some elements, however, that showed particularly poor agreement, *e.g.* P, where WDXRF indicated there was 21.6 mg kg^{-1} whereas ICP-MS gave a value of 85.7 mg kg^{-1}; which is closer, but still far away from the certified value of 62 mg kg^{-1}. Hafnium was also noted to provide a biased result.

The *analysis of platinum group elements* has also been undertaken by several workers. An example, by Harouaka *et al.* determined Th-229 and Th-232 as well as U-233 and U-238 in gold, iridium, platinum and tungsten matrices using a triple quadrupole ICP-MS instrument with oxygen as the reaction gas.[59] A thorough investigation was undertaken of the polyatomic interferences that may arise through the combination of matrix ions and either ions from the dissolution media or with the oxygen. In single quadrupole mode, numerous possibilities were identified over the mass range 227–239. The full list was tabulated, however the most important were: $^{194}Pt^{35}Cl^{+}$ on Th-229, $^{198}Pt^{40}Ar^{+}$ on U-238, $^{193}Ir^{40}Ar^{+}$, $^{197}Au^{36}Ar^{+}$ and $^{184}W^{16}O_3H^{+}$ on U-233 and $^{195}Pt^{37}Cl^{+}$, $^{197}Au^{35}Cl^{+}$ and $^{192}Pt^{40}Ar^{+}$ on Th-232. Scanning at a higher mass range (227–270 a.m.u.) showed that higher oxides of matrix elements did not form or, if they did, they did not interfere with the analytes. The mass shift method of measuring Th-229 (*i.e.* measuring ThO at *m/z* 245) provided data with 96% accuracy at a concentration of 100 fg g^{-1}, but that this decreased to 83% accuracy at 10 fg g^{-1} and to 73% at 1 fg g^{-1}. The corresponding figures for U-233 were 95%, 94% and then sharply decreasing to 51% at the 1 fg g^{-1} level. Absolute detection limits were 2.74 fg and 12.9 fg for Th and U, respectively which, depending on sample type analysed, corresponded to LOD at the pg g^{-1} range. The method was applied successfully to the analysis of electronic components.

Habibpour *et al.* constructed a single-shot, spark-assisted LIBS instrument for the soul purpose of *measuring the purity of gold*.[60] The details of the instrument were discussed in detail, but briefly, a Nd:YAG laser combined with a spark generator and a single channel CCD spectrometer were used. The spark assists

the LIBS in forming a more energetic plasma, even at low energy single shots. The more energetic plasma increases the plasma temperature by up to 20% and that, combined with the elongated lifetime of the plasma, leads to an increase in sensitivity by an order of magnitude. Using the method, the grade of gold could be determined with an analytical error of less than 0.5%. An added advantage was that stylus profilometry demonstrated that the damage caused by the laser shot was less than that caused during normal LIBS.

The analysis of *silver alloys or silver* has been reported in two papers. One, by Brocchieri *et al.* used a number of methods, all employing a hand-held EDXRF instrument, to estimate the silver coating thickness on materials.[61] Calibration standards were prepared by covering metal plates (copper, iron and lead) with silver foils of known thickness, ranging from 0.2 to 15.7 μm. Methods of determining the thickness included a partial least squares regression, and ratios of the Kα, Kβ, Lα and Lβ intensities of both the silver and the base metal. The partial least squares method provided the best thickness estimates, although it was noted that the other methods also provided good data. The method was then applied to the analysis of a Roman coin and to a modern coin. The other paper was prepared by Gao *et al.* who applied a calibration-free, high repetitive rate laser ablation spark induced breakdown spectroscopy method for the quantitative elemental analysis of a silver alloy.[62] Sample was ablated by a fibre laser operating at a repetition rate of 30 kHz and then a spark was applied to enhance the plasma emission. The usual plasma diagnostics were used, *i.e.* the Stark broadening of spectral lines was used to calculate electron number density (1.11×10^{17} cm^{-3}) and a Saha–Boltzmann plot was used to estimate plasma temperature (7355 K). Analytical data obtained from the system for the analysis of the alloy were compared with those obtained using a dissolution procedure followed by ICP-OES analysis. Agreement was within 15%, which was deemed acceptable, especially as a standard sample was not required. The method described therefore had the advantage of speed since dissolution was not required.

3 Organic chemicals and materials

3.1 Organic chemicals

There have been two main research topics in this area over the last review period. One is the forensic analysis of materials and the other is the analysis of pharmaceutical materials and/or cosmetics. Both areas have had a number of good applications presented.

The *preparation of certified reference materials* is always welcome as it continues to be the gold standard for validating methodology. The preparation of certified materials that are pure organic compounds is especially welcome given that there are so few. The preparation of natural and Se-82 labelled selenomethionine reference materials (SENS-1 and SEES-1, respectively) was reported by LeBlanc *et al.*[63] The high purity natural isotopic abundance SENS-1 was available as a powder, whereas the SEES-1 was a solution. The SENS-1 material was purchased from a commercial manufacturer and bottled without further

sample manipulation. This was produced as a primary standard (for traceability) by the certifying body (NRC Canada). The SEES-1 was made using an in-house method that was described fully in the paper. For certification purposes, 10 mg aliquots from different bottles of SENS-1 were weighed into microwave bombs and then digested with microwave assistance using a mixture of nitric acid and hydrogen peroxide. The resulting solutions were spiked with Se-82 and then an isotope dilution analysis undertaken using a triple quadrupole ICP-MS instrument employing oxygen as the reaction gas to quantify the Se present. The selenium-containing impurities were quantified by coupling HPLC with the ICP-MS instrument. These and other impurities were identified using LC-MS. An assessment of purity was also made using NMR. The purity of SENS-1 was 0.961 ± 0.007 g g^{-1} ($k = 2$). Having established the purity of SENS-1, it was used as a primary standard for the reverse isotope dilution analysis of SEES-1. This contains 1556 ± 60 μg g^{-1} ($k = 2$).

Both copper and zinc have been ingredients of anti-fouling paints for many years. At present, there are two standard methods used to determine their leaching rate from paint films, both of which have been questioned recently. Lagerstrom and Ytreberg developed a new method for determining *Cu and Zn based on XRF analysis of the paint films*.[64] Unfortunately, the paint formulations vary significantly, with different concentrations of Cu or Zn, different fillers, *etc.* and will also vary in thickness. This means that the X-rays could potentially have different amounts of self-absorption, leading to potential errors. The work described the preparation of standards made from seven different paints and with different thickness coated on Mylar® film. A calibration curve was therefore prepared for each of the seven paints. Two different portable EDXRF spectrometers were compared to test the transferability of the method between instruments. Both instruments produced data that were within 5% of the figures produced through wet chemical analysis; indicating good transferability. The study also showed that universal calibration curves could be created that had a prediction uncertainty of approximately ±130 μg cm^{-2} for both analytes.

Simultaneous compound-specific isotope analysis of S-33 and of S-34 in organic compounds using GC-MC-ICP-MS was described by Kummel *et al.*[65] The isotopic reference standards IAEA S-1, IAEA S-2 and IAEA S-3 were transformed into SF$_6$ so that they could be used as standards. The transformation reaction and the instrumental operating conditions were described in full. The determination of S is potentially fraught with problems arising from polyatomic interferences. The instrument was therefore operated in both low resolution ($m/\Delta m = 300$) and medium resolution ($m/\Delta m = 4000$). Although small amounts of the interferences occurred, the low resolution data were not significantly different to those obtained using medium resolution. The low resolution mode was therefore adopted since it offered greater sensitivity. The method developed was applied to the analysis of the organic compounds thiophene, tetrahydrothiophene, diethyl sulfide and dimethyl disulfide. These were dissolved in pentane and then aliquots with concentrations in the range 170 to 580 pmol for each analyte were injected

into the GC-ICP-MS system. The simultaneous and precise determination of $\delta^{33}S$ and $\delta^{34}S$ in individual organic compounds by GC-MC-ICPMS was demonstrated. The method provides a simpler and faster tool than existing techniques to obtain $\Delta^{33}S$ values for the evaluation of mass-independent isotope effects in organosulfur compounds.

Glow discharge-mass spectrometry is conventionally used for the analysis of solid samples. A new methodology was reported by Gubal *et al.* who used *microsecond pulsed glow discharge in a copper hollow cathode followed by TOF-MS detection for the ionization and subsequent determination of volatile organic compounds.*[66] The discharge cell of the system was modified slightly to incorporate a quartz capillary into the argon input channel. This enabled the analysis of the vapours of the compounds in air to be determined. The method was applied to the determination of vapours of acetonitrile, benzene, toluene, *o*-xylene, *p*-xylene, *m*-xylene and *n*-heptane. The ionization mechanism was studied at length and new mechanisms of chemical and electron ionization resulting in the formation of associate ions with the copper cathode material were identified. The Penning process and proton transfer reactions also played a part. Operating conditions such as the effect of repelling pulse delay, the effect of pulse duration and discharge power and the effect of air humidity were all studied and helped elucidate ionization mechanisms. Calibration graphs were prepared and yielded R^2 values of greater than 0.99. Detection limits were not magnificent (typically just sub-ppm or single figure ppm, depending on the ionization mechanism), but the calibrations spanned four orders of magnitude.

3.1.1 Forensic analysis. The forensic analysis of organic materials has been a popular area of research in this review period. An example, by Ahmed *et al.* used LIBS to *analyse black toners.*[67] A total of 23 toners of eight printers and six different photocopiers were used to print onto the same paper type. Each sample was then analysed using LIBS, with the hardware and the operating conditions being discussed in full in the paper. The analytical data obtained from the samples were then analysed statistically using PCA, where the input to PCA was 30 LIBS spectra per sample, and another chemometric tool called graph clustering. A brief description of the latter was given in the paper. The PCA was easily capable of discriminating between different brands of toner, although sometimes a second iteration of PCA was required. The graph clustering model also managed to classify the majority of toners with 100% accuracy with all except one of the others being classified correctly 97% of the time. One sample was classified 87% correctly though.

Inks from 17 pens were analysed using LIBS followed by PCA treatment of the data in an attempt to distinguish the inks.[68] The LIBS operating conditions such as the delay time, laser pulse energy and number of pulses per point, were optimized using a factorial design and a second order regression model. The data obtained from LIBS was corroborated by acid digestion of the inks followed by ICP-OES analysis. It was noted that the ICP-OES instrument was capable of determining P, which acted as a very good discriminating element. Unfortunately, the LIBS instrument used was not capable of this. Data from only 20 spectral lines were collected using LIBS and subjected to PCA.

This was sufficient to be able to distinguish between two inks of the same colour. The method was applied to the analysis of a cheque in which a 10 had been converted to 100. The last zero was identified as being added by a different pen because it contained large concentrations of Cu whereas the one and the first zero did not. Such a measurement clearly could not be undertaken using a standard ICP-OES experiment.

Amorim *et al.* used both ICP-MS and ICP-OES to study the *inorganic profiles of street cocaine samples.*[69] A total of 52 samples were collected from three regions of the Espirito Santo state, Brazil and these were acid digested in a closed vessel microwave system. The digests were then analysed using ICP-OES (for Al, Ca, Cu, Fe, Mg, Mn and Zn) and ICP-MS (for Co, Mo, P and Pb). Analytical data obtained were interrogated using hierarchical cluster analysis (HCA) and PCA. Although some analytes were found to form strong clusters, it was impossible to discriminate between samples from the different sites. The authors suggested that future work could perhaps try to separate impurities from the cocaine prior to the analysis. Spike tests indicated good recoveries for the majority of analytes (typically 90–115%). However, there were examples of extremely poor recovery, *e.g.* a Ca result of 186% and a Mg recovery of 71%. It was also possible to identify that region three diluted the drug more than the other two regions.

Another paper to span both cosmetic and forensic analysis was presented by Horiguchi and Kunimura, who used both *surface enhanced Raman scattering (SERS) and XRF to characterise hair dye products on single hairs.*[70] Hog hair was used for the experiment in which five hair dye products were used. The SERS identified clear differences between them when analysing solutions of the dyes, but sometimes produced very similar spectra when analysing the treated hair. Occasionally different dyes on the hair could be differentiated, but those containing similar ingredients or types of dye produced similar spectra. However, the XRF identified clear differences in the metallic signatures for many of the dyes, even on a single hair. For instance, product A yielded a Fe signal, product B both K and Mn and product C Ti. A combination of SERS and XRF was more efficient at differentiating the dyes than either technique alone.

3.1.2 Pharmaceutical and cosmetic samples. A method for the determination of *Bi in lake waters and some drugs* was reported by Yu *et al.*,[71] who employed liquid cathode glow discharge-optical emission spectrometry (LC-GD-OES) for the analysis. Three drugs were analysed: bismuth pectin, bismuth aluminate and bismuth magnesium sodium bicarbonate. Sample (0.4 g) was digested using nitric acid and hydrogen peroxide at elevated temperature. The digests were then evaporated to dryness and the residue dissolved and diluted to 25 mL for analysis. The effects of the presence of low molecular weight organic substances, *e.g.* formic acid, acetic acid, methanol and ethanol were tested. Formic acid at a concentration of 3% performed the best and increased sensitivity by a factor of 23. It had the additional benefits of removing interferences arising from the presence of chloride, bromide and iodide ions as well as improving LOD by a factor of 9. Unfortunately, the presence of the formic acid improved the interferences from Cu, but did not ameliorate them completely, *i.e.* recovery improved

from 180% to 116%. Recoveries were reported as being between 106 and 113% in the absence of Cu, which was deemed satisfactory. Results from the analysis of the drug samples were compared with those obtained using ICP-OES and were in agreement at the 95% confidence level.

The speciation of *Sb in injectable leishmanicidal drugs using hydride generation (HG)-AAS* was reported by Fabrino *et al.*[72] Total Sb was determined by reducing the Sb^V to Sb^{III} using 0.1 M hydrochloric acid and potassium iodide. Then, HG-AAS analysis took place using hydrochloric acid and a mixture of sodium tetrahydroborate in sodium hydroxide. To optimise the detection capability of Sb^{III}, a factorial design followed by a central composite design was used. The presence of citric acid in the system to stabilise the Sb^V and to prevent it from forming hydrides resulted in the blocking of the capillary at concentrations commonly used in other studies. The concentration was therefore decreased by a factor of between 4 and 20 and was still capable of the task, but did not cause blockages. The LOD for total Sb and Sb^{III} were 0.15 and 0.05 µg L^{-1}, respectively. Precision was, at best 3.1% rising to 19.6% closer to the LOD. Recovery from spike experiments were 95.6–102.3% for total Sb and 89.1–108.1% for Sb^{III}. The total Sb content of the drugs was between 0.08 and 0.21% m m^{-1}, with the Sb^{III} comprising only a very small proportion.

Three types of *surgical thread (absorbable polydioxanone and polyglycolic acid as well as non-absorbable polypropylene) were analysed* for total Al, Cu, Pb and Zn as well as the amounts of the same analytes extracted into 0.1 M hydrochloric acid.[73] For total metal analysis, sample (0.25 g) was acid digested using nitric acid with microwave assistance and then the digests analysed using ETAAS. For the extractable concentrations, 1 g of sample was used. Studies of the effects of temperature (25, 37, 50, 75 and 100 °C), time (15, 30, 60, 90, 120 and 240 min) and of the pH (2, 4, 7, 8 and 10) on the amounts extracted were also undertaken. In general, the temperature had little effect until 50 °C, whereupon the analytes were extracted much more efficiently. The pH had a big effect, with the highest extraction occurring at pH 2 and then decreasing rapidly at pH 4 and then decreasing further at higher pH. The effect of time was more variable, with some analytes increasing up to 60 min and then decreasing again, whereas others, *e.g.* Al remaining vaguely constant. The LOD were 2.8, 1.5, 2.9 and 1.5 µg L^{-1} for Al, Cu, Pb and Zn, respectively. The only method validation was through the analysis of QC-026, an aqueous standard which, although not ideal, is better than nothing.

A method for *discriminating between ZnO nanoparticles and Zn^{2+} in cosmetic samples* (eye shadow) was described by Garcia-Mesa *et al.*[74] The method was based on solid sampling high resolution continuum source GFAAS (SS-HR-CS-GFAAS). Sample was first dried in an oven and then vortex mixed to ensure homogeneity. Then, between 0.1 and 0.3 mg was transferred to a platform which was then inserted to a GFAAS atomiser and a temperature program, that had been optimized using central composite design, run. Calibration was against aqueous standards. The absorbance from the less sensitive Zn line at 307.590 nm was exported as a CSV file and then the data were converted to a standard data transfer format for surface

chemical analysis. It was now that the deconvolution was made using Multipak software, resulting in a peak for the Zn^{2+} and a second for the ZnO nanoparticles. The LOD were 0.06 µg for Zn^{2+} and 0.13 µg for the ZnO. These, of course, had the potential to be improved had the more sensitive Zn line at 213.857 nm been used. Precision for 10 replicates of Zn^{2+} at 0.6 µg in an aqueous standard was 2.5% RSD. The corresponding value for ZnO nanoparticles was 6.9% RSD. Recovery values were between 98 and 115% for aqueous standards of Zn^{2+} and between 80 and 100% for the nanoparticles. The total Zn result was verified by an acid dissolution prior to GFAAS. In general, good agreement between the sum of Zn^{2+} and ZnO and the "total" Zn was achieved.

3.2 Fuels and lubricants

In this section the number of papers seemed similar to last year but there was an increase in papers relating to crude oil and coal with the majority of papers on coal coming from China and employing LIBS for the analysis. A decrease in papers relating to alternative fuels was also noticed which seems at odds with the current environmental trend for alternative fuels.

3.2.1 Petroleum products – gasoline, diesel, gasohol and exhaust particulates. A review paper of note in this section this year was presented by de Souza *et al.*[75] It contained 130 references and looked at *analytical strategies for spectrometric determination of V in the petroleum industry*. Other reviews of relevance to this section may be found in the Introduction.

Four other papers were of interest in this section this year. One, by Andreu *et al.*[76] described a *comparison of nebulisers using ICP-OES for the direct determination of trace levels of P in petroleum products with high particulate content*. The purpose of the study was to develop a method to determine P below 0.1 mg kg^{-1} in petroleum products with a high particulate content in the shortest analysis time. Seaspray™, TSP OptiMist®, and OptiMist XL® nebulizers were compared in order to determine which provided the best performance for the method. The OptiMist XL® nebulizer was the only device that provided a quantification limit lower than 0.1 mg kg^{-1} with a 1 : 3 sample dilution ratio without clogging and had the shortest analysis time. The time period for the sample preparation and analysis was approximately 60 min for a batch of four samples. Identifying the nebuliser type least likely to cause problems whilst providing the relevant sensitivity is clearly of use to workers in the field.

A paper by Ferreira *et al.*[77] described a *method for the determination of Cu, Mn, Ni and Pb in diesel samples using reversed-phase vortex-assisted liquid–liquid microextraction with EDXRF spectrometry*. In this method a nitric acid solution was used to extract and isolate analytes from the samples. After a centrifugation step, the aqueous phase was added dropwise to a filter paper disc for EDXRF determination. The following variables were optimized: type of extraction phase solution, concentration of the extraction phase, stirring time and sample volume. The instrumental parameters of atmospheric conditions, irradiation energy and irradiation time were also evaluated. Using 100 µL of a 0.075 mol L^{-1} nitric acid solution as the extraction

phase and a sample volume of 5.0 mL with a stirring time of 45 s, the limits of detection were 14, 8, 10 and 7 μg L^{-1} for Cu, Mn, Ni, and Pb, respectively. The LOD were impressive thanks to the enrichment factors obtained (34 (Cu), 62 (Mn), 59 (Ni) and 64 (Pb)). The precision expressed as RSD was calculated from ten replicate analyses under optimized conditions using standard solutions containing 200 μg L^{-1} and 400 μg L^{-1} of the four analytes and ranged between 2.1 and 6.4%. The results of recovery tests ranged from 87 to 112%. The procedure was applied to the determination of the four analytes in diesel oil samples. The results were compared with those obtained using ICP-OES after sample digestion. A paired *t*-test *p* > 0.05 indicated that no significant differences were found.

The *determination of Cd in used engine oil, gasoline and diesel using ETAAS after employing magnetic ionic liquid-based dispersive liquid–liquid microextraction* was investigated by Aguirre *et al.*[78] The solvent used for the microextraction procedure was a magnetic ionic liquid which presents a paramagnetic property and allows easy phase separation using a magnet. A back-extraction procedure was then performed to transfer the analyte into an aqueous phase. The main experimental factors affecting the extraction of Cd were optimized using a multivariate analysis consisting of two steps, a Plackett–Burman design followed by a circumscribed central composite design. The optimal conditions were: 6.2 g of sample 119 mg of magnetic ionic liquid, 1 min extraction time, 200 mg of 1 mol L^{-1} nitric acid and 1 min back-extraction time. The proposed analytical method was validated using three samples: used engine oil, gasoline and diesel. The three samples were spiked at two levels 10 and 20 μg kg^{-1} of Cd for used engine oil and 1 and 3 μg kg^{-1} of Cd for gasoline and diesel. Precision and recovery values were produced within the range of 6–11% RSD and 95–110%, respectively.

The paper by Sanchez *et al.*[79] described a method for *Si speciation in light petroleum products using GC-ICP-MS/MS*. Silicon in petroleum products is a 'hot topic' following historic contamination issues and its presence in re-processed fuels. The only useable isotope for Si, ^{28}Si suffers from interferences mainly related to the polyatomic ions ^{12}C^{16}O and ^{14}N^{14}N. These interferences were reduced by adding hydrogen as a reactant gas in the octopole reaction cell and the optimization of the operating parameters such as carrier gas, optional gas and hydrogen gas flow rates. A test mixture of 11 Si compounds was used for this work and included cyclic and linear siloxanes, silanols and silanes. Calibration curves ranging from 0 to 500 μg kg^{-1} were produced with correlation coefficients up to 0.9999. The LOQ ranged from 8–60 μg kg^{-1}. The results were compared with those obtained using ICP-OES and XRF and no significant differences in total Si concentrations were found. The light petroleum products contained cyclic siloxanes, D3–D6 mainly hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4). The paper is a useful contribution to this evolving topic.

3.2.2 Coal, peat and other solid fuels. There were many more papers on this subject than last year; mostly of Chinese origin which may reflect the current interest in coal in this part of the world. The analytical technique of LIBS features highly

this year and much research is in the field of improving the measurement of calorific value for the optimal control of coal blending and combustion in thermal power generation. The calorific value of coal is positively correlated with the content of C, H, and S involved in combustion, but is also closely negatively correlated with the ash content (oxides of Si, Al, Ca, Fe, Mg, *etc.*).

A contribution by Li *et al.*[80] was in the field of calorific value measurement and described a method of determining *light elements associated with the organic fraction using LIBS and inorganic ash forming elements using XRF.* The combined approach greatly improved the measurement repeatability of the coal calorific value. The prediction model used PCA and multiple regression. The experimental results showed that the SD of calorific values predicted is 72 J g^{-1} which is an order of magnitude lower than the 700 J g^{-1} of traditional LIBS. This method could be applied in power plants and other fields that need to pay close attention to coal quality. The quick, reliable and on-site analysis afforded by LIBS is therefore an ideal solution to the problem of obtaining best combustion from coal.

The next contribution in this section, from Xie *et al.*,[81] described a method *for As and Se distribution and speciation in coal and combustion by-products from coal fired power plants*. In this study, a mixture of 1 M H$_3$PO$_4$ and 0.1 M ascorbic acid was used to release As from coal and related solid wastes. The Se in coal and fly ash samples was extracted using 0.1 M NaOH, and gypsum was extracted using 0.2% (v/v) HCl. After extraction by sonication, the extracts were diluted and then analysed using LC-ICP-MS. Stability experiments showed that inorganic As and Se species were almost unchanged during the extraction procedure with the recoveries ranging from 89.7% to 90.6% for inorganic As^{III} and As^V and from 98.5% to 112.9% for inorganic Se^{IV} and Se^{VI}. The recovery was calculated by dividing the sum of different species of As and Se by the total As and Se concentrations measured directly using ICP-MS after microwave digestion. The dominating species was As^V, however, the more toxic As^{III} was detected in the gypsum by-product most of which ends up in landfills or stockpiled in open areas. The results suggest that proper disposal of these wastes is needed.

The next three papers are on the subject of LIBS. The first, by Zhang *et al.*[82] described a method for *the determination of Fe, Ni and V in petroleum coke using LIBS*. This paper established a novel calibration model by using a genetic algorithm optimized support vector regression. The traditional AAS and ICP-AES methods of analysis for these elements have some disadvantages such as use of reagents, long turnaround time and possible contamination. Although LIBS technology has a gap in measurement precision and detection limits compared with AAS and ICP-AES it has unique advantages in rapid detection and simplicity which meets the demands of industrial production monitoring. The characteristic wavelengths of Fe, Ni and V were found by comparing the LIBS spectrum of petroleum coke with the NIST database. Feature selection was then carried out by modelling and sorting root means square error (RMSE) after cyclically removing one feature wavelength. After feature selection, support vector regression modelling was performed again.

The prediction accuracies of V and Ni with feature selection were close to that of standard ASTM D6376. It was therefore concluded that it is feasible to determine Fe, Ni, and V in petroleum coke using LIBS in an industrial environment.

A paper by Dong et al.[83] described *coal discrimination analysis using tandem LIBS and LA-ICP-TOF-MS*. This tandem approach allows simultaneous determination of major and minor elements in coal. The research focused on coal-classification strategies based on PCA combined with K-means clustering, partial least-squares discrimination analysis (PLSDA) and support vector machine. Correlation analyses performed using TOF-MS and LIBS spectra from the coal samples showed that most major, minor and trace element emissions had negative correlation with the volatile content. Suitable variables for the classification models were determined from these data. The individual TOF data, LIBS data and combined data from TOF and LIBS as the inputs for different models were analysed and compared. In all cases the results obtained with the combined TOF and LIBS data were found to be superior to those obtained with the individual TOF or LIBS data. The nonlinear support vector machine model combined with TOF and LIBS data provided the best coal-classification performance, with a classification accuracy of up to 98%.

Deng et al.[84] described a *method for N and S determination in coal using LIBS*. The detection of N and S in coal is essential for the evaluation of its quality. This study employed LIBS to test coal quality and combined two variable selection algorithms, competitive adaptive reweighted sampling and the successive projections algorithm to establish the corresponding partial least square model. The partial least square modelled with the full spectrum of 27 620 variables had poor accuracy. The coefficient of determination and RMSE of the test set for N were 0.5172 and 0.2263, respectively. For S they were 0.5784 and 0.5811, respectively. The competitive adaptive reweighted sampling and the successive projections algorithm screened 37 and 25 variables respectively in the detection of N and S but the prediction ability of the model did not improve significantly. Successive projections algorithm partial least square finally screened 14 and 11 variables respectively through successive projections and obtained the best prediction effect among the three methods. The coefficient of determination of the test set and root mean square error of N were 0.9873 and 0.0208 and those of S were 0.9451 and 0.2082 respectively. In general, the predictive results of the two elements increased by about 90% for root mean square error and 60% for coefficient of determination of the test set compared with partial least square treatment. The results showed that LIBS combined with successive projections algorithm-partial least square has good potential for detecting N and S content in coal and is a very promising technology for industrial applications.

A method developed by Mketo et al.,[85] described an improved microwave assisted sequential extraction method followed by ICP-OES/MS detection. The study aimed to develop a rapid and eco-friendly microwave-based sequential extraction procedure for heavy metal distribution determination and mobility in coal samples. The steps for the sequential extraction were: (1) water, (2) 5 M HCl, (3) 2 M HNO$_3$, (4) 7 M HNO$_3$–3 M H$_2$O$_2$. The most influential extraction parameters, *i.e.* coal amount (0.1 g), extraction time (5 min) and temperature (200 °C) affecting metal sequential extraction efficiencies were successfully optimized by using 2^3 full factorial design and response surface methodology. The optimized method was then applied to three coal CRMs (SARM 18, 19 and 20) and three metal ions Ga, Sr and Ba showed solubility towards water irrespective of the CRM. These three metals were regarded as highly mobile metal ions and are therefore expected to leach out into water bodies. The rest of the metals were only mobile in acidic conditions; therefore, these metals can be regarded as immobile.

3.2.3 Oils – crude oil, lubricants. This section appears to have more contributions this year generally but, in particular, in reference to bitumen and asphalt which were hardly looked at a few years ago. Papers discussing the analysis of lubricants appear to have decreased.

A review, by Mdluli et al.[86] contained 113 references and provided a *critical review of extraction methods published between 2005 and 2020 for the determination of trace metals in oily matrices with spectrometric determination*. Information gathered from the literature showed that liquid/liquid extraction was the more favoured extraction method over solid phase extraction and extraction induced emulsion breaking was the most studied method over the past 16 years.

The first paper in this section by Li et al.[87] described a procedure for the *direct determination of Ni in crude oil samples using a miniaturized electrothermal AAS system*. A fast and direct analysis was achieved using dilution in cyclohexane followed by the pipetting of a 20 μL aliquot onto the tungsten coil of the atomizer. The detection limit was 0.01 mg kg^{-1}, similar to that of other comparable methods. The portable nature of this method means it could be useful in the field, for exploration analysis, environmental monitoring or emergency assessment.

The next contribution, by Vinic et al.,[88] described a method using *LIBS for the quantification of heavy metals in oils*. Thin oil films were produced on silica wafer substrates by rotation. The more rotation the thinner the film and the fewer the matrix effects encountered. Different film thicknesses were studied with the optimum being 0.74 μm. The oil volume sampled by each laser pulse was 0.3 nL. Detection limits for Cd, Cr, Cu and Zn were 0.49, 0.082, 0.16 and 3.9 ppm, respectively. Although this is an interesting paper, all work was done on standards produced in base oil and no CRMs or 'real world' samples were analysed. Methods tend to work well on very controlled samples, and it would have been useful to see some analysis of 'real samples' included.

A paper by Hasme et al.[89] described an *integrated method for the analysis of in-service lubricants for particle size and metal content*. This article discussed adding a liquid particle counter in-line with an ICP-OES system to analyse wear metals and particles in lubricant samples in one run. This approach streamlines the monitoring of in-service lubricants and meets the ASTM D5185 standard.

A paper discussing the analysis of asphalts and bitumens was presented by Adolfo et al.[90] It described a *method for the determination of Co, Fe and Ni in petroleum asphalt cement using high-resolution continuum source AAS after extraction using*

emulsion breaking. Optimized conditions were: 0.08 g of the sample dissolved in 1.5 mL of toluene with 3.5 mL of mineral oil, this was then vigorously mixed with the extracting solution containing 40% (v/v) of HNO_3 and 40% (v/v) of Triton-X-100. The emulsions were then broken by heating just after their formation and the aqueous extracts collected for analysis. Simultaneous determination was carried out using the secondary lines of Co (352.685 nm), Fe (352.604 nm) and Ni (352.454 nm). For this purpose, the best pyrolysis and atomization temperatures were 700 and 2400 °C, respectively. Calibration was performed with standard aqueous solutions and no matrix effects were observed. The LOD was 0.003 mg L^{-1} for Co, 0.018 mg L^{-1} for Fe and 0.027 mg L^{-1} for Ni. This method was then compared with conventional acid digestion. Recoveries ranged from 100 to 107%, 103 to 109% and 95.5 to 98.9% for Co, Fe and Ni, respectively.

Chauhan et al.[91] investigated *dissolution methods for the quantification of metals in oil sands bitumen*. Seven different dissolution methods were investigated: direct dilution, dry ashing, sulfated ashing, ultrasound assisted extraction, extraction induced emulsion breaking, detergentless micro-emulsification and acid decomposition in closed vessels. Of these methods only direct dilution and sulfated ashing were recommended for the determination of Ni and V in bitumen and of these two methods, only sulfated ashing produced samples with good storage stability. The analysis of bitumen diluted in toluene found that 40–50% of the V-containing species separated from the bulk solution after a storage period of 28 days. It was not established whether instability of dilute bitumen in toluene was due to toluene insolubility or aggregation leading to separation, but this behaviour could have implications for the removal of metals from bitumen.

A paper by Gonzalez et al.[92] studied *very high molecular weight asphaltene clusters in THF solution using GPC-ICP-HRMS*. Three Venezuelan heavy crudes (Hamaca, Cerro Negro and Boscan) were investigated. The results showed very clearly the presence of asphaltene clusters in the THF solution. As expected these clusters occur at very low retention times indicative of cohesive long structures resulting from aggregation of species. These results provide strong support to current models regarding cluster formation. Isotopes monitored were ^{58}Ni, ^{32}S and ^{51}V, at a medium resolution of 4000. The spectrometer was fitted with a commercial micro-flow total consumption nebulizer mounted with a laboratory-made jacketed spray chamber whose temperature was set at 60 °C. Large quantities of clusters were detected in Boscan crude and its toluene soluble and toluene insoluble subfractions both at room temperature and after heating. Dilution experiments showed no significant change of these profiles suggesting that these clusters, as well as the other lower molecular weight aggregates and molecules, are not in equilibrium with each other and behave as independent units. A temperature cycle was then used to monitor possible changes of GPC-ICP-HRMS profiles with temperature. Here Boscan crude samples were heated from 25 to 200 °C, left standing for 24 h and then cooled back to 25 °C before measurement. Small changes were found for Boscan crude asphaltenes however vast changes in the profiles were detected for toluene soluble and

insoluble subfractions indicating interchange of material between the cluster and the other components of the solution. These results were discussed in terms of different arrays that may result when asphaltenes are separated into the two sub-fractions, and nanoaggregates are relocated within the cluster before and after heating.

Another paper that utilised GPC-ICP-HRMS was presented by Garcia-Montoto et al.[93] These authors also monitored ^{58}Ni, ^{32}S and ^{51}V to understand their *removal in crude oil from atmospheric residues during hydrodemetallization and hydrodesulfurization*. The Ni, S and V species size distributions were studied to track their evolution during the catalytic processes. For the Ni and V aggregates, it was found that high molecular weight compounds are more refractory compared with low molecular weight and medium molecular weight compounds which were removed at low temperatures. For the S aggregates a slightly different behaviour was observed, the low molecular weight and medium molecular weight aggregates are not as easily hydrotreated compared with the high molecular weight aggregates. This phenomenon illustrated the inherent difference in chemical composition of the metallo-organic compounds compared with the S-containing compounds and their reactivity.

3.2.4 Alternative fuels. There was only one contribution worthy of note in this section this year which seems somewhat at odds with the current drive for environmental alternatives. There were very few papers in this field in total this year.

The sole paper, by Arthur et al.[94] investigated the *monitoring of dissolved active trace elements in biogas plants using TXRF*. Natural plant biomass or biowaste plants in many cases show deficiencies in Fe, Co and Ni and they are supplemented with trace elements to guarantee stable gas and energy production. In this study a procedure was developed to monitor dissolved elements in these processes to prevent an overdose or underdose of these elements. The digester liquid is comparable to sludge with a high solids content and a high salt concentration. A series of two centrifugation steps followed by microwave assisted digestion was used prior to analysis using TXRF. The centrifugation steps also significantly separated carbonates and sulfides which are deemed to be not bio-available for microbial uptake. The calculated lowest LOD was 2–4 µg L^{-1}. The developed method was first tested in laboratory scale biogas digesters with wheat straw as substrate. After that, it was tested in a full-scale biogas plant for several months to estimate the dynamics of "active" trace elements in the range of 2–1000 µg L^{-1}. This demonstrated that cost-effective biogas plant management is possible through the application of TXRF spectrometry to monitor trace elements.

3.3 Polymers and composites

Research into the atomic spectrometric analysis of polymers and composites has followed two main themes: the analysis of micro or nano-plastics in the environment and classification for recycling purposes. The second category has made significant use of the varying forms of LIBS; usually in combination with a chemometrics method. There are, however, several other unrelated but interesting applications to be discussed.

For some time now there has been concern that micro/nanoparticles of polymers that enter the environment may act as sinks for toxic organic compounds and for heavy metals. This has led to a huge increase in the number of papers undertaking their analysis. An example was presented by El Hadri *et al.* who employed *LA-ICP-MS to determine the trace element distribution in marine microplastics*.[95] The operating conditions of the Nd:YAG laser used were optimized in terms of signal intensity and precision through the analysis of the reference material NIST 612 glass. It was possible to distinguish analytes that were additives (Cu, Pb and Sb) from those that were adsorbed to the surface (As, Cd, Cu, Fe, Pb, Sb, Sn, U and Zn). The authors proposed a spatiotemporal correlation of the sorption pattern comparing microplastics in terms of relative exposure time and time-weighted average exposure concentrations.

Single particle ICP-MS analysis has normally been applied to the analysis of engineered nanoparticles. However, in a paper by Jimenez-Lamana *et al.*[96] it was employed for the detection and quantification of nanoplastics. The polymer particles were attached to functionalized gold-containing nanoparticles. This was achieved by using the negatively charged carboxylate groups on the plastics surface with a positively charged gelatin moiety attached to the gold nanoparticle. The Au was then detected using ICP-MS operating in single particle mode enabling the nanopolymers to be quantified with <5% error. The model was developed using polystyrene particles of nominal diameter of 759, 990 and 3030 nm which mimic the natural breakdown of plastics in the environment. The quantification limit was 8.4×10^5 nanoparticles per litre and the calibration was linear up to 3.5×10^8 nanoparticles per litre. Once developed, the method was applied to the detection of nanoparticles in drinking, tap and river waters. Assuming a fully functionalized nanoplastic, the theoretical limit of detection for size of the proposed strategy was 135 nm and the maximum size that could be quantified was 1000 nm.

A paper by Chen *et al.* described the *use of LIBS for the analysis of single microplastics*.[97] The LIBS system used was discussed and a schematic diagram provided. The methodology was optimized using pure polypropylene particles of 150 μm diameter that had been treated with different concentrations of lead acetate and cadmium sulfate. Analytical signals were normalised to the C signal at 247.9 nm to compensate for any laser energy fluctuation or particle morphology effect. The Cd and Pb signals were proportional to the concentrations of analyte the polymers were exposed to. The methodology developed was applied to particles collected from seawater through filtration, the polymers identified using Raman and then the LIBS system to determine trace metal content. The advantages of the system were described as: its ability for multi-elemental determination, its speed (100 ms acquisition time – but this was limited by the speed of the laser used and could probably be reduced further), not having the requirement of chemical treatment of the samples (unlike other techniques) and its ability to analyse individual particles of micron size. The size LOD was 70 μm, but that was restricted because of the need to transfer the particle from the Raman microscope to the LIBS setup. It was thought that the particle size LOD could be improved further if a hybrid

system was developed. In that case, size would be determined by the resolution of the LIBS system and could be as low as 1 μm.

An interesting application of microplastic analysis was reported by Holmes *et al.* who developed a method for the determination of the *in vitro avian bioaccessibility of metals adsorbed to the pellets*.[98] Polyethylene pellets were collected from beaches and then exposed to an acidified (pH 2) saline solution of pepsin for 168 h at 40 °C. The extracted Co, Fe, Mn and Pb as well as their residual concentrations, *i.e.* those that could be extracted using dilute *aqua regia*, were quantified using ICP-MS. Time-based studies indicated that the Co, Fe and Mn were mobilised quickly at the beginning of the pepsin leach, but slowed to a quasi-equilibrium. The Pb leaching was more complex, with evidence of secondary maxima and re-adsorption. After the full 168 hours, the concentrations of metals extracted from the solid material were 0.014, 0.81, 38.9 and 0.10 $\mu g\ g^{-1}$ for Co, Fe, Mn and Pb, respectively representing an extraction efficiency of 50, 80, 60 and 80%, respectively.

A *metrologically traceable protocol for the quantification of trace metals in different types of micro-plastics* was described by Hildebrandt *et al.*[99] Three different microwave digestion systems, that differed in their temperature and pressure regulation as well as the number of samples that could be processed simultaneously, were compared. Also compared were different acid digestion mixtures as well as different temperatures and hold times of the digestion procedure. The digestion and analysis stages were validated by the use of six CRMs: two polyethylene CRMs (ERM1-EC680m and ERM1-EC681m), a PVC (NMIJ CRM 8123-a), two polypropylene (NMIJ CRM 8133-a and lead in plastic-QC) and an acrylonitrile butadiene styrene (ABS) CRM (BAM-H010). Determination of a total of 56 analytes (although the certified ones were: As, Cd, Cr, Hg, Pb, Sb, Sn and Zn) was by ICP-MS/MS. Recovery in the certified materials fell in the acceptable range of 95.9 ± 2.7% to 112 ± 7% for all analytes except for Cr in ABS. After optimization of the procedure, these figures improved marginally to be between 103 ± 5% and 107 ± 4% for all analytes. However, this further optimization also brought the Cr result in ABS to much more acceptable levels.

The other main topic of research has been the *analysis, characterisation and identification of waste plastics*. An example by Junjuri and Gundawar used a low-cost LIBS system to obtain analytical data and then the chemometric tools of principal component analysis (PCA) and artificial neural network (ANN) to analyse the data and to characterise 10 types of polymer.[100] The two LIBS setups used were described in detail. One comprised a Nd:YAG laser, an Echelle spectrometer, an intensified CCD, optics and an X–Y translational stage. The other comprised a low cost, compact, and portable non-gated Czerny–Turner CCD spectrometer. Data were recorded in two modes: single shot using both CCD and intensified CCD and an accumulation of 10 shots using only the intensified CCD. Spectra were collected that obtained data for Ca at 393.33 nm, H at the 656.36 nm line, K at 766.69 nm, Mg at 279.51 and 280.33 nm, N at 742.42, 744.35 and 746.90 nm, Na at 589.52 and 589.61 nm and for O at the 777.23 nm line. In addition, the C_2 Swan band and the band for CN were also measured. Data analysis using PCA was described as having "excellent discrimination".

However, use of ANN demonstrated even better performance, with discrimination rates of up to 99% being achieved. The Echelle-based instrument equipped with the intensified CCD and using 10 laser shots provided data that had 97% discrimination. However, the Czerny–Turner-based instrument equipped with the ordinary CCD and using only one laser shot provided a similar performance. This latter instrument was therefore much lighter, smaller, was more portable and less expensive than the Echelle instrument. It also provided data much more quickly (by a factor of 15) because of a reduced amount of time required to train and test the ANN model.

A paper by Brunnbauer *et al.* described the use of *LIBS combined with PCA and K means clustering to classify bulk polymers as well as individual layers of layered polymer composites*, *e.g.* two-sided sticky tape.[101] The LIBS parameters (laser energy, gate delay, laser spot size and the gaseous atmosphere) were all optimized. A short gate delay resulted, in increased emission intensities of the elements C, H and O and longer gate delays improved the signal-to-noise ratio especially in the wavelength range of the C2 swan band. The compromise conditions were tabulated. Bulk polymer sample types from a 3-D printer included polyethylene, polyacrylate, acrylonitrile butadiene styrene, polyvinyl chloride (PVC) and polylactic acid. The two-sided sticky tape was known to comprise four different layers: a polyethylene liner, polyacrylate adhesive layer, PVC support and a second polyacrylate adhesive layer providing a total thickness of 250 μm. The PCA was incapable of discriminating between PVC and polyacrylate. However, the K means clustering discriminated between all polymer types. The obtained 3D distribution of the different polymers present in the multilayer sample was compared with data obtained from a microscopic cross-section of the investigated sample. The sequence of the different layers present in the sample was correctly classified and also the thickness of each layer is in good agreement with the microscopic cross-section.

An array of different spectroscopic techniques (attenuated total reflection (ATR)-FTIR, near IR reflectance spectroscopy, LIBS and XRF) and seven different classification methods were used by Michel *et al.* to classify different polymers.[102] Classification methods included: naive spectral matching and three machine learning classifiers (support vector machine (SVM), *k* nearest neighbours (kNN), and linear discriminant analysis (LDA)), each of which was also coupled with PCA: PCA-SVM, PCA-kNN, and PCA-LDA. Polymer types tested were: polyethylene terephthalate (PET), high density polyethylene, PVC, low density polyethylene, polypropylene and polystyrene. The success rates for the different techniques using the different classifiers were tabulated. Linear discriminant analysis proved to be the best classifying method for the ATR-FTIR, near IR-reflectance and LIBS analyses with a success rate of 99 ± 1, 91 ± 1 and 97 ± 2%, respectively. The best classification success rate for XRF analysis was obtained using *k* nearest neighbour; but was much lower at 70 ± 4%. The last paper of interest in this little sub-section was provided by Liu *et al.* who described the development and use of a software system to be used in conjunction with LIBS analysis to analyse different plastics.[103] Partial least squares discrimination analysis (PLS-DA) and

partial least squares regression (PLSR) were used for qualitative and quantitative analysis of plastics. The LIBS devices, including laser, spectrograph, delay generator and sample holder, were automatically controlled by the software. The plastic database was created with the capability of input, query, modify, delete and storage. It included a basic element database based on NIST and a dedicated plastic database which contains industrial plastics, plastic bottles and standard samples. A denoising method, a baseline correction method and a peak detection method enabled material identification based on PLS-DA and quantitative analysis based on PLSR were all realized by the software. The software performance was excellent with an identification accuracy of 99.80% for industrial plastics being achieved.

Several other applications of interest have been published. One by Costa described *LIBS calibration strategies for the determination of Pb* in polypropylene recycled from car batteries.[104] The LIBS parameters were optimized using central composite design, a multivariate approach to optimization and the calibration strategies evaluated were: partial least squares (PLS), principal component regression (PCR) and two point calibration transfer. The "percent trueness" was calculated by comparing the data obtained using the different calibration strategies with the Pb concentration in the samples obtained by using a microwave-assisted acid decomposition method followed by ICP-OES analysis. This reference method was validated through the analysis of the certified reference material ERM-EC681k polyethylene. Results for the calibration strategies ranged between 74 and 139% for PLS, 74 and 123% for PCR and 100 and 127% for two point calibration transfer. Precision was also very variable, ranging between 3 and 37% for PLS, 5 and 30% for PCR and 6 and 21% for two point calibration transfer. Although the results and precision were very variable, the authors still concluded that they were fit for purpose.

A *forensics application of polymer analysis* was reported by Nishiwaki *et al.* who described the non-destructive analysis of individual white polyester clothing fibres using synchrotron radiation microbeam XRF with vertical focussing.[105] A Kirkpatrick–Baez mirror was used to focus the 20 keV X-ray beam onto individual fibres from clothing commonly sold in Japan. A focussed beam of dimensions 2 μm × 300 μm was approximately 12.8 times more sensitive than synchrotron radiation XRF with an un-focussed 300 μm × 300 μm beam. Scatter plots of the Ti k_β/Sb $L_{\alpha\beta}$ against the Zr k_α/Nb k_α X-ray intensities were used to discriminate between individual fibres. These elements originate from catalysts used during the manufacture of the material, *e.g.* polymerization catalysts, transesterification catalysts, delustering agents (titanium dioxide) and their contaminants (*e.g.* Br, Co, Cu and Zn). The fibres can therefore be classified according to the methods used to synthesise them. Precision for the Ti k_β/Sb $L_{\alpha\beta}$ and Zr k_α/Nb k_α intensity ratios was in the range 1.5–7% RSD and 1–8% RSD, respectively. Using these ratios as well as the extra elements for classification, 98% of the fibres were differentiated.

Although XRF is a powerful analytical tool, most instruments cannot *quantify analytes with very low atomic number* (*i.e.* less than 11, Na). Aidene *et al.* published a paper reporting a method

whereby scattering of monochromatic X-rays at different incident radiation angles provided quantitative information on both physical and chemical properties of the plastics.[106] The XRF instrument contained both a copper and a molybdenum tube and both were used at radiation incident angles of 0.5, 1 and 2°, yielding six different measuring modes. Such radiation incidence angles provided scattered radiation angles of 90.5, 91 and 92°. The polymer blocks were placed in the cell holder without undergoing any treatment and were analysed using a spectral accumulation time of 300 s. The chemometric tool of partial least squares (PLS) regression was used to relate the scattered spectral radiation with the concentrations of C and H, hence enabling physical sample properties such as density, mass per atom and water absorption to be elucidated. Root mean square error of cross validation was used as the performance metric and provided values of approximately 4% for C.

Calibration of LA-ICP-MS measurements is known to be problematic and has been tackled in a paper by Kuczelinis *et al.* who employed a method of *standard addition using dried picoliter droplets* of aqueous standards.[107] A dosing device based on a modified commercial ink cartridge and dosing interface was developed to deliver a droplet on demand. Once dried, the residue had dimensions in the low μm range, yielded LOD at the fg level and provided a calibration that spanned six orders of magnitude. Since it is a standard additions method, there is a necessity to measure the sample mass ablated. This was achieved using microscopical analysis of the crater diameter and depth, *i.e.* its volume, and then using its density to calculate a mass. The methodology was applied to the successful analysis of polymeric thin films and to a glass cover slip.

Rodrigues *et al.* described a method for the determination of analytes (Cr, Fe, Mg, Mn, Na and Ni) in *samples of diphenylmethane diisocyanate*, a material used during the formation of polyurethane polymers.[108] Samples (0.5–23 mg) were weighed using a balance capable of 0.01 mg resolution into a solid sample introduction device and then analysed using GFAAS. Calibration was achieved by pipetting aqueous standards onto a solid sampling platform and then running the normal furnace program. Zeeman background correction was used in all cases. Extremely low LOD were obtained with values ranging from 0.06 ng g^{-1} for Fe up to 3 ng g^{-1} for Ni. The results obtained using the method were compared with those obtained using a microwave assisted acid digestion in which 400 mg of sample was digested using a mixture of nitric and sulfuric acids. A second alternative method was also employed in which 200 mg of sample underwent a microwave induced combustion. Both alternative methods used ICP-OES and ICP-MS to obtain the data. No significant difference was observed between the data obtained from the proposed method and those from the alternatives.

The *measurement of polymeric thin film thickness using EDXRF and multivariate analysis* of the raw data was reported by de Almeida *et al.*[109] Nine polymeric films with thickness ranging from 1.5 to 7.6 μm and of differing composition were used for calibration and validation processes. A univariate approach was first adopted, but failed to determine thickness adequately with the coefficient of determination being, at best, 0.873 (for the Rh-

k$_\alpha$ Compton counting rate against film thickness). Other spectral regions yielded even poorer coefficients. The multivariate regression was achieved by employing PLS, with three different regions of the X-ray spectrum being used. Eight of the films were used for training the model and one for validation. The coefficients of determination ranged between 0.993 and 0.998, indicating excellent ability and this was achieved with an acceptable precision of 4% RSD. Scanning electron microscopy was used as an alternative technique to validate the results.

4 Inorganic chemicals and materials

4.1 Catalysts

The review period has seen an uptick in papers reporting the *coupling of electrochemical flow cells with ICP-MS for the tracking of electrocatalyst stability under operating conditions*. The configuration enables potential- and time-resolved dissolution monitoring of individual metal counterparts with extremely high sensitivity. It has been effectively employed to monitor Pt dissolution in gas diffusion electrode (GDE) half-cells,[110] carbon supported single atom catalysts,[111] bimetallic PtRu/C alloy[112] and PtNi alloy[113] catalysts and proton-exchange membrane fuel cells.[114,115] The technique was also employed to assess the stability of IrO$_2$ coated TiO$_2$ core–shell microparticles used as oxygen evolution reaction catalysts in water electrolysers.[116] In each case, the mechanistic insights gained improved understanding of the operation and limitations of the electrochemical fuel cells tested. It also highlights how atomic spectrometry can play a role in sustainable development.

The accurate and precise determination of *PGMs in catalytic convertors* remains an area of interest, likely driven by their sustained high market price. This is a very mature topic, and it is difficult to find truly novel work. Rather, papers are often minor extensions of well-established procedures. For example, an 'optimized' microwave extraction procedure for determination of Pd in Pt in spent auto catalysts by ICP-OES and GFAAS failed to enthuse this author.[117] Preconcentration methods continue to be reported to allow reduced limits of detection. Zhang *et al.* described a bismuth fire assay method for the preconcentration of precious metals for analysis using ICP-OES.[118] Ground samples were mixed with 48 g Bi$_2$O$_3$, 25 g Na$_2$CO$_3$, 5.5 g wheat flour and 80 g slag silicate. The mixture was transferred into fire-clay crucibles and fused at 1080 °C for 25 min followed by dissolution of the cupel in *aqua regia*. Measurement of multiple preparations indicated a repeatability better than 0.21% at ~2000 ppm concentration for Pt. As well as reporting an optimized method, the group discussed at length the thermodynamic mechanism of the process. Anthemidis and Tzili reported a quick and simple online flow injection technique for the preconcentration of Pd prior to determination using FAAS.[119] The method was based on the in-line formation of palladium diethyldiphosphate and sorption on a PTFE turning column packing. Elution with MIBK prior to atomisation and quantification achieved a preconcentration faction of 114 for a 60 s run time. The detection limit was 0.9 μg L^{-1} with an RSD of 2.8% at 20.0 μg L^{-1}.

An interesting collection of papers reporting the use of ICP-MS/MS as a screening reactor to monitor intermediate species formed during gas phase reactions was reported by Zhu *et al.*[120-122] Catalytic metal ions of interest were generated in the plasma and isolated using the first quadrupole mass filter. These were then introduced into the collision-reaction cell with gaseous reactants where reactions took place. The product ions and newly formed metal adducts were then immediately analysed *via* mass spectrometry using the second quadrupole, allowing rapid assessment of the possible formation pathways. The technique was used to understand reaction pathways for the conversion of ethanol to butanol catalysed by a Ce, Ir, Ru, Zr, and TiO catalyst and the TaO catalysed coupling of methane with ethane and ethylene.

A quick, flexible and reliable method was developed, based on *LA-ICP-MS, for accurate assessment of nanoparticle catalyst materials* with sample amounts in the picogram to nanogram range.[123] The calibration and quantification was a variation of a micro-dried droplet approach, where self-aliquoting wells were used to avoid common drawbacks, such as the "coffee stain" effect and size discrimination due to increased evaporation rate towards the rim of the droplet. Wells were prepared as 20×5 arrays using a NWR213 nm laser to cut 50 μm holes in polycarbonate plate. Plates were loaded with 10 μL of sample and any excess removed with a glass slide. The small volume of liquid in each well evaporated within seconds allowing almost immediate analysis. Accuracy of the method was assessed by the analysis of AUROlite reference material, with results for Au (0.74% wt ± 0.13% wt) in good agreement with the certified value (0.8% wt). The study highlighted the difficulties in obtaining a genuinely homogenous sample when significantly reduced sample sizes, as low as 3 pg, are used for analysis. In the reported case, a minimum 300 pg of material was required to cancel out any micro-heterogeneity.

4.2 Forensic applications

The *interrogation of gunshot residue (GSR)* continues to be a major inorganic forensic application of atomic spectrometry, serving as alternatives to the established SEM-EDX analysis. Madeira *et al.* reported the successful discrimination of GSR collected from the hands of shooters of four different firearms using WDXRF.[124] Statistical analysis of trace component concentrations and Rh tube Compton scattering arising from the organic components in the sample allowed identification of the GSR examined, including those that were Ba, Pb and Sb free. Analysis was performed using a standard laboratory sequential spectrometer equipped with a 4 kW Rh target X-ray tube and a range of diffracting crystals. Spectral data were processed using smoothing, baseline correction, normalisation and scaling prior to analysis by HCA, PCA and nearest known neighbour techniques. Detailed elemental mapping of tape-collected GSR was achieved using LA-ICP-MS equipped with a 213 nm Nd:YAG pulsed laser.[125] A 4 mm² area was scanned in 33 minutes with the ablation of 100 lines, 2000 μm in length, and a spot size of 20 μm. A constant flow of He was used to carry ablated material to the plasma. Accurate determination of

[137]Ba, [121]Sb and [208]Pb allowed for the visualisation of collected samples, whilst ternary distribution plots allowed discrimination of collected GSR particles from other sources of characteristic elements such as brake dust and fireworks. The mapping of 15 elements associated with GSR using LA-ICP-MS was also reported by Aliste *et al.*[126] Sampling was performed using swab devices impregnated with EDTA, with the material collected from the nostrils of shooters where GSR persisted for longer periods in the nasal mucus than on the hands. Particles were detected 6 h after shooting occurred.

Trace elemental profiling coupled with chemometric and other statistical techniques was utilized to *characterise and discriminate a variety of pyrotechnic sparklers used in the production of homemade explosive devices*. The concentration of 50 elements in 48 sparkler samples from eight brands available in Australia were determined using ICP-MS. Ground up samples were extracted in 10% nitric acid for 24 prior to analysis and a seven-element profile, consisting of Co, Ni, Sb, Sn, Sr, V and W, developed to identify the correct brand. The paper demonstrated the potential of using trace element data and chemometrics to correctly identify the origin of materials for forensic evaluation.

Several papers have reported forensic applications of glass analysis. Akmeemana *et al.* discussed the *standard method ASTM E2927-16e*, which is a consensus-based approach to sampling, sample preparation, quantitative analysis and "match" comparison of chemical properties.[127] Using glass from different manufacturers prepared days, weeks and months apart and analysing using LA-ICP-MS enabled the analytical data to be studied using chemometrics. Likelihood ratios were established that range between 10^{-3}, where the glass comes from different manufacturers or from the same manufacturer months apart, to 10^3 where the glass samples are from the same manufacturer and prepared on the same day. The paper was very light regarding the analytical chemistry detail and concentrates more on the chemometric side of the work. However, is worth mentioning simply because it is a standard method. The method requires a glass fragment with dimensions of approximately $400 \times 200 \times 100$ μm. A paper by Becker *et al.* reported attempts to reduce the size of the glass particle required.[128] Ten small fragments of glass along with the standard reference materials FG1, FG2, NIST SRM 610 and NIST SRM 612 were mounted on a 3D moveable stage. Float glass standard FGS 2 was used as external standard, FGS 1 was used as a quality control sample and NIST SRM 612 served as a standard to quantify elements not certified in FGS 2. The samples were then analysed using LA-ICP-TOF-MS using an ArF excimer laser, the operating conditions for which were tabulated. The spot size of the laser was only 90 μm so the dimensions of the glass particles required for analysis could be reduced to $100 \times 100 \times 33$ μm. This represented a sample mass reduction from 20 μg to only 0.8 μg. A total of 110 laser shots were made on each sample, with data from the first 10 being ignored because of potential surface effects. Data for 18 analytes were obtained and a modified 5-sigma criterion was used to identify match and no match samples from different sources.

A total of 17 laboratories participated in three *inter-laboratory comparisons for the forensic analysis of glass fragments from car windshields*.[129] The report, by Corzo *et al.* reported the assessment of the data obtained using refractive index as well as from LIBS and μ-XRF. Every laboratory was sent three fragments of each of several samples, some of which were known samples and others were "unknown". The exact details of each of the comparisons were given in the paper. The most interesting was in comparison three, where the participants were given a case scenario where three questioned glass fragments (Q1) from suspect one and three fragments (Q2) from suspect two were sent to the participants. Participants were asked to follow ASTM E1967 (for RI) and ASTM E2926 (for μXRF). In this example, all laboratories using refractive index correctly associated Q1 to K1, resulting in no false exclusions. All labs also correctly excluded all K1/Q1 and K1/Q2 pairs, resulting in no false inclusions. Similar results were obtained for those laboratories using μ-XRF and the labs using LIBS. Overall, the correct association rate was greater than 92% for all three techniques for samples that originated from the same source. For samples that originated from different vehicles, the correct exclusion rate is 82, 96 and 87% for refractive index, μ-XRF and LIBS, respectively.

Almirall *et al.* published a paper reporting the results of 17 major and trace elements in new *float glass materials intended to be used as matrix matched standards for LA-ICP-MS forensic analysis* of glass.[130] Three Corning glasses, one each at low, medium and high concentrations of analytes (CFGS1–CFGS3), were distributed to seven laboratories who then analysed them using the standard ASTM E2927-16e1 method. A range of ICP-MS instruments and LA units were used during the study, with the diameter of the laser sampling spots being in the range 50–100 μm. A total of eight sets of data were obtained using the standard LA-ICP-MS methodology along with one set obtained using the standard ASTM E2926-17 μ-XRF method. Precision was typically better than 3% RSD within each laboratory and better than 5% RSD between labs. Given the laser spot size and the precision achieved, it was concluded that the glasses were homogeneous. Results were checked against the existing SRMs NIST 1831 and FGS2. At present, the materials developed in this study are not yet regarded as being SRMs. However, work is on-going with NIST to make them so.

Scatter is a problem associated with the forensic μ-XRF analysis of glass fragments, a problem exacerbated by their small size (typically <1 mm). A study by Corzo and Steel attempted to *improve the signal to noise ratio of μ-XRF measurements by reducing the scatter produced by the sample stage*.[131] This was achieved by using 3D printing to produce a plastic mount that enabled the sample to be as raised as possible from the sample stage. Results for LOD from the analysis of NIST SRM 1831 were compared between a simple sample cup, a stage and two different mounts as well as for two different instruments. In both instrument cases, the LOD improved for the cup and the mount when compared with the standard stage, although the improvement was not uniform across the analyte mass range. Instead, the light elements, *e.g.* Mg and Na as well as the heavy elements Sr and Zr, were improved by a factor of approximately two using the mount.

Other analytes, *e.g.* Ca, Fe, K, Mn and Tl showed no improvement in LOD. Raising a specimen above the stage can improve the analysis of any type of sample that is partially transparent to the primary beam or small relative to the primary beam, as this will ensure that the background scatter is predominantly from the specimen itself and not the instrument. As particles approach bulk thickness (*i.e.* they become opaque to the primary beam), the stage plays an insignificant role and raising the specimen above the stage is not necessary. A second method to improve the LOD, that of using primary beam filters, was also tested during the study. Elements with lines in the high energy range (*e.g.* Rb, Sr and Zr) showed the greatest improvement in LOD. Unfortunately, different elements demonstrated an improvement whilst employing different filters.

A standardized method for the in-*air particle induced gamma-ray emission (PIGE) analysis of glass fragments that uses a tantalum window material as a current normaliser* was reported in a paper by Sharma *et al.*[132] Glass fragments were irradiated in air using a 3.5 MeV proton beam and simultaneous measurement of the prompt gamma rays from proton-induced reactions of isotopes of low atomic number elements *e.g.* Al, B, Mg, Na and Si as well as those at 135 or 165 keV from the tantalum window were measured. The results were compared with those obtained using a conventional (in vacuum) PIGE method in which sample in pellets of cellulose were analysed. Both methods were validated through the use of soda lime and borosilicate glass reference materials. The external (in air) method was both rapid and non-destructive and was able to discriminate between the two different glass types qualitatively and quantitatively. The only analyte capable of discriminating soda lime (automobile) glasses was Al. Therefore, an instrumental neutron activation analysis (INAA) method was also developed that enabled 13 analytes (including some transition and REE) at both major and trace levels, to be determined. Statistical analysis of the data using dendrograms and cluster analysis indicated that the glasses used in the study fell into three distinct groups. This gave the methods developed the potential to be used for forensic analysis.

4.3 Building materials

The application of LIBS in the field of civil engineering continues to receive attention due to its portability, speed of analysis, minimal sample preparation and multi-element capability. Bryukhova *et al.* reported its used for *the evaluation of aging of reinforced concrete structures*.[133] The paper focused on the detection of the corrosion products Cr, Fe and Mn, emerging on the structures surface. However, this was limited to surface areas painted with corrosion products. The application of LIBS for the identification of concrete type was reported by Volker *et al.*[134] Measurements were performed with a diode-pumped low energy laser (1064 nm, 3 mJ, 1.5 ns, 100 Hz) in combination with two spectrometers covering the UV and NIR spectral range. A linear discrimination model effectively allowed classification of 10 different cement types. However, the analysis was found to be sensitive to moisture and sample matrix and thus required further work.

Sulfur can occur in concrete aggregates in the form of sulfate (gypsum and anhydrite), as well as sulfides (pyrites, marcasite and pyrrhotite), the latter being linked to concrete degradation. Cruz-Hernandez and colleagues exploited the variation in intensity of the *S Kα, S Kβ and S Kβ′ peaks due to changes in the electronic environment of S in different oxidation states to determine sulfate/sulfite ratios in cement using WDXRF*.[135] Measurements were performed using a basic laboratory WDXRF spectrometer calibrated using mixtures of $CaSO_4$ and FeS blended with synthetic cement matrix. Since S should only be present as S^{6+}, sulfate, and S^{2-}, sulfide, the impact of matrix effects was investigated by comparing the summed ratio of each species to total S as determined by an independent method. Any significant deviation from 1 indicated an error. This method was validated for S concentrations between 0.1 and 2 wt%, so long as the lead content was below 8 wt% since the Pb Mβ and Pb Mα lines overlap with S Kβ, S Kβ′.

A detailed overview of the optimization and validation of an EDXRF method for the determination of metals in cement leachates by means of chemometric evaluation of the analytical variables was reported.[136] The method enabled the determination of As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb and Zn in liquid leachates, with uncertainty ranging from 9.1% for Cr to 19.1% for Zn and LOD from 0.022 mg L^{-1} for Pb and 0.080 mg L^{-1} for Cu. The researchers concluded that the mass of liquid samples presented to the spectrometer significantly affect the quality of the analysis. Given the extensive fundamental knowledge of critical depth, this is hardly ground-breaking.

4.4 Fertilizers

The rapid, standoff analysis capability of LIBS lends itself well to the application of *quality monitoring on production conveyer belts*. One such example was reported by Zou *et al.* for the online monitoring of H_2O and KCl in potash fertilizers.[137] The research focussed on the development and application of machine learning models, including back-propagation neural networks and convolutional neural networks, to overcome the challenges caused by water on the collected LIBS spectrum. A compact LIBS setup was installed on a potash production line, continuously collecting spectra at a rate of approximately 3 per second. Offline samples were collected at hourly intervals with H_2O and K concentrations determined by gravimetric and ICP-OES methods. In total 119 samples were collected, and the corresponding LIBS spectra combined to train the data models. With the rapid evolution of data science and machine learning, this looks like an area that could see major developments in the near future.

In a more conventional approach to the analysis of fertilizers, Patidar *et al.* detailed the development and validation of an ICP-MS method for the determination of 11 trace elements.[138] The work focused on the utilisation of an Argon Dilution Kit, available with most modern instruments, to address the issues associated with high dissolved solids. The optimized method had LODs ranging between 1 and 7 ppb with typical repeatability of 2–5% RSD at 80 ppb. A method of microwave assisted digestion for the determination of 19

elements in phosphate fertilizers and related materials by MIP-OES was reported.[139] Whilst not particularly novel in approach, the paper does document the capability of MIP-OES for the determination of trace analytes in these complex matrices.

4.5 Other inorganic materials

The diversity of the applications of atomic spectrometry was once again evident in the review period, with studies ranging from the analysis of high-purity germanium oxide semiconductor material[140] to a review of heavy metals in children's chalk sticks in China.[141] The former utilised the reactivity, and subsequent volatility, of Ge and chlorine gas to remove matrix interference by distillation of $GeCl_4$ at 120 °C. Nguyen *et al.* reported a simple separation system for the elimination of polyatomic interferences encountered during the determination of ultra-trace rare earth elements (REE) in high-purity Eu_2O_3 and Yb_2O_3 using ICP-MS.[142] Whilst many REE impurities could be determined with a standard ICP-MS setup, monoisotopic $^{169}Tm^+$ and the most abundant $^{175}Lu^+$ isotope suffered from significant interference from $^{153}Eu^{16}O^+$ and $^{174}YbH^+$ ions formed in the plasma. Interference removal was achieved using chromatographic separation of the high concentration of matrix elements by reverse-phase HPLC using a C18-silica column impregnated with 2-ethylhexyl, 2-ethylhexyl phosphonic acid and a dilute HNO_3 mobile phase. This separation method was ideal for coupling with ICP-MS. The optimized method allowed for complete separation of analyte and interferents within 3.5 minutes.

The *matrix plays a crucial role in trace determination of analytes by all atomic spectrometry* techniques and the skill of the analytical chemist is knowing how to overcome matrix effects. A simple approach, based on the standard dilution analysis method, was presented by Sloop *et al.*[143] Unlike conventional standard dilution analysis, where two solutions are mixed during measurement, the team's approach consisted of a 50% sample 50% standard solution and a 50% standard 50% blank solution to produce a matrix matched two-point calibration curve. The method was used to determine Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in four matrices: 1% v/v HNO_3, 20% v/v HNO_3, 0.1% m/v Na, and 0.1% m/v Ca solutions using MIP-OES, ICP-OES and ICP-MS. Results were shown to be consistent with those obtained using other calibration methodologies such as external standardisation, internal standardisation and standard additions. In many cases, improved recovery was obtained for the proposed method compared with the conventional calibration methods. The role of the matrix in trace analysis using TXRF, often marketed as 'matrix free', was studied by Dhara.[144] Dilute multielement ICP standards were measured with varying concentrations of the matrix elements Al, U and Zr. Recovery rates were calculated against theoretical concentrations and were within 7% for analytes up to 20 μg mL^{-1} and within 12% for higher concentrations. Of the three matrix elements studied, the most pronounced effects were observed with increasing atomic mass and concentration, *i.e.* 1000 μg mL^{-1} uranium.

Accurate determination of *impurities in a bulk matrix using glow discharge mass spectrometry (GD-MS) requires a sample and*

standard of identical matrix to be measured. Alternatively, relative sensitivity factors, RSFs, can be calculated from reference materials of similar matrix. However, these are sensitive to variations in the discharge conditions (amongst other things). Paudel and Sabatino studied the impact of changes in current, voltage and argon flow on the determination of 16 elements in silicon pressed onto an indium sheet.[145] The variation in argon flow was quantified along with impurity elements to identify a range of discharge conditions where the deviation is minimum. Further, the discharge settings leading to an optimum crater in a flat silicon sample were also considered before finalizing the optimum discharge parameters for RSF determination. The RSFs were estimated and verified by subjecting the CRMs NIST 57b and 195 to the discharge condition of 2.3 mA and 1.2 kV and comparing with certified values. The estimated RSFs were further verified by ICP-MS analysis, where comparable data were obtained with errors below 20% for most elements.

The varied applications of LIBS continued to feature during the review period. The approach of sampling salt solutions by drying on filter paper prior to LIBS analysis was used for the determination of Ba, La and Sr in LiCl–KCl salt mixtures.[146] Using Yb (369.42 nm) as an internal standard, linear calibration curves were obtained from 50–800 ppm for Sr (421.55 nm), 50–1000 ppm for Ba (455.40 nm) and 300–4000 ppm for La (394.91 nm) with a detection limit of 21, 19 and 68 ppm, respectively. The same approach was used by Kumar *et al.* to determine Sr in sea salt samples using a weak Na I line at 330.2 nm for signal normalisation.[147] The team found that preparation and analysis of samples in triplicate significantly improved the quality of analysis and optimized conditions enabled the determination of Sr with an LOD of 2 ppm and precision of 5%. The direct analysis of liquid boric acid solutions was achieved by creating a laminar liquid jet of sample using a nebuliser and peristaltic pump.[148] A double pulse LIBS setup was used to excite the sample, with molecular emission bands for BO and BO_2 interrogated by laser ablation molecular isotopic spectrometry. The use of a double pass laser increased the intensity of molecular emissions tenfold compared with the single pass configuration, enabling determination of B with an LOD of 72 ppm.

An interesting and novel technique for the *suppression of self-absorption effects in LIBS measurements* was reported.[149] The experimental setup consisted of a 1064 nm YAG laser focussed laterally 6 mm above the sample surface generating a He gas plasma with flowing helium. A second 355 nm YAG laser focused directly on the sample surface created the target plasma. Ablated sample ions arrive at the secondary He plasma in the ground state, where they were excited through a Penning-like energy transfer with excited He ions. The approach was demonstrated for the determination of K and Na in salt samples, where concentrations would normally be beyond the linear range of standard LIBS.

Yang *et al.* reported the use of *reactive gas LA-ICP-MS/MS to overcome the isobaric interferences encountered when determining trace level Rh and Pd in copper minerals*.[150] Single quadrupole ICP-MS suffered from $^{63}Cu^{40}Ar^+$ and $^{65}Cu^{40}Ar^+$ overlaps on the ^{103}Rh and ^{105}Pd analyte masses that were only partially removed by

kinetic energy discrimination. Ammonia reactive gas used in the analysis by MS/MS mode allowed quantitative removal of interference through reaction with Cu ions to form $Cu(NH_3)^+$ ions. The optimized method enabled the accurate determination of Rh and Pd with LODs 1.7 ng g^{-1} and 7.0 ng g^{-1}, respectively.

4.6 Ceramics and refractories

In truth, there has been relatively few papers of interest in this section published during the current review period. Following on from last year, archaeological ceramics or those of cultural heritage have been discussed in their own section (Section 5.3). Several papers have been published describing diffusion experiments with data being obtained using SIMS or TOF-SIMS. However, the novelty arises in the ceramic type rather than the atomic spectrometry for which diffusion analysis using these techniques is routine. Those papers of interest that have been published are of diverse subject areas.

A *dried droplet calibration approach for the LA-ICP-MS* analysis of glass and ceramic was described by Guo *et al.*[151] A dispersant had to be used to ensure uniform distribution of analyte in the droplet and its residue once dry. The optimized conditions were a Pluronic F-127 (dispersant) concentration of 2% and a drying temperature of 85 °C. Precision was better than 20%. Analysis of the dried droplets did not affect ablation of the sample material and the residue from the droplet could be ablated in one raster of the laser. Regression coefficients of calibrations were excellent, ranging between 0.9936 and 0.9999 without the requirement of an internal standard. The method was applied to a YAG crystal and the NIST SRM 612 glass. Data in good agreement with the certified values were obtained for the glass sample. As a further method validation step, the samples were also analysed using ICP-OES and ICP-MS. Results from the proposed method were again in good agreement with those from the alternative methods.

An interesting application presented by Yahiaoui *et al. correlated the hardness of a sample with its spectrographic properties*.[152] During the study, XRD and Raman spectroscopy determined structural properties, such as the grain size and phase of crystallization, of the alumina samples. A morphological study was also undertaken using SEM. In addition, LIBS with a Nd:YAG laser and XRF were used to analyse three alumina samples which had purities of 99.990, 88.869 and 73.842%. A commercial microhardness tester and a nanoindenter were used to calculate the Vickers hardness and Young's modulus of the three samples. After optimization of the LIBS operating conditions based on the best signal to noise ratio, a gate width of 4 μs and a delay time of 2 μs, were used for all samples. After accruing several LIBS spectra for each sample, correlation curves of the surface hardness were plotted against the Al, Ca and Mg ionic to atomic line intensity ratios, the plasma temperature, the electron density and the vibrational temperature of AlO radical. Linear relationships with correlation coefficients of greater than 0.98 were achieved for the ion to atom line intensity ratios, of 0.92 for the electronic temperature, 0.82 for the electron number density and 0.99 for the vibrational temperature of the AlO radical.

Ceramics are generally regarded as being inert. However, a study by Reclaru *et al.* questioned whether *zirconia bioceramics and ceramics intended to come into contact with skin are inert.*[153] Zirconia ceramics can change from a stable tetragonal phase to a less stable monoclinic form over time. Different preparation methods using various additives containing different contaminants, grain boundaries and porosities may all have an influence on the corrosion behaviour leading to the samples potentially not being as inert as first thought. To this end, the authors studied the ceramics using several different methodologies. In one, the ceramics were dissolved in a mixture of nitric and hydrofluoric acids (60 : 40). Other methods looked for leaching from the bioceramics using various media designed to mimic biological fluids. These included 0.07 M hydrochloric acid (for dental bioceramics and ceramics used in jewellery and in watches), 0.1% sodium fluoride and 0.1% potassium fluoride, and an artificial sweat medium (undertaken according to the standard EN 1811-2011). For all cases, a suite of elements (24) was determined using either ICP-OES or ICP-MS after a 10 or 100-fold dilution, respectively. Numerous ceramic types were tested including some cermets (composites of ceramics and metals), in all cases, the "inert" ceramics were found actually to have numerous toxic elements leached from them. The elements and their leached concentrations varied, but in some cases, the concentrations were extremely high.

Zirconia-based ceramics were also studied by Prymak *et al.* who synthesised and then analysed them, magnesium oxide ceramics and mixtures of magnesia/zirconia.[154] Methods of analysis to determine the incorporation of Mg into the zirconia included SEM, XRD, EDXRF and, after dissolution in sulfuric acid, AAS. The hardness and Young's modulus were also determined. Although the AAS analysis demonstrated incomplete dissolution and hence, lower Mg results than expected, the samples were homogeneous. Porosity was between 30 and 37%. Once thoroughly characterised, the samples were tested for their osteogenic potential *in vivo*. The mechanical analysis, alkaline phosphatase activity and calcium and collagen production indicated that the zirconia/magnesia ceramics hold a great potential for bone tissue engineering.

4.7 Glass

Various applications of the analysis of glass have been prepared during this review period, but the most common theme has been of a forensic nature. For those applications, minimally damaging methods of analysis are required to preserve the evidence. Therefore, techniques such as XRF, LIBS or LA-ICP-MS are the most common. The forensic applications of glass analysis have been placed in Section 4.2, the reader is referred there for those.

The *production of reference materials* is always useful as it helps validate methodology. A paper by Chen *et al.* reported the production of two silicate glass standards containing precious group elements (Au, Ir, Os, Pd, Pt, Re, Rh and Ru) at relatively high concentrations.[155] The materials were prepared at very high oxygen potentials, *i.e.* at elevated pressure. Experimental details of their preparation were provided. The samples were then analysed using SEM, electron probe microanalysis (EPMA) and LA-ICP-MS. Although EPMA is not a sensitive technique, it could be used because the concentration of the analytes were sufficiently high. This is important because the correction procedures needed with this analytical method are well understood and so good accuracy is achievable using only pure metal or similar readily available substances as standards. The LA-ICP-MS was undertaken using an ArF laser operating at 193 nm and at a frequency of 5–10 Hz with an energy of 60–80 mJ. This provided craters of between 47 and 100 μm diameter. Calibration was achieved through the analysis of the SRMs NIST 610 and 612. The SEM data indicated that there were no remaining metal nano-nuggets, although this was limited by the resolution of the instrument (10 nm). It was declared that the glasses were homogeneous down to at least the micron scale. Chemical analysis indicated that Pt was present in both materials at between 400 and 5000 mg kg^{-1}, with the other analytes being less. The data obtained using EPMA and LA-ICP-MS were in good agreement.

Another paper to discuss *classification of glasses* was published by Devangad *et al.*[156] These authors used a LIBS system (described and shown schematically in the paper) to obtain analytical data for iron phosphate simulated nuclear waste glasses and then used assorted chemometric tools to analyse the data. The chemometric tools were PCA, partial least squares-discriminant analysis (PLS-DA), partial least squares regression (PLSR) and the support vector machines support vector classification (SVC) and support vector regression (SVR). The paper provided a brief but useful introduction to each of the chemometric methods that a new worker in the area could find useful. The main elements of interest were Cr, Sr and Ti. Classification studies were made using PCA, PLS-DA and SVC. The PCA was unsuccessful in classifying all groups of glasses. The supervised techniques of PLS-DA and SVC were more successful, with PLS-DA classifying 90% successfully, and the SVC 100% (for both calibration and validation sets of samples). For quantitative analysis, SVR and PLSR were used. For PLSR, the root mean squared error of prediction (RMSEP) was 0.16, 0.20 and 0.08% for Cr, Sr and Ti, respectively. This was marginally better than those obtained using SVR. It was concluded that such an analytical approach could usefully be employed for process control of nuclear waste, nuclear forensics *etc.*

An interesting application of LIBS was reported by Stefanuk *et al. who increased the sensitivity of the analysis of glass by coating it with a few layers of graphene* prior to analysis.[157] This is an extension to the now accepted nanoparticle enhanced LIBS analyses reported in previous years. The graphene layers were deposited onto copper foils using cold vapour deposition by CVD using methane and hydrogen as precursors. All depositions were performed at atmospheric pressure at 1000 °C for a duration of 30 min. After deposition, the copper foils were dissolved in a chemical solution of iron nitrate and, after repetitive washing cycles, the graphene layers remained floating in distilled water. They were then transferred to the sample to be analysed (Corning microscope slides). Each round of deposition resulted in six or seven layers of graphene being deposited. Using a Nd:YAG laser operating at 355 nm, the sensitivity

of the LIBS determination of several analytes including Ca, Mg, Na and Si was enhanced significantly. Six-seven layers provided a much higher intensity than the plain glass surface and 12–14 layers enhanced sensitivity even further. The method was described as being cheap, rapid and easy to implement.

The *surface contamination on optical glass* was determined by Gerhard *et al.* using a sensitivity-improved calibration-free LIBS system.[158] The LIBS system, employing a Nd:YAG laser operating at 266 nm was described in full with the aid of a schematic diagram. Calibration-free LIBS can suffer from reduced sensitivity. The authors overcame this by recording two spectra with different delays between the laser pulse and the detector gate. The first measurement was performed in full local thermal equilibrium conditions, when the electron density is large enough to ensure Boltzmann equilibrium distributions of all plasma species. Since this has a low signal-to-noise ratio, this spectrum enables the quantification of major and minor elements only. To obtain data for trace analytes, a second spectrum was recorded with a longer delay. The lower electron density means that the equilibrium condition is not fulfilled for all elements. Atoms such as oxygen are characterised by large energy gaps between their electronic excitation levels. They are therefore out of equilibrium. Contrarily, the equilibrium condition is still fulfilled for metallic atoms because their energy levels lie closer to each other. Since the number of charged particles are reduced, the continuum emission intensity is lower and hence low-intensity emission lines are observable with an improved signal to noise ratio. The system enabled depth-resolved measurements to be made. Method validation was achieved by combining the depth-resolved measurements to give a bulk concentration, this was then compared with data obtained using a nitric/hydrofluoric acid etching followed by ICP-OES analysis.

A method of *standard addition calibration for LA-ICP-MS analysis* of glass and polymers films was reported by Kuczelinis *et al.*[107] In brief, it employed deposition of pL volumes of aqueous standard onto the sample, drying and then LA-ICP-MS of the residue and sample surface. The paper was discussed in detail in the Polymers section so will not be repeated here. Readers are referred to the Polymers section for a lengthier discussion.

4.8 Nuclear materials

The properties of materials used in nuclear fusion reactors remains a popular topic, with LIBS a dominant technique, either used alone or in combination with other techniques. The safe and efficient operation of existing nuclear reactors was also a key topic, including assessing the condition of reactor components and quantifying the impurities in fuel. The drive to expand the number of measurable radionuclides to contribute to safe, cost-effective decommissioning continues, with destructive mass spectrometric techniques commonly used, in some cases supported by rapid, online radiochemical separation of the radioanalytes. Finally, isotopic ratio measurement was a popular area for identifying the source of nuclear contamination and for the safeguarding of nuclear materials.

Whilst TIMS and MC-ICP-MS were dominant analytical techniques for isotope ratio measurements, several destructive and non-destructive alternatives were presented.

4.8.1 Nuclear fusion. A popular technique for remote monitoring of material properties used in fusion reactors is LIBS. A review of LIBS for analysis of plasma facing components (PFCs) was published by Maurya *et al.*[159] The review included the role of factors such as pressure and atmospheric effect on LIBS measurement, as well as spatial and depth profile studies of key elements in PFCs including Al, Be, C, Li, Mo and W. Other elements investigated included Fe,[160] Ti[161] and graphite.[162] The accumulation of fuel particles in PFCs is an important area of research for reasons including material degradation over time and monitoring of the fuel inventory. The technique of LIBS offers contact-free measurement in harsh thermonuclear conditions using an *in situ* or *ex situ* laser head.[163]

Tungsten-based material properties were the focus of multiple publications. Picosecond LIBS was investigated by Zhao *et al.* for high depth resolution diagnosis of W.[164] Three ablation regimes in laser fluence were identified based on average ablation rate changes and surface morphology variations, with SEM used to investigate crater morphologies and microstructures from the three regimes. One regime was identified as superior based on the limited average ablation rate of <40 nm per pulse, the small thermal effect and therefore a potentially high depth resolution capacity. Further investigation showed the average ablation rate to be weakly dependent on crater diameter at the same laser fluence, with spectral intensities increasing with crater diameter. The formation of a rectangle-like cross section in the crater achieved by the first regime was considered beneficial for depth analysis. Veis *et al.* quantified H/D content in beryllium/tungsten mixture (67/33) coatings on molybdenum substrates using calibration-free LIBS, which was not known to have been performed previously.[165] Different pressures were used to enhance resolution to distinguish H and D, with Be and W lines free from interference and self-absorption selected for evaluation of the electron temperature of the plasma using Boltzmann plots. The electron density was extracted from the Saha equation using the average electron temperatures obtained from the Stark broadening of the H(alpha) line. The D content of the sample (4.7 ± 2.9%) agreed with thermal desorption spectroscopy measurements (4–5%), with the depth profile in agreement with SIMS measurements.

Deuterium retention in compact, porous W–O coatings was successfully assessed using LIBS.[166] The coatings were exposed to a D plasma, with strong signals measured in the laser shot corresponding to the surface layer, reducing to noise levels deeper in the coating, with higher signals in the central region. The results were supported by SIMS measurement of the lateral surface, while SEM and XRD data also supported the measured change in surface morphology. The LIBS was used as an *in situ* monitoring tool by Sattar *et al.* to assess tungsten heavy alloy (97% W, 2% Ni, 1% Fe) hardness after exposure to different plasma irradiations.[167] The results achieved suggested *in situ* LIBS could be applied to estimate the hardness of such materials. Calibration curves were generated using the ratio of ionic to atomic line intensities of W *versus* the Vickers hardness. The

ratio of ionic to atomic spectral emission line intensity and plasma electron temperature increased with hardness. The obtained Pearson correlation coefficient values in measuring hardness of all investigated samples had good approximation, which was a positive indicator of the LIBS approach.

Jin *et al.* used several techniques (focussed ion beam-SEM, TEM, GD-OES and thermal desorption mass spectrometry (TDS)) to analyse *He pre-implantation on deuterium (fuel) retention in tungsten* from microstructure and concentration depth profiles.[168] The GD-OES showed He ion pre-implantation increased the diffusion depth of D in tungsten, whilst TDS showed the pre-implantation increased D retention due to defects produced providing new trap sites. Deposition of Be and D retention in tungsten divertors was studied by Catarino *et al.* following several exposure campaigns in JET with International Thermonuclear Experimental Reactor (ITER)-like wall divertors.[169] Ion beam analysis techniques including proton induced X-ray emission and nuclear reaction analysis were used during the study. The results showed D retention not to be cumulative and was determined mainly by the most recent campaign, whilst total Be deposition differed to the sum of the deposits from individual campaigns for different tiles. Moon *et al.* investigated the fuel retention on tungsten tiles with a castellated structure, which are present for thermo-mechanical durability and integrity under high heat flux loads.[170] Carbon deposition was modelled with the impurity transport code 3D-GAPS, with different concentrations at the tile groove entrance depending on the shaping, and an exponential decrease inside the gap. The highest C and D densities were measured at the plasma-exposed side of the flat tile and aligned gap, with modelled deposition profiles reproducing experimentally observed trends.

The *D retention and permeation characteristics of dispersion-strengthened tungsten containing 1–10 wt% TaC, TiC or ZrC* was investigated using GD-OES by Lang *et al.*[171] The D depth profile was dependent on the second phase added, but was observed beyond the implantation depth in many samples. Reduced retention with increased O was observed using XPS. A study by Pisarev *et al.* measured tungsten tile surfaces after decommissioning using several techniques (LIBS, SEM/EDA, XRD, TDS and NRA).[172] A deposited film was measured in 5 mm and 1 mm gaps to their full depths of 22 mm and 15 mm, respectively. The films were mainly formed from the Li limiter and C from sputtered volatile hydrocarbons from the Tokamak walls. Chemical interactions led to the formation of W_2C, WC, WO_2, and Li_2WO_4, while trapping of D and He was also found.

Molybdenum is a second element used in PFC materials. Quantitative analysis of Mo–Zr–Ti alloy by CF-LIBS was carried out by Miskovicova *et al.*,[173] with Mo acting as a substrate and support for W thin layers. The LIBS spectra were measured under air, Ar and N_2 flow at the sample laser spot, with the evolution of plasma parameters (electron density and electron temperature) observed by choosing different gate windows and delays relative to the laser pulse. The elemental concentration calculated by CF-LIBS showed the most suitable conditions for elemental analysis to be with gate delay and gate width equal to

750, 1000, 1500 ns respectively, where similar elementary concentrations in all three conditions were observed.

Wu *et al.* focused on *molybdenum as a PFC in the Experimental Advanced Superconducting Tokamak (EAST)*, using TF-MS to investigate the characteristics of multi-charged ions emitted from a Mo plasma produced by a nanosecond laser at various power densities.[174] The density ranges (0.85–7.9 GW cm^{-2}) were commensurate with that used by LIBS and laser induced ablation spectrometry (LIAS), with the charge state increasing with laser power density up to a maximum charge of seven. Greater velocities of higher charged ions due to separation between charged ions during plasma expansion were also observed. Plasma shielding from strong laser absorption and reduced ablation rates with increased laser power density were the explanations given for multi-charged ion origins. Picosecond laser-based techniques were used to study the ablation features of Mo by Zhao *et al.*[175] Confocal microscopy was used to determine the ablation depth and morphology, with FIB-SEM assessing the craters structural features, leading to information on ablation threshold, depth resolution and minimum depth of bulk Mo. The paper went on to discuss the application of picosecond laser-based techniques for current and future fusion devices.

Liquid metals offer the potential for PFCs to overcome issues with material erosion inside a reactor. Veis *et al.* analysed the performance of a liquid lithium divertor module based on capillary porous system technology in the COMPASS Tokamak.[176] Lithium-coated Ni–Cr based screws located around the vacuum vessel were analysed to assess the migration of liquid elements, using laser ablation in air at atmospheric pressure, focusing on Li, Ca and Fe spectral lines using CF-LIBS. Zaplotnik *et al.* assessed D retention in liquid Sn (250 °C) following D exposure[177] using thermal desorption spectroscopy and ToF-SIMS. Deuterium was not detected in pure tin, but up to 165 µg g^{-1} D/Sn was detected in the SnO layer, peaking with a D fluence of approximately 5×10^{25} m^{-2}. At larger fluences the D concentration decreased below the detection limit ($\sim$50 ng g^{-1}), which was explained by the reduced oxide film. The impact of the plasma in reducing the SnO layer therefore means the retention of H isotopes in a liquid Sn divertor is unlikely. Tin and lithium were combined as $Sn_{70}Li_{30}$ alloy as a potential liquid metal PFC by de Castro *et al.*[178] Wetting temperatures from 360 °C to 405 °C were determined for fresh alloy on stainless steel, Mo and W, with alloy conditions strongly affecting wetting characteristics. Several techniques (ICP-OES, TOF-SIMS, SEM, EDX and 3D laser microscopy) were used for characterization of deposited droplets, including composition, depth profile and the nature and composition of boundaries between the substrate and alloy. The results showed good compatibility of alloy with Mo and W following <3 hour exposure at 550 °C, whilst under the same conditions, corrosion through Li–Cr association and Fe–Sn mixing was observed on 316 stainless steel.

The *corrosion behaviour of steel materials in fusion reactors* was investigated in several studies. Two studies by Cao *et al.* characterized Li-induced corrosion behaviour of China Low activation Ferritic steel (CLF-1), one using calibration-free LIBS

for depth profile analysis,[179] and the second using an improved internal standard LIBS method.[180] Following 500 hours exposure at 500 °C liquid Li, CF-LIBS effectively showed the non-uniformity of the corrosion layer and gradient distribution of elements, including the weight% of elements along the longitudinal corrosion depth for the corroded sample. In the second study by Cao et al., the same steel sample and exposure conditions showed that the matrix effect caused by a non-uniform surface microstructure could not be neglected, causing a fluctuation of spectral intensity. To eliminate this, neutral and ionised Fe atoms were selected as an internal standard, with the trends of relative concentrations between elements used to deduce the relative mass loss during the matrix elements to be Fe > Cr > V and Mn. Wang et al. also measured CLF-1, focusing on H isotope permeation reduction in steel corroded by Li_4SiO_4 following long-term high temperature exposure.[181] A combination of XRD, SIMS and spherical aberration corrected TEM showed a three-layered corrosion product, with a middle $LiFeO_2$ layer and inner $LiCrO_2$. Deuterium permeation tests showed a decrease in permeability with an increase in corrosion period based on results from 15 and 30 day periods, with a cracking and reoxidation process proposed to explain reduced permeability during Li_4SiO_4 corrosion. Ye et al. used a combination of SEM, ED-XRF and self-designed LIBS to measure Type 316L stainless steel in stagnating liquid lithium under elevated temperatures.[182] After 500 hours exposed to 350 °C liquid lithium a porous and rugged corroded layer was formed on the substrate surface. The Cr on the corroded sample decreased when the depth reached ∼2.8 μm, gradually restoring at ∼5.6 μm, compared with Li intensity that reduced to zero at 4 μm. The stability of the corrosion layer of low activation steel by contact with a ceramic breeder was studied by Hernandez et al.[183] The layer was characterized using SEM, XRD, SIMS and Mössbauer spectroscopy to verify oxide formation and modification following 164 hours exposure at 550 °C in a He/H_2O gas purge simulation mixture (99.8/0.2% volume). The study also identified different Fe states and H isotope traps that could be generated in the corrosion layer, with results showing no additional defects to those generated by hematite transformation to wüstite, the fundamental compound of the corrosion layer by environmental D.

4.8.2 Fuel impurities and reactor operation. The safe and efficient operation of nuclear reactors is of critical importance to minimise risk to the workforce and the public, as well as ensuring the operation is as cost-effective as possible. The *quality assurance of nuclear materials for safe reactor operation* was the motivation for some studies. Saha et al. measured trace impurities (B, Cd, Dy, Eu, Gd, Hf and Sm) using ICP-MS in uranium silicide dispersed in aluminium.[184] A three-step matrix separation was applied prior to sample introduction, with an online nebulisation-assisted solvent extraction setup used for online U extraction that reduced liquid waste generation. Analyte recoveries in three real samples were >95% with RSDs of better than 8%. Cong et al. also used ICP-MS for trace impurity analysis of nuclear grade UF4 using standard addition and [103]Rh internal standardization.[185] The method detection limit ranged from 0.0004–0.072 μg g^{−1} for the 42 trace impurities

measured, with recoveries from 92–111% and RSDs less than 10%. In future work, the verified method will be used for analysis in a molten salt reactor.

A D.C. arc carrier distillation atomic emission spectrometric (D.C. Arc AES) was used for determination of multiple trace metallic *impurities in uranium silicide dispersion fuel*.[186] A 5% AgCl carrier gas was used to sweep away trace constituents into the arc, leaving the major matrix as a refractory material. A charge coupled device detector improved the analytical performance, in particular by enabling additional analytical lines that are valuable for trace level measurements, to be monitored. The method was validated using synthetic samples, with EDXRF being used for comparative evaluations. Wavelength dispersive XRF was applied by Pandey et al. for non-destructive trace U determination in plutonium oxide.[187] Following pelletisation of PuO_2 powder, the U Lα X-ray was used as the analytical line, which provided a reproducibility of better than 5% at U concentrations of 200–1000 μg g^{−1}. There was good agreement between results from WDXRF and ICP-OES.

Namitha et al. focused on the *detection and identification of failed fuel pins and sodium-water reaction in fast reactors* using LIBS.[188] The presence of the gaseous fission products Kr and Xe, or He (for He-bonded fuel pins) in the core cover gas indicates fuel pin failure, with H_2 indicating possible sodium–water reactions. Detection of these gases is therefore an important part of safe fast reactor operation. LIBS was applied to the measurement of H_2, He, Kr and Xe in ultra-high purity Ar (similar to fast reactor cover gas) using their characteristic emission lines. Good linearity and correlation coefficients were reported for all elements. However, an interference from moisture in the LIBS sample chamber was observed during the determination of H_2.

4.8.3 Difficult to measure radionuclides. Utilising the *latest generation sample preparation and measurement techniques for detection of difficult-to-measure radionuclides* was the subject of a number of studies. A popular technique for measurement of medium and long-lived radionuclides is ICP-MS. Diez-Fernandez et al. reviewed the role of collision-reaction cell ICP-MS for online interference removal and radionuclides analysis, including actinides and fission products.[189] Direct quantification of [129]I in Hanford tank wastes using Dynamic Reaction Cell ICP-MS was studied by Adams et al.[190] Instrument parameters were optimized to minimise the background signal at mass 129 and sample cross contamination. The results are believed to be the first reporting of [129]I in Hanford tank waste.

Tandem ICP-MS/MS was successfully used for detection of several radionuclides. Xing et al. combined ICP-MS/MS with the testing of different sample preparation techniques for measurement of Pu in soil.[191] Acid leaching, *aqua regia* and lithium metaborate fusion were tested for different soil samples, focusing on the influence of the major interference elements (U, Hg, Pb, Tl, and Bi) that can prevent accurate measurement of Pu by ICP-MS. Combined with chemical purification, the tandem quadrupole setup with NH_3 and He gases in the collision/reaction cell reduced the contribution of interferences, with values of <0.01 counts per second for Hg, Tl and Bi across the digestion methods tested. Russell et al. tested the

capabilities of ICP-MS/MS for ^{41}Ca detection, which suffers from significant interferences, some of which cannot be removed by offline chemical separation (stable Ca, Ar plasma gas).[192] Concrete samples were digested using lithium borate fusion followed by multi-stage chemical separation prior to measurement. Using a combination of NH_3, He and H_2 in the collision/reaction cell, successful detection was achieved at activity concentrations down to 0.67 Bq g^{-1} (0.21 ng g^{-1}) at ^{41}Ca/^{40}Ca ratios of 10^{-6} to 10^{-7}. This represented the first known measurement of ^{41}Ca using any ICP-MS design. Tandem ICP-MS/MS was also tested for the rapid assessment of ^{93}Zr and ^{93}Mo in concrete rubble following solid phase extraction.[193] Zirconium and Mo recoveries of >90% were achieved, with method detection limits of 1.7 mBq g^{-1} and 0.2 Bq g^{-1} for ^{93}Zr and ^{93}Mo, respectively, based on measurement of inactive concrete. A decontamination factor of the Nb interference that affects both ^{93}Zr and ^{93}Mo was of the order of 10^{-5}, which was deemed sufficient for rapid, low-level measurement in real samples.

Long-lived ^{135}Cs and ^{135}Cs/^{137}Cs isotopic ratios for source identification were measured using ICP-MS/MS in different waste samples (steel, zirconium alloy, reactor coolant, ion exchange filter paper and spent ion exchange resin) by Zhu *et al.*[194] A multi-stage separation scheme achieved decontamination factors ranging from 2.1 × 10^5 (Sn) to 7 × 10^5 (Co). Yields of greater than 85% and a ^{135}Cs detection limit of 3.1 × 10^{-14} g g^{-1} for 0.2 g stainless steel or spent resin were obtained. Caesium-135 and ^{135}Cs/^{137}Cs were the focus of other studies using alternative mass spectrometric techniques. Dion *et al.* employed TIMS for the determination of radioactive Cs and Sr isotopes.[195] Based on stable Sr and Cs measurements, a minimum ^{90}Zr decontamination factor of 2 × 10^8 was achieved, compared with 5 × 10^7, 5 × 10^6 and 8 × 10^6 for Y, ^{135}Ba and ^{137}Ba, respectively. Sample dissolution and chemical separation techniques were tested on a soil matrix, whilst the ^{89}Sr/^{90}Sr and ^{135}Cs/^{137}Cs values from measurement of an irradiated target agreed with published Evaluated Nuclear Data Files (an IAEA database), with a 5–10 times reduction in isotopic ratio uncertainties using TIMS. The same measurement technique was used by Shibahara *et al.* for neutron capture reaction studies of ^{135}Cs.[196] Several additive agents were investigated for their impact on Cs ionization, with silicotungstic acid the most effective of those tested, at the expense of higher polyatomic ion interference levels. The optimized setup was validated through testing of two radioactive Cs samples. Asai *et al.* measured ^{135}Cs directly in spent adsorbent used for water decontamination using LA-ICP-MS.[197] The aim was to address the challenges of irreversible sorption and the relatively high ^{137}Cs radiation dose. A crushed sample was coated with a nitrocellulose based curing agent to provide a flat surface for stable sampling using laser ablation. This was combined with gamma spectrometry measurement of ^{137}Cs. The method achieved a ^{135}Cs/^{137}Cs ratio in good agreement with the results obtained using solution nebulisation whilst having the advantage of only requiring small (<10 mg) samples.

The *measurement of difficult to measure radionuclides using AMS* was successfully demonstrated in several papers.

Strontium-90 was determined by Sasa *et al.* as a rapid, sensitive alternative to traditional decay counting techniques.[198] Strontium was recovered as SrF_2 to provide sufficient negative ions. As well as ion exchange separation prior to measurement, a five-anode gas ionization detector was used to avoid isobaric ^{90}Zr interference. The ^{90}Sr/Sr atomic ratio background of approximately 6 × 10^{-13} was comparable to other AMS facilities, with good linearity from 1.75 × 10^{-10} to 3.38 × 10^{-9}. Schiffer *et al.* investigated projective X-ray AMS (PXAMS) for measurement of ^{63}Ni and ^{90}Sr through their characteristic X-rays, studying production yields in a projectile ion energy range of 0.35 MeV u^{-1} to 1.80 MeV u^{-1}.[199] A paper by Gong *et al.* focused on ^{129}I measurement using AMS at the China Institute of Atomic Energy.[200] The measurement efficiency of the system was calculated to be 28% following optimization of ion transport, gas stripping, charge state selection and interference removal, with a ^{129}I/^{127}I sensitivity of 1 × 10^{-14}. Pacesila *et al.* outlined the extended capability of the AMS facility based on the 1 MV Tandetron at the Romanian institute IFIN-HH, with preliminary results for plutonium isotopic ratios (^{239}Pu/^{242}Pu and ^{240}Pu/^{242}Pu) being obtained.[201]

Plutonium isotopes were also the focus of a study investigating solution loaded laser ablation modified sources for TIMS analysis.[202] A Parafilm coating was applied to the filament surface and then ablated through the film to the metal beneath creating a central point source. A Pu solution can then be applied to this area and slowly dried. This simplifies the sample loading process for TIMS, with a 10% uncertainty (2σ) for ^{240}Pu/^{239}Pu from a 5–7 fg CRM sample, with an average sample utilisation efficiency of 1.3%.

4.8.4 Radiochemical separation. Depending on the measurement technique and sensitivity required, *radiochemical separation may be required prior to measurement, focusing on rapid, automated procedures.* Wang *et al.* developed a procedure for Am and Pu determination in soil and sediment samples prior to sector field ICP-MS measurement, combining low detection limits with short analytical time (14 hours).[203] Iron hydroxide precipitation was followed by extraction chromatography using several resins to separate Pu and Am from interferences and each other. Chemical recoveries of 71–91% (Pu) and 70–88% (Am) were achieved through testing with four reference materials, with decontamination factors of 4.2 × 10^2 for Pu in the Am fraction and 7.0 × 10^3 for Am in the Pu fraction. Kolacinska *et al.* also focused on Pu measurement, developing a sequential injection analysis system combined with ICP-MS for ^{239}Pu determination.[204] The system used DGA resin for removal of ^{238}U that can form a ^{238}U^{1}H interference. The total analysis time was 45 minutes, with a method detection limit of 88 mBq L^{-1} from a 100 mL sample, which was deemed satisfactory for technological and environmental samples.

Gadolinium, Nd, Pu and U were quantified in uranium oxide and Gd-enriched spent fuel using isotope dilution sector field ICP-MS following high performance ion chromatography separation.[205] Uranium was present at higher concentrations and required off-line dilution and measurement, whilst an online approach was used for the other analytes. The final method was compared against routinely used techniques, namely isotope

dilution TIMS and alpha spectrometry. In a paper by Manard *et al.*, U was the analyte of interest for an automated separation method prior to ICP-OES and ICP-MS/MS measurement of uranium ore concentrate samples.[206] Seventeen samples, two quality control reference material samples and 26 process blanks were sequentially run through a single extraction chromatography column, with the resin separating trace elemental impurities. The column was successfully regenerated even after a total of 50 mg U had been processed, with the results showing good correlation to previously reported data. Liu *et al.* also studied U separation, specifically electroseparation from lanthanides on a liquid gallium electrode.[207] The motivation for this work was the identical reduction potentials of U and lanthanides in multi-component melt systems that could not be resolved on the Ga cathode. The study applied different electroseparation techniques, followed by ICP-OES measurement in molten salts and alloy deposits. Separation factors of up to 1000 was achieved for U/La and U/Sm, compared with approximately 350 for U/Nd. Current pulse electrolysis achieved a larger separation factor than galvanostatic and potentiostatic methods.

Green radiochemistry was highlighted in some studies as an alternative to more established separation materials. Mortada *et al.* investigated an eco-friendly alternative for the extraction and separation of Th from U and lanthanides in wastewater and phosphate rocks prior to ICP-OES measurement.[208] Morin formed a complex with Th^{4+} at pH 2–4 that quantitatively extracted it into the surfactant-rich phase in the presence of 0.1% (v/v) Triton X-114 and 0.1% (w/v) KI at room temperature. The analytical range and detection limit compared favourably to other cloud point extraction procedures for Th, with an enrichment factor of 49.5 for a 50 mL sample and a recovery of at least 95% in Th-spiked samples. Phillip *et al.* investigated palm oil fly ash as a green supplementary material for cementitious backfill in disused sealed radioactive source borehole disposal, focusing on ^{226}Ra confinement.[209] Multiple techniques were used to measure the performance of ordinary Portland cement with and without the palm oil fly ash, with 30% ash replacement found to improve geochemical conditions by reducing competitive Ca release into the disposal environment. Samples with up to 50% fly ash replacement met the mechanical and hydraulic performance requirements, and ^{226}Ra confinement was improved owing to the higher fraction of active sites. This suggested that the use of palm oil fly ash may reduce the radiological hazard.

4.8.5 Nuclear accidents and security. Measurement of fuel debris and the environment surrounding the Fukushima Daiichi Nuclear Power Plant remains a popular topic one decade after the accident. *Accurate and precise isotopic ratio measurement of nuclear materials also continues to be extensively investigated for source attribution and verification.* Nakanishi measured various Gd concentrations in surrogate mixed oxide nuclear fuel debris in the damaged Fukushima reactors using fiber optic LIBS.[210] Optical emission lines at 501.5 nm and 510.3 nm were determined to be suitable, with further tests under 0–10 kGy h^{-1} gamma irradiation that resulted in reduced spectral intensities due to radiation-induced optical fibre damage. The Gd detection limit was in the range of 0.03–0.08 wt%, demonstrating the potential for *in situ* remote fuel debris analysis. Ikeda *et al.* also used LIBS for Fukushima fuel debris screening, focusing on microwave-enhanced fibre coupled LIBS for remote sensing in active environments that will be an important tool during decommissioning of the site.[211] The radiation-induced reduction in spectral intensity was improved using 2.45 GHz semiconductor oscillated microwaves to the induced plasma of fibre coupled-LIBS. Although transmission losses through the fibre still occurred, the increased intensity of the emission from the plasma, led to an overall intensity enhancement of 1160 times using aluminium oxide test material.

Measurements of *Cs-bearing microparticles emitted from Fukushima* were the subject of studies by Miura *et al.* and Kurihara *et al.* The study by Miura *et al.* focused on measuring a larger number of particles emitted from Unit 2 or 3 (0.1–10 μm diameter particles termed Type-A) and Unit 1 (50–400 μm diameter particles termed Type-B).[212] Micro X-ray computed tomography and XRF revealed multiple voids and Fe-rich parts of Type-B particles, whilst the ^{137}Cs activity was approximately 10 000 times higher in Type-A particles compared with Type-B. The differences suggested different formation routes for the two particle types, which contributes to improved understanding for decommissioning and environmental assessment. Kurihara *et al.* used SIMS and LA-ICP-MS to measure U and Cs isotopic ratios in five spherical Cs microparticles (approximately 2 μm diameter) sampled 50 km west of the Fukushima plant.[213] The ^{235}U/^{238}U ratios were close to the estimated values for Units 2 and 3 fuel cores and identical in the case of Cs isotopic ratios. The results were combined with atmospheric release information to conclude that the particles originated from the Unit 2 reactor on the night of March 14th and the morning of March 15th 2011.

Nuclear forensics remains a very popular topic, with a large number of publications on measurement of U isotopic composition in fuel and particle samples. This was reflected in a publication by Jovanovic *et al.* who reported the results from the fifth collaborative materials exercise of The Nuclear Forensics International Technical Working Group.[214] Two uranium dioxide fuel pellets were prepared and sent to participating laboratories to independently analyse their characteristics using different techniques.

Varga *et al.* published two papers on the measurement of U using mass spectrometric techniques. One used LA-MC-ICP-MS to study heterogeneity of solid UO_2 pellets at micrometre levels as part of the Nuclear Forensics International Technical Working Group.[215] Despite the identical source material of the two pellets, different production routes could be observed at micron-scale and the U isotopic ratios determined, with the imaging helping to assess the lateral dimensions of individual grains which can be used as an indicator of the production route. A second study by Varga used MC-ICP-MS to determine the U production date from a swipe sample of a highly enriched U seizure.[216] Measurements following acid leaching were used to calculate the 'bulk' composition (72.51 ± 0.03 wt% ^{235}U) and the production date, which was similar to other cases seized earlier in Europe. A separate study by Krachler *et al.* used LA-

MC-ICP-MS for the measurement of U isotopic composition in five contaminated scrap metal samples found in the EU.[217] Two U isotopic reference materials (CRM U-020 and CRM U-030) were also measured for quality assurance, ion counter gains and mass bias correction. Similar to the study by Varga et al.,[215] LA-MC-ICP-MS was highlighted for its ability to identify inhomogeneous distribution of U within samples, with the large range of ^{235}U enrichment confirmed using SIMS, and four of the five samples tested containing ^{236}U, indicative of the presence of reprocessed U.

The technique of LA-MC-ICP-MS with an extended dynamic range was used for U isotopic analysis by Yamamoto et al.[218] Three Faraday detectors with 10^{-11} and 10^{-13} ohm resistors were tested for a series of solid materials on transient signals with LA durations of <3 seconds to minimise sampling volume. Using a tau correction technique, the ^{235}U/^{238}U values were approximately 3% higher than the literature values, which was ascribed to incomplete correction of the slow response of the Faraday amplifiers. When continuous ion monitoring was applied, precision for ^{235}U/^{238}U improved to 1 part per thousand and for ^{234}U/^{238}U to 7% (2σ), showing good agreement with literature values. It demonstrated the suitability of the technique for measuring transient signals in high-gain amplifiers. Craig et al. also investigated transient signal isotope ratio analysis, in particular the limitations of 'blind time' on LA-MC-ICP-MS.[219] A high speed integrated ablation cell and dual concentric injector design was tested for U isotopic ratios. When compared with a slower washout, established low-volume cell design, the highly transient signals of the new design introduced a new bias, a major component of which was referred to as the 'blind time'. The impact was modelled on UO$_X$ particles, with average precisions in sub-micron particles of 3% (1σ) and 8% (1σ) for ^{235}U/^{238}U and ^{234}U/^{238}U, respectively.

The application of TIMS for U isotope ratio measurement was demonstrated by Bhatia et al. through the design and development of a compact instrument.[220] The sector radius of the magnetic sector analyser in the compact instrument was 20 cm compared with 30 and 27 cm in the conventional and commercial geometries, respectively. A U200 standard was measured to compare the conventional and compact instruments. A sensitivity improvement of 1.5 for the compact instrument and an improved precision of 0.05% for ^{235}U/^{238}U for the compact instrument were obtained. Lee et al. assessed the signal-detection performance of TIMS with continuous heating for isotopic U measurements in the fg to pg range for nuclear safeguards.[221] Peak jumping mode with a single detector was compared with static mode using multiple detectors, with ^{235}U/^{238}U measured down to 1 fg and 3 fg in the two modes, respectively. Both modes could only measure down to 100 fg for ^{236}U/^{238}U. The similar capabilities demonstrated that continuous heating during TIMS measurement offers the advantage of exhibiting the properties of multiple detectors within a single detector.

Both TIMS and MC-ICP-MS remain popular techniques for isotopic analysis, but a number of alternative analytical methods were applied to isotopic analysis. Rinaldi et al. carried out U isotopic analysis using LIBS, citing the speed of detection and identification of elements in a sample using this approach.[222] The combination of LIBS with Chemometrics to determine isotopic ratios at atmospheric pressure could achieve precisions of 4–10% depending on the enrichment level, which is applicable in the measurement of certain special nuclear materials. Fast, quantitative analysis of U using LIBS was also employed by Rollin et al.[223] The detection of trace and minor elements is challenging owing to the large number of actinide emission lines in the UV–visible region. Rollin et al. therefore investigated the vacuum UV (VUV) range below 200 nm as an alternative, estimating the detection limits of C and V. The results agreed with findings from non-nuclear samples, with the technique not suitable for metal impurities with useful spectra in the VUV, whilst offering improved detection limits for non-metals that have intense VUV lines.

In situ TOF-SIMS analysis of uranium oxide was presented by Yu et al. as a method for surface analysis of liquid and solid–liquid interactions as a neat, non-destructive alternative or support to destructive techniques such as ICP-MS.[224] Initial results were presented for liquid uranium oxide standard solutions. Paing et al. presented rapid U isotopic measurement in cotton wipes using a planar surface reader coupled with a liquid sampling-atmospheric pressure glow discharge microplasma ionization source employing an Orbitrap mass spectrometer.[225] A 30 second extraction step achieved quantitative recovery with approximately 100 ng sampled per extraction. The intra sample variability was around 30% RSD, which the authors claim was offset by <10% RSD for ^{235}U/^{238}U and (for enriched samples) ^{234}U and ^{236}U ratios. An additional benefit was that it is a convenient, versatile approach for swipe samples in a range of applications. A final alternative technique published by Hoegg et al. was liquid sampling-atmospheric pressure glow discharge with Orbitrap mass spectrometers, aimed at meeting the international target values for U uncertainty.[226] The system was tested on a series of uranium CRMs, with measurement of ^{234}U and ^{236}U related species that had not been achieved previously. In the case of CRM U-800, the measured ^{235}U/^{238}U value of 4.266922 compared favourably to the expected value of 4.265622, with the instrument showing promise for forensics and safeguard applications.

4.9 Electronic materials

An enormous amount of research has been put into electronic materials recently. Many of the papers describe the development of new lithium ion batteries, their alternatives and their components and so most do not describe the analytical chemistry in huge detail. Many of the papers use the atomic spectroscopy as a tool to characterise their product. These papers are therefore not included because they do not represent an advance in the analytical aspect of the work. Papers that are included are those that describe new or improvements to existing methods of depth-profiling.

Several review papers have been published over the last year or so. An excellent overview entitled "Laser ionization mass spectrometry at 55: Quo Vadis?" prepared by Azov et al.[227] The paper was extremely long (>50 pages) and contains 274

references, but covered the historical aspects as well as more modern instrumental designs (Orbitrap *etc.*). Also covered were recent applications and more theoretical aspects, for example, the effects of different lasers and their powers. The review would be a good place to start for anybody entering the research area.

A review (212 references) by Giurlani *et al.* covered the *different methods of measuring the thickness of metal coatings*.[228] The review was split into two main sections: destructive and non-destructive methods, with each of those being split into numerous sub-sections covering the techniques available. The destructive methods were: mechanical cross-sectioning, focused ion beam cross-sectioning, angle lapping, TEM, Calo tester, optical microscopy, scanning ion microscopy and chemical dissolution. The non-destructive techniques were: XRF, EPMA, ellipsometry, RBS and resonant methods. Each of the methods were described in terms of their pros and cons, their accuracy, simplicity, time required *etc.*

4.9.1 Wafers, thin films and multi-layer materials. Techniques capable of depth-profile analysis are the most commonly used for these sample types. Therefore, techniques such as LA-ICP-OES/MS, LIBS (both of which use the laser to "drill" through the sample by successive firings), SIMS, TOF-SIMS and assorted X-ray-based techniques proliferate.

Research into the analysis of wafers impregnated with substances is still on-going. An example was a paper presented by Czyzycki *et al.* who used *GIXRF to analyse three silicon (111) wafers that had been deeply implanted* with 200 keV argon ions of nominal dose 10^{15}–10^{16} cm^{-2}.[229] The technique is usually used to analyse implants with a depth of <25 nm. However, this paper reported the analysis of depths far greater than that. This was achieved using a new mathematical model that did not rely on X-ray standing wave. The calculated concentrations were in agreement with nominal values and were further validated using an ion beam analysis method. The authors concluded that their new model would expand the use of GIXRF into areas not previously explored.

Several papers have reported the analysis of thin films. Included in this number was a paper by Huang *et al.* who *determined residual dimethyl sulfoxide (DMSO) in methyl-ammonium lead iodide perovskite thin films* using high resolution continuum source graphite furnace molecular absorption spectrometry.[230] The sample was placed in the graphite furnace which was then heated to 160 °C converting the DMSO to the molecule CS, which was then detected at 258.055 nm. Calibration was against aqueous standards of DMSO and Pd was used as the matrix modifier. The characteristic mass was 17 ng. The DMSO content was normalized to the Pb content. For this, the Pb in the perovskite was reduced to metallic Pb using zinc powder and then measuring the signal at the weak line 261.418 nm using HR-CSAAS. The Pb content remained constant with increasing annealing time but the S/Pb ratio decreased, indicating better removal of the DMSO.

Refractory transition metal nitrides have many uses, *e.g.* as protective coatings for industrial machine parts. However, they are also gaining increasing interest in the microelectronics world as diffusion barrier layers. Their applications and desired performance require precise control of the film thickness and

elemental depth profile. Torrengo *et al.* used a combination of XRR and GIXRF for the non-destructive analysis of titanium tungsten nitride films that had been prepared using physical vapour deposition.[231] This approach is normally undertaken using a reference-free approach which requires knowledge of the whole experimental system. This can be problematic in a laboratory or workplace where parameters may be difficult to control precisely or to access. The authors developed a reference-based method in which known standard samples close in composition and structure to the samples are analysed so that key parameters of the instrumental setup are identified. These parameters are then used for the combined XRR/GIXRF analysis of the samples of interest. The method was very successful and met the requirements for both qualitative and quantitative depth-profiling analysis while being easier to implement in laboratories than the reference-free method.

Copper oxide thin films are used in many types of solar cells. *Analysis of Al or Co-doped copper oxide films using LIBS* was reported by Wu *et al.*[232] The films, prepared by radiofrequency magnetron sputtering deposition, were analysed using LIBS in a rapid manner enabling qualitative and quantitative determination of the doping elements. The emission intensity ratios of Al/Cu in the copper oxide–aluminium films and of Co/Cu in the copper oxide–cobalt films were used for the analysis.

Aluminium–indium-tin oxide thin films are formed by doping Al into the well known indium tin oxide material and are promising materials for deep ultra-violet optoelectronic devices. A paper by Liu *et al.* described the preparation and subsequent analysis of such films prepared under different magnetron sputtering powers, pressures and times.[233] The concentration ratios of Al/Al + In + Sn and Sn/Al + In + Sn were determined using LIBS. The accuracy of a comprehensive calibration protocol was determined using samples prepared under random sputtering parameters and with data obtained using EDXRF. There was less than 5% error in the data between the two techniques, indicating the accuracy of the LIBS methodology.

The work into *laser ablation of solids in liquid (LASIL) followed by either ICP-OES or ICP-MS detection* has continued to be a subject of interest for researchers in the field of thin films. A paper by Herzig *et al.* used a LASIL system built in-house coupled with ICP-MS detection for the analysis of complex metal oxide thin films.[234] The system required sample transport with as little particle dispersion as possible so that a spatial map of the film could be made. This 2D mapping ability was applied to films of varying composition with a thickness of 220 nm that had been deposited using pulsed laser deposition. The workers then extended the study so that a simultaneous on-line quantification using standard additions was developed. This helped correction for instrumental drift during long-term measurements.

The analysis of layered structures and depth-profiling studies have, as always, featured heavily in the literature. The techniques capable of depth profiling are mature now and therefore many of the applications simply use them as characterising tools. As such, they offer no advances in the atomic spectroscopy and will not be discussed. A useful contribution

was presented by Lobo *et al.* who used *pulsed GD-TOF-MS for the depth-profile analysis of Ge_xNi_{100-x}/Ni/Nd_yNi_{100-y} thin films*.[235] The technique of GD-TOF-MS is ideally suited to the task because it offers rapid elemental determination whilst also specialising in the capture of transient signals. The thin films, of total thickness between 15 and 75 nm were deposited on two different substrates: non-conducting glasses and conducting silicon wafers. The operating conditions for the glow discharge were optimized for each substrate to ensure best instrumental performance. Short pulse width (*e.g.* 0.16 ms) and periods (1.32 ms) enabled the best depth-profile resolution for the layers deposited on glass. However, the pulse width was not such an important parameter when analysing films on wafers.

The technique of *TOF-SIMS is gaining increased attention for depth-profiling studies*. An example, by Smentkowski and Goswami, reported the Al depth-profile in silicon carbide wafers.[236] The paper indicated that TOF-SIMS was capable of replicating the quantitative data obtained using dynamic SIMS, although at the lowest concentrations, a greater number of spectra needed to be collected. Until now, TOF-SIMS had been regarded as being excellent for the analysis of thin films, but only in a qualitative manner. Applications utilising TOF-SIMS were also reported by Miyayama and Iida[237] and by Priebe *et al.*[238] In the former paper, low energy (2 keV) bismuth cluster ions (Bi_3^+) at an incident angle of 65° were used to generate bismuth adducted secondary molecular ions $(M + Bi)^+$, which are not observed under normal TOF-SIMS operating conditions.[237] The method was applied to multi-layers of Irganox 1010/Irganox 1098 thin films and provided a better dynamic range for both layers. It was concluded that the low energy bismuth cluster is more suitable for organic films than the normal 54 keV bismuth cluster. The paper by Priebe *et al.* investigated the matrix effects exhibited during the TOF-SIMS analysis of two element inorganic thin films.[238] Matrix effects can be severe in TOF-SIMS, with the sensitivity of analyte signals changing depending on their surroundings. This is the main reason it has hitherto been regarded as being capable of qualitative analysis. The work undertaken in this study found that Zr ionization efficiency was four times higher in the silicon matrix compared with a copper matrix and two times higher than an aluminium matrix, the topography of the film can also affect TOF-SIMS measurements. An interesting paper by Spampinato *et al.* combined the use of a scanning probe microscope and TOF-SIMS in an attempt to overcome this problem.[239] The scanning probe microscope provided high resolution topographical information whilst the TOF-SIMS analysed the thin layers. Rapid alternation between the scanning probe microscope and the TOF-SIMS instrument enabled far better accuracy to be obtained during the analysis of 3D structures.

Hybrid organic–inorganic perovskite devices are known to be unstable and hence have not, as yet, been commercialised. An additional problem is that their complexity makes it difficult to analyse them fully, so mechanisms of failure can be hard to elucidate. A paper by Higgins *et al.* described the depth-profile analysis of the interface between methylammonium lead bromide perovskite and the gold electrode.[240] The authors used TOF-SIMS in conjunction with a machine learning workflow that combined the Hough transform and non-negative matrix factorization and non-negative tensor decomposition. The TOF-SIMS enabled chemical composition characterisation whereas the chemometric approach enabled interpretation of the multi-dimensional data obtained while avoiding some of the limitations. This enabled salient features of the chemical changes to be extracted whilst separating the voltage- and light-dependent dynamics.

Oxygen diffusion behaviour through a commercial A-site deficient lanthanum strontium chromium iron oxide delta perovskite was studied by Sha *et al.*[241] These materials can be used as solid oxide fuel cells. It had been suggested that atmospheric parameters such as humidity can affect the chemistry and hence performance and durability of such devices. The technique used for the study was isotopic exchange depth-profiling SIMS. An O partial pressure of 200 mbar was used with a constant water pressure of 30 mbar. A temperature range of 600–900 °C was also used. Only very limited O diffusion was observed above 800 °C. To study this phenomenon in more depth, the authors used angle resolved XPS, SEM and scanning TEM. Strontium segregation was found to be one of the causes for suppressing the water surface exchange.

A paper by Yi *et al.* reported the use of *picosecond LIBS for depth-profiling studies in an attempt to improve the depth resolution* which, for many LIBS applications, can be poor.[242] The ablation depth was measured and then correlated with the laser pulse number. A series of layered graphite samples was analysed under a residual pressure of 1×10^{-5} Pascals and a resolution of 24 nm and 102 nm was obtained for Mo and C, respectively. This represented a significant improvement over standard LIBS analysis.

4.9.2 Solar cells. Some references pertinent to this section will have been discussed in the previous section, since many are thin films. However, there has been one review of note published in this period. The review (with 194 references) was by Liu *et al.* and was entitled "*Secondary ion mass spectrometry for the chemical characterisation of metal halide perovskites*".[243] The capability of TOF-SIMS for the analysis of these structures was summarized and analysed. Topics included basic chemical composition analysis, mechanistic studies, distribution of analytes, ion migration, interference composition and degradation mechanisms and products. A section on future developments was also provided.

A *variant of calibration-free double pulse LIBS was used by Shakeel et al. to analyse gadolinium/germanium/silicon alloys and solar cells*.[244] The method was both simpler and faster than conventional calibration-free LIBS. The inter-pulse delay was optimized and a Boltzmann plot used to calculate plasma temperature and subsequently the concentration of the analytes. The results obtained were compared with those obtained using conventional calibration-free LIBS and were in agreement. The method was applied to the analysis of three unknown polycrystalline silicon solar cells. Traces of Al, C, Ca, Fe, In, Sb, Sn and Ti (at the mg kg^{-1} level) were observed. The authors stressed the possibility of their method being used in real time during the manufacture of the materials.

Perovskite quantum wells (a bulk 3D perovskite layer combined with a reduced dimensional perovskite layer) have been shown to improve the efficiency and stability of perovskite-based solar cells significantly. A study by Hu *et al.* used *time-resolved grazing incidence WAXS to study the formation mechanisms of these quantum wells*.[245] The technique enabled real-time insights into phase-transition during the organic cation (in this case hexyltrimethylammonium bromide) and the perovskite assembly formation process. An ionic reaction between the 3D perovskite and the long-chain organic cation occurs rapidly forming an intermediate phase in just a few seconds. The optimal conditions can be elucidated from evidence obtained using TOF-SIMS. By controlling the second ionic reaction during the long-chain cation coating process as well as the fluorinated poly(triarylamine) as a hole-transport layer, the efficiency of the perovskite solar cells exceeded 22%.

4.9.3 Analysis of electronic components. A popular area of research has been the analysis of scrap electronic equipment. This is required because it often contains a complex mixture of elements, many of which are toxic, others can be re-cycled for future use in electronic materials and others are precious. The *Waste Electrical and Electronic Equipment (WEEE) directive along with the Restriction of Hazardous Substances (RoHS) directive* govern what can be released into the environment. Remeteiova *et al.* tested the US EPA method 3052 microwave acid digestion procedure (and modifications thereof) for the sample preparation method for the analysis of printed circuit boards from mobile phones.[246] Significant quantities of Cu (22.6%), Fe (5%), Ni (2%) and Zn (2.6%) were found. The best digestion procedure was the non-modified version, but even then, acid decomposition was not complete. The residue contained oxides of Al, Ca and Mg as well as fluorides of Ca and Mg. In addition, there were also minor amounts of Cu and Fe. Another example was presented by Babos *et al.* who used LIBS with several calibration strategies for the analysis of waste printed circuit boards.[247] Matrix-matching calibration, two-point calibration transfer, one-point and multi-line calibration, single-sample calibration and calibration free were the methods used for the LIBS determination of Al and Pb in the solid samples. Each strategy had its advantages and disadvantages when overcoming matrix effects and these were discussed at length. The matrix matching calibration and calibration free methods provided the best results, with recoveries between 80 and 120% being obtained. Another paper, by Garcia *et al.* used LIBS for the determination of Cu in discarded printed circuit boards.[248] The method was used for the monitoring of Cu leaching from the material. Once the data have been obtained using LIBS it is common for a chemometric package to be required to aid the interpretation. Castro *et al.* used parallel factor analysis (PARAFAC) to aid the interpretation of the spectra obtained from the LIBS analysis of printed circuit boards and hard disk drives.[249] The analytes were Al and Cu (base metals) and Ag and Au (noble metals). A board was cut into 77 fragments and then a matrix comprising four rows and four columns with 10 laser pulses at each point was made. The data for each of the analytes were inserted to PARAFAC to enable modelling to ensure interference-free data. A map of the board could then be constructed enabling easy visualisation of where the analytes were located. In addition, once PARAFAC had removed the interferences, the Ag and Au data were treated using Partial Least Squares Discriminant Analysis (PLSDA). Good figures of merit were obtained for calibration, cross-validation and validation data sets with accuracy ranging from 0.94 to 1.00.

Lithium ion batteries and their components have received a huge amount of research. This is because assorted different anode and cathode materials have been developed in an on-going attempt to improve efficiency. However, the vast majority of this work does not involve atomic spectrometry and, of those papers that do use some form of atomic spectrometry to characterise the material, most use basic techniques and hence, do not further knowledge. Consequently, those papers will not be discussed. Instead, those few papers that do describe an interesting application or modification of a method will be discussed at greater length, the temperature-dependent chemical and physical micro-structure of lithium metal anodes was investigated by Adair *et al.* who used synchrotron-based techniques for the task.[250] X-ray computed tomography and energy-dependent X-ray fluorescence mapping were utilised to assess the surface morphology. Another technique employed was μ-XANES. This was used to determine the chemical composition of the solid electrolyte interphase in quasi-3D space combined use of the techniques enabled information to be gleaned for the origin of cycling performance at different temperatures through analysis of coulombic efficiencies, surface morphology and the chemical composition of the solid electrolyte interphase in quasi-3D space.

Lithium lanthanum zirconium oxide garnets are regarded as being promising solid state electrolytes for next generation lithium ion batteries. Their analysis using LA-ICP-OES was reported by Smetaczek *et al.* who first prepared matrix-matched standards and then characterised them using an acid dissolution procedure followed by conventional ICP-OES analysis.[251] Once characterised, the standards were used for calibration of the LA-ICP-OES protocol. An internal standard-independent calibration strategy based on 100% normalization was applied, enabling the quantification of all cations within the material. Results from LA-ICP-OES were compared with those obtained using LA-ICP-MS and were found to be superior. Results from the analysis of an Al-doped material using the method were compared with those from a fusion-based dissolution ICP-OES method and were in good agreement.

A paper by Yamagishi *et al.* reported the use of *operando TOF-SIMS for visualizing the Li distribution and degradation of composite electrodes in sulfide-based all-solid-state batteries*.[252] Two types of electrode materials were analysed during cell operation: lithium nickel cobalt aluminium oxide ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) and lithium phosphorus sulfide ($75Li_2S \cdot 25P_2S_5$). Evolution of the non-uniform reaction of the lithium cobalt aluminium oxide particles during charge and discharge cycles was successfully visualized by mapping fragments containing Li. In addition, degradation of the interface between the materials was investigated by mapping PO_x^- and $SO(x)^-$ fragments. Results indicate that there was a redox active component at the interface. The paper is a good example of how atomic

spectrometry can be used to elucidate mechanistic aspects of processes.

Another paper to explore *mechanistic aspects of processes* was presented by Cheng *et al.*, who used *in situ* synchrotron XRD and small angle X-ray scattering (SAXS) to investigate copper oxide/graphene oxide anode materials.[253] Different copper oxide morphology could be obtained by reacting at 83 °C for different times. The analytical techniques were then used to characterise the materials during the first cycle. As the Li becomes incorporated into the material the copper oxide Bragg peak shifted indicating a higher angle in the crystal lattice. In addition, the growth of the solid electrolyte interphase increases with increased lithiation dose to the extent where cracks form. Another example was presented by Haridas *et al.*[254] who examined the effects of the electrolyte additives tris(trimethylsilyl) phosphite and fluoroethylene carbonate on lithium nickel manganese cobalt oxide–silicon lithium ion batteries. The analytical techniques of TOF-SIMS and XPS were used to study the electrode–electrolyte interface and to investigate the depth profiles of the species. Results indicated adequate hydrogen fluoride scavenging. Different ratios of the two electrolytes were tested. A three-fold excess of fluoroethylene carbonate over the other electrolyte led to a two-fold increase in life cycle compared with an even greater proportion. Lithium titanium oxide ($Li_4Ti_5O_{12}$) has also been proposed as an alternative for the negatively charged electrode of lithium ion batteries. The different states of lithiation were investigated using energy dispersive inelastic X-ray scattering spectroscopy in a paper by Robledo *et al.*[255] The technique was used to differentiate between the lithiated and de-lithiated forms of the compound with good sensitivity and was regarded as being a reliable tool for undertaking such speciation work. The results were compared with those obtained using XANES and were in good agreement.

Alternative battery types to lithium ion ones exist and studies have also been undertaken on these. A battery type that has very benign components is *zinc/alpha-manganese dioxide*. This battery type has been investigated by Wu *et al.* who used operando spatiotemporal resolved synchrotron X-ray fluorescence mapping measurements to provide direct evidence of a Mn dissolution–deposition faradaic mechanism that governs the electrochemistry.[256] Analysis of the electrolyte found an aqueous form of Mn during battery discharge and a depletion when charged. The results were confirmed by an assortment of other analytical techniques that included TEM, XANES and EXAFS. The mechanism was therefore different to the Zn insertion or conversion reactions that had previously been assumed.

Several other applications have been published that are worthy of mention. One by Miner and Beauchemin described the ICP-MS determination of *Ni in an alkaline electrolyte solution*.[257] This is not a straightforward analysis because the presence of high concentrations of concomitant elements leads to signal suppression of the analyte. An additional problem is that the alkaline nature tends to de-vitrify the glassware of the instrument sample introduction system. The method developed utilised an on-line system comprising a column of Dionex™ IonPac™ CS-10 cation exchange column to retain the Ni whilst allowing the interfering ion (K, Na *etc.*) to elute to waste. The system was first tested on standards of Ni in sodium and potassium hydroxide solutions. The Ni was eluted using 6 M nitric acid. The whole process lasted only 260 s yielding a detection limit of 0.1–0.2 μg L^{-1}. Strangely, there did not seem to be much quality control.

Secondary ion mass spectrometry has been used for diffusion studies several times in this review period. An example, by Wojcik *et al.*, determined the depth profiles of hydrogen-passivated and active Zn in gallium arsenide/aluminium gallium arsenide.[258] This work used ultra-low impact energy SIMS for the task of measuring the zinc-arsenic signal as a marker for active Zn and the H signal to provide information about the hydrogen-passivated impurity profile. The method could potentially be used for optimizing the growth process and controlling the level of impurity activation in such materials. Another example by Duan used TOF-SIMS for the analysis of the boehmite layer of resistive switching random access memory.[259] A 3D map of the H ion distribution was obtained during the high/low resistance states. This enabled the mechanism of H ion diffusion to be elucidated. A third paper used TOF-SIMS to elucidate degradation mechanisms of organic light emitting diodes.[260] Although popular, the organic light emitting diodes are renowned for failure and so information into the mechanisms of failure is required. The paper, by Iida *et al.*, used depth-profiling analysis of degraded materials. The MS/MS mode was used to try and minimise the mass spectral interferences often observed during analysis of this type of material. The results identified a number of small hydrocarbon molecules that were degradation products of either the starting material or contaminants at the indium tin oxide interface.

The purity of the *room temperature semiconductor radiation detector material caesium lead bromide was determined using ICP-MS* by Makanda *et al.*[261] The analysis for this sample type is more frequently undertaken using GD-MS and so a quick, easy and reliable alternative is welcomed. The sample was ground using a mortar and pestle and then dissolved in 2% nitric acid, first at room temperature overnight and then at 95 °C on a hotplate to ensure complete dissolution. After dilution the sample was analysed using ICP-MS. Method validation was through spike recovery experiments with recoveries obtained for the 12 analytes being generally close to 100%. Limits of detection were 0.0004 (Tl) to 0.377 (Cr) μg kg^{-1} and regression coefficients were better than 0.99 for all analytes. The method developed was applied to a high temperature zone-refined sample. The concentration of contaminants varied depending on the part of the ingot, with the heel being the most contaminated. In all cases, the chief contaminants were Rb and U. Strangely, U was by far the highest in the tip of the ingot, whereas Rb was far higher in the middle and the heel.

The composition of *contamination deposited on transmission line insulators can affect their surface flashover voltage*, currently, to estimate the extent of the contamination requires an electrical shutdown while the insulators are sampled and taken to a laboratory for analysis. An on-line method that does not require power shutdown would therefore be of huge benefit. The technique of LIBS could possibly provide such an analysis

capability, but can potentially run into problems from the different forms of salts present giving different sensitivity. Lu *et al.* described a LIBS method of analysis that first tested whether the different forms of elements, *e.g.* Na_2CO_3, $NaHCO_3$, $CaSO_4$ and $CaCO_3$ affects the sensitivity of the analysis.[262] Samples containing different proportions of Na and Ca were prepared and the linear correlation coefficients for the calibration curves calculated. No significant change of the linearity of the calibration was observed, indicating that matrix effects were minimal. However, the laser energy density had a very large effect. Partial least squares regression helped improve the accuracy of the analysis significantly.

4.10 Nanostructures

Atomic spectrometry, through techniques such as XRD, XPS, XRF, single nanoparticle (sNP) ICP-MS and ICP-OES has a key role in the characterization and detection of nanoparticles (NPs) with over 200 papers published in the period covered by this ASU. However, many of these articles only mention the technique(s) used without any further analytical detail and as such are not reported on here.

4.10.1 Reviews. A number of *reviews covering NP measurements* have been published this year. The first of these described here was presented by Laborda *et al.* and covered the detectability of NPs and the estimation of detection limits in sNP-ICP-MS from a metrological approach.[263] The paper summarises and reviews, citing 48 papers, the different approaches that have been applied to determine whether NPs are detectable using sNP-ICP-MS and proposes a holistic approach for the estimation of the different critical values and LOD values. In addition, a calculation tool for estimating and predicting these critical and LOD values under different experimental conditions is also presented. The paper focuses more on the discrimination of particle events and the calculation of size LOD values, with less attention given to particle number concentrations and the associated dissolved element LOD values. The authors concluded that the discrete nature of the detected signals from individual particles and the distributions involved, which are governed by Poisson statistics, introduce additional levels of complexity in data treatment that have been overlooked in many publications. They also concluded that sNP-ICP-MS still lacks a standardised metrological approach to express and calculate its detection capabilities. A review by Mozhayeva and Engelhard, with 241 cited references, covering sNP-ICP-MS assessed the steps needed to be taken for it to become an "ideal method for nanomaterial characterization".[264] Most of the citations are summarised in tabular format with the text mainly devoted to sample introduction systems, the behaviour of NPs in the ion source, ion transport to the detector and the mass analysers in between the ion source and the detector, NP quantitation and the coupling of NP separation systems to ICP-MS instruments. The authors concluded that a careful optimization of the plasma conditions and dwell time is required to achieve improved NP size LOD values as well as accurate particle size and number values from a sample. Whilst sNP-ICP-MS is currently a very useful method for NP analysis there is still

room for fundamental studies, instrumental improvements, and methodological advances to bring the technique closer to the goal of being an ideal method for nanomaterial characterization. The paper by Galazzi *et al.* that reviews, with 80 cited references, ICP-MS for NP detection and characterization reported on the evaluation of NPs in distinct biological samples and the behaviour of NPs and their toxicity in organisms.[265] As well as sNP-ICP-MS the review has significant sections covering the use of LA-ICP-MS, HPLC-ICP-MS, FFF-ICP-MS and single-cell ICP-MS. The authors concluded that ICP-MS based strategies can help, to a large extent, in many studies and applications involving NPs and in analytical, biological, medical and environmental areas. A discussion paper by Wojcieszek *et al.*, entitled what "To-Do and Not-To-Do in Model Studies of the Uptake, Fate and Metabolism of Metal-Containing Nanoparticles in Plants", which cites 54 articles, has also been published this year.[266] The paper covered in detail areas such as NP transformations in growth media, sample preparation and the extraction of intact NPs from solid samples, NP uptake, translocation and biotransformation in plants. Speciation studies of NP and spatial distributions were also covered. The review is a welcome and timely addition to the NP focussed literature given the ever increasing number of studies involving NPs. The authors presented a number of recommendations on how to undertake such studies in the conclusion section with probably the most important being that initial studies should verify that the NPs under study are stable in the growth media used and that NP stability in the extraction protocols to be used should also be assessed.

Further *reviews on the use of atomic spectroscopy for NP characterization* and detection have also been published this year. One of these, by Semenova and Silina, covers the various techniques that can be used to investigate the manufacture of organic–inorganic nanohybrids.[267] The review, which cites 93 papers, gives an overview of a number of techniques that can be used for this purpose, namely FT-IR, Raman spectroscopy, surface plasmon resonance, ICP-MS, sNP-ICP-MS, LA-ICP-MS, TOF-SIMS, LC-MS and laser desorption ionization mass spectrometry. The authors concluded that the nanoanalytical techniques mentioned in the review require a fundamental understanding of the physical processes between nano-objects and these detection techniques. Developments in this field will help the extraction of a maximum of analytical information from a single run. To address this, developments in both nanoanalysis tools (instrumentation), as well as new nano-analytical methodologies, are to be expected. Two reviews covered different aspects of X-ray-based techniques for NP characterization and detection. The first of these, by Bleiner *et al.* with 128 articles covered, was a tutorial review of soft X-ray LA for nano-scale chemical mapping microanalysis.[268] The review gave a good overview of the topic, including differentiating between imaging and mapping, spatial resolution and the trade off with chemical resolution, mechanisms of laser sampling, laser-plasma emission spectrometry and laser MS with a wealth of information included. Detailed conclusions on the benefits and drawbacks of the techniques discussed were given. The authors concluded that the results presented show

that XUV/SXR-laser desorption spectrometry shows promise as an alternative to XUV/SXR-laser ablation spectrometry although 'engineering robustness' of the instrumentation needs to improve for this to be achieved. The other aspect of X-ray-based techniques that has been reviewed is angle resolved XRF, as given by GE-XRF and GI-XRF.[269] This review by Baumann et al., which cited 158 papers, gave a good introduction to the fundamentals of these two allied techniques, with sections on excitation sources including X-ray tubes, synchrotron radiation, laser produced plasmas, ion beams and the various detectors in current use. The review also had an extensive section on applications of GI-XRF and a smaller section on coupling of GE-XRF with other techniques such as microfocus excitation. In separate reviews, the preparation of nanoparticles for TOF-SIMS and XPS analysis was presented by Bennett et al. (54 references)[270]. The detection of TiO_2 in aquatic samples by Heilgeist et al.[271] and a historical perspective on the synthesis, investigation techniques and properties of Ag NPs, by Pryshchepa et al.[272] (with 159 and 255 articles cited, respectively) have also been published in the period covered by this update.

4.10.2 Fundamental papers. For particles with dimensions at the size limit of detection (LOD_{size}) the generated ion signals lie within the standard deviation of the background signal, which arises from the signal from ionic species of the analyte present in the sample and electronic noise. Thus, there is considerable interest in *improving sample transport to the plasma and increasing ion transmission in the MS for SP-ICP-MS to improve obtainable figures of merit*. One way of improving the ion transmission is to increase the mass bandwidth of the quadrupole mass filter and this approach has been described and used by Meyer et al. for Au and composite REE NPs.[273] After optimization the sensitivity for ^{197}Au increased by a factor of 8.4 with a decrease in the LOD_{size} from 7.0 to 4.9 nm. Increasing the quadrupole bandwidth decreases the mass resolution, allowing spectral overlap from adjacent m/z ratios and this factor allowed the sensitivity for the REES under study to increase by differing factors e.g. Er by a factor of 12 and Gd by a factor of 33. As the authors pointed out, one of the drawbacks of this approach is the potential for spectral interferences from other elements present in the samples under study. These therefore need to be carefully considered and it is possible that this approach is only suitable for suspensions of single element NPs and ions and not for multielement solutions.

An alternative approach to *improving sensitivity for single NP analysis, using a newly developed conical torch* as opposed to the parallel path of the conventional Fassel type torch fitted to most modern instruments, has been reported by Alavi et al.[274] The torch was fitted into what appears to be an in-house built ICP-OES instrument, with axial monitoring of the produced emission signals. A microdrop generator was used to produce monodisperse 50 μm Ø droplets containing NPs from one of eight elements, Ag, Al, Be, Ca, Fe, Mg, Na or Sr, which were desolvated and introduced into the plasma *via* an Ar gas carrier stream. A detailed description of the conical torch, which operates at a reduced RF power and gas flow rates compared with a Fassel type torch, is given in a cited reference and the sample introduction system is described in ESI. After

optimization of the system for both conical and Fassel torch types, it was found that the conical torch gave a 1.5 to 8 times larger peak intensity, a two to four times greater peak area and higher precision (on average a 1.5 times lower RSD for peak intensity and a 1.8 times lower RSD for peak width) than the Fassel type torch. The authors concluded that these improvements observed using the conical torch were due to a much higher electron density in the plasma, a higher excitation temperature and plasma robustness and an improved particle trajectory which led to more rapid vaporization, atomization and ionization of particles with a lower atom/ion cloud diffusion. The capability of analysing single particles at a rate of at least 2000 particles per second was also demonstrated. It remains to be seen if any of the major instrument manufacturers or component suppliers will offer this conical torch design commercially. A microdrop generator has also been used to produce monodisperse droplets, containing different amounts of a dissolved element, to expand the versatility and the general understanding of sNP-ICP-TOF-MS measurements.[275] In this work by Gundlach-Graham and Mehrabi, the temporal durations and elemental sensitivities obtained from the produced microdroplets and NPs were very similar such that microdroplets were used as proxies for NPs by controlling the absolute mass of elements injected into the plasma in each droplet. The paper described how microdroplets can be used to calibrate sNP-ICP-MS, in terms of both NP mass and particle number concentration and shows that, when combined with sNP-ICP-TOF-MS, online microdroplet calibration can be a powerful method for untargeted quantitative single-particle analysis. The use of microdroplets as a tool to study approaches for split event correction and single-particle detection with ICP-TOF-MS was also demonstrated. The authors concluded that microdroplet-based sample introduction, giving total consumption and quantitative transport of analyte in each microdroplet, could reduce sampling bias and thus improve quantification of element-mass distributions in analyte particles or cells. They also pointed out that the low volumetric throughput for microdroplet sample introduction remains a challenge for the detection of anthropogenic NPs at environmentally relevant particle number concentrations (10^2 to 10^6) but anticipate improvements in this direction.

A *general factorial design, with nebuliser gas flow, plasma RF-power and sampling depth as the independent variables* and the intensity of ^{197}Au as the response variable, was used by Kinnunen et al. to improve the sensitivity of sNP-ICP-MS for Au NPs.[276] The optimization was performed using both Au NPs and solutions of ionic Au and the instrumental parameter values after optimization were found to be in a good agreement for both analyte types, indicating a similar behaviour of the NPs in the plasma when compared with the dissolved analyte. The results obtained showed that significant interactions occur between the main instrument parameters under study hence consecutive single parameter optimization approaches may not be suitable for optimizations of sNP-ICP-MS instrumental conditions. The authors also point out that for more challenging analytes, such as Fe or Ti NPs, the potential for polyatomic interferences and doubly charged ions also needs to be

included in the optimization routine. In sNP-ICP-MS the ion cloud produced from each particle is detected as a transient signal and, due to the size range of NPs that can be detected, this can span many orders of magnitude of the detector response. Non-linear detector responses can therefore cause biased results and this has recently been investigated by Strenge *et al.* using an in-house constructed data acquisition system fitted to a commercially available ICP-MS instrument.[277] The device was used to assess the suitability of applying dead time correction to time resolved signals from gold NPs of both milli- and microsecond durations generated by a microdroplet sample introduction device. The results were compared with those obtained from the analysis of 11 Au NP suspensions, covering a size range of 10–100 nm, introduced *via* regular solution nebulisation. Applying a dead time correction routine to µs time resolved data increased the maximum number of counts tolerated per particle by four to fifteen-fold which resulted in the linear dynamic range increasing from 10–40 nm to 10–60 nm for Au NPs. It was also found that an accurate cross-calibration between pulse and analogue counting detector modes could extend the linear range up to 100 nm. The authors concluded that the results obtained support the theory of dead time related count losses being the main reason for nonlinear response in pulse counting sNP-ICP-MS. However, applying a dead time correction can lead to slightly distorted measured particle size distributions. In addition, despite the fact that counting electronics with ultra-low dead times could further improve the linear dynamic range, other ways must be explored to extend the top end of the tolerated particle mass range and, thereby, the methods' applicability and usability. The five papers covered in this paragraph provide a wealth of information and interest for those who wish to explore the fundamentals of sNP-ICP-MS.

A number of reports of *attempts to improve the figures of merit achievable using sNP-ICP-MS* have been published this year. The use of IR energy to heat the sample introduction system, with the aim of reducing the LOD values obtainable, has previously been described in conjunction with ICP-OES. Williams *et al.* have now investigated whether this approach can improve the sample transport efficiency for sNP-ICP-MS.[278] It was found that the number of detected Au NPs per min increased from 540 at room temperature to 600 at 60 °C and 840 at 80 °C. However, as it was only possible to use IR heating outside of the torch box, condensation could subsequently occur as the aerosol cooled on the way to the torch and no significant change in the LOD_{size} resulted at 60 °C and degradation of this parameter occurred at 80 °C. The authors then investigated mono-segmented flow analysis (MSFA), in which a discrete sample volume is injected into a flow of air, in conjunction with sNP-ICP-MS for the same purpose. It was found that, with IR heating the transport efficiencies rose from 3.7 ± 0.3% to 10 ± 1% at 20 °C and 4.1 ± 0.2% to 12 ± 2% at 60 °C for sNP-ICP-MS and MSFA-sNP-ICP-MS, respectively. In all cases the measured size of the Au NPs, which ranged from 50 ± 13 to 54 ± 6 nm, were in statistical agreement with the certified size of 49.9 ± 2.2 nm. The same research group have also published a paper which described a different approach for calculating NP masses from sNP-ICP-

MS data.[279] If external calibration with standard solutions is used to find the mass of NPs, the average signal intensity for each standard solution is typically used, which requires measurement of the transport efficiency of solutions through the spray chamber. In this new approach the signal is integrated over a constant time period for all standards and samples and the mass of analyte aspirated can be calculated from the analyte concentration in each standard, the gravimetrically determined sample uptake rate and the integration time used. The line of best fit through the calibration curve of integrated signal *versus* sample mass can then be used to find the total mass of NPs nebulised during the integration time, and the mass of each NP then corresponding to the fraction of the total integrated signal caused by the NP. Measurement of the transport efficiency is only required if the concentration of NPs is desired. An alternative approach to improving sample transport efficiency is to directly nebulise NP suspension into the plasma, which obviates the need for transport efficiency measurements. These two papers contain a good explanation of the theory of IR heating and the calculations involved for the new approach for estimating transport efficiency and are well worth a read. A demountable direct injection high-efficiency nebulizer introduction system hyphenated to a flow-injection valve and a gas displacement pump was used by Tharaud *et al.* for this purpose with sample flow rates as low as 8 µL min^{-1}.[280] Measurements made using this system were described as accurate and repeatable and the average measured diameters of Ag, Au and Pt NPs were in agreement with the manufacturers' reference values. The system was also used to analyse for Au NPs in surface waters.

A study by Yamashita *et al.* reported on a *new approach to extend the quantifiable size range of Au NPs in sNP-ICP-MS*, which is typically limited by detector saturation.[281] To achieve this, the signal intensities of Au related polyatomic ions such as $^{197}Au^{12}C^+$, $^{197}Au^{14}N^+$, $^{197}Au^{16}O^+$ and $^{197}Au^{40}Ar^+$, instead of the $^{197}Au^+$ signal, were used for the size calibration of Au NPs. Using the $^{197}Au^{40}Ar^+$ for example, the signal intensities emanating from the Au NPs were reduced to the 10^5 level for 400 nm Au NPs. This allowed the $^{197}Au^+$ signal to be used for the analysis of samples containing Au NPs in the 10 to 100 nm size range and the $^{197}Au^{40}Ar^+$ signal for the 200 to 400 nm size range. The use of different collision/reaction cell gases to allow the reliable detection of Fe, which suffers from a number of polyatomic interferences, was reported by Rua-Ibarz *et al.*[282] Based on the figures-of-merit obtained for the different approaches evaluated, an on-mass approach, *i.e.* measuring the Fe isotope directly rather than as an adduct at higher mass, using NH_3 as the reaction gas in single quadrupole-ICP-MS, an on-mass approach using H_2 as the collision/reaction gas in ICP-MS/MS and pseudo-medium resolution in SF-ICP-MS were found to be the best-suited approaches for fast interference-free monitoring of the ion signals generated by Fe_3O_4 NPs in single particle mode. The authors stated that the use of H_2 as a reaction gas provided accurate and precise results for custom-made 50 nm Fe_3O_4 NPs whilst the use of NH_3 was less successful, due to a lower signal-to-background ratio.

4.10.3 Method validation. Several *studies focussed on improving the validation of data acquired using sNP-ICP-MS* have been published this year. Usually, the sample transport efficiency in sNP-ICP-MS is measured using a suspension of pure NPs, often of a single size. However, for some NPs pure suspensions are not available, particularly for those consisting of two or more elements or compounds. Therefore, an alternative approach, in which the transport efficiency is determined gravimetrically and termed a dynamic mass flow approach, has been developed by Cuello-Nunez *et al.*[283] Initial studies used well characterized spherical Au NPs of 30 and 100 nm nominal diameter and the particle number results obtained by the dynamic mass flow approach, the conventional particle frequency approach and a laser-based (405 nm) particle tracking analysis method were all in good agreement within uncertainty limits. Subsequently, the dynamic mass flow method was applied to the particle number determination of triethanolamine stabilised bipyramidal shaped TiO_2 NPs for which no reference standard was available. Again, the results obtained for the dynamic mass flow and particle tracking analysis methods were in good agreement within uncertainty limits. For all approaches investigated, the uncertainties of the measured particle number concentrations, which are fully traceable to the SI, were between 10 and 15% relative, with the number of detected NP in the ICP-MS time scan being the major contributing factor to the overall measurement uncertainty. The use of microdroplet generators is increasing in laboratories investigating fundamentals of sNP-ICP-MS and a report of a combined microdroplet generator/conventional nebulisation sample introduction system was published by Rosenkranz *et al.*[284] The system allowed rapid switching between the two devices, with each being able to introduce either NPs or their dissolved ion solutions to the plasma, such that various signal types could be monitored in a single time resolved run allowing rapid assessment of the total metal concentration and particle number and mass concentrations to be made, even when well characterized NPs are not available. After optimization the system was tested using Ag, Au and CeO_2 NPs in three different modes, termed counting mode (mode I), sensitivity ratio mode (mode II) and the well-established analysis mode in which both ionic standards and NP-containing suspensions were introduced *via* the microdroplet generator (mode III). For all three modes the measured particle sizes for the Ag, Au and CeO_2 NPs were all in statistical agreement with each other and the supplier's data for the Ag and Au NPs. However, the determined average value for CeO_2, 69 ± 6.4 nm, was much higher than the expected 28.4 ± 10.4 nm. The authors attributed this to possible NP agglomeration and/or the inability to detect NPs existing within this lower size range. For the Ag and Au NPs particle number concentrations were in agreement with the supplier's data when measured using modes I and II, with recoveries of between 91 and 100%. However, this was not the case for mode III where the recoveries were between 70 and 88%. For the CeO_2 NPs the authors concluded that this latter measurement was not possible due to these NPs' polydiversity, size and polyhedral shape.

4.10.4 Clinical studies. *Nano-carrier systems, such as liposomes used to deliver specific oncology drugs to tumour cells, have promising biomedical applications* but characterizing these complex samples can be a challenging analytical task. One approach developed for this purpose by Hachenberger *et al.* is a coupled hydrodynamic chromatography sNP-ICP-MS system and the proposed methodology was validated based on the ISO 19590:2017 technical specification.[285] The hydrodynamic chromatography column used was capable of separating NPs in the size range 0.1 to 300 nm, with a mobile phase of 0.5% Tween-20, 0.13% sodium dodecyl sulfate and 5 mmol L^{-1} ammonium acetate flowing at 1.5 mL min^{-1}, with 10% of this flow directed to the ICP-MS instrument used *via* a flow splitter. A Y piece was also inserted post-column to allow calibration solutions to be directly introduced to the ICP-MS instrument during chromatographic dead times. After optimization the LOD$_{size}$ values were 12.7 and 10.3 nm for Au NPs by sNP-ICP-MS and hydrodynamic chromatography-sNP-ICP-MS, respectively. Method validation using NIST:8013 60 nm Au NPs at two concentration levels, 500 and 50 pg mL^{-1}, showed no differences within uncertainty limits for particle number and recovery measurements. The values obtained for transport efficiency sNP-ICP-MS and hydrodynamic chromatography-sNP-ICP-MS, also showed no difference. The actual transport efficiency was lower for the sNP-ICP-MS method (2.54%) compared with the HDC-sNP-ICP-MS method (6.86%). The found particle size measurements agreed with the certified values, within uncertainty limits, for both approaches. Further validation and cross calibrations between the two methods described were also undertaken and are described in detail in the paper. Finally, as a proof-of-concept application, various liposomes with embedded Au NPs were analysed and the hydrodynamic sizes and metallic/inorganic content of lipid-based nano-carrier systems were determined. It was shown, which is again described in detail, that the HDC-sNP-ICP-MS setup was able to differentiate between similar sized lipids, the liposome inorganic content could be evaluated, that the particle uptake distribution of the loaded liposomes could be obtained in parallel with the actual hydrodynamic size of the nano-carrier systems and that liposome loaded and free NPs could be distinguished which is not possible with conventional sNP-ICP-MS. Due to instrumental developments it is now possible to use sub-millisecond dwell times for sNP-ICP-MS and the effect of this on the LOD$_{size}$ obtainable for sNP-ICP-MS was investigated by Mestek *et al.* using Ag NPs as the target analyte.[286] Using dwell times of 10, 20 and 50 μs did not lead to a statistically significant decrease in the obtainable LOD$_{size}$, which ranged between 9.4 ± 1.2 and 11 ± 4.7 nm, when compared with the value obtained using a dwell time of 100 μs, 12.4 ± 2.4 nm. When analysing for Ag NPs close to the LOD$_{size}$, a low detection yield was observed, with only 5% and 44%, for 14 and 20 nm NPs, respectively, of the expected number of NPs as estimated from the transport efficiency, being detected. For 30 nm NPs the detected and estimated particle number concentrations were in statistical agreement leading the authors to conclude that, when using very short dwell times for NP sizes near the LOD$_{size}$, the apparent transport efficiency value changes sharply and subsequently affects the particle concentration detection limit and that these measurements should be made with caution.

4.10.5 Multiple isotope analysis. Typically, sNP-ICP-MS is used to determine a NP comprised of a single element but, as NPs and microparticles can be comprised of more than one element or may contain isotopic information that can lead to source apportionment, the research field is expanding to account for this. Reports of ICP-MS being used to detect C, due to poor sensitivity and generally high background levels in reagents, are few and far between. Therefore it is good to see a paper where *sNP-ICP-MS has been used to detect microparticles on the basis of the ^{13}C signal.*[287] In this work, by Laborda *et al.* a flow focussing nebuliser was used in conjunction with a spray chamber designed for single cell analysis to improve the transport of the microparticles to the plasma. A range of dwell times, from 50 to 200 µs, were employed to analyse suspensions of latex and polystyrene microparticles, extracts of personal care products and teabags and Au NPs. Very high purity Ar (99.9999%) was used in an attempt to minimise background signals, which ranged from 80 000 to 100 000 cps for high purity water with a typical sensitivity of 1000 cps per 1 mg L^{-1} ^{13}C. After careful optimization of the system for both particle transport and atomisation efficiency, a LOD of 0.8 mg L^{-1} was achieved, illustrating the challenges involved. The authors stated that acidification and inert gas purging of the samples was not considered appropriate. The reasons for this are not given and would be interesting to know but an LOD of 0.1 mg L^{-1} for dissolved organic carbon, using combustion/IR based instruments, can be readily achieved. It would seem that further work on this aspect could reduce the background to more manageable levels. The transport efficiency for 2.22 µm polystyrene microparticles was 29.9 ± 0.9% which was in fair agreement with the efficiency calculated using 50 nm Au NPs of 28.2 ± 0.4%. This fell to 12.5 ± 0.6% for 4.82 µm polystyrene µPs, showing that transport efficiency is dependent on size for polystyrene microparticles over *ca.* 3–5 µm. For size measurements of the polystyrene microparticles recoveries ranged from 90 to 95% for particles ranging from 1.98 to 5 µm but were 163% for 1.04 µm particles. Particle number concentrations were accurately measured up to 2 × 10^9 L^{-1} for 3 µm particles and a good discussion of the steps needed to achieve accuracy in both particle size and number measurements was given in the paper. The size of the particles detected in the personal care products and teabag extracts ranged between 2 and 3 µm with 10^7 to 10^{11} particles per g released from the former and 10^4 particles per g released from the latter. Although, as the authors stated, the technique has limitations, particularly for environmental samples where particle number concentrations are often much lower than those measured here, it also shows promise if the challenges of high background levels of C can be reduced.

A *multi-method approach to characterize metal nanoparticles contained in nanoplastic colloids*, which were described as composite particles, was reported by Barber *et al.*[288] The techniques FFF-sNP-ICP-MS, TEM, Asymmetric Flow Field-Flow Fractionation-UV–Vis (AF4) and centrifugal field-flow fractionation (CFFF) were employed. The in-house synthesised target analytes were Au polystyrene-*block*-polyacrylic acid (Au-PS-*b*-PAA), Au-PS and Au-citrate NPs. The metal NP size and particle number concentration were obtained using sNP-ICP-MS whereby AF4 and CFFF were used to separate and size the composite particles based on their hydrodynamic diameter and buoyant mass, respectively. Off-line sNP-ICP-MS analysis of fractions obtained by the FFF separations facilitated measurement of the mass and number of Au-PS NPs (from 1 to >8) contained in the composite particles. Differences or similarities in the NP size results obtained by AF4 and sNP-ICP-MS were used to further characterize composite particles, with the use of AF4 also allowing the detection of organic material associated with the inorganic NPs. In CFF, using a carrier that was density-matched to the polymer component of the composite particles allowed the measurement of multiple gold NPs in the composites. The authors concluded that to effectively apply the developed methodology to the environmental behaviour of nanoplastics in model systems, the mass of metal NPs in the composite particles should be kept small compared with the overall mass of the polymer in the nanoplastic.

Various analytical techniques, FFFF, sNP-ICP-MS, dynamic light scattering (DLS) and TEM were used by Maknun *et al.* for *the size analysis of SeNPs coated with either proteins, giving positively charged NPs, or sodium dodecyl sulfate, giving negatively charged NPs.*[289] A commercially available detergent, FL-70, was used as the symmetrical channel carrier in FFFF with a 10 kDa regenerated cellulose membrane to minimise particle–membrane interactions. The synthesised SDS coated SeNPs ranged in size from 30 to 190 nm whilst the protein coated Se NPs were in the 30 to 75 nm size range. The measured hydrodynamic sizes by both asymmetric and symmetric FFFF were always statistically lower (as tested using a *t*-test), than those obtained using DLS whilst the core diameters estimated using sNP-ICP-MS were always in agreement with the TEM method used. Due to the slow response time of Faraday detectors, MC-ICP-MS is rarely considered for sNP-ICP-MS. However, if the instrument is fitted with ion counting detectors, which are much faster to respond, then using MC-ICP-MS for the determination of the isotopic ratio of a NP becomes possible and this has been described for Pt NPs.[290] In this work the instrument was fitted with three electron multipliers and three Daly detectors, which allowed four isotopic signals to be monitored in any combination, and high-time resolution amplifiers which allowed dwell times as short as 10 µs to be used to monitor the four Pt isotopes, *m/z* 194, 196, 197 and 198. Data presented for the ^{195}Pt : ^{194}Pt isotope ratio, which is naturally close to unity thus minimising the effects of mass bias, was always in agreement with, but lower than, the natural ratio. The uncertainties (2 SD) on the isotope ratios were 35% for 30 nm NPs, 17% for 50 nm NPs and 10% for 70 nm NPs with the precision obtained presumably improving due to the increasing ion signal with increasing NPs size for a given particle number concentration. The measured sizes for 30 and 50 nm Pt NPs were 30 nm ± 3 nm and 47 nm ± 5 nm which was in agreement with the data acquired by TEM. The authors suggested that the effect of dead time correction can account for part of discrepancy in the measured ^{195}Pt : ^{194}Pt ratio from the natural value. The dead time correction factor was calculated using a solution of

dissolved Pt and it may be that alternatives to this, using NPs, needs investigating. The aim of the work was to develop a method which could be applied to the measurement of isotope ratios in the small metallic grains (<500 nm) found in meteorites and the authors concluded that the approach described shows promise in this direction.

4.10.6 Particle sizing and other applications. The *various forms of FFF are probably the most common technique used for the separation of NPs based on size and this is often coupled with ICP-MS as the detector.* Velimirovic *et al.* used a combination of ultracentrifugation and hexane washing, thermal destruction of the matrix, and surfactant assisted particle extraction to extract TiO$_2$ NPs from sunscreen products.[291] Particle size distributions in the extracts were assessed using AF4 hyphenated with Multi-Angle Light Scattering (MALS) and ICP-MS based on size calibration of the particle retention time in the AF4. The accuracy of the methodology was assessed by two internal reference samples: TiO$_2$ NPs (EC JRC NM104) and similar TiO$_2$ nanoparticles dispersed in a sunscreen matrix. In each case the particle mass concentration recovery was greater for ICP-MS, 83–93%, than for MALS, 71–79%. When the developed methodology was applied to two commercial sunscreen samples TiO$_2$ NPs <100 nm were detected. In a separate study reported by the same group, an intra-laboratory assessment was carried out to establish the effectiveness of a method for the detection of TiO$_2$ NPs and particles of a larger size, 200–500 nm in sunscreens.[292] The extraction procedure involved the addition of a commercially available cleaning agent to aliquots of the sunscreens under test, shaking, ultrasound-assisted extraction (UAE), the addition of 0.2% SDS (m/v) at pH 8.5–9, further UAE, dilution with 0.1% (v/v) SDS, filtration through 0.02 μm disc filters and a final step of UAE. Quantitative AF4-MALS and AF4-ICP-MS measurements of the hydrodynamic radius of the NM104 and the extracted TiO$_2$ NPs were then undertaken with the values obtained for the NM104 NPs used as reference values for the spiked sunscreen samples. It was found that there was a shift in the size distribution towards larger sizes for the spiked sunscreen extracts when compared with the reference values. Uncertainties, based on the method precision, were 3.9–8.8%. Finally, the bias data showed that the trueness of the method (5.5–52%) can only be taken as a proxy due to the lack of a sunscreen standard containing certified TiO$_2$ NPs. The paper contains a wealth of detail and should be read by those wishing to undertake this type of analysis.

An alkaline extraction procedure was reported by Ojeda *et al.* for the extraction of TiO$_2$ NPs from photocatalytic products and crab sticks.[293] The procedure consisted of the suspension of the sample in TMAH (10% v/v) with UAE at 37 kHz for 2 hours followed by centrifugation and then dilution of the supernatant (1 : 10) in the AF4 carrier (Novachem, 0.05%) or storage at 4 °C for analysis by sNP-ICP-MS. Particle sizes in the range of 50–90 nm and 160–170 nm were estimated in the different photocatalytic products by AF4-DLS, which were in good agreement with the sizes predicted by calibration *versus* SiO$_2$ and polystyrene standards. In the crab sticks, particle sizes of between 140 and 350 nm were estimated by AF4-DLS. These results were also compared with those obtained using sNP-ICP-MS. The size

value obtained using sNP-ICP-MS was about a quarter of that for AF4-DLS. This difference is explainable by the different parameter measured by the two techniques, mass spherical equivalent diameter *vs.* hydrodynamic diameter, respectively and the higher LOD$_{size}$ obtainable with AF4-DLS. Silicon dioxide is a permissible food additive and a method for the extraction of SiO$_2$ NPs from coffee creamer and their subsequent characterization using AF4-ICP-MS was reported by Li *et al.*[294] The dominant primary size of the extracted SiO$_2$ NPs was 36.5 nm and the NP fraction, compared with the total SiO$_2$ content, was 18.6% for the dominant primary nano-silica particles by prechannel calibration and 35.7% for total SiO$_2$ NPs (<100 nm) by post-channel calibration, with recoveries of 90% for the former and 75% for the latter. Possible reagents to assist in the extraction of Ag and CeO$_2$ NPs spiked into river waters were investigated by Loosli *et al.*[295] Of the extractants investigated, which included NaOH, Na$_2$C$_2$O$_4$ and Na$_4$P$_2$O$_7$, the greatest recovery was achieved using Na$_4$P$_2$O$_7$ which the authors attributed to the greater efficiency in the break-up of natural and engineered nanomaterial heteroaggregates by this reagent. The size distributions of the extracted suspensions, assessed using AF4-ICP-MS, showed that the spiked Ag NPs were extracted from the river water as both primary particles and small (<100 nm) aggregates, whilst the spiked CeO$_2$ NPs produced aggregated particles in the size range 0–200 nm.

An analytical methodology based on AF4-ICP-MS was developed by Sanchez-Cachero *et al.* for monitoring *citrate coated PtNPs* (5, 30 and 50 nm) in water samples.[296] After optimization of the carrier composition, AF4 separation program, the focusing step and cross flow values, the PtNPs were fractionated in less than 30 min with quantitative recoveries of 100 ± 7%, $n = 5$. The optimized method was then used to study transformations, in terms of size and surface modifications, of PtNPs in synthetic and natural water samples over time and in the presence of organic matter. This was found to be a critical parameter in this regard. In AF4 the dissolved fraction passes with the cross flow through the membrane of the separation channel and is usually not analysed which is a disadvantage when compared with centrifugal field flow fractionation and chromatographic techniques. Thus, an AF4-ICP-MS system which allows the conversion of the discontinuous cross flow into a continuous flow to the ICP-MS for analysis was developed by Tan *et al.*[297] Quantification was performed both for aqueous standard solutions and for environmental water samples using ultrafiltration as a reference method. In addition, a combined method including monitoring of the dissolved fraction in the cross flow and the particulate fractions in the detector flow was also established. Comparison of the dissolved fraction data obtained with the new method and *via* ultrafiltration gave recoveries in the range of 87% to 120% for Ca, Mg and Si. For Al and P the dissolved fraction, which was in the low μg L^{-1} range, elevated recoveries were observed, presumably due to contamination from the AF4 system, but their values obtained still agreed with the ultrafiltration values within confidence intervals. This fraction is relevant to determine the ratio of free and particle bound nutrients or toxicologically relevant elemental species, to establish the dissolution rate of non-stabilised

(nano)particles and to establish a mass balance for quality control of the fractionation results. Fraction collection of the cross flow followed by off-line elemental analysis is rarely performed to determine the dissolved fraction because of delayed elution through the frit of the channel, dilution and elevated blank levels for some elements. The authors concluded that the system could be used to determine the ratio of free and particle bound nutrients or toxicologically relevant elemental species, for NP dissolution rate studies and for determining a mass balance for quality control purposes.

A number of studies have used *X-ray-based techniques to characterize and/or detect NPs* in different matrices. The fungicide activity of chitosan–silver nanocomposites (Ag–Chit-NCs) against *Penicillium expansum* from feed samples was evaluated by Alghuthaymi *et al.* using XRF, SAXS, XPS and TEM.[298] It was shown that Ag–Chit-NCs, in sizes ranging from 4 to 10 nm, were internalised into the *P. expansum* in cells, formed agglomerates in the cytoplasm, and were bound to cell organelles. The ability of the Ag–Chit-NCs to influence protein and DNA fragmentation in *P. expansum* was also assessed using sodium dodecyl sulfate–polyacrylamide gel electrophoresis (SDS–PAGE) which explained the apparent cellular protein response to the presence of the Ag–Chit-NCs. The intensity of *P. expansum* hyphal cell protein lines treated with Ag–Chit-NCs was very thin. This indicated that high molecular weight proteins were largely prevented from entering the electrophoretic gel, reflecting cellular protein modification and the possible damage caused by the binding of protein fragments to Ag–Chit-NCs. The *in vivo* percutaneous permeation and dermal safety of cosmetic cream containing Au nanosheets, and Au nanosheets extracted from cosmetic creams were investigated by Cao *et al.*[299] Imaging by SR-XRF showed that the Au nanosheets in cosmetics penetrate mainly through hair follicles in a time-dependent manner. Cosmetic creams, rather than the extracted Au nanosheets applied separately, decreased the cell viability of keratinocytes and slightly induced apoptosis/necrosis of keratinocytes and skin dermal fibroblasts. Hair growth was also inhibited by the cosmetic cream and the extracted Au nanosheets. A soft XRF-based methodology that allowed both a dimensional reconstruction of nanostructures and a composition characterization using GI-XRF was presented by Honicke *et al.*[300] The capability of this technique for this purpose was demonstrated by performing an element-sensitive reconstruction of a lamellar grating made of Si_3N_4, with GI-XRF data for the O-K alpha and N-K alpha fluorescence emissions allowing a thin oxide layer to be reconstructed on the surface of the grating structure. In addition, the technique was also applied to three dimensional nanostructures to derive both dimensional and quantitative compositional parameters. A semi-analytical approach for the characterization of ordered 3D nanostructures using GI-XRF has been reported by Nikolaev *et al.*[301] A computational scheme based on the dynamical diffraction theory in many-beam approximation, which allows a semi-analytical solution to the Sherman equation to be derived in a linear-algebraic form was used for this purpose as well as recently published GI-XRF data measured on 2D Si_3N_4 lamellar gratings, and on periodically structured 3D Cr nanopillars. Both the dimensional and

structural parameters of these nanostructures were reconstructed by fitting numerical simulations to the experimental GI-XRF data and the results of this showed good agreement with the nominal parameters used in the manufacturing of the structures, as well as with reconstructed parameters based on the previously published finite-element method simulations.

The application of *a convolutional neural network to in vivo XRF images of Au NPs* obtained using a benchtop instrument to eliminate Compton-scattered photons was reported by Jung *et al.*[302] The XRF imaging system comprised a 2D CdZnTe gamma camera, a pinhole collimator and fan-beam polychromatic X-rays. An architecture of the 2D convolutional neural network model for Compton background elimination was optimally designed and trained with data sets obtained by the measurements of water only and Au NP-embedded imaging phantoms. The XRF images generated by the trained 2D convolutional neural network were compared with those generated by a direct subtraction method. The developed 2D convolutional neural network was also applied to generate *in vivo* XRF images of Au in living mice exposed to Au NPs. The *in vivo* XRF images generated by the two methods were then compared in terms of the difference in Au NP concentration and it was shown that the 2D convolutional neural network model could be successfully applied to *in vivo* XRF images for detecting the concentration and location of Au NPs in living mice. Pulsed laser ablation in liquids (PLAL) is a hierarchical multi-step process to produce pure inorganic nanoparticle colloids. Controlling this process is hampered by the partial understanding of individual steps and structure formation. *In situ* X-ray methods were employed by Reich *et al.* to resolve macroscopic dynamics of nanosecond PLAL as well to analyse the distribution and speciation of ablated species with a microsecond time resolution.[303] High time resolution was achieved using 'single shot' synchrotron-based methods. X-ray multi-contrast imaging by a Shack–Hartmann setup and small angle X-ray scattering (SAXS) resolved evolving NPs inside the transient cavitation bubble, while the total material yield and the chemical state of the ejecta was monitored by dispersive mode XAS. It was observed that nanoparticles are produced directly during ablation and that reactive material was also detected. This was identified as Zn atoms. The NPs within the cavitation bubble exhibited a metal signature for a few milliseconds before gradual oxidation occurs.

A range of *other techniques has also been used for investigations involving nanomaterials*. One of these is GF-AAS which was employed by Brandt *et al.* to determine activation energies for ionic Au and Au NPs, by constructing Arrhenius-type plots from absorbance signals.[304] Ionic Au atomisation is governed by a two-precursor mechanism. For the first precursor no release order can be determined, but an estimated activation energy of 211 ± 26 kJ mol^{-1}, corresponding to atomisation from small atomic clusters was found. A release order of 0.3 showed that larger *in situ* formed aggregates are the second precursor. By varying the temperature ramp programme, the ratio of the precursors was altered resulting in different shapes of the absorbance signals. In contrast, the atomisation of Au NPs followed a one precursor atomisation mechanism. A "pseudo-

first" atom release order was found for all NP sizes and atomisation behaviour was found to be similar for each heating rate. The activation energy of Au NPs smaller than 20 nm increased with increasing NP size, while for larger sized NPs the activation energy was constant and approached the heat of sublimation of the bulk material. On the basis of the different atomisation mechanisms, discrimination of ionic Au and Au NPs, as well as sizing of nanoparticles seemed to be independent of the used atomisation temperature program, *i.e.* primarily the heating rate. A second paper by the same research group reported the use of GF-AAS for examining non-spherical Au and Ag NPs, such as rod and prism structures, as well as Fe, Pd and Pt NPs.[305] Using the methodology developed for Au and Ag NPs, the Fe NPs could be distinguished from ionic Fe^{III} and rod-shaped Au NPs and Ag nanoplates could be differentiated from their ionic forms. Discrimination between rods and plates was not possible as the rods and plates were converted to spheres during the temperature ramp program prior to atomisation. The determined diameters of spheres formed *in situ* were in good agreement with the theoretical values and diameters determined by SEM. For Pd and Pt neither a differentiation between ions and NPs nor a size evaluation was possible. A report on single-cell imaging of Au and Ag NPs by near-field desorption ionization mass spectrometry (NDI-MS) was published by Cheng *et al.*[306] A mean crater diameter of 310 nm on the cellular surface and single cell imaging with a 250 nm pixel size were achieved. Some compounds originating from surface ligands or endogenous substances were simultaneously imaged with Au NPs. Additionally, the location of the Au NPs was compared with the images from confocal laser scanning microscopy, which were in good agreement. The NDI-MS data showed a unique advantage of simultaneously imaging NPs and ligands at subcellular lateral resolution and the authors proposed that it can be extended to other NP systems and thus used as a general method for the exploration of the use of engineered NPs in biomedicine.

A *CE-ICP-MS/MS method for the determination of superparamagnetic iron oxide nanoparticles (SPIONs)* was reported by Kruszewska *et al.* with the aim of assessing changes in these NPs after incubation with proteins under simulated physiological conditions.[307] The SPIONs were added to a 10 mmol L^{-1} phosphate buffer, pH 7.4, containing 100 mmol L^{-1} NaCl and 1 mg mL^{-1} albumin, to give a final concentration of 30 μg mL^{-1} and the mixture incubated at 37 °C. A polyimide coated fused silica capillary (i.d. 75 μm; o.d. 375 μm; length 70 cm) was used for the CE separations with ammonium bicarbonate (20 mmol L^{-1}, pH 7.4) as the running buffer and an applied voltage of +18 kV. Oxygen was used as the ICP-MS cell gas to allow $^{32}S^{16}O$ to be monitored as a marker for proteins and V was added to the sheath liquid for use as an internal standard. Under these conditions the repeatability of migration times and peak areas ranged from 0.23–4.98% RSD, spike recoveries were 93 to 97% and the LOD values were 54 ng mL^{-1} and 101 ng mL^{-1} for SPIONs with carboxyl and amino terminal groups, respectively. The carboxyl coated SPIONs were found to be stable in the buffer solution for 24 hours whilst some of the amino coated SPIONs transformed into a form with higher electrophoretic mobility which matched the retention time of $FeCl_2$. Monitoring of the $^{32}S^{16}O$ signal led the authors to conclude that the majority of the carboxyl SPIONS and albumin present in the sample formed a conjugate. A CE-ICP-MS application was developed by Wroblewska *et al.* for monitoring the formation of cisplatin targeting delivery systems with Au NPs.[308] In this work cisplatin was bound to Au NP with 11-mercaptoundecanoic acid as a nanomaterial surface modifier, the electrolyte was 40 mmol L^{-1} HEPES at pH 7.4, the applied voltage was +15 kV, the sample injection pressure was 30 mbar for 5 s and the capillary length was 70 cm (i.d. 75 μm) with a total run time of 40 minutes. The results showed that an activated form of Au-cisplatin could be produced. Details of this procedure were given in a cited reference. All of the Au NPs were incorporated in the Au-cisplatin produced by this method. Taylor dispersion analysis is a microcapillary flow-based technique whereby a nanolitre-scale sample pulse is injected into the laminar flow of running buffer, which then undergoes axial dispersion. Detection of the equilibrium concentration profile of the dispersed sample pulse allows the molecular diffusion coefficient and hence hydrodynamic radius of solute molecules to be calculated. This technique has been coupled with ICP-MS to allow the determination of the hydrodynamic radius of Gd containing NPs, including sub 5 nm particles, in urine, cerebrospinal fluid, and undiluted serum. Precision of the measurements (RSD) was less than 10%. The authors stated that the specificity of the method provided the opportunity to perform measurements in complex biological media.

The physicochemical properties and applications of C based nanomaterials are dependent on the amount of carboxyl group on their surfaces, and it remains a challenge to *determine the amount of carboxyl groups on the surface of these structures*. A strategy to achieve this, comprising coupling carbon dioxide vapour generation to a microplasma OES, was developed by Yang *et al.*[309] The carboxyl group on multiwall carbon nanotubes (MWCNTs), graphene or its oxide was converted to carboxylic acid with HCl, the generated carboxylic acid was then purified, reacted with $NaHCO_3$ to generate CO_2, which was swept into a miniaturized point discharge OES for the detection of C atomic emission lines. Potassium hydrogen phthalate was used as a calibration standard and the LOD was 0.1 μmol g^{-1} for the carboxyl group based on a sample mass of 10 mg. Quantitative imaging of amyloid beta (A beta) in brain tissues is important in the development of Alzheimer's disease treatments. A method using antibody-conjugated Au NPs for quantitative imaging of A beta peptide in the brain of a mouse suffering from Alzheimer's disease using LA-ICP-MS was presented by Gao *et al.*[310] A beta antibody (anti-A beta) was labelled with Au NPs to form the conjugate Au NP–anti-A beta which was immunoreactive with A beta in the brain slice of mouse. Quantitative imaging of Au was acquired with homogenised brain slice matrix-matched standards as external calibrants. The stoichiometric ratios between metal conjugates and A beta were optimized and the immunoreaction efficiency after labelling was also investigated. According to the molar relationship between Au NPs and anti-A beta (1 : 4.3) and the ratio of anti-A beta to A beta (1 : 1), quantitative imaging of A beta in brain was accomplished. The

Table 1   Applications of nanomaterial characterization and/or detection

Analyte	Matrix	Technique	Comments	Reference
Au NPs		sNP-ICP-MS	Use of various NP sizes to determine membrane pore size. A mixture of 20, 30, 40 and 60 nm gold particles, at a concentration of approximately 7 $\times 10^7$ particles per mL for each nominal size or 2, 8, 19, 66 µg L^{-1} gold, respectively was used to determine the filtration performance over a wide size range	312
Au NPs		sNP-ICP-MS	Assessment of NP aggregation and colloidal stability under physiological conditions. The technique was used to quantify aggregate size and aggregation kinetics at the individual aggregate level. Potential applications may include nanoparticle aggregation in environmental samples and the preparation of colloidally stable nanoparticle formulations for bioanalytical assays and nanomedicine	313
Au NPs	Cell culture medium	sNP-ICP-MS	Characterization and quantification of AuNPs in only one minute of analysis at concentrations at the ng L^{-1} range. Sample preparation involved only a dilution step. Precise determinations of particle size and concentration (1% RSD) were reported with 22.4 nm and 2.1×10^5 particles per L as limit of detection for particle size (LOD$_{size}$) and for particle-number concentration (LOD$_{NP}$), respectively	314
Ag NPs	Nano-textiles	sNP-ICP-MS	Study of the release behaviour of silver from nanotextiles. Simulated sweat and water were the extracting media. Different extraction behaviour was observed between the two extractants, with the sweat releasing larger nanoparticles. However, the particle size extracted was related to the dilution factor. Hence, a standardized method was required to obtain reliable data	315
TiO$_2$ NPs	Confectionery products	sNP-ICP-MS, TEM	Inter-laboratory test using seven experienced food analysis laboratories, employing different instruments and software packages for particle size analysis of TiO$_2$ NPs confectionery products. Bias of the data was estimated using TEM	316
Te NPs	Bacteria	sNP-ICP-MS, single cell ICP-MS	Single cell and single particle analysis evaluating uptake and biotransformation of Te NPs in bacteria S. aureus and E. coli. Both strains converted nanospheres to nanorods. The amount of Te taken up was at the fg range, with E. coli taking up marginally less	317
ZnO NPs	Food packaging materials	sNP-ICP-MS, TEM	Study of effect of different types of food (orange juice and chicken) on the fate of ZnO NP migration from food packaging materials. Nanoparticle diameter LOD were 26 nm, 95 nm, 108 nm and 129 nm for aqueous solution, chicken breast extract and for oral and intestinal extracts, respectively	318
Au, Ag, ZnO, and CeO$_2$ NPs	Simulated gastric fluid	sNP-ICP-MS, SAXS, TEM	Study on the fate of NPs in simulated gastric fluid. Size detection limits for Ag-NP, Au-NP, ZnO-NP, and CeO$_2$-NP ranged from 15 to 35 nm. The particle concentration detection limit was 135 particles per mL. The ZnO-NPs dissolved completely and rapidly, whereas Au-NPs and CeO$_2$-NPs showed apparent aggregation and did not dissolve significantly	319

Table 1 (Contd.)

Analyte	Matrix	Technique	Comments	Reference
CeO_2	Natural waters	sNP-ICP-MS	Analysis of natural waters for CeO_2 NPs using a sector field instrument with a dwell time of 50 µs. CeO_2 NPs in rainwater at a concentration of $2.2 \pm 0.1 \times 10^8$ L^{-1} with a mean diameter of 10.8 ± 0.2 nm; and in a river water at a concentration of $1.6 \pm 0.3 \times 10^9$ L^{-1} with a higher mean diameter 21.9 ± 0.8 nm	320
Ag–Au, Au and SiO_2 NPs		sNP-ICP-MS	Determination of the porosity of nano- and sub-micron particles. Accuracy and precision were comparable to those of the reference methods, small angle X-ray scattering (SAXS), gas adsorption or TEM imaging	321
Pt NPs		sNP-ICP-MS, TEM	Characterization of Pt NPs for fuel cell applications. Results for particles with diameters of 30, 50 and 70 nm were compared with those from TEM. Technique then used for the characterization of 10 nm Pt NP	322
Ni NPs		sNP-ICP-MS	Characterization of Ni NPs which included a flow injection approach	323
Au NPs and Au–DNA conjugates		sNP-ICP-MS	DNA assay *via* Au NPs based on a hybridisation-chain-reaction-mediated spherical nucleic acid assembly. The assembly process generated large gold nanoparticle aggregates, and the number of aggregates could be counted by SP-ICPMS, which was closely correlated to the concentration of the target DNA. This simple homogeneous assay could analyse DNA within the range of 5 fM to 10 pM with excellent selectivity	324
Se NPs		sNP-ICP-MS, TEM	Size determination of Se NPs. Data obtained using SP-ICP-MS were consistent with those from TEM for the core diameter. Consecutive size analysis by SP-ICP-MS for the fractions collected from flow FFF was proposed for sizing of SeNP mixtures	289
Various NPs	Waste water	sNP-ICP-TOF-MS	A holistic study of particle behaviours during wastewater treatment. A new data analysis approach was reported. Waste water treatment plants had average of 90% and 94% removal efficiencies of single-metal and multi-metal NPs, respectively	325
Fe_3O_4 NPs		sNP-ICP-MS, TEM	Detection of Fe_3O_4 NPs in petroleum hydrocarbon materials. Helium used as a collision gas to control spectral interferences from ArO and CaO on Fe at m/z 56. Different cell gas flow rates (3, 3.5, and 4 mL min^{-1}) were tested and 4 mL min^{-1} was optimal	326
Ag NPs	Toothpaste	sNP-ICP-MS	Ultrasonic extraction combined with SP-ICP-MS was developed to detect the size distribution, number concentrations and mass concentrations of silver nanoparticles. After optimization, detection limits of particle size, number concentration and mass concentration were 23 nm, 3.9×10^8 particles per kg and 26 ng kg^{-1}, respectively were obtained	327
TiO_2 NPs		sNP-ICP-MS, TEM	Characterization of 15 batches of E171 food additive. After optimization of the sample preparation with method validation, a significant variation in the particle size and shape distributions, the crystallographic structure (rutile *versus* anatase), and the physicochemical form (pearlescent pigments *versus* anatase and rutile), was identified	328

Table 1 (*Contd.*)

Analyte	Matrix	Technique	Comments	Reference
Graphene oxide–Au NPs composite		sNP-ICP-MS	Bio-marker assay using graphene oxide–Au NPs with thrombin as the target analyte. AuNPs modified with thrombin aptamers were first non-selectively adsorbed onto the surface of graphene oxide (GO) to form GO/AuNPs composites. In the presence of thrombin, the AuNPs desorbed from the GO/AuNPs composites. The desorbed AuNPs were proportional to the concentration of thrombin	329
CeO$_2$		sNP-ICP-MS	Study of CeO$_2$ number and size distribution from different chemical mechanical planarization processes. Particle number concentrations were measured for the 21 to 559 nm size range at 1 nm size resolution	330
Pd NPs		ICP-MS, XRD, HR-TEM, EDX, SEM	Pd NPs synthesised and characterized to produce a risk assessment of particulate pollution on the murine macrophage cell lines	331
TiO$_2$ NPs	Personal care products	CE-sNP-ICP-MS	Screening for TiO$_2$ NPs in personal care products. Sensitivity was enhanced by cysteine which acts as a nanoparticles stabiliser. Method applied to lip balm and toothpaste samples	332
Halloysite-doped ZnO NPs	Sunscreen products	ICP-OES, TEM XRD	Synthesis and characterization of Halloysite-doped ZnO NPs for use in sunscreen	333
CuO, NiO, TiO$_2$ NPs	Cell culture medium and water	ICP-OES	Dissolution behaviour of metal oxide NPs in water and Dulbecco's modified Eagle's medium. Solubility of the metal oxides decreased in the order CuO ≳ NiO > TiO$_2$ in both media, solubility trends displayed by nano-TiO$_2$ were the opposite of those displayed by nano-CuO and nano-NiO	334
Ag NPs		TOF-SIMS	Proof-of-concept study. Different shapes (spherical, triangular and rod) of silver nanoparticles embedded within a hydrogel matrix of polyacrylamide. Anti-bacterial and mechanical properties studied	335
Au nanorods		Solution cathode GD-OES	Evaluation of solution-cathode GD-OES for the analysis of NP suspensions. Metallic nanoparticles with diameters from 5 nm to 150 nm were directly analysed and found to exhibit lower, and size-dependent, elemental sensitivity when compared with dissolved free-ion standard solutions. Correlation of NP boiling point with difference in sensitivity between free-ion and NP solutions supported the conclusion that delayed vaporization of nanoparticles is the source of the morphological matrix effect	336
Cu$_x$S NPs		SEC-ICP-MS, TEM	Study on the effect of natural organic matter (fulvic acid) on copper sulfide NP growth, stability and dissolution over a period of four weeks. At low Cu and S concentrations, fulvic acid restricted particle growth by up to 25%. The Cu$_x$S nanoparticles exhibited great chemical stability against oxidative dissolution and were only dissolved when both fulvic acid and oxygen were present	337
Ag and Au ions and NPs		HDC-ICP-MS	Evaluation of HDC-ICP-MS for the speciation of dissolved and NP Ag and Au. Optimization of the mobile phase identified that the addition of 0.05 mM penicillamine allowed the quantitative recovery of ionic gold and gold nanoparticles up to 50 nm, whereas 1 mM penicillamine was necessary for quantitative recovery of ionic silver	338

Table 1 (*Contd.*)

Analyte	Matrix	Technique	Comments	Reference
			and silver nanoparticles up to 40 nm. Best-case mass concentration detection limits for gold and silver species were 0.05 and 0.75 μg L^{-1}, respectively	
Au–Ag NPs		ICP-MS, TEM, SAXS	Determination of the morphology and concentration of core–shell Au–Ag NPs. The shell thickness, overall size polydispersity and number particle concentration obtained by the various methods were in good agreement	339
Au NPs		TOF-SIMS	Inkjet printing of Au NPs onto porcine gelatin coated Si wafers to create quantitative test materials. Spatially resolved quantification using TOF-SIMS was achieved for 30, 80, 100, and 150 nm particles deposited onto gelatin with loadings ranging from 34 fg up to 67 000 fg per spot	340
Au NPs		TOF-SIMS	Study on the detection of Au cysteine thiolate complexes on Au NPs. The presence of NaCl or a 2-(*N*-morpholino)ethanesulfonic acid buffer disabled the detection of Au NPs on the Al foil. In their absence, TOF-SIMS was demonstrated to be a good tool for the study	341
Al NPs	Copper thin film	TOF-SIMS, scanning TEM EDX	Elemental characterization of Al NPs buried under a copper thin film. The capability of TOF-SIMS to spatially resolve individual tens of nanometer large nanoparticles under ultrahigh vacuum as well as high vacuum conditions was demonstrated	342
Bronze NPs		LIBS	Optical trapping LIBS characterization of NPs generated by laser ablation of bulk targets in air. The main advantages of the technique were the circumvention of possible material losses owing to transference into the inspection instrument while providing the high absolute sensitivity of single-particle LIBS analysis	343
Au NPs		TOF-SIMS	Numerical evaluation of polyethylene glycol ligand conjugation to Au NPs. Statistical correlation values calculated from the signals of PEG and Au measured using TOF-SIMS imaging on the sample spots made by a micro-liquid inkjet printing system had better reproducibility and improved correlation values compared with the pipette spotting	344
Pt NPs		sNP-ICP-MS	Study on the effects of NP size and natural organic matter composition on aggregation of polyvinylpyrrolidone coated Pt NPs. The effects of nanoparticle size (20–95 nm) and different sources/compositions of natural organic matter were tested; with the latter being the key factor	345
Pt–Ti NPs		GI-XRF, NEXAFS	Study on the interaction of nanoparticle properties and X-ray-based analytical techniques. NEXAFS measurements were performed to investigate the binding state of titanium in the core–shell nanoparticles. This was amorphous TiO$_2$. The nanoparticles were characterized using reference-free GIXRF employing radiometrically calibrated instrumentation	346

Table 1 (Contd.)

Analyte	Matrix	Technique	Comments	Reference
Ag, Au, Cd, Eu NPs		LA-ICP-MS, ICP-MS	A study of different metal NPs for immune-analysis. Commercial kits of gold nanoparticles were the most suitable for the preparation of conjugates model monoclonal antibody (DO-1, recognizing p53 protein). The LA-ICP-MS detection gave a long linear range (0.1–14 ng) and had a LOD of 1.3 pg of P53 protein	347
CdTe quantum dots		CV-AFS, ICP-MS	Study on the use of nanomaterials for use as fluorescence label-free multimode bioassays	348
Ag_2S, ZnS NPs	Environmental waters	LC-ICP-MS	Speciation of Ag_2S and ZnS NPs in environmental waters by cloud point extraction. Precision was <4.9% RSD. Detection limits were 8 ng L^{-1} for Ag_2S-NPs and 15 ng L^{-1} for ZnS-NPs. Recoveries of 81.3–96.6% for Ag_2S-NPs and 83.9–93.5% for ZnS-NPs were achieved when spiked into three environmental water samples	349

method displayed the location and concentration of A beta aggregation in the brain tissues, and this was consistent with traditional immune-histochemical staining methods. The proposed methodology was stated to have potential for investigating the quantitative imaging of biomarker heterogeneity, and could also be useful for understanding complex brain mechanisms in the future. Analysis for NPs directly in solid biomatrices by LA-sNP-ICP-MS can produce erroneous results if non-optimal operational conditions are used. A report offered insights into the analysis for NPs by LA-SP-ICPMS, based on modelling the chain of events from NP release to LA cell washout to ICP-MS detection as a function of the biomatrix characteristics, instrumental specifications and variable operational settings was published by Metarapi and Van Elteren.[311] By processing the computational data *via* an "outlier" filter to differentiate between NPs and dissolved ions, guidelines have been established to achieve the optimal instrumental setup and operation. This assumes the measurement of homogeneously distributed metal NPs and dissolved metal and uses a laser fluence ≤ 1 J cm^{-2} to circumvent NP degradation.

Table 1 shows other applications of nanomaterial characterization and/or detection presented in the literature during the time period covered by this review. For those applications where a sample matrix was analysed, the material has been inserted to the table. However, for those applications where nanoparticles were analysed directly, this field has been left blank.

5 Cultural heritage

The analysis of cultural heritage samples continues to be a very popular topic. As with most years, the majority of the papers do not discuss the analytical experiments in any great detail, concentrating instead on the archaeological or historical aspects. These papers are therefore not discussed in this section. Instead, those papers that do go into greater detail will be discussed and others, that have some novelty, *e.g.* the use of chemometrics to discuss the provenance, manufacturing process, *etc.*, or those that show a good level of method validation, will be discussed in brief in tables. It is usual to want to preserve most of these samples. Therefore, techniques such as LIBS, LA and XRF that are either non-destructive or minimally destructive, proliferate.

5.1 Metallic artefacts of cultural heritage

A lengthy review containing 160 references of the *use of non-traditional heavy stable isotopes (e.g. Ag, Cu, Fe, Hg, Sb and Sn) in archaeological research* was made by Stephens *et al.*[350] Although the stable isotopes of these analytes do not have any radioactive parents, their ratios may undergo limited fractionation from various causes. The review was split into numerous sections, including sections for each of the analytes. The paper reviewed the recent work (since 2010) for archaeological purposes and investigated whether or not they may be used for determining the geological provenance of materials such as bronze and glass. The conclusion from the literature was that, in general, they could not. The Cu and, to a lesser extent thus far, Ag was useful for determining the type of ore (supergene or hypogene) the material had been made from though. Applications as well as future developments were discussed.

Dechlorination is a method of stabilizing archaeological iron artefacts. Reguer *et al.* investigated the use of *XANES as a technique for the analysis of Cl K-edge during the dechlorination treatment* of wrought iron bars raised from Roman shipwrecks.[351] The paper presented new results but also gave a summary of the work undertaken using X-ray absorption spectroscopy over the last 10 years. The historical work has aimed to decipher the corrosion patterns of Cl ions in iron artefacts and also to understand the dechlorination process. Samples complete with corrosion products were subject to dechlorination in either aerated solution (five samples) or de-

Table 2 Applications of the analysis of metallic cultural heritage artefacts

Analyte	Matrix	Technique	Comments	Reference
C	Archaeological ferrous materials	LIBS	A large laser spot enabled the bulk C concentration. However, it was not capable of analysing different steel phases. Therefore, micro-LIBS was developed that enabled C to be determined in the different phases and even for non-equilibrium structures	352
Pb and Sn	Copper alloys from the bronze age/iron age transition	Hand-held LIBS, p-XRF	Hand-held LIBS was compared with pXRF for the analysis. Hand-held LIBS was affordable, rapid and micro-destructive and was thought to have the potential for significant usage. However, results from pXRF were deemed to be better, despite its limitations in penetrating corrosion	353
Pb isotopes	Twelve bronze coins and 10 lead objects from 2nd to 1st century BCE	TIMS	Lead isotopes used to elucidate provenance of materials, All of the coins have Pb isotopes indicating that it originated from the mining district of Cartagena-Mazarron. The lead objects were more diverse and were split into three clusters. All of the objects from the bath complex also originated from the same place. However, workshop and household objects were unresolved; potentially because of re-smelting	354
Various	Armour from 13th to late 16th century from Italy, Germany and France	LA-ICP-MS	Microscopic silicon slag inclusions in the armour were analysed. Two LA systems used: one operating at 193 nm and the other at 257 nm. Analytical data interrogated using PCA and Linear Discriminant Analysis (LDA). Different provenance groups identified	355
Various (Ag, Au, Bi, Cu, Fe, Pb and Zn)	Incuse coins (31) from four cities from Southern Italy from 550 BCE to 470/440 BCE	XRF	Both PCA and HCA used to interrogate XRF data. All coins contain Ag (>95%) and Cu. All coins had a similar trace metal signature, indicating the ore originated from the same mine. Some coins appeared to have been overstruck	356
Various and Pb isotopes analysis	Warring states period bronze bracelets from Huili county, China	pXRF, MC-ICP-MS	Small spot on bracelets polished for pXRF analysis and then the pieces removed during polishing acid digested and analysed using ICP-MS. All bracelets contain approx. 85% Cu and 15% Sn. The Pb data indicate two main groups: one that used local copper without adding Pb and the other added Pb. The Pb isotope ratios indicate that this may originate from the middle reaches of the Yangtse region	357
Various	Early iron age ferrous remains from Arabia	XRF, ICP-MS, LA-ICP-MS	Slag inclusions analysed using LA-ICP-MS. Rocks and ores from different origins fused using lithium metaborate and then analysed using XRF for the major elements and ICP-MS for the minor/trace ones. Analytical data treated using PCA and HCA using Ward's method to enable provenance determination. Long distance trade with Iran, UAE and Oman potentially identified	358
Various (6)	Seal dies made from copper alloy	EDXRF	Samples (95) from 13th to 20th century underwent EDXRF analysis for Ag, Cu, Pb, Sb, Sn and Zn. Data interrogated using PCA. The elemental composition was correlated with the historical data and the location of manufacture	359
Various (8)	Mixed iron–copper chunks and iron objects from Jordan	LA-ICP-MS, TIMS	Two stage analysis: LA-ICP-MS to detect Au, Ir, Os, Pd, Pt, Re, Rh and Ru and then TIMS analysis for Os isotopes. No connection between high analyte concentrations and Os isotopes. The conclusion was that the objects were not locally produced. In addition, it provided evidence that an exchange network existed in the iron age Eastern Mediterranean	360

Table 2 (Contd.)

Analyte	Matrix	Technique	Comments	Reference
Various	Early medieval silver jewellery	LA-ICP-MS, SEM-EDX	Metallic components determined using SEM-EDX. Then, to obtain provenance, LA-ICP-MS used to determine Pb isotope ratios. Analytical data treated using LDA. Results indicated that all artefacts were made using re-melted metal from multiple sources. The most likely origin of the Ag was from Uzbekistan, Afghanistan or Germany	361
Various	Ancient silver coins	μ-XRF, LA-ICP-MS	μ-XRF used to detect Ag and Cu enrichment/depletion on coin surfaces. Achieved using Ag Kα/Ag Lα, Cu Kα/Ag Kα, and Cu Lα/Ag Lα for the coins and comparing with Ag–Cu standards of a similar composition. Those coins demonstrating Ag enrichment were analysed using LA-ICP-MS to measure trace elements in the core compared with the surface. Surfaces found to be enriched in Au, but depleted in As, Co, Ni and Pt	362
Various	Silver coins	LA-ICP-MS	Chronological discrimination of 266 coins based on inter-element ratios. NIST 610–617 series glasses used for calibration. Elemental composition and visual inspection helped identify many coins. Those that remained unknown had their data inserted to LDA. This enabled the sovereign and hence approximate age of the coin to be identified	363
Various	Silver coins from colonial Brazil	p-XRF, μ-XRF	Samples (17) of 960 Reis coins were analysed. Analytical data input to robust PCA so that they could be classified according to their elemental composition. The surface enrichment of Ag is a known phenomenon and this could potentially interfere with the XRF measurements which only measure the surface few microns. Initial experiments were conducted to ensure that this was not the case	364

aerated solution (two samples). In both cases, the solution was 0.5 M NaOH. The dechlorination process was stopped for some samples so that the dechlorination front could be located. Samples were dried at 50 °C for 10 min using a heat gun prior to analysis. As well as XANES, XRF and EXAFS were also performed. The XANES enabled the chemical form of the Cl, its distribution and its role in each phase's stability to be determined. The Cl ions maybe trapped inside the structure of the iron oxyhydroxide as akageneite (beta $FeO_{1-x}(OH)_{(1+x)}Cl_x$) and beta or gamma-ferrous hydroxychlorides, *e.g.* beta-$Fe_2(OH)_3Cl$. Some may also be adsorbed to the surface of the grains of the various phases present. It was concluded that XANES was very suitable for the task.

Other applications of the analysis of metal artefacts of cultural heritage are summarised in Table 2.

5.2 Cultural heritage samples of organic origin

Several *reviews or overviews of the analysis or restoration of artworks* have been produced during this review period. Included in this number is one by Borg *et al.* who reviewed (with 131 references) the application of state of the art technologies to support artwork

conservation.[365] Some of the technologies discussed were: XRF, holographic interferometry, Raman spectroscopy, thermal quasi-reflectography, FT-IR and terahertz imaging. The techniques allow analysis of the paintings, statues and murals, providing information about the pigments, restoration history and media constituents. The review was conveniently split into sections covering each of the techniques, so any reader could simply read the section applicable to them. Another paper, by Dudeja, containing 18 references, gave an overview of laser technology for analysis, cleaning and restoration of artworks.[366] Although by no means a comprehensive review, it did highlight the use of techniques such as LIBS, micro-Raman spectroscopy, optical coherence tomography, LIF, *etc.* and would, perhaps, be a useful read for anybody interested in the area.

Macro-XRF is a very useful technique for the analysis of artworks and other historical artefacts and is employed almost routinely by many workers. This is because it can give valuable information on pigments but also, because of the penetrative nature of X-rays, it can give information on layers beneath the surface. It can therefore potentially identify pictures that have been painted over. The development and application of a highly mobile

Table 3   Applications of the analysis of organic cultural heritage artefacts

Analytes	Matrix	Technique	Comments	Reference
Various	Wall paintings in Rome	XRF, time-gated LIF, reflectance spectroscopy, Raman, FTIR	A multi-technique approach where the experimental data was interrogated using PCA (for LIF and spectral angle mapper) and partial least squares discriminant analysis (PLSDA) for reflectance spectrometry. Raman and XRF used to characterise the pigments. It was also possible to identify areas that had been touched up using acrylic-based compounds	371
Various	Ancient murals	LIBS	Green painted layers of different pigment sizes were analysed using LIBS. Preliminary experiments optimising the LIBS parameters and minimizing signal fluctuations were undertaken. Then, LIBS analysis on different pigment size was performed on simulated samples. When real murals were analysed, the data were input to PCA so that different pigment sizes were classified	372
Various	Pictorial layers of a harpsichord	XRF, LIBS, FTIR	Numerous restorations identified. Vermillion was used for the red areas, lead white, copper-based pigments for the blue and violets (as well as Prussian blue), chromium oxides for the green tones and iron oxides for the red, yellow and ochre colours. Examination of samples cross-section indicated the presence of up to 10 layers	373
Various	Leonardo da Vinci drawings	XRF, macro-XRF, Raman	The combination of techniques allowed an improved description of the drawing technique to be made. In addition, it identified an unusual copper-based metalpoint and a peculiar bone preparation	374
Various	Historical paintings	Macro-XRF	Curvature of a painting surface can affect the measurement process of a macro-XRF scanner, hence changing sensitivity of the analytes. This work used NIST 610 at different distances from the instrument to set up an algorithm that could correct this. Once derived, it was applied to the analysis of some Rembrandt paintings	375
Various	Historical inks	LA-ICP-MS	Iron gall inks can damage the paper they are written on. This study used standards of historic iron gall inks and then used test papers containing bathophenanthroline to extract the metals. The Fe could be detected colorimetrically (a red colour forms). Other elements detected using LA-ICP-MS. This enabled an approximation of the trace element concentration on historical documents	376
Various	Cross-sections of paintings	TOF-SIMS	Dual beam TOF-SIMS using both a bismuth cluster liquid metal ion gun and an argon gas cluster beam was used to determine whether the binding medium of each layer of the painting was oil, egg yolk (oil and protein) or glue (proteinaceous). Unexpectedly, it turned out to be oil-based. Pigments also analysed and several metal-based components identified. Sub-μm resolution obtained	377
Various	Surface and interface treatments for wooden artefacts	XRF, FTIR, Raman, optical coherence tomography	Multi-analytical, non-invasive approach adopted to study the potential and limitations for analysis of surface treatments. The abilities and limitations for each technique were nicely summarised in tabular form. Mock-up pieces of wood were treated and then exposed to different lengths of artificial aging before analysis. Analytical data from FTIR and XRF interrogated using PCA. Valuable insights into aging and light effects obtained	378

Table 3 (*Contd.*)

Analytes	Matrix	Technique	Comments	Reference
Various	Sixteenth century illuminated printed book	pXRF	Portable XRF combined with Monte Carlo simulations for depth assessment of painted objects. Spectra obtained from painted and non-painted areas. Data compared with simulations. Results provided quantitative compositional and stratigraphic data. Although limitations exist, these preliminary results encourage future work	379
Various	Ceiling paintings	pXRF, XRD, FTIR, optical coherence tomography	Multi-technique, non-invasive approach that was performed *in situ* with portable instruments. Pigments identified using XRF and XRD included hydrocerussite, vermillion, smalt, copper-based blue or greens; lead-tin yellow and iron oxide. The FTIR and optical coherence tomography enabled the condition of the varnish layers to be established	380

and versatile macro-XRF scanner for the *in situ* analysis of painted works of art was reported by Pouyet *et al.*[367] The system enabled the real-time elemental mapping of large painted surfaces. This was facilitated by the system having an XRF head that was capable of moving 84 × 84 × 20 cm in the *X*, *Y* and *Z* directions, respectively. The technical details of the scanner were described in detail in the paper. Briefly, the X-ray beam size was adaptable and the detection system comprised a 50 mm² active area coupled to a CUBE preamplifier and DANTE digital pulse processor. The system was controlled using a custom software including a graphical user interface that had been programmed in Python. Detection limits for K-lines of elements with an atomic number of <50 were typically at the 10s of mg kg⁻¹, but this increased rapidly at higher *z*. For these higher *z* elements, L-lines were required. The authors applied it to the successful analysis of paintings.

Another paper to have utilised *macro-XRF was presented by Watteeuw et al. who combined it with multi-light reflectance imaging* to study medieval illuminated manuscripts.[368] The combination of the complementary techniques enabled the analysis of the pigments to be made in an advantageous way compared with normal analysis. Comparing and combining the macro-XRF data and the reference datasets for the multi-light reflectance imaging, enabled the ink and paint layer compositions to be characterised. The genuine 13th century materials and the areas that had been retouched in the 19th century could clearly be distinguished. This is just one example of the numerous papers that have employed complementary techniques for the analysis of materials in an attempt to glean as much information as possible. This use of complementary techniques is probably used most in the analysis of artworks.

A third paper to report the use of macro-XRF for the analysis of pigments was presented by Orsilli *et al.*[369] These authors combined *macro-XRF with Statistically Tailored Elemental Angle Mapper for the analysis of a painting* by Giotto. The paper is partially an overview (with 54 references) that discussed the relative merits and limitations of using macro-XRF. The data handling aspect is based on the spectral angle mapper

algorithm and on global spectrum analysis. It first maps the elemental distribution and then, in synergy with XRF data at set points, it exploits the information gathered from the mapped area(s) as a database to extend the comprehension to data outside the scanned region(s). The methodology was explained fully in the text of the paper.

A paper by Lazic *et al.* discussed the *pitfalls associated with LIBS depth-profiling of painted layers*.[370] Simply taking into account the line intensities or applying a single normalization approach based on the analyte line and a matrix reference line, *e.g.* Ca, led to misleading results. This was attributed to the crater formation and different overlaid materials affecting the plasma dynamics and hence, sensitivity. The authors set about picking Cu and Ca atom lines that were less affected by variations of the plasma temperature and that had a similar energy gap between ground and excited state. Each analyte therefore had its own reference Ca line. A total of 20 analytes were determined per laser pulse. In this way it was possible to detect thin over-painted layers of similar colour and to recognise the painting technique used. In some instances, it was even possible to establish geographical origin of the materials used.

Other applications of the analysis of organic samples of cultural heritage are described in Table 3, below.

5.3 Ceramic objects of cultural heritage

The analysis of ceramic objects is always a popular area of research in cultural heritage studies. A paper by Niedzielski *et al.* evaluated the *effects of sample processing on the XRF results from archaeological pottery*.[381] A total of 41 samples of pottery from the late bronze age/early iron age were used in the study. Of these, some were hand made and others had been wheel-thrown pottery. All had been collected from western Andalusia, Spain. The results from intact samples had significantly higher levels of Al, Ca, Co, Fe, K, Nb, S, Sb, Si, Sn and Sr compared with pulverised ones. Cluster analysis and PCA were used with the datasets. Cluster analysis failed to identify any clusters. However, PCA identified two outlying

samples in the intact (*i.e.* non-destructively prepared) samples; indicating that they had a different chemical composition. Analysis of the same samples that had been pulverised did not make that distinction. The clear conclusion was that grinding the sample loses vital information (as well as destroying part of the sample).

Table 4 Applications of the analysis of ceramic cultural heritage samples

Analyte	Matrix	Technique	Comments	Reference
Pb isotopes	Roman lead glazed archaeological artefacts	SIMS	$^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$, $^{208}Pb/^{204}Pb$, $^{208}Pb/^{206}Pb$ were measured on the glazed coatings of each sample. No mass bias correction was necessary. Treatment of data using PCA and comparing with the OXALID database indicated that since the 2nd century, the Pb in the glaze most probably originated in Britain. The technique of SIMS has several advantages over other techniques such as easy sample preparation, quick acquisition times, minimal destruction of samples and the possibility to choose the location of each analysis point	385
Various	Thirty four archaeological ceramics from 17th century shipwreck	ICP-MS, XRD, SEM	Sample pulverized and fused using lithium borate and then the melt was acid digested using 1N nitric acid containing a few drops of hydrofluoric acid prior to analysis, reference materials JB-3, JG-2, JG-1a and JA-2 used for method validation. The ICP-MS data were treated using PCA. Samples identified as coming mainly from Seville but also from northern Portugal	386
Various (10 major oxides and 12 minor analytes)	Ancient pottery from Hachijojima Island, Japan	WDXRF	Samples cleaned, pulverized, fused into a glass bead and analysed. Analytical data obtained input to PCA and cluster analysis (using Ward's method). The two chemometric techniques produced similar results. Of 47 samples analysed, 36 originated in Honshu. It was concluded that cultural exchange was happening 14 000 years ago between the island and Honshu, 190 km away	387
Various	Byzantine pottery from Romania	PIXE	Shards (45) of pottery from Romania were milled and pressed into a pellet. Samples analysed using PIXE with Basalt BHVO-2 as a CRM. Data input to PCA. Two groups identified. One made from kaolinitic clays (high Al) and the other from alluvial sediments	388
Various (37)	Roman amphorae fragments	pXRF, ICP-MS, FTIR, Voltammetry	Sample (1 g) was pulverized into a powder for XRF determination of Al, Ca, Fe, K, Si and Ti. For ICP-MS analysis, a total acid dissolution employing hydrofluoric acid was used. Validation for both methods was achieved using GBW07408 soil CRM. Analytical data input to PCA enabled classification of amphorae types	389
Various	20 ceramic artefacts from eastern Siberia	TXRF, GIXRF, ICP-MS, WDXRF	Several sample preparation methods compared for TXRF analysis: suspension after dry grinding, suspension after wet grinding, acid leaching and acid decomposition. All preparation methods ended by injecting an aliquot onto a quartz carrier and air drying prior to analysis. The TXRF data were validated through analysis of GeoPT33 ball clay CRM. Both suspension methods and acid decomposition provided good data. Data from TXRF compared with those from other techniques. Data from TXRF analysis input to PCA for provenance classification	390

Table 4   (Contd.)

Analyte	Matrix	Technique	Comments	Reference
Various (15)	142 ceramic artefacts and local clays from Greece	pXRF	Non-destructive analysis of ceramic artefacts and eight local clay sources and their mixtures using pXRF. Clays made into briquettes and fired between 750 and 1050 °C prior to analysis. Results input to hierarchical cluster analysis, biplots, boxplots, PCA and Euclidean and Mahalanobis distances. Results indicated the ceramics were made from local clays and their mixtures	391
Various	Chinese blue and white pottery sherds	WDXRF, pXRF	Comparison of two techniques for the analysis of 12 sherds of pottery. Chemical composition of the body, blue pigment and glaze determined. Provenance classification possible using both major (Al, Ca, K, Mg and Si) and minor (Rb, Sr and Zr) analytes	392
Various (42)	On-shore and offshore Roman ceramics from Croatia	ICP-MS, FTIR, SEM-EDS	Samples (20) were fused and then diluted with nitric acid prior to analysis. Of the 20 samples, five came from the excavation site at Crikvenica and 15 came from the coastline. Those from the sea also underwent a desalination process prior to analysis. Analytical data input to PCA and box and whisker plots. Although the provenance of all the samples was known to be the same, the samples recovered from the sea formed a very different group using PCA than those from the land	393
Various	Black glazed wares from two archaeological excavations in Sicily	μ-XRF, μ-XANES	Possible elemental variations in the glaze and materials evaluated. Speciation of Fe investigated using XANES. Cross-sectional analysis indicated a range of compositions of the black glaze, including some containing Zn. Samples from the attic had glaze that is mainly composed of magnetite (Fe_3O_4) and hercynite ($FeAl_2O_4$). Colonial samples had mainly magnetite with minor amounts of hematite (Fe_2O_3)	394

The use of LIBS has become popular in cultural heritage studies because it is quick, cheap and quasi-non-destructive. It does, however, suffer from problems associated with calibration and the production of huge amounts of information that can require powerful computing capacity. Some researchers therefore use statistical techniques to help remove redundant or insignificant data, thereby improving the efficiency of data interpretation. Such a paper has been produced by Ruan et al. who developed a *novel hybrid filter/wrapper method for feature selection for the LIBS analysis of archaeological ceramics*.[382] The method was based on the mutual information algorithm-based filter method (to remove redundant or insignificant data) and the bi-directional selection algorithm-based wrapper method (to obtain the optimal feature subset with good productive performance). The method was implemented through a random forest-based non-linear multivariate classification method. A total of 35 archaeological ceramics were analysed in the study. Prior to the use of the method, the LIBS spectra were treated using wavelet transform de-noising. The overall method

was compared with other methodologies and was found to have superior performance in terms of classification ability.

A study presented by Odelli et al. used portable XRF followed by data analysis using an assortment of chemometric methods to *classify the provenance of 73 transport amphorae*.[383] These authors used PCA, cluster analysis and a method called graph clustering for the classification. The analysis took place on a fresh cut surface. Classification using the new method was by no means universally successful. A success rate of approximately 75% was achieved. However, the authors did note that the majority of failures were for samples that had coarse grained clay pastes, implying that the method is especially useful for fine-grained materials. Despite this obvious flaw, the method was rapid, easy and relatively non-destructive.

Vannoorenberghe et al. used LA-ICP-MS for the analysis of the clay fraction of archaeological pottery samples with a view to elucidate provenance.[384] Assorted different calibration strategies were tested on the reference material NIST 679 brick clay before being applied to the archaeological samples. These strategies were: external calibration with no internal standard, external calibration

with Si as an internal standard, sum normalization approach with estimation of the Si concentration as internal standard and another sum normalization method. The calibration materials tested were a matrix matched clay and five glass reference materials. When no internal standard was used, the glass materials provided incorrect data. The matrix matched material did, however, produce reliable data. When the normalizations or the internal standard were used, either the glass materials or the matrix matched sample could be used for calibration. Once the method had been developed, it was applied to a series of Mesolithic and early Neolithic ceramic materials from the Scheldt valley. Data for 44 analytes from these analyses were treated using linear discriminant analysis (LDA). This was capable of classifying the different sediments used.

Other applications of the analysis of ceramic cultural heritage objects are shown in Table 4.

5.4 Glass samples of cultural heritage

This has been a relatively quiet area of research in this review period with only two papers of note to be discussed. One, by Comite *et al.*, used LA-ICP-MS, SEM-EDS, FTIR and XPS to *identify the degradation products that show up as iridescent black patinas or incrustations on Byzantine glasses* from Northern Tunisia.[395] All of the analytical techniques were either non-destructive or, at worst, minimally destructive. The LA-ICP-MS was used to identify the chemical composition of the glass and the degradation products whereas the XPS was used to identify the elements present at the surface and their chemical state. The iridescent areas were found to be depleted in alkali and alkaline earth elements. The incrustations were a result of deposits of calcium carbonate or oxyhydroxides.

A paper that critically compared the *performance of four non-invasive techniques for the differentiation of glass types in historical leaded windows* was presented by Cagno *et al.*[396] The techniques were: macro-XRF, UV–Vis-IR, Raman and IR thermography. All of the techniques could be used *in situ* but the macro-XRF was least portable. The non-quantitative nature of macro-XRF and its inability to measure low z elements such as Mg and Na meant that it was not ideal. However, it was capable of distinguishing two glass types based on their K content. It was also the technique that provided the most chemical information. The UV–Vis-IR broadly matched the macro-XRF findings. The Raman spectroscopy has had a good previous track record of historical glass analysis. However, in this case where colourless glass was analysed, there was very little fluorescence detected.

6 Abbreviations

2D	two dimensional
3D	three dimensional
AAS	atomic absorption spectrometry
ABS	acrylonitrile butadiene
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
ANOVA	analysis of variants
ARECV	average relative error of cross-validation
ASTM	American Society for Testing of Materials
ATR	attenuated total reflection
BCR	Community Bureau of Reference
CCD	charge coupled device
CE	capillary electrophoresis
CFFF	centrifugal field flow fractionation
CIGS	copper indium gallium selenide
CRM	certified reference material
CS	continuum source
CT	computerised tomography
CV	cold vapour
DA	discriminant analysis
DLS	dynamic light scattering
DLTV	diode laser thermal vaporisation
DP-RLIBS	double pulse resonance laser induced breakdown spectrometry
DMSO	dimethylsulfoxide
DRC	dynamic reaction cell
EAST	experimental advanced super conducting tokamak
EDS	energy dispersive spectrometry
EDXRD	energy dispersive X-ray diffraction
EDXRF	energy dispersive X-ray fluorescence
ELM	extreme learning machine
EPMA	electron probe microanalysis
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
FFFF	flow field flow fractionation
FI	flow injection
FIB	focused ion beam
FI-CVG	flow injection chemical vapour generation
FTIR	fourier transform infrared
FWHM	full width at half maximum
GC	gas chromatography
GD-MS	glow discharge mass spectrometry
GD-OES	glow discharge optical emission spectrometry
GF-AAS	graphite furnace atomic absorption spectrometry
GI-SAXS	grazing incidence small angle X-ray scattering
GIXRD	grazing incidence X-ray diffraction
GIXRF	grazing incidence X-ray fluorescence
HDC	hydrodynamic chromatography
HG	hydride generation
HPLC	high performance liquid chromatography
HR-CSAAS	high resolution continuum source atomic absorption spectrometry
IAEA	International Atomic Energy Agency
IBA	ion beam analysis
ICA	independent component 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-TOFMS	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 ratio mass spectrometry
ISO	International Organisation for Standardisation
ITER	international thermonuclear experimental reactor
JET	Joint European Torus
K-SVM-RFE	k-fold support vector machine recursive feature elimination
LA	laser ablation
LASIL	laser ablation of sample in liquid
LC	liquid chromatography
LDA	linear discriminant analysis
LIAS	laser induced ablation spectrometry
LIBS	laser induced breakdown spectrometry
LIBS-LAMS	laser induced breakdown spectrometry-laser ablation mass spectrometry
LIF	laser induced fluorescence
LIPS	laser induced plasma spectroscopy
LOD	limit of detection
LOQ	limit of quantification
MALDI-TOF	matrix-assisted laser desorption ionisation time-of-flight
MALS	multi-angle light scattering
MC	multicollector
MIBK	methylisobutylketone
MIP	microwave induced plasma
MIP-AES	microwave plasma atomic emission spectrometry
MS	mass spectrometry
MSFA	mono-segmented flow analysis
MWCNT	multi-wall carbon nanotubes
NAA	neutron activation analysis
NAAR	neutron activation autoradiography
ND	neutron diffraction
NDI-MS	near-field desorption ionization mass spectrometry
Nd:YAG	neodymium doped-yttrium aluminium garnet
NEXAFS	near edge X-ray fine structure
NIST	National Institute of Standards and Technology
NMR	nuclear magnetic resonance
NRA	nuclear reaction analysis
OES	optical emission spectrometry
PARAFAC	parallel factor analysis
PBS	phosphate buffered saline
PCA	principal component analysis
PCR	principal component regression
PET	polyethylene terephthalate
PFC	plasma facing components
PGAA	prompt gamma neutron activation analysis
PGM	platinum group metals
PIGE	particle induced gamma ray emission
PIXE	particle-induced X-ray emission
PLAL	pulsed laser ablation in liquids
PLS	partial least squares
PLS-DA	partial least squares discriminant analysis

PLSR	partial least squares regression
ppb	parts per billion
ppm	parts per million
RAFM	reduced activation ferritic/martensitic
RBS	Rutherford backscattering spectrometry
RDA	regularised discriminant analysis
REE	rare earth elements
rf	radiofrequency
RIMS	resonance ionisation mass spectrometry
RMSECV	root mean square error of cross validation
RMSEP	root mean squared error of prediction
RoHS	restriction of hazardous substances
RSD	relative standard deviation
RSF	relative sensitivity factor
SDS–PAGE	sodium dodecyl sulfate–polyacrylamide gel electrophoresis
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SEM-EDS	scanning electron microscopy-energy dispersive spectrometry
SF	sector field
SIA	sequential injection analysis
SIBS	spark induced breakdown spectrometry
SIMCA	soft independent modelling of class analogy
SIMS	secondary ion mass spectrometry
SNR	signal to noise ratio
SP	single particle
SPION	superparamagnetic iron oxide nanoparticles
SR	synchrotron radiation
SRM	standard reference material
SXRF	synchrotron X-ray fluorescence
SVR	support vector regression
STXM	scanning transmission X-ray microscopy
TEM	transmission electron microscopy
TDS	thermal desorption mass spectrometry
TGA	thermogravimetric analysis
TIMS	thermal ionisation mass spectrometry
TOF	time of flight
T-PGAA	time-resolved prompt gamma activation analysis
TPR	temperature programmed reduction
TXRF	total reflection X-ray fluorescence
UAE	ultrasound assisted extraction
UV–Vis	ultra-violet–visible
WDXRF	wavelength dispersive X-ray fluorescence
WEEE	waste electrical and electronic equipment
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

7 Conflicts of interest

There are no conflicts to declare.

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