

2020

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

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<http://hdl.handle.net/10026.1/19976>

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10.1039/d0ja90067b

Journal of Analytical Atomic Spectrometry

Royal Society of Chemistry (RSC)

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## ASU REVIEW



Cite this: *J. Anal. At. Spectrom.*, 2020, **35**, 2410

Received 23rd September 2020

DOI: 10.1039/d0ja90067b

rsc.li/jaas

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

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1	<b>Metals</b>
1.2	<b>Non-ferrous metals</b>
1.2.1	<b>Copper and copper-based alloys</b>
1.2.2	<b>Aluminium and aluminium-based alloys</b>
1.2.3	<b>Nickel and nickel-based alloys</b>
1.2.4	<b>Other non-ferrous materials</b>
2	<b>Organic chemicals and materials</b>
2.1	<b>Organic chemicals</b>
2.2	<b>Fuels and Lubricants</b>
2.2.1	<b>Petroleum products – gasoline, diesel, gasohol and exhaust particulates</b>
2.2.2	<b>Coal, peat and other solid fuels</b>
2.2.3	<b>Oils – crude oil, lubricants</b>
2.2.4	<b>Alternative fuels</b>
2.3	<b>Pharmaceutical and personal care products</b>
2.4	<b>Polymers and composites</b>
3	<b>Inorganic chemicals and materials</b>
3.1	<b>Inorganic chemicals</b>
3.2	<b>Fertilisers</b>
3.3	<b>Forensic applications</b>
3.4	<b>Catalysts</b>
3.5	<b>Building materials</b>
3.6	<b>Ceramics and refractories</b>
3.7	<b>Glasses</b>
3.8	<b>Nuclear materials</b>
3.8.1	<b>Fusion</b>
3.8.2	<b>Reactor materials</b>
3.8.3	<b>Nuclear forensics and security</b>
3.8.4	<b>Nuclear de-commissioning</b>
3.9	<b>Electronic materials</b>
3.9.1	<b>Wafers, thin films and multi-layer materials</b>
3.9.2	<b>Solar cells</b>
3.9.3	<b>Electronic equipment and devices</b>
3.10	<b>Nanostructures</b>

4	<b>Cultural heritage</b>
4.1	<b>Metallic artefacts of cultural heritage</b>
4.2	<b>Cultural heritage samples of organic origin</b>
4.3	<b>Ceramic materials of cultural heritage</b>
4.4	<b>Glass materials of cultural heritage</b>
5	<b>Conflicts of interest</b>
6	<b>Glossary of terms</b>
7	<b>References</b>

This review has been modified somewhat compared with its predecessors in that the cultural heritage applications have been grouped together in their own section rather than being split between assorted other sections throughout the review. Hopefully, this will enable readers interested in that topic to locate all of the relevant papers more easily. There is no doubting that laser induced breakdown spectrometry (LIBS) is still the most rapidly expanding technique of interest for “industrial” samples. Its use for on-line or standoff analysis covers many topic areas including the metals production, scrap metal and plastic sorting industries, nuclear applications, *in situ* analysis of remote systems, e.g. power cable insulators, etc. It is also regarded as being minimally damaging to samples and has therefore found extensive use in the analysis of cultural heritage samples; especially when used in conjunction with chemometric tools to identify provenance or chronology. For the analysis of fuels, it was disappointing to see so many papers re-inventing the wheel, with numerous applications being published that offer little improvement on existing standard methods. In many cases, the protocols described were very lengthy or complicated and succeeded only in obtaining a similar result to an existing method, but with poorer precision and with no benefit to the end user. Other areas, e.g. catalysts has a huge amount of interest. However, the techniques used to characterise the materials are mature and often, many of the papers published do not discuss the analytical science in any detail. The analysis of pharmaceuticals and personal care products has had a large increase in research interest during this review period. This is

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potentially because of traditional methods, e.g. atomic absorption, slowly being replaced by more modern techniques, e.g. ICP-MS. Other growth areas of research have been the analysis of thin films, semiconductors and solar cells. Here, it is often X-ray-based analytical methods that are most commonly used, although some depth-profiling applications will use either LIBS or LA-ICP-MS. Another very popular area of research is that of nanoparticles. Here, the research focus has shifted from toxicological studies to the analysis of nanoparticles being used as carriers for drugs. This area is likely to increase further over the coming years. Consequently, analytical methods have also changed from using field flow fractionation to X-ray-based techniques such as XPS and XANES that describe the chemical composition of the particles rather than their size. Single particle ICP-MS for particle sizing is still an area of interest though.

## 1 Metals

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<sup>1</sup> and is part of the Atomic Spectrometry Updates series.<sup>2-6</sup>

### 1.1 Ferrous metals

Following on from the last review period, Laser Induced Breakdown Spectroscopy (LIBS) has been the technique of choice for most workers researching into the analysis of steels or iron products. This is certainly true for those describing automated and/or on-line measurements. This is because LIBS is easily automated, may not require lengthy calibration protocols, inflicts little damage on the sample itself and may obtain reliable data in a "stand-off" mode, *i.e.* may be employed on a production line where conditions may be inhospitable for humans. For studies investigating corrosion processes, X-ray-based techniques are still the most common.

A review paper was presented by Legnaioli *et al.* who discussed, with the aid of 95 references, *industrial applications of LIBS*.<sup>7</sup> Particular emphasis was made to the steel industry and to the characterisation of coal; although sections on the nuclear, pharmaceutical, building, mining, food, waste management and electronics industries were also present. Although far from comprehensive, the review does give the reader a taste of the capabilities of the technique.

As with all sample types, *certified reference materials (CRM)* are of utmost importance because they provide the best way of assuring that quality data are produced. This statement is dependent on several variables, not least of which is that the CRM should be as closely matched matrix-wise to the samples under analysis as possible. A paper by Shehata *et al.* described an intra- and inter-laboratory approach for the certification of reference materials of low-alloy steel samples.<sup>8</sup> Seven low-alloy steel reference materials were developed by the National Institute of Standards, Egypt. The homogeneity of the samples was studied using XRF and atomic emission spectrometry, and the results indicated that they were sufficiently homogeneous to

establish traceability of measurement results. The materials were characterised by different laboratories and by using four independent analytical methods: gravimetry, XRF, optical emission and atomic absorption spectrometry (AAS). The mass fractions of each analyte as well as their associated uncertainty were calculated using the weighted mean approach.

Two papers have described the *LIBS analysis of steels for the C content*.<sup>9,10</sup> The paper by Sturm *et al.* used a compact passively Q-switched laser operating at 1064 nm, with a power of 0.6 mJ, a frequency of 1000 Hz and a duration of 5 ns and a hand-held spectrometer (of dimensions 110 × 80 × 21 mm) to collect the data.<sup>9</sup> The spectrometer had a very limited wavelength range (188–251 nm), but had an instrumental broadening at the C 193.09 nm of only 36 pm. There was also a facility to introduce an argon flow so that sensitivity in the vacuum UV region could be improved. Calibration curves for C as well as Cr, Ni and Si were obtained using CRMs. A total of 39 samples were used in the study. Set A contained CRMs from reliable sources of pure iron, alloy steel and one cast iron. Four of the samples from set A were used to form sub-set B and were used for the broadening experiments. A third set, set C contained 15 CRMs that had very low C content, of which the lowest C content was 5.1 µg g<sup>-1</sup>. This set was used to calculate the LOD. Initially, set A samples were used to form a calibration curve to >2% C. Five replicate readings were made and the signal was normalised to the intensity of the iron ion wavelength at 193.1845 nm. Calibrations obeyed either linear or second order polynomial fitting with *r*<sup>2</sup> values of greater than 0.98. The LOD was 34 µg g<sup>-1</sup>, which although inferior to larger instruments, was still impressive. Overall, the technique was capable of discriminating between similar samples, e.g. stainless steels 304 and 304 L. The other paper, by He *et al.* determined C in steels using LIBS with a genetic algorithm and back propagation neural network models.<sup>10</sup> Unfortunately, there is an Fe emission wavelength coinciding with the C wavelength at 247.86 nm. This means that interference is a probability during the analysis of iron or steel samples. In general, the C wavelength at 247.86 nm is more sensitive than the 193.09 nm line, and is therefore often preferred because it gives lower LOD. This paper proposed a method that used a genetic algorithm to help overcome the interference problem. Using the model developed, the root mean square error was 0.0114 and the linear correlation coefficient showed a significant improvement compared with that obtained without the algorithm. This led the authors to conclude that as well as being rapid and easy to implement, it was effective for the determination of C in steels and iron-based alloys.

As eluded to above, calibration can be problematic for LIBS when analysing samples such as steels or iron alloys, because iron has a plethora of wavelengths in the visible and near UV region of the spectrum. Consequently, there have been several papers that *tested different methods of calibration*. Many of these have relied on a statistical correction to ensure optimal results are obtained. An example of this approach was presented by Zhang *et al.* who used multivariate calibration models using a machine learning approach as well as univariate approaches to determine Cr, Mn and Ni in steel samples.<sup>11</sup> These authors

used 25 CRMs as “training” samples so that the model could be constructed. They then used a further four samples as validating materials, to ensure that the model was functioning correctly; *i.e.* to determine whether or not the calibration was adequate. Each sample was analysed 400 times and the average for each element in each sample calculated. The background was then fitted and subtracted for each of the elements in each sample. The regressions for the univariate approach were between 0.8796 (for Mn) and 0.9852 (for Ni), but these values improved to 0.9405 (for Mn) and 0.9996 (for Cr) once signal intensity normalisation to an iron wavelength was performed. For the multivariate approach, back propagation neural network was used; which yielded  $R^2$  values of at least 0.99969. This is a clear improvement over the univariate approach. Precision was also improved using the multivariate calibration. Two further examples from another research group were also published. In one by Liu *et al.* interference during LIBS analyses was corrected for using an algorithm based on an iterative discrete wavelet transform and Richardson–Lucy deconvolution.<sup>12</sup> The authors provided a summary of what the Richardson–Lucy algorithm is and then gave a stepwise guide to how to use it and supplemented the text with a flow diagram. The method was applied to the determination of Mn in iron alloys and to the determination of Fe and Si in aluminium alloys. For the analysis of the iron alloys, the regression without applying the method was 0.973, improving slightly when either the transform or the deconvolution were used individually. When both the transform and the deconvolution were used, the regression improved to 0.993. Similarly, the root mean square error of calibration (RMSEC) improved from 0.057 to 0.032. The results for the analysis of the aluminium alloy were even more striking, with  $R^2$  values improving from 0.816 to 0.985 and RMSEC improving from 0.101 to 0.041. The  $R^2$  value of 0.985 is a clearly significantly better than that obtained without the algorithm. However, there may still be room for further improvement. The second paper by this research group used an image quantitative analysis to overcome matrix effects during the determination of Ni in 17 stainless steel samples.<sup>13</sup> The authors again discussed the experimental setup, how the algorithm works and what needs to be done to ensure optimal data acquisition. Another flow diagram was provided to aid the reader. Improvements to the  $R^2$  value (from 0.9833 for a conventional spectrum to 0.9996 using the algorithm), to the average relative error of cross-validation (ARECV, from 56.80% to 1.0818%) and to the root mean square error of cross-validation (RMSECV, 15.93% to 0.9866%), were obtained. The authors concluded that their approach was very effective at providing an improvement to the quantitative performance of LIBS analyses. Another research group also used a plasma-image – assisted method to correct for matrix effects during LIBS analyses.<sup>14</sup> The authors used the re-arranged Lomakin–Scherbe formula to calculate the temperature of the plasma from the intensity of the emission from the wavelengths of interest. The area of plasma analysed yielded information on the mass of sample ablated. The authors applied their method to the determination of Cu and Mg in certified metal samples GSB 04-1661-2004 aluminium alloy and a range of cast iron

samples (GBW 01131a–GBW 01137a). To show the broad applicability of the technique, Cr and Mn were determined in some pressed pellet samples (soils GBW 07408 and GBW 07446) and a rock sample (GBW(E) 070164). The  $R^2$  values for Cu and Mg improved from 0.726 and 0.942 to 0.992 and 0.988 when the image assisted LIBS technique was used. Large improvements were also observed for the pressed pellet samples, where  $R^2$  improved from 0.364 and 0.098 to 0.975 and 0.98 for Cr and Mn, respectively using normal LIBS and image assisted LIBS. Improvements to average relative errors and RMSECV values were also observed for all analytes in both sample types. Sun *et al.* experienced problems when calibrating a LIBS instrument during the determination of Fe in an iron–zinc coating of galvanized steel samples.<sup>15</sup> Although the method was suitable in terms of spot size produced ( $\sim 50$   $\mu\text{m}$  in diameter), the calibrations obtained using the Fe intensity alone was extremely poor, with  $R^2$  of 0.7713 being obtained. When using the intensity ratio of the Fe 404.58 nm to Zn 468.01 nm lines, a significant improvement was observed, with  $R^2$  improving to 0.9511. The root mean square error also decreased from 0.4832% to 0.1509%. The influences of laser fluence and elemental depth distribution were also studied. Since the Fe is not uniformly distributed in the coating, the laser fluence had to be sufficiently high to ensure that sufficient sample was ablated. A fluence of 170  $\text{J cm}^{-2}$  gave the optimal results and was therefore used for the rest of the study.

Wang *et al.* compared three quantitative analysis methods for the LIBS determination of Cr, Mn, Ti and V in steel.<sup>16</sup> The three methods were single variable calibration, partial least squares regression and support vector regression. The partial least squares regression adds interference spectrum lines to the model to enable linear modelling. The support vector regression also adds interference spectrum lines, but enables non-linear modelling. All of the models were discussed at length in the paper. Both the partial least squares regression and the support vector regression gave better data than simply using the spectral intensity and concentration. However, of the three, the support vector regression model provided the best quantitative data, yielding  $R^2$  values of 0.995, 0.993, 0.992 and 0.990 for Cr, Mn, Ti and V, respectively. The root mean square errors of prediction were: 0.045, 0.044, 0.014 and 0.011 for the same analytes. In addition, it had virtually no elemental bias whereas the partial least squares regression and single variable calibration had different degrees of influence on the spectral lines.

Jia *et al.* devised the physical method of laser beam shaping for improving the calibration during the LIBS determination of Cr and Mn in certified steel samples.<sup>17</sup> A Nd:YAG laser operating at 1064 nm, a 7 ns pulse duration, 1 Hz repetition rate and an energy of 50 mJ was used with a peak shaping lens placed in front of the focussing lens. This peak shaping lens transformed the Gaussian shaped laser beam into a “top hat” shaped beam. This beam uniformity meant that there was less unwanted heating and therefore the crater produced was much flatter at the bottom and had smoother walls than that produced by the normal laser beam. This was shown using electron micrographs and other images. The intensity of Cr at the 425.43 nm line was ratioed to the Fe intensity at 283.16 nm line. Similarly, the Mn

signal at 403.45 nm was ratioed to the Fe intensity at 404.58 nm. The data produced was then treated using the “leave one out cross-validation” protocol to calculate relative error, precision and RMSECV. These values were tabulated and showed clear improvements for both elements compared with the Gaussian laser beam using both the peak area and the amplitude. Similarly, the LOD observed for the “Top hat” laser were typically half those observed for the Gaussian laser beam.

Two papers discussed the *analysis of alumina inclusions* in steel samples.<sup>18,19</sup> In the paper by Imashuku and Wagatsuma, both alumina and magnesium oxide centre dot alumina spinel inclusions were visualised using X-ray excited optical luminescence.<sup>18</sup> The technique is capable of rapidly identifying sizes, shapes and compositions of non-metallic inclusions in such samples and can be performed in air. A model steel sample was prepared by melting iron, aluminium and magnesium oxide powders together at 1550 °C in an argon atmosphere. Application of the X-rays made the alumina inclusions emit red (at 695 and 750 nm) and blue (at 380 and 485 nm) luminescence. After attaching a filter to the camera that blocked light above 650 nm, only the blue light was observed. In contrast, the magnesium oxide.alumina spinels emitted green light at 520 nm. Using the filter therefore enabled both species to be determined simultaneously over the wavelength range 420–650 nm. The sample was also analysed using SEM-EDS. The results of this were largely in agreement with those obtained using X-rays. In one area of the sample, that emitted red light, *i.e.* it contained only alumina, the EDS showed the presence of both Al and Mg. This was attributed to alumina and magnesium oxide being present, but not the mixed alumina-magnesium oxide spinel. The other paper, by Matsuda *et al.*, reported the use of LIBS to detect alumina inclusions in stainless steel.<sup>19</sup> A schematic diagram of the setup was given. The sample was placed on an XYZ stage and a Q-switched, high frequency, low energy (1 kHz and 1 mJ per pulse) Nd:YAG laser, operating at 532 nm was used to produce trough like craters in parallel lines, 50 µm apart, across the sample surface. The Al was detected at 396.152 and 394.403 nm, which are wavelengths that are not spectrally overlapped by iron lines. A histogram was therefore produced of the Al signal, where spikes indicate the presence of an inclusion. The method was rapid, with a 4.5 mm<sup>2</sup> area (3000 × 1500 µm) being analysed in 20 min. This compared very favourably with the conventional method of counting the inclusions using optical microscopy.

Huang *et al.* described a *hybrid model combining wavelet transform with recursive feature elimination for running state evaluation* of heat-resistant steel using LIBS.<sup>20</sup> The analytical data from LIBS underwent a chemometric transformation which was a hybrid of wavelet threshold de-noising and k-fold support vector machine recursive feature elimination (K-SVM-RFE). Fourteen samples, including four industrial samples obtained from a power plant boiler that had seen different extents and conditions of service, were analysed. The data first underwent an evaluation of the noise component, which was removed using the wavelet threshold de-noising. Then the K-SVM-RFE approach was applied to obtain the optimal feature subset and to build the classification models of aging grade and

hardness grade. The assessment matrix obtained using the indicators from the aging grade and hardness grade was used to evaluate the running state of the steel.

A very interesting paper was prepared by Shin *et al.* who used *LIBS to improve the classification accuracy* of waste stainless steel alloys.<sup>21</sup> The scraps were placed on a conveyor belt and a laser shape sorter was used to identify a flat area fit for analysis. The scraps were then passed to the LIBS side of the operation that utilised a Nd:YAG laser operating at 1064 nm, at 10 Hz and at 26 mJ; placed 70 mm above the conveyor belt. Light emitted from the plasma formed was detected using a dual channel spectrometer capable of operating between 200 and 430 nm with a resolution of 0.1 nm (channel 1) or between 415 and 900 nm with a resolution of 0.3 nm (channel 2). A charge coupled device (CCD) detector was used in both cases. A total of 17 wavelengths were used for the classification, of which seven were for Fe, six were for Cr, two were for Ni and then there was one each for Mn and Mo. A total of 16 line pairs were chosen to be ratioed. All of the Cr wavelengths were ratioed to different Fe lines, but other elements used different species to be ratioed with, *e.g.* the Ni 352.4 nm line intensity was ratioed to the intensity at the 360.5 nm Cr wavelength. A table described the line pairings in full. The data so produced were then treated using principal component analysis (PCA) and checked using linear discriminant analysis (LDA). Method validation was through the use of eight stainless steel reference materials. It was concluded that this procedure offered a low cost and efficient method that was suitable for industrial purposes.

Makino *et al.* developed a new analytical method by which major and trace elements in low alloy steels, stainless steels and tool steels were determined using a *solid mixing calibration method and multiple spot LA-ICP-MS*.<sup>22</sup> The system used a high repetition rate laser and galvanometric optics; *i.e.* a device that can change the laser spot focus in the X and Y axis in a very short time period. The multiple spot laser system enabled two different sample types to be ablated almost simultaneously. Therefore, a sample could be analysed at virtually the same time as a reference material of known composition and then the aerosols combined prior to ICP-MS detection. A further advantage was that using a high repetition rate laser led to large quantities of material being ablated in a short time period. This means that improved signal to noise ratios were obtained. The analytes Co, Cr, Cu and Ni were determined in a total of 13 samples. The concentrations calculated showed good agreement with reference values (within 10%) even over very large concentration range, *e.g.* µg g<sup>-1</sup> up to percentage levels. It was concluded that the methodology could become a powerful tool in the future.

One last laser-based application was presented by Luo *et al.* who *compared three different laser systems for ablation of steels into an ICP-MS instrument* for detection.<sup>23</sup> The lasers were: a 257 nm one operating at 300 fs, a 213 nm Nd:YAG operating at 3 ns and an argon fluoride laser operating at 193 nm and at 15 ns. Under typical operating conditions, the signal intensity for the 257 nm laser was 10 and 3.6 times greater than that for the 193 nm and 213 nm lasers, respectively. The femtosecond laser also showed a greater signal stability compared with the

nanosecond lasers. The different systems also showed significant differences in melting and elemental fractionation, with the 193 nm laser providing the worst performance. In contrast to this, once normalisation to the  $^{57}\text{Fe}$  signal was undertaken, the 257 nm laser provided elemental fractionation indices close to one for most analytes, with no significant melting. In this work, NIST 610 glass was used as a non-matrix matched external calibration standard. The femtosecond laser enabled far more accurate results to be obtained when compared with the nanosecond lasers.

The corrosion of steels has received considerable attention. However, most of the papers in this area are very routine with respect to the atomic spectroscopy and hence will not be detailed in this review. An exception to this was published by Wongpanya *et al.* who studied the corrosion of 1045 and J55 low alloy steels in crude oil.<sup>24</sup> Since the crude oil can also contain sand, some was added in different concentrations with particle sizes ranging from 500 to 2000  $\mu\text{m}$ . Therefore, erosion of the steel pipes was also studied. An impingement jet system was used to bring the steels into contact with the oil/sand matrix. The corrosion was measured gravimetrically thus giving a weight loss with units of mass per square area. The surface of the pipes were analysed using SEM and X-ray photoemission spectrometry (XPS). Both ICP-OES and electrochemical measurements were made on the oil to determine material leached/abraded from the steel surface. The Fe content of the oil as determined using ICP-OES showed that the 1045 steel had a much greater release than the J55 steel. It also had a greater depth penetration. The sand particles size had a significant effect, with larger particles causing much greater abrasion of the surface. Analysis of the oil for CHN as well as K, Na and Si was undertaken. It was found that the  $\text{Fe(II)}/\text{Fe(III)}$  was a useful indicator of whether corrosion or erosion dominated. A high ratio indicated better erosion resistance (more corrosion) whereas a low ratio indicated a better corrosion resistance.

*Matrix-assisted photochemical vapour generation* was used by Zhen *et al.* to determine Bi in iron–nickel alloy samples using ICP-MS detection.<sup>25</sup> The alloys (0.5 g) were digested using aqua regia (10 mL) on a hotplate at 60 °C for an hour and then the digests heated to almost dryness at 90 °C. They were then reconstituted to 10 mL with water and an aliquot of 150  $\mu\text{L}$  removed, mixed with formic acid and acetic acid and pumped at a rate of 3.8 mL  $\text{min}^{-1}$  into a reactor. The reactor had a volume of approximately 0.7  $\text{cm}^3$  and was surrounded by a 19 W lamp. Once inside the reactor sample flow was stopped and irradiation for 10 s was allowed. The pump was then re-started, transporting the sample to a gas liquid separator where the Bi vapour (thought to be  $(\text{CH}_3)_3\text{Bi}$ ) was transferred to the plasma of an ICP-MS instrument by a flow of argon. The concentrations of the acetic and formic acids were optimised, with the optimum being 4% and 15%, respectively. This method enhanced the formation of the bismuth vapour and also the transport efficiency to the plasma yielding an impressive LOD of 0.54  $\text{ng g}^{-1}$ . Precision was also determined with seven replicate measurements of 0.5  $\mu\text{g L}^{-1}$  in a sample matrix giving a value of 1.1% RSD. Method validation was achieved through the successful analysis of the reference materials GBW 01621 and GBW 01622.

An asymmetric flow field flow fractionation combination with ICP-MS (AF4-ICP-MS) was used by Itabashi *et al.* to measure the concentration and size distribution of *nanometer-sized particles of titanium and vanadium carbides in sheet steel*.<sup>26</sup> Often, a sulfur-based dispersant is used during AF4 separations. However, the presence of sulfur will lead to polyatomic interferences on the Ti and V isotopes. It was therefore necessary to identify a dispersant that was sulfur-free. The authors first used gold nanoparticles of known sizes to determine the resolution of the separation using a sodium cholate dispersant. Careful optimisation was undertaken, including controlling the zeta potential of the particles to above  $-30$  mV to avoid particle agglomeration and to ensure the zeta potential of the RC 30 kDa membrane was between  $-20$  and  $-30$  mV to prevent particle adhesion to the membrane surface. The steel samples were then decomposed using selective potentiostatic etching by electrolytic dissolution. This dissolved the iron matrix but not the carbide particles. Using the RC 30 kDa membrane with a 1.16 mM sodium cholate dispersant, the authors identified particles of both TiC and VC that had a size of less than 5 nm.

A paper by Misnik *et al.* discussed how secondary ion mass spectrometry (SIMS) *depth-profiling* analyses can be affected by matrix effects and that these can be overcome by using the “storing matter” technique.<sup>27</sup> The storing matter technique is where the sample is sputtered onto a rotating disk and then ionization of this stored matter occurs when it is exposed to ion beam bombardment. A separation of the sputtering and ionization processes is therefore obtained, decreasing the matrix effects. The method was demonstrated by determining Cr, Fe and Ni in oxidised austenitic steel 304 and steels with an aluminium covering which are known to give severe matrix effects at the metal oxide interfaces. The storing matter SIMS method was compared with conventional SIMS and gave a better depth resolution and greater sensitivity. For steels that had been baked at 500 °C, the storing matter SIMS showed that Cr, Fe and Ni were uniformly distributed throughout the steel. However, conventional SIMS did not show this, instead indicating that there were hotspots of Cr and Fe. This disparity was attributed to the presence of matrix effects encountered during conventional SIMS.

## 1.2 Non-ferrous metals

This area has received significant amounts of interest during this review period. The analysis of copper-based, aluminium-based and nickel-based alloys have all received significant attention. Another common theme has been studying corrosion, either in an attempt to prevent it or to study the mechanism by which it occurs.

**1.2.1 Copper and copper-based alloys.** One of the most common topics to receive research attention has been the *analysis of copper-based alloys*. An example of such an analysis was presented by Arnquist *et al.* who reported the development of a method to determine  $^{232}\text{Th}$ - and  $^{238}\text{U}$  in copper using ICP-MS.<sup>28</sup> An automated, off-line matrix separation/analyte pre-concentration method was developed in which the anion

exchange resin AG 1X4 (100–200 mesh) was packed into a low-pressure chromatography system. This system was capable of cleaning the resin column, sample loading, matrix removal, analyte elution and collection with no input from the operator other than the initial programming. After pre-conditioning the column using 2 mL of 8 M HNO<sub>3</sub>, the sample digest (9 mL) was loaded onto the column at a reduced flow rate to ensure maximal interaction with the column. The matrix was removed by flowing through 0.5 mL of 8 M HNO<sub>3</sub> and the analytes eluted in 1.8 mL of 2% HNO<sub>3</sub>. A five-fold preconcentration was therefore established. Analyte eluates were collected in pre-cleaned vials ready for analysis. An isotope dilution methodology was adopted for the quantification. This led to the extremely low method LOD of 3.7 and 9.4 fg g<sup>-1</sup> being obtained for the Th and U, respectively. The preparation procedure was not rapid, with the whole pre-conditioning, sample loading, washing and elution protocol taking just over 60 min per sample. However, since it was fully automated, this is less of a problem. Arcidiacono *et al.* reported the use of a neutron-based quantitative method entitled time-resolved prompt gamma activation analysis (T-PGAA) for the analysis of copper-based alloys.<sup>29</sup> This is a relatively new, technique developed by the authors and undertaken on an instrument designed and built in-house. A high purity germanium detector maintained at 77 K was used to acquire both the photon energy promptly emitted by the irradiated sample and the time at which the prompt gamma ray is detected. The authors briefly described the process and the instrumentation. It is based on a radiative capture reaction where the incident neutron hits a target nucleus which becomes activated and then emits prompt gamma rays during the irradiation. The main advantages of the technique are that it is non-invasive and is sensitive for major, minor and trace analytes. The authors applied the technique to the analysis of certified brass and bronze samples. In general, agreement with certified values was good. However, there was a significant error observed for the determination of Zn in the bronze sample, where the experimental result of 0.01% was a huge underestimate of the certified value of 4.92%. This was attributed to the background subtraction method used.

The improvement in sensitivity for the determination of Pb in five copper-based alloys by using *double pulse resonance LIBS* (DP-RLIBS) compared with RLIBS was discussed by Tang *et al.*<sup>30</sup> For the DP-RLIBS, a beam splitter was used to split a tuneable laser into a transmission and a reflection beam. The reflection laser pulse was used to ablate the sample (similar to the front edge of the pulse in RLIBS) and the transmission beam was used to resonantly excite the atoms within the vaporised plume (similar to the back edge of the pulse in RLIBS). A detailed description of the instrumentation including a schematic diagram was given to aid the reader. Careful optimisation of the operating conditions in terms of laser wavelength (huge increase at Pb 405.78 nm when the laser was tuned to the resonance line 283.31 nm), laser energy and acquisition delay. The Pb signal increased with increasing laser energy, but the signal to noise ratio (SNR) decreased. The optimal delay time was in the nanosecond range, which is significantly shorter than traditional LIBS (μs range). Using five reference materials,

calibrations were established for DP-RLIBS and two version of RLIBS. These two versions were: using the reflection beam (RLIBS-1) and the transmission beam only (RLIBS-2). The *r*<sup>2</sup> value was 0.992, 0.947 and 0.859 for DP-RLIBS, RLIBS-1 and RLIBS-2, respectively. Similarly, the LODs for the three configurations were 9, 29 and 13 mg kg<sup>-1</sup>, demonstrating the clear sensitivity and general performance enhancement exhibited by DP-RLIBS. Damage to the sample was also not significantly worse, with the diameter of the crater being 66 μm for the DP-RLIBS compared with the 62 μm for the RLIBS.

Another LIBS-based application was reported by Jabbar *et al.* who used a *long duration single pulse version of LIBS* for the analysis of brass alloys that were submersed in water.<sup>31</sup> A Nd:YAG laser was used at 1064 nm and with a pulse duration, frequency and energy of 100 ns, 0.05 Hz and 50 mJ, respectively. The experimental setup was described, again with the assistance of a schematic diagram. Reference brass samples were placed in a beaker of distilled water and the laser shot fired perpendicularly through the surface of the water. The beaker was on a rotating table to ensure that the laser did not sample from the same spot, so causing a deep crater. The water was changed every 50 shots to avoid contamination from the vaporised plume. Plasma parameters such as electron number density and plasma temperature were calculated and used to enable calibration-free, quantitative LIBS measurements. The spectral profile of the copper lines was investigated and was found to be severely affected by self-absorption in the underwater measurements. Two versions of the analysis were therefore tested – before and after self-absorption correction. Results after self-absorption correction were superior with the Cu data having better than 2.4% relative error to the certified values after correction compared with better than 4.4% before it. The Zn data were less impressive with one sample in particular (ZBY 926) yielding very poor data. The relative error for Zn after correction was 21.3% whereas before correction it was 49.5%.

A related technique to LIBS is *laser ablation spark-induced breakdown spectroscopy (LA-SIBS)*. Jiang *et al.* described the use of a high repetition rate fibre laser operating at 30 kHz and at 1064 nm to ablate samples and then a spark between a tungsten rod anode and the sample plate cathode excited the plume further so that light emitted could be detected.<sup>32</sup> Optimisation of the ablation and excitation processes as well as the geometry and distance between the anode and the sample was undertaken. The system was tested using five standard copper alloy samples and the performance compared with that of just using the LA component. Use of the spark secondary excitation yielded sensitivity and LOD that were improved for Al, Fe and Pb at 396.15, 358.12 and 368.35 nm, respectively, by a factor of between 3 and 9. Using the combined system, the LOD were 106, 1022 and 1309 ppm for Al, Fe and Pb, respectively. Although not massively impressive, these LOD were better than those obtained using a standard LIBS system and, given that the device is portable, it offers several advantages. An extension to the work was published by Kang *et al.* who used a similar device in addition to a lock in amplifier and detector.<sup>33</sup> In this study a high repetition rate Nd:YAG laser was used rather than a fibre laser. Therefore, a repetition rate of only 4 kHz could be

obtained. The spark discharge extended the duration of the light emission to approximately 10  $\mu\text{s}$  per pulse. The gated preamplifier used enabled the continuum background to be reduced significantly. The device was used to determine Al and Pb in brass samples and Cr and Mn in aluminium alloy samples. Detection limits were 178, 112, 235 and 202 ppb for Al, Pb, Cr and Mn, respectively, which were a factor of between 9 (for Mn) and approximately 70 (for Al and Pb) better than conventional LIBS.

**1.2.2 Aluminium and aluminium-based alloys.** Another popular sample type has been aluminium and aluminium-based alloys. In an extension to the work above on LA-SIBS, Kang *et al.* analysed aluminium alloys for several analytes.<sup>34</sup> Again, a high repetition rate laser was used operating at 30 kHz was used for the ablation and this time detection was achieved using a compact fibre spectrometer in non-gated mode. The median filtering method was used to reduce the contribution of the continuum background to the emission signal. The electron density measurements were determined according to the Stark broadening of the atomic lines and Saha-Boltzmann plots indicated that the plasma temperature was 11 800 K. These two fundamental parameters were used to enable calibration-free quantification. Analytical error was less than 0.5% for the major elements, but up to 35% for minor analytes with concentrations up to 0.1%. A final paper of this type was presented by He *et al.* who determined Cr, Cu, Mg, Mn and Zn in aluminium alloys.<sup>35</sup> This time calibration curves were constructed and the setup yielded LOD of 4.4, 5.6, 8.3, 4.9 and 31.1 ppm.

Two papers have been published that have utilised glow discharge (GD) with MS detection. In one, Gonzalez-Gago *et al.* used GD-MS to determine impurities in three different matrices: aluminium, copper and magnesium. The paper explained the quantification models used for GD-MS and then went on to explain the experimental part of the work. Reference materials of the three matrices (four each for aluminium and copper and three for zinc) were used and the operating conditions in terms of argon flow rate, voltage and current were optimised for highest relative sensitivity factor for each. The voltage and current had only marginal effect, but the gas flow rate was critical, with the relative sensitivity factor changing by 40% over the gas flow rate range tested. Improved standard relative sensitivity factors were calculated when optimisation based on multi-matrix calibration was undertaken. Also presented in the paper was an attempt to use GD-MS as a method of determining O in the materials. The O was present as a result of the sintering process. The LOD was very poor (1.5–7.0  $\text{g kg}^{-1}$ ), but this was dependent on the matrix. The worst sensitivity was obtained for the magnesium sample. The poor LOD was attributed to the high ionisation energy of O and the high background signal intensity. However, the authors acknowledged that further fundamental studies were required to test this. A paper by Pisonero *et al.* used GD-SF-MS in the pulsed mode for the multi-elemental (major, minor and trace) depth-profiling analysis of heat-treated zinc coatings on extruded aluminium.<sup>36</sup> Parameters including the GD source design, the discharge conditions and the mass spectra acquisition

conditions were optimised to obtain low sputtering rates, high mass spectra acquisition rates, high speed and improved depth-profiling resolution. Relative sensitivity factors did not change with the matrix when the GD was operated in pulse mode. This is important because the relative sensitivity factor is used to convert ion signals into elemental concentrations. Numerous reference materials were analysed and, as a further quality control method, the data were compared with those obtained using femtosecond LA-ICP-MS. The results were in reasonable agreement.

An interesting forensic application was reported by Nishiwaki and Takekawa, who discriminated between different aluminium automobile wheel fragments using the non-destructive technique of synchrotron radiation XRF.<sup>37</sup> The samples comprised tiny fragments (less than  $500 \times 500 \mu\text{m}^2$ ) from 45 different kinds of wheels. Each sample was packed into polypropylene films, sealed and then placed in a sample holder with a 3 cm aperture. The XRF was undertaken using two different energy X-ray beams. These were 18 keV and 116 keV. For the 18 keV work, pairwise comparison was made between the analyte and Ga. This led to 10 analytes being determined with all except Fe having a precision of better than 15%. It was impossible to do a pairwise comparison with Ga for the data obtained using 116 keV because it was not detected in all samples. In addition, the Pb gave a large background signal because of the lead collimator in front of the detector. Samples were also analysed using SEM-EDS. A pairwise comparison of Mg/Al was successful and with a good RSD of 3.4%. However, other elements had a very poor precision and were useless analytically. It was therefore concluded that although the Mg/Al ratio obtained using SEM-EDS was potentially a good indicator, the overall results were not sufficiently reliable. The high energy XRF data enables an 82.9% success in identification. However, the data obtained using 18 keV was much more successful, with a 92.9% identification rate. Combined use of the data from the two different energies yielded an identification rate of 98.2%.

A paper by Vrabel *et al.* compared a high-end LIBS instrument with a low-cost one for their performance in classifying aluminium-based alloys.<sup>38</sup> The low-cost instrument comprised a Czerny–Turner monochromator with an integrated non-intensified detector that covered the range 190–1100 nm. The high cost instrument had an Echelle spectrometer covering the range 200–900 nm with an electron multiplying CCD detector. The alloys were analysed in two forms – powders or printed parts. Once the data had been acquired, the spectra were analysed and inserted into multivariate data analysis tools such as PCA and Support Vector Machine. The PCA was used first to reduce the number of variables required for analysis. It was found that 89% of the variability could be found in just four principal components. These four components were then passed to the support vector machine algorithm for further analysis. The results were impressive. The high-cost instrument correctly identified 100% of sample types in both printed part and powder forms. The low-cost instrument also performed well, with 94.7% of samples in powder and 100% in printed part form being correctly classified.



A LIBS-based application was reported by Gudmundsson *et al.* who reported the use of the technique at an aluminium smelter site to *determine 14 analytes in molten aluminium*.<sup>39</sup> Each measurement comprised 70 shots of a Nd:YAG laser operating at 1064 nm, at 10 Hz and with an energy of 100 mJ. Real-time quantification at the ppm level was achieved for some of the analytes (Cr, Cu, Mn and Sn). Inspection of the correlations of the calibrations indicated that the analytes with higher vapour pressure (*e.g.* Mg, Na, Sb and Zn) tended to have poorer  $r^2$  values ( $<0.95$ ), whereas those that had a much lower vapour pressure had  $r^2$  values of greater than 0.97. The on-line measurements were compared with those obtained using OES in the laboratory, with reasonable agreement being obtained. Even analytes with poor calibration curves, *e.g.* Na that had a regression of 0.6, could still be reliably determined in a relative way, *i.e.* it was possible to compare different batches of aluminium with each other.

**1.2.3 Nickel and nickel-based alloys.** The *production of reference materials* for all sample types is necessary to ensure that analysis is accurate. Dvoretzky *et al.* reported the development of reference materials for new grades of nickel super-alloys.<sup>40</sup> The authors pointed out that until now, there was a complete lack of reference materials for many modern, heat-resistant nickel superalloys. The authors prepared the samples and then polished the ends and studied the homogeneity. Samples were rejected if they had defects, *e.g.* cracks, non-metallic inclusions, separate zones, different contents of alloying elements and impurities or had high micro-porosity. If they were rejected, they were melted and then re-cast, adjusting the smelting mode as necessary. Certified values were established using two XRF measurements from the same place on the surface and two measurements by AES from different places on the surface. Two series of reference materials were prepared. These were entitled the VZHM and the VKNA series. Each contained five separate samples of slightly differing composition.

Harrington analysed nickel-based samples using the *technique of ETV-ICP-OES*.<sup>41</sup> Between 2 and 2.5 mg of nickel foam was cut and placed on a graphite boat before being inserted to the ETV device. It then underwent an ETV temperature programme comprising a char stage at 400 °C, a cool period of 15 s and then vaporization at 2300 °C. The vapour was transported to the plasma torch by a flow of argon (0.12 L min<sup>-1</sup>) fortified with 9 mL min<sup>-1</sup> carbon tetrafluoromethane to aid the volatility (particularly useful for analytes such as Cr) and 20 mL min<sup>-1</sup> hydrogen. An additional 45 mL min<sup>-1</sup> of nitrogen was added to the central channel of the plasma *via* a sheathing device. This improved the stability of the plasma and led to enhanced sensitivity and lower LOD. Calibration was achieved by inserting different masses of the reference material NIST 2710 Montana soil. Clearly, this is not the ideal material in that it is not matrix matched to the sample. In addition, it is recommended that a minimum of 250 mg is used to ensure homogeneity. Despite this, the authors succeeded in calibrating even though less than 10 mg was used. The argon 415.859 nm line was used as an internal standard to account for sample loading effects on the plasma. The analytes determined were Cd, Cr, Mn, Mo, Pb, V and Zn. The results obtained were in agreement with those

obtained following an acid digestion of the samples followed by pneumatic nebulisation into ICP-OES.

An *on-line LIBS application* was reported by Sdvizhenskii *et al.* who used it to analyse metal-particle powder during additive manufacturing (also known as three-dimensional printing or layer manufacturing).<sup>42</sup> A lightweight and compact LIBS instrument was designed and installed on a robot arm in a laser cladding setup and then used to analyse particles of nickel alloys reinforced with tungsten carbide particles. The setup was described in reasonable detail with the aid of a clear diagram and photographs. Compared with the analysis of solid metal materials, very poor precision was achieved when metal powders were analysed. This was attributed to the low probability of the powder particle being ablated/vaporized by the central part of the laser beam. Two different calibration regimes were tested. The first used spectral counting (counting the number of spectra with meaningful LIBS signal) and spectral averaging (LIBS spectra summed during multiple laser shots). In terms of the root mean square error of cross validation (RMSECV) and the linearity measured in the form of  $r^2$ , the spectral averaging approach provided by far the better data. The overall result was a system that could be used reliably on-line, thus saving time (and money).

**1.2.4 Other non-ferrous materials.** One paper described methodology to *determine the provenance of gold*, a task that is difficult but necessary to ensure a responsible supply chain.<sup>43</sup> This paper, by Pochon *et al.* described the use of a commercial hand-held LIBS system to determine Ag in 13 samples of gold and gold alloys from five different areas of French Guiana. The small spot size of the laser enabled analysis of very small gold grains. Calibration was through the use of six commercial gold alloys with a Ag content of up to 16%. The authors studied different calibration models including univariate and multivariate (principle component regression and partial least squares regression). After normalisation against the signal from a gold wavelength, the quadratic univariate approach was adopted. Several wavelengths were monitored, but the 546.58 nm line was chosen for quantification because it provided the best sensitivity. Using the method developed, an  $r^2$  value of 0.99991 was achieved with a mean average error of 0.36% Ag for the prediction. Results were compared with those obtained using electron probe microanalysis (EPMA), with good agreement being achieved. It was possible to distinguish between the different samples through the determination of the Ag content and this could be extended to even tracing the origin of unknown samples. The method was described as being very fast and easy.

Two papers from the same research group described the technique of *laser ablation ionization mass spectrometry* for the depth-profiling analysis of tin-silver solder bumps.<sup>44,45</sup> The surface and near-surface regions of the bumps are the most difficult to analyse because they are often rough and can accumulate contaminants from the plating bath. Such an approach should yield an in-depth understanding of the plating process. A laser with a pulse width of ~190 fs and with a fundamental wavelength of 775 nm operating at its third harmonic (258 nm) was used for the ablation. Both papers used the reference

material BCS 347 as a closely matrix matched calibrant and both discussed a novel 2D binning approach. The results obtained using the protocol discussed were compared with those obtained using ICP-MS. Results were similar, but the ICP-MS provided details of the composition of the bulk sample whereas the LA-ionization mass spectrometry could give detail with 10  $\mu\text{m}$  lateral resolution. Two different sampling protocols were compared. In one, the single crater approach was adopted. This is where the same spot is repeatedly sampled. The other method used a layer by layer approach. This approach was discussed in detail in the publications.

An interesting application was proposed by Kang *et al.* who discussed the use of LIBS for the evaluation of stress on the surfaces of a magnesium alloy and a steel plate.<sup>46</sup> Stress was induced to the magnesium alloy by ultrasonic peening, whereas bending was used to stress the steel plate. The ion to atom line intensity ratios were used as the basis of the analysis, with Mg being the analyte in the magnesium alloy and Cr being used for the steel sample. The experimental setup was described and the delay between the laser shot and the acquisition of data optimised. Successive shots of a Nd:YAG laser at the same point on the sample enabled different depths to be analysed. The depth was estimated using the position of the objective lens of a microscope. The authors explained how the data had to be treated to account for the different depths. The data obtained were compared with those obtained using XRD, with similar trends being identified; especially for those samples that had been stressed through bending. The authors did acknowledge that further work was required because the laser treatment also caused surface damage.

## 2 Organic chemicals and materials

### 2.1 Organic chemicals

A review containing 173 references highlighted the broad applications of atomic absorption spectrometry which have been driven by developments in designs of high-resolution continuum source atomic absorption spectrometers.<sup>47</sup> Such instruments allow sequential as well as simultaneous multi-element analysis. In addition, these spectrometers are suitable for atomic and molecular absorption analysis utilising flame or graphite furnaces. The authors further summarised the developments concerning the analysis of solids, solutions, and liquid samples. The applications reviewed included biological objects, pharmaceuticals, oil and petrochemicals, water, dust and soil, cosmetics, polymers, fertilisers and plants. These applications were collated summarising analyte, matrix, LODs obtained and analysis conditions. A second review of interest summarised applications of LIBS for organic compounds (258 references).<sup>48</sup> It provided an overview of the life cycle of organic plasmas and discussed the factors and mechanisms responsible for the features exhibited within the spectrum. In addition, different variables that influence the formation and expansion processes of organic plasmas are discussed and an in-depth summary about atomic and molecular spectral bands of organic compounds observed in LIBS was given. The focus of this review was with regards to emitting species. However, the

importance of non-emitting species (for example  $\text{CN}_2$ ,  $\text{C}_2\text{N}$  and  $\text{C}_2\text{N}_2$ ) which can participate in the overall physio-chemical process was also discussed.

It is essential to monitor the exposure to radioactive material by both nuclear plant workers and the general public. The long-lived  $^{129}\text{I}$  isotope is an indicator for the long-term accumulation of radioactive iodine. The determination of iodine in general has several challenges. This is because of its high volatility, active chemical properties and the complex behaviour of iodine, resulting in iodine species often being lost during chemical processes. To overcome these challenges, an extraction method of  $^{129}\text{I}$  from charcoal cartridges was developed.<sup>49</sup> The charcoal cartridges had previously been used to collect gaseous emissions from the Canadian Nuclear Laboratories. An extraction system was derived, which consisted of a 50 mL Erlenmeyer flask (reactor) connected via a low-density polyethylene tube to a 20 mL glass vial (collector). The reactor, which contained 0.1 g of the charcoal sample and a spike of  $^{125}\text{I}$ , was located in a metal bead bath (85 °C). Once  $\text{HNO}_3$  (10 mL of 68–70% v/v) was added iodine vapours were produced. By bubbling compressed air through the system (for 2 hours), the vapours were transported to the collection vessel, which contained  $\text{AgNO}_3$  (10 mL, 0.1 mol  $\text{L}^{-1}$ ). Consequently, an AgI precipitate was formed. A gamma counter was employed to measure the activity of the  $^{125}\text{I}$  yield tracer both in the reactor and collector to calculate the  $\text{I}_2$  recovery. In addition, accelerator MS was utilised to determine  $^{129}\text{I}$  recoveries. The  $^{129}\text{I}$  mass was compared with predicated values based on previous  $^{131}\text{I}$  measurements which allowed the calculation of the minimum amount of  $^{129}\text{I}$  expected in each sample. Recoveries ranged from 34–100% and 13–85% for  $^{125}\text{I}$  and  $^{129}\text{I}$ , respectively. In some cases, the substantial loss in recovery was associated with leaks in the system, variations in air flow rate and differences in absorption of  $^{125}\text{I}$  by charcoal which will be further optimised in future studies. The developed simple procedure consisted of basic laboratory equipment, making it cheap and highly accessible. It would have been intriguing to see if preliminary experiments had been performed to optimise the extraction parameters such as the amount and type of acid used, the ratio of charcoal to  $^{125}\text{I}$  spike, and the bath heating temperature. In addition to the extraction methods the possibility of directly determining  $^{129}\text{I}$  in the charcoal powder from the collection cartridge was assessed. For this purpose, 10 mg of charcoal samples were mixed with 2 mg of  $^{127}\text{I}$  carrier in the form of NaI solution and allowed to dry overnight (<50 °C). To aid target stability Ag powder was added to dried and spiked charcoal samples (ratio 4 : 1). This mixture was loaded onto copper targets and analysed in duplicate. The results showed large variations in replicate analysis, which was associated with sample inhomogeneity and needs to be overcome for future applications. The large variation in duplicate results made the comparison of the direct and extraction method more difficult. In addition, in multiple cases results obtained after extraction differed by an order of magnitude compared with those obtained after direct analysis. Nonetheless, future optimisation could result in a promising sample pre-treatment for  $^{129}\text{I}$  determination. The main challenge that

needs to be overcome will be that of obtaining representative samples from the charcoal filters.

*The analysis of explosives* is often needed in remote areas and in non-laboratory environments. Therefore, it is essential to develop analytical systems that are portable and robust that enable the rapid analysis of unknown samples *in situ*. A system was developed in which a Nd:YAG laser (1064 nm, 7 ns pulse at a power of 100 mJ) with a spot size  $\sim 5000 \mu\text{m}$  was utilised for the identification of explosives.<sup>50</sup> A Bi-concave ( $f = -10 \text{ cm}$ ) and a Plano-convex lens ( $f = 20 \text{ cm}$ ) were used to focus the beam onto the sample surface. Spectral emissions from the sample were collected using a single Plano-convex lens and transmitted to a non-gated spectrometer (350–1000 nm, resolution 1 nm at 500 nm) *via* an optical fibre (core diameter 600  $\mu\text{m}$ , numerical aperture 0.22). To avoid transfer of the excitation source to the spectrometer, a notch filter was placed in front of the optical fibre. The signal could be maximised, by optimising the fibre position and lens selection for a brass sample. Standoff LIBS spectra were obtained at a distance of 6.5 m. The highest intensity was obtained when a lens with a focal length of 50 cm and a diameter of 10 cm was utilised. This system was applied to analyse 5 explosive samples as well as 19 non-explosives, which included common plastics that are known to interfere in identification of explosives due to their use in transport containers. Sample size permitting, up to 30 to 100 single laser shot spectra were acquired. To correct for background effects a fifth order polynomial fit by an iterative least square-based curve fitting algorithm (MatLab) was employed. Principal component analysis (PCA), two-dimensional scatter plots and the application of an artificial neural network (ANN) were compared for their ability to classify spectra obtained from both the explosive and non-explosive samples. Correct prediction rates of 99.83% and 94.18% were obtained when utilising the ANN approach for non-explosives and explosives, respectively with false alarm rates of  $\sim 6\%$ . It would be beneficial to assess if the stand-off distance of 6.5 m could be improved with further adjustments to the system.

To identify forgeries or to establish the order in which pen and toner lines have been applied to a document could prove to be useful in forensic investigations. For this purpose, data obtained using MeV SIMS analysis in combination with results of particle induced X-ray emission (PIXE) was applied to determine the deposition order of toners, inkjet inks and blue ball point pen.<sup>51</sup> The mock samples were created using different combinations of blue ballpoint pen, laser printers and inkjet printers. Utilising 8 MeV  $\text{Si}^{4+}$  ions (lateral beam resolution  $\sim 5 \mu\text{m} \times 5 \mu\text{m}$ ) samples (area 100  $\mu\text{m} \times 100 \mu\text{m}$ ) were scanned initially far away from the ink intersection to obtain mass spectra. These were utilised to define each individual ink and toner in a first step. After this, the actual intersection area (1200  $\mu\text{m} \times 1200 \mu\text{m}$ ) was scanned. Both measurements were obtained in pulsed mode with a beam current of 0.2 fA and a primary ion fluence of  $2 \times 10^7$  ions per  $\text{cm}^2$  resulting in a measurement time of 15 min. The obtained hyperspectral images were analysed using PCA, which enabled the identification of all samples except for those containing inkjet ink. These were further investigated using PIXE. The intersection

regions (800  $\mu\text{m} \times 800 \mu\text{m}$ ) were scanned utilising a 2 MeV proton beam with a lateral beam resolution of 5  $\mu\text{m} \times 5 \mu\text{m}$ , and a beam current of 80 pA. The primary ion fluence of  $4.6 \times 10^{13}$  ions per  $\text{cm}^2$  resulted in a measurement time of 10 min. In contrast to MeV-SIMS, which is a surface technique, PIXE obtains information from layers located at greater depth. The PCA of PIXE maps could help resolve some of the unidentified deposition order. However, it was not possible to distinguish all of the samples reliably. Further optimisation of the MeV-SIMS and the use of a wider range of inkjet inks in combination with other writing tools is to be the subject of further studies.

Similar to document fraud, *counterfeit bank notes* are commonly encountered by authorities. Assessing the topographical properties of bank notes might potentially help to distinguish counterfeit from genuine ones. A high resolution TOF-SIMS methodology was developed, which assessed the height distribution of a sample surface by monitoring one secondary ion and its spectral signature throughout the area under investigation.<sup>52</sup> Different heights result in varying time of flights for the secondary ions enabling topographical measurements. Bismuth clusters at 25 keV and an intensity of 0.09 pA were utilised to produce a pulse beam hitting the target at a 45° incidence angle. Secondary cations were collected at  $-2 \text{ keV}$ . A microchannel plate in combination with a scintillator and a photomultiplier were utilised for detection. Sodium was chosen as secondary mass ion as it is found in the low mass region where the background is low. In addition, Na is considered to be a surface contaminant and so is present on most surfaces. The concept was proven by analysing a model consisting of two post-it notes that had been stuck together. Sodium ions detected from the upper layer reached the mass detector earlier than those resulting from the bottom post-it. The differences in TOF between the two peaks' centre indicates distance between the areas of interest. The importance of experimental aspects such as changes in the extraction field, the presence of flood gun electrons, the extraction gap relative to the layers and the adjustment of the analyser deflection were discussed in detail. It was shown that the orientation of the topographic step relative to the primary ion and the flood gun beam did not influence its analysis. The optimum reflector voltage to obtain best mass separation, was between  $-60$  and 0 V. The developed approach was applied to study the security feature of a 1000 Lebanese Lira bank note, the blue and green stripes created by intaglio printing as well as a Braille dot were studied. The average difference in TOF between the stripes was 3 ns. For the Braille dot it was noticed that due to its previous circulation more than two different height areas were detected. The difference between the dot and the upper left and lower left side of the banknote were 4 and 7.4 ns, respectively. In addition, a Franz Schubert–Fitaglio was assessed to determine height variabilities. Three layers were detected, the TOF difference between the first and second layer was 2.7 ns and was 7.3 ns between the first and the third layer. Results obtained were compared with measurements taken using a Schaefer optical profiler. A linear correlation was observed between TOF measurements (ns) and these height measurements in the range of 20–180  $\mu\text{m}$  which shows that it is possible to utilise

TOF measurements to quantify heights. Based on the difference between the peaks observed in the region of interest, the LOD was calculated to be 0.6 ns; equal to 1–2  $\mu\text{m}$ . This is an interesting approach which could be useful in forensic investigations. However, the encountered matrix and experimental conditions need to be considered in detail. In addition, due to the nature of this technique it is only suitable for insulating samples.

*Chemical profiling has long been an important tool in forensic science* as it can, for example, help link illicit drugs to precursors used in their production. A common technique to achieve these determines the stable isotope ratios of drug samples by means of isotope ratio mass spectrometry (IRMS). However, the availability of the required instruments can be a challenge for forensic laboratories. Therefore, assessing chemical information by other means could help overcome this. One example could potentially be LC-MS. This technique was investigated for its ability to determine abundance ratios of ephedrine and pseudoephedrine samples.<sup>53</sup> The abundance ratio of  $\{M + 2H\}^+$  ion to  $[M + H]^+$  was determined by selective ion monitoring in positive mode. Separation was achieved on a Poroshell 120 EC-C18 column and an isocratic separation utilising a mixture of acetonitrile and 20 mM ammonium formate solution (6 : 94 or 15 : 85). For the determination of *D*-methamphetamine, trifluoroacetic acid was added to the mobile phase (0.05% v/v). The stable isotope ratio of ephedrine correlated to carbon and hydrogen stable isotope ratios previously determined by IRMS at  $R^2$  of 0.7902 and 0.8437, respectively. The analysis of ephedrine of known origin, used as precursors for methamphetamine showed good linkage between their respective abundance ratios. Furthermore, using LC-MS, it was possible to identify methamphetamine groupings based on ephedrine nature: synthetic, biosynthetic, and semi-synthetic. The developed method is by no means a substitute for conventional methods. However, it is a good way of obtaining useful chemical data for drug intelligence purposes based on a commonly used technique. Another facet of this paper was the determination of Sr using ICP-MS. The Sr was found only in semi-synthetic samples of ephedrine prepared from molasses and in biosynthetic samples. However, it was not found in synthetic samples made using pyruvic acid. This ICP-MS method was to be investigated further in future work, where the use of isotope ratios may help clarify further the origin of the drugs.

One last forensic-based application was *the LIBS determination of assorted analytes in carpets from car boots and tyres*.<sup>54</sup> The LIBS instrument used was equipped with a Q-switched Nd:YAG laser operating at 532 nm, with a pulse width of 6–8 ns and at a repetition rate of 10 Hz. It was used to determine many of the decomposition products from bodies (Ca, Fe, Mg and Na) in the carpets. Interestingly, when blank carpet values were subtracted, a Ca : Mg of 3.5 : 1 was obtained early in the decomposition process, whereas the Na concentration did not increase significantly. This was also an indication of early stage decomposition. The technique of GC-MS was also used to detect the presence of chloroform in the air or in the carpet. This too was an indication that a decomposing body had been present.

## 2.2 Fuels and lubricants

A lot of the papers in this section this year were focussing on instruments that have been superseded with the adoption of ICP technology. Many contributions used AA, particularly graphite furnace techniques, with a lot of 'reinvention of the wheel'. In industrial production and assessment labs the technology has moved on with the use of ICP-MS now being the 'go to' technique for low level analysis. Researchers are urged to evaluate the current techniques in use in industry for the analysis they wish to research (American Society for Testing of Materials (ASTM), Institute of Petroleum (IP), Universal Oil Products (UOP) methods) prior to undertaking a research project using AA technology as this is of little benefit to industrial settings and the instrumentation they are currently using. It was surprising how few papers were using ICP-MS in this topic when it is now a mature technique and used extensively in the field. This year the numbers of papers citing LIBS and coal seem to have dropped while those on the subject of crude oils seem to have increased. However, the quality of many of these methods for the analysis of oils was disappointing.

**2.2.1 Petroleum products – gasoline, diesel, gasohol and exhaust particulates.** Emulsion breaking methods proved popular in the papers in this section and are seen as a 'green' alternative to solvent methods. However, most were not novel and were variations on a fairly well described theme with many using flame AA or graphite furnace instrumentation. However, two were of note, the first by Vicentino *et al.*, described a method for the *simultaneous determination of Cd, Mn, Pb and Sb in gasoline samples using ICP-MS with discrete sample introduction*.<sup>55</sup> In this method 20  $\mu\text{L}$  aliquots of the sample solution obtained after micro-emulsion breaking were introduced into the injection system of the ICP-MS instrument by micropipette producing a transient signal. Calibrations curves were matrix-matched to the simulated extract (70 : 25 : 5, ethanol : water : 7 mol L<sup>-1</sup> HNO<sub>3</sub> solution) and 20  $\mu\text{g L}^{-1}$  of Rh was used as an internal standard. This preparation procedure resulted in a pre-concentration factor of 1.75. The timing parameters, such as dwell time, sweeps/reading and readings/replicates were optimized, producing an integration area of 300 points and a total acquisition time of 36 seconds. Detection limits for Cd, Mn, Pb and Sb were 0.06, 0.9, 0.1 and 0.04  $\mu\text{g L}^{-1}$  respectively. Due to the lack of gasoline CRMs, spiked samples were analysed and recoveries were within 80–120%.

The second paper on the emulsion breaking theme, by Meira *et al.*, explored *the determination of Cd, Cr, Cu and Pb in gasoline using micro-emulsion-breaking and solid-phase extraction using magnetic nanoparticles and determination by EDXRF*.<sup>56</sup> The CoFe<sub>2</sub>O<sub>4</sub> nanoparticles were synthesized by co-precipitation using iron nitrate and cobalt nitrate with an Fe : Co fixed ratio of 2 : 1. The micro-emulsions were prepared by mixing 2.0 mL of gasoline, 6.5 mL of *n*-propyl alcohol and 1.5 mL of nitric acid (0.01 mol L<sup>-1</sup>) in a centrifuge tube. Buffer (3.0 mL) was then added to promote the micro-emulsion-breaking. Then, 100 mg of nano-ferrite was added to the centrifuge tube and shaken manually for 10 min. The solid phase was then separated from the supernatant using a magnet. The solid phase was dried for

10 min at 60 °C and the determination performed directly using EDXRF. Detection limits for Cd, Cr, Cu and Pb were 24, 2.8, 16 and 9.7  $\mu\text{g L}^{-1}$  respectively. Recoveries of spiked samples varied from 89–115%. This method, although interesting, is somewhat complicated and probably of limited use in industry where direct methods routinely used for these elements are simpler, more sensitive and more cost effective.

An interesting paper was submitted by Cinosi *et al.* who proposed a *method for trace element quantification in light fuels by total reflection XRF spectrometry*.<sup>57</sup> The paper focussed on 8 elements Cr, Cu, Fe, Mn, Ni, Pb, V and Zn with Ga being used as an internal standard. A benchtop TXRF spectrometer equipped with a 600 W X-ray source monochromated to Mo-K $\alpha$  (17.44 keV) by a W/Si multilayer was used to produce the fluorescence signal from the sample. A 20 mm<sup>2</sup> Silicon Drift Detector with a 900 nm graphene window, collimator and polymeric foil was placed about 2 mm above the sample to collect the spectrum. Analysis software featured automatic background correction, spectrum identification and fitting. In contrast to traditional analytical techniques for trace element identification where calibration curves were required quantification was performed by the internal standard method and relative sensitivity curves. Outlier detection was performed by using modified Z-score and the acquisition time was 1000 s. The samples were prepared using between 3 and 30 injections of 8  $\mu\text{L}$  sample aliquots pipetted onto a siliconized quartz reflector. These were then dried on a hotplate between 100–150 °C. This sequential aliquot addition and drying pre-concentrated the analytes of interest. Using 30 injected aliquots the LOD for these elements by this method were all 1 ng g<sup>-1</sup> or below. Recoveries for a spiked sample of the fuel Jet A1 were between 78 and 112%.

**2.2.2 Coal, peat and other solid fuels.** The first contribution in this section, by Rondan *et al.*, described a new method for the *determination of Se and Te in coal at trace levels using ICP-MS after microwave induced combustion*.<sup>58</sup> In this method, between 300 and 550 mg samples of coal were pressed into pellets and placed on disks of filter paper on quartz holders containing 50  $\mu\text{L}$  of 6 mol L<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub> solution. The holders were placed inside quartz vessels containing 6 mL of an absorbing solution containing HNO<sub>3</sub> and HCl at various concentrations. After closing the vessels, they were placed on a rotor and pressurized with 20 bar of oxygen. The following heating program was used, 1400 W for 5 min followed by 20 min for cooling. Final solutions were diluted with water to 25 mL and the Se and Te determination performed using ICP-MS. This method produced a LOD of 0.002  $\mu\text{g g}^{-1}$  for Se and 0.007  $\mu\text{g g}^{-1}$  for Te. The results compared well with those obtained from the analysis of the same samples using microwave assisted wet digestion and ETV-ICP-MS detection. Method validation was achieved using NIST CRM 1632c with the results comparing well with the certified values.

The second paper in this section, by Chubarov *et al.*, described a *method for the determination of Fe and S valence states in coal ashes using WDXRF*.<sup>59</sup> The proposed X-ray fluorescence method described the determination of ferrous iron and the estimation of the S valence state in coal concentrates and ashes from a pressed pellet without additional sample

preparation. By increasing the S valence state from S<sup>2-</sup> to S<sup>6+</sup> the intensity of satellite SK $\beta$  increased and in the pyrite spectrum the satellite SK $\beta$  is absent and the chemical shift of the SK $\beta_{1,3}$  line energy is observed. The S valence state can be qualitatively assessed in ashes by comparison with the spectra of pure compounds, anhydrite and pyrite. The CRM SO-1 coal ash produced by the West Siberian Testing Center (Yekaterinburg, Russia) and CRM CTA-FFA-1 fine fly ash, produced by the Institute of Nuclear Chemistry and Technology (Warsaw, Poland), were analyzed three times using both a certified titrimetric technique and the proposed XRF method (FeO content in the CRMs is not certified). The deviation between the results of the titrimetric and XRF determinations of FeO was less than 0.21 and 0.09 wt% and did not exceed that of the titrimetric method (0.25 wt%). Using the ratio of FeK $\beta$  satellite and FeK $\beta_{1,3}$  line intensities provided less accurate results, but allowed semiquantitative determination of the FeO content in the ashes. The ratio of FeK $\beta_5$  and FeK $\beta_{1,3}$  lines intensities in contrast provided a good quantitative determination.

The last paper in this section, by He *et al.*, described a *method for the measurement of Li isotopic compositions in coal using MC-ICP-MS*.<sup>60</sup> In China, some coal-associated lithium deposits have been suggested to be a promising Li source especially in countries with limited Li-bearing brines and pegmatites. Additionally, Li isotopes in coal can be used to trace the source of fossil fuels contributing to atmospheric haze. Coal samples were prepared by HNO<sub>3</sub> and HF microwave digestion followed by H<sub>3</sub>BO<sub>3</sub> addition and further microwave digestion followed by evaporation to dryness and dissolution in 10 mL of 2% v/v HNO<sub>3</sub>. After digestion the samples were then purified using Savillex® columns (0.64 cm I.D. × 25 cm height, 30 mL reservoir) packed with 8 mL of Bio-Rad® AG 50 WX-12 cationic resin. The sample was finally eluted into 25 mL of 0.5 M HNO<sub>3</sub> which was then taken to dryness and then diluted in 2% v/v HNO<sub>3</sub> for analysis. The CRMs SARM 18, 19 and 20 were analysed for total Li and the results showed good agreement with the certified values. Using MC-ICP-MS, Li isotope data were obtained with an intermediate precision better than  $\pm 0.30$  parts per thousand. The delta <sup>7</sup>Li values determined for SARM 18, 19 and 20 were 1.35  $\pm$  0.23, 2.16  $\pm$  0.27 and 1.48  $\pm$  0.17 parts per thousand, respectively. The non-certified coal samples analysed revealed a similar range in lithium isotopes delta <sup>7</sup>Li = 6.02–6.77 parts per thousand; suggesting limited lithium isotope fractionation in the coal locally.

**2.2.3 Oils – crude oil, lubricants.** There appeared to be more papers this year related to this subject however a large percentage were not new or novel. A number of examples described hugely long, complicated sample procedures and difficult instrument configurations only to replicate (usually with worse detection limits) standard ASTM methods that have been around for many years. Resources would be better targeted at ‘problem areas’, ‘difficult’ elements and ‘greening technology’ for which methods are badly needed. However, a number of papers were of interest. The first, by Garcia *et al.*, described a *method for the analysis of wear metals in used lubricating oils using a multi-nebuliser and standard dilution analysis with ICP-OES detection*.<sup>61</sup> The nebulizer used in this study was

a multi-nebulizer (MultiNeb®, Ingeniatics, Seville, Spain) which incorporates two independent liquid inlets into a single nebulizer body with a common nebulization gas inlet and a unique outlet orifice. The liquid streams are mixed at the tip of the nebulizer prior to exiting. In this analysis the used lubricating oil samples were diluted 1 : 10 with petroleum ether prior to analysis to reduce their viscosity. These samples entered the nebuliser through one nebuliser inlet and the other was used for the aqueous standard/internal standard addition. The sample is continually pumped through one inlet while the aqueous standard in the other is continually diluted with a blank solution. The internal standard, Y is used to quantify the standard dilution at points over time and this is used to calculate the standard concentration at those individual points. This is then used to construct a standard addition plot with many points, thus giving the unknown concentration in the sample. The continuous dilution of the standard was performed using the peristaltic pump that transports the solutions to the nebuliser. Limits of detection for this method for Cd, Cr, Cu, Fe, Mn, Ni and Pb were 20, 10, 6, 20, 4, 30 and 200 ng g<sup>-1</sup>, respectively. Spiked lubricating oils analysed using this method produced recoveries of 91–108%. This is possibly a 'greener' approach to the conventional ASTM D5185 method, however it would be more time consuming.

The next paper in this section, by Nelson *et al.*, described a method for the *determination of Cl in crude oils by direct dilution using ICP-MS/MS*.<sup>62</sup> To avoid corrosion in refineries the concentration of Cl in crude oil feed stocks should be less than 1 mg L<sup>-1</sup>. However, their level in most crude oils ranges from 3 to 3000 mg L<sup>-1</sup>. Therefore, the need to monitor the presence of chlorinated compounds in petroleum crudes is essential. The measurement of Cl is difficult using ICP-MS and becomes even more difficult in petroleum matrices. However, ICP-MS/MS using the mass-shifting technique was found to be able to achieve low LOQs and good spike recoveries off mass at <sup>37</sup>Cl using H<sub>2</sub> in the reaction cell. The crude oil samples were diluted 1 : 5 or 1 : 10 in *o*-xylene to bring the Cl concentrations within the calibration range. The reference material NIST 1634c was examined at both a 1 : 5 and 1 : 10 dilution. All samples were shaken for two of hours in a mechanical shaker to ensure the samples dissolved in the *o*-xylene diluent. The calibration standards were prepared using different concentrations of an organic Cl standard in an *o*-xylene diluent. Internal standards of Sc and Y were added at a concentration of 0.1 mg kg<sup>-1</sup>. Multiple calibration standards ranging from 1 to 1000 mg kg<sup>-1</sup> were prepared by weight and the diluent was run as a blank. The LOQ for this method was 40 µg kg<sup>-1</sup> and the recovery of NIST 1634c at the two different dilution factors of 5 and 10 produced recovery values of 98.5% and 107.3%, respectively.

The paper by Oropeza *et al.*, described a *method for the analysis of asphaltenes using simultaneous LIBS and LA-ICP-OES*.<sup>63</sup> The LIBS was used for the determination of the major elements C and H while the LA-ICP-OES was used for the determination of Ni, S and V. The asphaltene samples were extracted using a modified ASTM D6560 test using a 1/20 sample/*n*-heptane ratio, the blend was then filtered at 80 °C. The precipitated material was washed using hot heptane before drying and

weighing. Each asphaltene sample was then weighed and mixed with KBr binder at a 1 : 9 ratio for 5 min to ensure homogenization. Preliminary results without a binder generated irreproducible ablation patterns which directly affected the emission signal. Following homogenization, the samples were then pelletized using approximately 7 tons of pressure. The LA was performed using a Nd:YAG laser at 213 nm. The samples were ablated at a repetition rate of 10 Hz while the sample was moved at a speed of 0.1 mm s<sup>-1</sup>. A five-line ablation pattern covering a 1 mm<sup>2</sup> surface was found to produce the best sensitivity and precision while taking into consideration the strongly heterogeneous character of the sample. Signals were acquired in time resolved analysis mode for 3.5 min. The transient signals were integrated using the instrument software and C was used as an internal standard and to normalise the calibration curves. This compensated for matrix effects and variations in the ablation process. The LIBS signals for C and H were obtained simultaneously with the ICP-OES analysis. The H : C ratio gave information about the aromatic/paraffinic nature of the sample and complements the elemental analysis. A high H/C ratio (>1.3) indicates a more paraffinic nature whereas low H : C (<1.0) indicates more aromatic type compounds. Limits of detection by this method were 5, 100, and 0.5 mg kg<sup>-1</sup> for Ni, S and V, respectively. There was good agreement between LA-ICP-OES and analysis by conventional microwave-assisted digestion followed by ICP-OES analysis of a series of asphaltene samples. Similarly, LIBS values were also in agreement with elemental analysis using a routine combustion technique. This demonstrated that simultaneous LIBS and LA-ICP-OES analysis is an alternative atomic emission technique for the direct elemental analysis of asphaltenes.

A paper by Pereira *et al.*, described *an assessment of extraction conditions for the determination of Hg fractions in oily sludge samples using CV-AFS*.<sup>64</sup> The toxicity of Hg depends largely on its species. The toxicity level associated with organic Hg compounds is significantly higher than the toxicity associated with its inorganic species and Hg may bio-accumulate in living organisms. It is assumed that most of the Hg species in petroleum products are in the form of particulates, followed by dissolved Hg<sup>2+</sup> and elemental Hg with organic species (monoalkylmercury and dialkylmercury) at trace concentrations. Common methods employed for the extraction of Hg species were evaluated in this paper in terms of their efficiency towards the analysis of oily sludge samples. Convective heating using dilute HNO<sub>3</sub> in a sealed vessel was demonstrated to be a simple, fast and inexpensive setup to carry out the extraction of ionic Hg. Multivariate optimization using a desirability function permitted the establishment of optimum extraction conditions. Despite the adoption of optimized conditions, the non-extractable fraction of Hg was substantial and likely associated with the presence of hydrophobic complexes, insoluble HgS and Hg<sub>0</sub>, which are of far lower toxicity and environmental importance than extractable ionic species. Overall, the developed method allowed the determination of very low concentrations of Hg<sup>2+</sup> with high sensitivity and precision when compared with more traditional approaches such as HPLC-ICP-

MS. In addition, the method developed has much lower operating costs.

The final paper in this section was a review paper by Gab-Allah *et al.*, that contained 172 references and is a critical review of the *Analytical methods for the determination of S and trace elements in Crude oil*.<sup>65</sup> This review discussed the most commonly used techniques and sample preparation methods and would be a good place to start for a student entering the field.

**2.2.4 Alternative fuels.** Contributions to this section were less numerous than expected this year bearing in mind the push for renewable fuels and green alternatives, however a number were of note.

The paper by Margui *et al.*, described a *method for the determination of S in biodiesel samples using ED-XRF after deposition on a solid support*.<sup>66</sup> The presence of S is a big issue in diesel and other fuel samples with regulators looking to reduce limits and hence to reduce engine emissions. In this work various types of solid support were evaluated, however many had significant blank issues. The best option was found to be 50  $\mu\text{L}$  of biodiesel on an Ultra-Carry® support. The LOQ for this method was 7  $\text{mg kg}^{-1}$  and spiked samples produced recoveries of 94.3–110.6%. This compares well with ASTM D4294 (standard test method for S in petroleum and petroleum products by ED-XRF) which has an LOQ of 16  $\text{mg kg}^{-1}$ .

The paper by Chen *et al.*, aimed to develop a new method for the *quantification of different forms of P in solid fuels via chemical extraction and acid digestion followed by ICP-OES or ion chromatography (IC) determination*.<sup>67</sup> This study developed a new three-step method for separating and quantifying the P in solid fuels into five major P-containing fractions. These were comprised of three organic P-containing fractions: acid-soluble organic P, P in lipids and P in nucleic acids and other acid-insoluble organic structures. There were also two inorganic P-containing fractions: acid-soluble inorganic P and acid-insoluble inorganic P. The new method was validated using a series of P standards with known concentrations and forms. It was also successfully applied to the determination of P content and forms in a wide range of solid fuels *i.e.* bio-solid, meat and bone meal, chicken litter, rice bran, algae, mallee leaf, and biosolid char. Recoveries of P concentrations ranged from 95–102%.

Rong *et al.*, undertook an *experimental study of Hg in flue gas based on LIBS*.<sup>68</sup> The Hg from coal burning plants is discharged into the atmosphere together with the flue gas. The Hg in the atmosphere has toxic persistence and bioaccumulation effects which can cause harm to human health and the environment. It is therefore necessary to monitor the amount of Hg discharged in this way. In this study an experimental system was used comprising an approx. 200  $\text{cm}^3$  vacuum measurement chamber with 4 quartz windows perpendicular to the direction of laser propagation. The emission signal of the plasma was collected from a window of the chamber and focused on the entrance of an optical fibre and transmitted to the spectrometer. A Q-switched Nd:YAG laser was used operating at 1064 nm. Straight calibration lines were constructed using C as an internal standard. The Hg detection limit was estimated by

evaluating the ratio of standard deviation of noise to the slope of the Hg calibration curve and was around 0.06 ppm (0.32  $\text{mg m}^{-3}$ ) at a gas pressure of 10 kPa. The detection limit of this system could possibly be reduced with optimized experimental conditions, such as the use of a short pulse width laser.

The last paper in this section by Foppiano *et al.*, described the *method development and speciation analysis of siloxane compounds in biogas from manure and mixed organic waste using GC-ICP-MS*.<sup>69</sup> A liquid quench sampling system was developed in-house to sample condensable trace compounds from biogas by concentrating them into a liquid solvent. In this study, 2-propanol was used. The instrument system used consisted of a GC with a split/splitless inlet connected to two HP5 type columns one connected to a conventional FID detector and the other by a heated transfer line set at 250 °C to the ICP-MS instrument. The oven temperature program of the GC was initially optimized for GC-FID with a single column connected to the FID detector. The optimized temperature program was then also used for the GC-ICP-MS analyses. The mixing of helium with hydrogen in the octopole reaction system of the ICP-MS instrument was found to be crucial to achieving high Si sensitivity, a low LOD and LOQ and a constant background signal over time. The GC-ICP-MS method showed very good linearity for all the investigated compounds ( $R^2$  between 0.999 and 1.000). The LOD and LOQ in the gas for cyclic compounds such as D5 varied based upon the sampling conditions (approximate range of 0.002–0.004  $\text{mg Si Nm}^{-3}$  and 0.007–0.014  $\text{mg Si Nm}^{-3}$  respectively). The GC-ICP-MS method was evaluated by comparing its performance with that from the FID. The GC-FID had much more complicated chromatograms and showed higher detection limits than the GC-ICP-MS method whose chromatograms which only contained  $^{28}\text{Si}$  were much simpler, cleaner and easier to interpret.

### 2.3 Pharmaceuticals and personal care products

A *review* containing 148 references summarised the developments in the analysis of toxic and potentially toxic elements in make-up articles.<sup>70</sup> Various analytical approaches in terms of sample preparation and analysis technique are generally applied. The most common ones combine conventional and microwave assisted digestion using concentrated acids and plasma-based atomic spectrometric techniques. Examples of these and other methods were summarised in terms of analyte of interest, sample preparation, analytical technique and limit of detection. In addition, trends and challenges encountered in this field were illustrated. It was noted that the method accuracy can often not be addressed due to the lack of available CRMs. A drawback of sample preparations involving concentrated acids is their incompatibility with the instrumental analysis. Consequently, high dilution factors and the resulting larger LODs are often encountered. To avoid this, digestion vessels can be pressurised with  $\text{O}_2$  or  $\text{H}_2\text{O}_2$  which minimises the amount of acid required by regenerating  $\text{HNO}_3$  during the digestion. Alternatively, microwave induced combustion and microwave-assisted ultraviolet digestion can be employed. A need for

speciation analysis was identified because of the different toxicities associated with different elemental species.

Due to the complex matrices often encountered in personal care products, *sample preparation* is a crucial step that needs to be optimised prior to the analysis. To simplify the procedures involved, a total reflection XRF approach was applied to the analysis of lipsticks, eye shadow and body creams.<sup>71</sup> In this study, since only a thin sample layer was deposited, matrix effects became negligible and concentrations could be calculated based on the internal standard added and the instrumental sensitivities for the different analytes. Preliminary experiments were performed to optimise the solvents, sample amount, deposition volume and drying mode. The best results for lipstick samples were obtained when utilising chloroform as solvent and Mo as internal standard. In addition, 5 min of sonication aided the formation of a homogenous suspension. The optimal deposition volume was 5  $\mu\text{L}$ , which was deposited on quartz glass disc reflectors and dried at room temperature. Eyeshadow and body cream samples were treated similarly except that 1% Triton X100 was used as solvent, Pb as an internal standard and an IR lamp was utilised for drying. The method was not suitable for determining elements at concentrations below 1  $\text{mg kg}^{-1}$  in lipstick. However, LODs were sufficiently low to allow general screening for legal thresholds. Since there is a lack of suitable CRMs, to assess the method's accuracy, lipsticks and eye shadow samples were also analysed using ICP-OES and ICP-MS following a microwave assisted digestion. Good agreement was reached between data obtained using ICP analysis and those obtained using suspension-TXRF; even though precision values of 15–20% RSD were encountered. In addition, it was pointed out that Ba determination is challenging because of overlap of the Ba-L lines with K-line of Ti, which is often present in lipstick at high concentrations and should be the subject of future studies. Eye shadow results obtained by suspension TXRF showed an overestimation compared with ICP methods, indicating that the method is applicable only as a first screening tool and requires a normalisation process for quantification purposes. Applying the suspension TXRF method to a body cream CRM (CHEK RM 619) with certified levels of Cd, Cr, Hg, Ni, Pb, Sb and Se resulted in recoveries of  $100 \pm 15\%$  for all but Cr, Hg and Pb. Mercury was not detected at all. This was attributed to its volatility and therefore it being lost during the sample preparation process. Lead concentration, on the other hand, was overestimated by 30%. The authors hope to improve this by employing a molybdenum X-ray tube rather than a tungsten one to achieve LODs lower by an order of magnitude for light-medium *Z* elements with K-line detection (Cr) and the high *Z* elements with L-line detection (Pb).

A vital aspect when analysing active pharmaceutical ingredients (API) within various formulation types is *overcoming matrix effects*. To enable the direct analysis of various low molecular weight compounds ( $180\text{--}325 \text{ g mol}^{-1}$ ) a system utilising a microwave argon plasma torch for ion trap mass spectrometry was developed.<sup>72</sup> The argon plasma torch consisted of a quartz tube through which argon flows at  $100 \text{ mL min}^{-1}$ . The torch was powered by a 100 W, 2450 MHz microwave power

generator. Optionally, analyte particles could also be thermally released from a heated crucible, operated at varying temperatures ( $100\text{--}250 \text{ }^\circ\text{C}$ ), and ionised by the microwave generated argon plasma. The system developed was applied to the analysis of various low molecular weight compounds, commercial tablets and molecularly imprinted polymers. Analytes were introduced into the crucible and heated to approximately  $200 \text{ }^\circ\text{C}$ . The LODs and LOQs ranged from  $0.002\text{--}0.005 \mu\text{g}$  and  $0.006\text{--}0.0015 \mu\text{g}$ , respectively. The linear range was  $0.008\text{--}3 \mu\text{g}$  for pure compounds and  $0.003\text{--}10 \mu\text{g}$  for tablets and molecularly imprinted polymers. It was noticeable that accuracy and precision were not addressed, which would have been beneficial to assess the method's performance. Nonetheless, this direct approach eliminates the need for sample preparation, saving time as well as avoiding the introduction of dilution steps.

A different *direct analysis approach based on LA-ICP-MS* of solid pharmaceutical materials was developed.<sup>73</sup> Samples were analysed by coupling the ablation unit (ArF excimer laser, 193 nm) to the He mode operated ICP-MS instrument *via* Tygon tubing. In-house matrix matched calibration standards, containing 21 different elements at a concentration range of  $0\text{--}200 \mu\text{g g}^{-1}$ , were prepared by drying metal standards under nitrogen. The obtained residues were dissolved in milli Q water and spiked to a placebo pharmaceutical matrix to obtain a stock matrix. This was diluted using the pharmaceutical matrix to obtain the additional concentration levels. Bismuth, In, Sc and Y were utilised as internal standards at a concentration of  $10 \mu\text{g g}^{-1}$ . The lack of commercially available CRMs again proved problematic, with method validation having to be achieved using a separate multi-element stock. Acceptance criteria of United States Pharmacopoeia were met for linearity, accuracy ( $83\text{--}118\%$  spike recovery at three different concentration levels), repeatability (1–12%), LOQ as  $0.3 \times$  the target level. The developed method surpasses the need for time-consuming digestion and was shown to produce results comparable to those obtained using conventional ICP-MS and ICP-OES methods.

In the field of pharmaceutical analysis, the need to meet legal requirements is often the main aspect to drive the development of new analytical methods. The EU Cosmetic Product Regulation No 1223/2009 requires nanomaterial-containing products to be labelled as such. Therefore, analytical methods that can assess the particle size and their quantity in cosmetic products are required. An example for such cosmetic products are sunscreens, which often contain the UV filter nanoparticulate titanium dioxide. The effect that sample preparation can have on these nanoparticles has been assessed.<sup>74</sup> The size of  $\text{TiO}_2$  nanoparticles as well as their concentration was determined utilising asymmetric flow field-flow fractionation (AF4) hyphenated with multi-angle light scattering (MALS) and ICP-MS instrumentation. This approach enabled the internal verification of the size measurement. The lack of specific reference material was overcome by utilising a well-characterised  $\text{TiO}_2$  material dispersed in a water and surfactant mixture as an internal reference during method development. The three sample preparation approaches evaluated were: (1) ultracentrifugation in combination with hexane washing, (2) the thermal destruction of the matrix in a muffle furnace at  $550 \text{ }^\circ\text{C}$  for ten



hours and (3) an anionic surfactant assisted particle extraction and dilution followed by particle stabilisation. The performance of these three sample preparation methods was evaluated based on the Ti bulk mass recovery and particle specific recovery. Bulk mass recovery was best for method (2) at 104% followed by 87% for (1) and 72% for approach (3). Particle specific recoveries after size separation showed best recoveries for methods (2) and (3) at 91%, and a slightly lower result for method (1) of 83%. However, this still far exceeded previously reported particle recoveries of 50% when applying a superficial fluid extraction sample preparation step. Following suspension stability studies method (2) was deemed unsuitable since particle size increased by 8% and the corresponding change in polydispersity index (0.21 to 0.28). This further highlighted a change in size heterogeneity. In addition, the mode and width of the mass-based particle size distribution increased when samples were prepared applying method (1) and (2). Only the third approach did not lead to a significant alteration of TiO<sub>2</sub> particle sizes. Applying sample preparation method (1) and (3) to two sunscreen samples resulted in bulk mass recovery ranged from 77–88% and 89–95 for methods (1) and (3), respectively, demonstrating that these methods were capable of extraction the TiO<sub>2</sub>. The authors have pointed out that it was not part of the scope of this preliminary investigation to provide statistical data to assess the developed methods, hence no replicate analysis was performed. Nonetheless, the most promising method, method 3, is currently being assessed in an inter-laboratory study and will be fully validated at a later date.

An important field of study within the pharmaceutical industry is that of *drug release* as it is vital to fully understand this to develop an efficient drug. The release in long-acting injectable drug formulation (implant) has been assessed utilising LIBS.<sup>75</sup> The API of the studied implant contains a fluoro-functional group allowing F to be used to chemically map the API. Utilising a 266 nm Nd:YAG laser with a 10 Hz repetition rate combined with a CCD detector, F LIBS spectra were acquired (685.60 nm atomic emission line) to quantify the API at pre-determined time points equivalent to 25%, 50%, 75% and 95% theoretical API release. A thin slice from the middle section of the implant (~100 μm thick) was placed directly into the helium purged (1 L min<sup>-1</sup>) sample chamber. One laser point was utilised per location, 440 × 60 locations over a 2.2 × 2.2 mm area at a 35 μm spot size. The obtained spatial resolution was 5 μm × 36 μm. This provided a unique direct spatial visualisation of the API within the implant during its *in vitro* release. A dissolution gradient was observed at the interface between the centre of the cross section and the outer surrounding ring of the cross section. These spatially resolved images showed that the API release begins from the outermost regions, and a dissolution front progresses uniformly towards the implant centre over time. The vertical spatial homogeneity was also assessed at five different points (0, 0.5, 1.0, 1.5, and 2.0 cm from the left end of the implant), which showed a relatively even distribution for all points. The results obtained using LIBS compared well with those obtained using ultra performance liquid chromatography (UPLC) analysis ( $R^2 = 0.9866$ ). This method is a very useful tool to illustrate API release from long-acting injectable drug

formulations and can be beneficial to highlight issues, should unexplained behaviours be observed in drug dissolution studies. Moreover, drug release modelling tools could be developed based on these imaging results.

In a similar approach, *TOF-SIMS was applied to study the depth profile of the oral drug delivery films* Naloxone and Buprenorphine.<sup>76</sup> The TOF-SIMS system utilised a 15 keV Bi<sub>3</sub><sup>+</sup> liquid metal ion source and an argon gas cluster primary ion beam. Sputtering was limited to 70–80 μm while scanning both sides of the film. Naloxone was found to be uniformly distributed, whereas the buprenorphine intensity varied as a function of depth. By dissolving the films in ultra-pure water, a matrix matched ink for printing was created at various concentrations of buprenorphine and naloxone. These calibration standards were analysed to assess if the method could be used for quantification purposes. The correlation between integrated depth profile ion intensity and printed mass was good with  $R^2 = 0.9963$  and  $0.9977$  for buprenorphine and naloxone, respectively. However, the concentrations determined experimentally did not compare well with the stated dose of the film. The authors attributed this to the small analysis volume used and it would be worth investigating if this can be improved. It is pointed out that currently the technique is useful to visualise and size APIs, however, accurate quantification remains a challenge due to the small sample volume and the heterogeneity of the samples in terms of particle size, shape and spatial distribution. Nonetheless, being able to visualise API *in situ* without the need for markers or sample preparation is highly beneficial for the pharmaceutical industry (Table 1).

## 2.4 Polymers and composites

This has been a popular area of research during this review period. The most popular area of research is that of classification of different polymer types for re-cycling or for forensic purposes. Many of these papers also employ chemometric tools on the analytical data to aid the classification.

*One review paper* pertinent to the analysis of polymers has been published by Alqaheem and Alomair.<sup>83</sup> The review, entitled “Microscopy and Spectroscopy Techniques for Characterization of Polymeric Membranes” contained 153 references and covered microscopy techniques such as atomic force microscopy (AFM), SEM and TEM. In addition, spectroscopy techniques such as XRD, small angle X-ray scattering (SAXS), wide angle X-ray scattering (WAXS), FTIR, XRF and XPS were also discussed. Both SAXS and WAXS can provide crystallographic data as well as information regarding pore size distribution and particle size whereas the XPS and XRF provides information on the chemical composition. In the review, each of the technologies is discussed in terms of operation, limitations, sample preparation requirements and data interpretation. The review gives an easily understandable account of each technique while using a good number of clear tables and figures. A second review paper discussed the use of LIBS for the real-time analysis of trace surface contamination of polymers and composites.<sup>84</sup> This review, by Ledesma *et al.* contains 53 references and discussed the capabilities of different LIBS systems, including μ-

Table 1 Applications of atomic spectroscopy for pharmaceutical and personal care products

Analyte	Matrix	Technique	Sample treatment/comment	Reference
Cd, Cr, Cu, Ni, Pb, Sn, Zn	Electronic nicotine delivery system	QQQ-ICP-MS	A full method validation assessing linearity, accuracy, precision and matrix effects was performed; with excellent method performance demonstrated. The developed QQQ-ICP-MS method, which utilised rhodium as an internal standard, was applied to the analysis of e-cigarette liquids. The lowest reportable levels ranged from 0.031 $\mu\text{g g}^{-1}$ for Cr to 3.15 $\mu\text{g g}^{-1}$ for Cu. SEM-EDXRF was utilised to evaluate device component composition which could be linked to metal concentrations in some e-cigarette liquid samples	77
Various	Anti-diabetic tablets	LA-TOF-MS, LIBS	Analysis undertaken using LIBS (250–870 nm) utilising an online calibration free method. The optically thin spectral lines were used to estimate atomic concentration applying a simple Boltzmann equation. The Saha–Boltzmann equation was utilised to calculate the contribution of ionised species. Contributors of both neutral and ionised species were included for the determination of elemental composition. Elements detected in the tablet were Ca (60.7%), Mg (24.2%), Si (5.8%), Na (4.3%), K (2.5%), and Ba (2.4%). LA-TOF-MS was utilised to verify LIBS results and confirmed the elemental composition	78
Na, P, S	Oligonucleotides	ICP-MS	Characterisation of synthetic phosphorothioate oligonucleotides based on quantification of P (five-point external calibration). In addition, the ratio of phosphodiester to phosphorothioate can be determined as an important quality attribute of the oligonucleotide. Oxygen was used as reaction gas for P and S determination. Recovery of P in thiophosphate potassium salt was used as a model compound because of the lack of an appropriate CRM. Recovery values ranged from 99.8 to 102.4% when tested at five different concentration levels (% RSD $\leq$ 0.4 $n$ = 3). Accuracy of phosphodiester to phosphorothioate ratio, based on comparison with the theoretical value, was excellent ( $n$ = 5, 99.1–101.2%). Overall method accuracy was excellent as shown by the mass balance assessment of two oligonucleotides based on P, Na and water content. A mass balance of 100.1% and 101.7% were obtained for these, respectively	79
Ca, Fe	Paper and ink	Confocal 3D micro XRF	A Mo target X-ray tube (30 kV, 1 mA) with a focal spot diameter of 16.5 $\mu\text{m}$ at 20 kV was utilised to analyse mock samples in which printed numbers had been covered by paper, black ink or paper with printed characters. In all cases, the hidden number printed in iron oxide-containing ink, could be identified when assessing the depth profile of the samples	80
Fluorescence spectra $k = 1-10 \text{ \AA}^{-1}$	Ni(II) complex	XAFS	Self-absorption and attenuation correction allowed greater insight into the structural determination and could spectroscopically differentiate bis( <i>N</i> - <i>n</i> -propyl-salicylaldiminato)nickel(II) from bis( <i>N</i> - <i>i</i> -propyl-salicylaldiminato)nickel(II). For each sample 33 spectra were collected from each pixel in a square-planar detector. Analysis revealed two new peaks in the XAFS spectrum at 4.4 and 5.4 $\text{\AA}^{-1}$ . In addition, the experimental data uncertainties were reported and propagated throughout the analysis	81
I	Tablets	XRF	Samples were ground to a fine powder and directly packed into the XRF sample cups (TF-160-255 film). XRF was operated at 45 kV, 50 $\mu\text{A}$ and 180 second scan time. The overall analysis took approximately 10 min. Excellent accuracy was shown when analysing multivitamin tablet (NIST SRM 3280) with recovery of $96 \pm 7.5\%$ ( $n$ = 10). The LOD was 20–30 $\mu\text{g g}^{-1}$ which could be improved further when prolonging the scan time. The author also investigated method robustness and potential effects of the tablet matrix	82

LIBS, the use of different laser types and the duration of the laser pulse. The limitations were discussed as were the future prospects.

Numerous authors have discussed the use of *atomic spectrometry to classify different polymer types*. The most common technique used was LIBS, usually in conjunction with a chemometric analysis of the data. An example of this approach was presented by Junjuri and Gundawar who used femtosecond LIBS followed by principal component analysis (PCA) and artificial neural network (ANN) to classify the polymers polystyrene, low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene and polyethylene terephthalate (PET).<sup>85</sup> The authors collected data from two areas of the spectrum; 220–450 nm and then from 450–800 nm. The first region contained emission wavelengths of C (247.85 nm) and three bands from the CN radical (385.13–421.61 nm). The second region contained emission lines from H, N and O as well as the Swan bands. Two dimensional scatter plots were first plotted and these showed good segregation abilities, although there were some overlaps (for instance, C and CN, C and C<sub>2</sub> and between C<sub>2</sub> and CN) – especially between LDPE and HDPE. The authors then used PCA and ANN on the same species as well as emission data from Ca, K, Mg, Na and Ti. The PCA showed an excellent segregation, although there was a very small overlap between LDPE and polypropylene. The ANN was even more successful, with 99.5–100% of the samples being correctly classified in less than five minutes. A second paper by Junjuri *et al.* reported the use of LIBS for the analysis of “post-consumer” plastics.<sup>86</sup> After obtaining the analytical data for the same analytes in the paper above from 10 different types of plastic, they used several statistical tests on them. These included correlation analysis and ratiometric analysis. The most successful of the tests used was partial least squares discrimination analysis (PLS-DA). This managed to identify nine of the plastics with a success rate of over 90%. However, identification of polycarbonate was slightly less successful, with a rate of only 87.2%. It was still concluded that the approach could potentially be used routinely. Liu *et al.* presented a paper using LIBS to analyse and classify polymer materials.<sup>87</sup> The analytical data obtained from the analysis of 20 plastic bottles was treated using spectral windows based on the algorithm continuous wavelet transform, and then inserted to PLS-DA. A full description of continuous wavelet transform is beyond the scope of this review, but briefly, it is a non-numerical tool capable of providing a representation of a signal by letting the translation and scale of the wavelets vary continuously. In the application described here, it was used to identify peaks in the LIBS spectra and then evaluate the detection performance. A longer description was presented in the paper. Use of the continuous wavelet transform reduced the influence of noisy variables on the classification results, *i.e.* it removed parts of the spectrum that are analytically useless. It also overcame many of the problems associated with manual data processing and enabled easy automation of data handling. When combined with the PLS-DA, itself a simple and stable multivariate analysis technique, a very powerful classification tool was obtained. A step by step guide of the process, including the training protocols for the model, was given. The method was

compared with PLS-DA without the use of spectral windows and with the classification tools Support Vector Machine and Random Forest. The spectral windows PLS-DA was the most successful of the classification techniques, with a rate of 93.93% being obtained, compared with 67.5% for the standard PLS-DA, 76.07% for Support Vector Machine and 57.15% for Random Forest. Another advantage claimed was that of speed. Only 10.1155 s to form its spectral windows was required and this only needed to be performed once, so no further calculations were required for the model. Another paper to use LIBS for recycling/classification purposes was presented by Costa and Pereira<sup>88</sup> who attempted to discriminate between three types of polyethylene (low and high density and re-cycled). The LIBS spectra were collected over the range 186–1042 nm, yielding 12 288 variables. These data were then pre-processed using mean centering prior to using Soft Independent Modelling of Class Analogy (SIMCA) to calculate the inter-class distances between the three types of polyethylene. Once this had been undertaken, PCA was used for the classification. Twelve normalisation modes were tested to help overcome problems associated with variations in the sample surface, the stability of the laser and the interaction of the laser with the sample surface. These 12 modes were discussed in detail and provided similar performance, with inter-class distances of between 5.5 and 7.5 being obtained. The authors averaged the 15 laser shots per sampling position and then normalised the average. This was because of the simplicity of the calculations. Once all of the normalisation had been applied, the PCA classification of the three types of polyethylene achieved a very clear segregation. Another paper to use LIBS to collect analytical data prior to chemometric analysis to classify polymers was presented by Wang *et al.*<sup>89</sup> Four types of plastics were analysed and seven chemometric methods (artificial neural networks (ANN) classification and regression tree (CART), k nearest neighbour (kNN), linear discriminant analysis (LDA), PLS-DA, support vector machine (SVM) and SIMCA) were tested. A brief description of each of the packages was provided, as was a description of the five data pre-processing methods that were also compared. Overall, 199 molecular and atomic emission lines were used for the analysis including C, CN, C<sub>2</sub>, H, N, O and the metals Ba, Ca, Cr, Fe, K, Mg, Na and Ti. The best data pre-processing method was Standard Normal Variate, although autoscaling, mean centering, normalising by the total area and normalising by the maximum also worked to lesser extents. Overall, the ANN along with the standard normal variate pre-processing provided the best performance, although LDA and PLS-DA also provided good classification.

Other techniques have also been applied to obtain the atomic spectrometric data. Among these is a paper by Tuccitto *et al.* who used *TOF-SIMS along with a probabilistic artificial neural network* classifier to classify four plastic types.<sup>90</sup> Data were obtained using a Bi<sub>3</sub><sup>+</sup> beam at 25 keV. The training of the model involved the analysis of 50 samples of each polymer type and an additional 100 spectra obtained from other polymer types. The testing part of the methodology included obtaining 150 spectra (30 from each of the four polymer types of interest and 30 from the “other” polymers). Overall, a mis-classification of 11.7% was

achieved, with most of those (7.5%) arising from non-distinction between polyethylene terephthalate-co-isophthalate and polymethylmethacrylate and the remaining 4.2% misclassification arising from confusion between polystyrene and polyalphanaphthylstyrene. Classification was very rapid and required very little computer processing capability.

An interesting forensic application was reported by Gupta *et al.* who used LA-ICP-MS to analyse different electrical tapes for 18 analytes.<sup>91</sup> A total of 90 different tapes that were known to come from different sources were analysed and the <sup>208</sup>Pb signal was used to transform the data. The 18-dimensional data was transformed so that the scale of the signals was altered and the transformed data had similar characteristics to a normal distribution. The transformed data were then input to PCA which decreased the number of variables (the principal components) to five. The likelihood ratio gave extreme values, indicating that it is unreliable and should not be used in court. However, using an established *post hoc* calibration procedure, the likelihood ratios obtained fell within an acceptable range. Using the first five principal components, 97% of the data variability was accounted for and the error rates were very low (3.65% false inclusion and 2.22% false exclusion). Although this on its own is unlikely to lead to a conviction, it is still compelling evidence. Further work was envisaged to improve the methodology further.

There have been several papers that described different or novel methodologies. An example was presented by Liu *et al.* who used LIBS to quantify toxic elements (Cr, Hg and Pb) in polypropylene samples and then used Random Forest Regression based on Variable Importance to extract as much information from the analytical data as possible.<sup>92</sup> Usually, the chemometric method Random Forest Regression, is used to classify polymers and other materials, so for it to be used in a full quantification is unusual. Random Forest Regression based on Variable Importance is a robust technique that has a good tolerance to noise and consequently does not suffer from the phenomenon of “over-fitting”, *i.e.* it does not adhere too rigidly to a particular set of data (often the training data) and so fails to fit additional or “test” data. As above, data pre-processing was used with mean centering and normalisation being used to improve the performance of the Random Forest Regression. The model was compared with partial least squares regression and Random Forest regression without the Variable Importance input. The newly proposed model had the lowest root mean square or error and the highest correlation coefficient, demonstrating its applicability.

An interesting paper from Aidene *et al.* used EDXRF to determine C, H and O in plastics.<sup>93</sup> This is a novelty because the large majority of commercial spectrometers cannot determine analytes with an atomic number less than that of Na. The authors analysed 40 samples comprising 13 different polymers using an instrument equipped with a rhodium anode X-ray tube. Two sets of spectra were obtained per sample: the “light” (15 kV) and the “heavy” (50 kV). These were then split into four datasets: spectra covering the energy range 0–15 keV and the scattering region of the “light” channel (2.6–2.9 keV) and the analogous ones for the “heavy” channel (0–40 keV and

17.7–23.6 keV). The data were mean centered before processing and partial least squares regression and PCA were used to visualise the data. In general, the PCA did a reasonable job in classifying the polymers, especially for the light channel spectra; but was confounded by elements present in the samples as additives and colourings. The PLS was more successful, but it too suffered from some problems. For instance, the  $R^2$  value for C content over the range 38.43–85.62% ranged from 0.67 to 0.86, again with the “light” channels providing better data. Despite this, the authors concluded that the methodology had potential for further use in classification of polymers. In addition, the study could be extended to include the determination of N.

In recent years, significant research has gone into single cell- and single particle-ICP-MS measurements. This is especially true for nanoparticles. However, that technology has been transferred and so Bolea-Fernandez *et al.* have reported the use of single event ICP-MS analysis of micro-polymers.<sup>94</sup> The dwell time was set at 100  $\mu$ s and a high efficiency, low flow nebuliser was used with an uptake rate of 10  $\mu$ L  $\text{min}^{-1}$ . Standards of metal-containing polystyrene beads (2.5  $\mu$ m diameter, doped with lanthanide ions) was used for the method development. In addition, no-spiked beads of 1  $\mu$ m diameter were also used. Both types of beads were diluted with ultra-pure water to ensure that double strike events were minimised. The particle size distribution was measured by monitoring the C-13 signal and this was compared with the data obtained using the Ho signal arising from the metal-doped microparticles. Agreement for the number density and for the transport efficiency was good. Despite the encouraging data, the authors warned that before the technique could be used routinely, standards of known size and calibration methodologies would have to be developed.

Grunberger *et al.* reported a LA-spark discharge-Optical Emission Spectroscopy method for the analysis of several sample types including human finger prints, mesoscopic layered samples and micro-patterned polymers.<sup>95</sup> In addition, certified materials such as aluminium, titanium, titanium alloys, molybdenum and tungsten were also analysed. A schematic diagram was provided in the paper, but essentially a Nd:YAG laser and a spark from a tungsten electrode placed 1–5 mm above the sample were used to initiate a plasma from which emitted light was transmitted through a fibre optic to either a Czerny–Turner or an echelle spectrometer. The laser shot triggered the spark with the delay lag being dependent on the distance above the sample surface the electrode was. Best performance and optimal spatial resolution was achieved when the laser spot size, the pulse energy and the spark gap were minimised. A useful table was provided that compared the performance of LIBS, Spark-OES and LD-SD-OES. Spatial resolution for the new technique was approximately 100  $\mu$ m, which was comparable to the other techniques. However, it was noted that emission lines from higher ionisation states, *e.g.* those with a double charge, could only be detected using the LA-SD-OES technique.

There are a number of relatively simple applications of interest that should be reported. This includes a LIBS analysis in which the type and quality of high voltage outdoor insulators were

Table 2 Applications of the analysis of inorganic materials

Analytes	Matrix	Technique	Comments	Reference
Fe	High purity rare earth metals	ICP-MS/MS	Mass shift reaction of $^{56}\text{Fe}$ with $\text{O}_2$ to produce $^{56}\text{Fe}^{16}\text{O}^+$ target ion for the removal of $^{40}\text{Ar}^{16}\text{O}^+$ , $^{40}\text{Ca}^{16}\text{O}^+$ and $^{37}\text{Cl}^{18}\text{O}^{1}\text{H}^+$ interferences (in Chinese)	114
Al, Fe, Mg, In, Si, Zn and K	Potassium hydroxide zincate electrolyte	Flow injection ICP-OES	A five-step procedure for the determination of trace, particulate and bulk components in concentrated (12 M) potassium hydroxide zincate electrolyte materials was described. Three calibration strategies were employed: spiked 12 M KOH for trace analysis, standard addition of ZnO to diluted electrolyte samples and a simple high dilution ratio of K determination. The procedure developed was used to understand the precipitation of components when samples were exposed to air over several hours	115
As	Titanium dioxide	ET-AAS	Paper described the use of ET-AAS with a pyrolytic graphite coated tube to determine trace levels of As in titanium dioxide samples following microwave digestion with $\text{HNO}_3$ and HF. The optimised method enabled analysis over a range of $5.0\text{--}100.0\ \mu\text{g L}^{-1}$ with an LOD of $0.2\ \mu\text{g g}^{-1}$	116
Cr	ZnS crystals	LA-ICP-MS	Utilisation of the high spatial resolution of lasers and the sensitivity of ICP-MS to quantitatively map the diffusion and spatial distribution of Cr ions doped in ZnS crystals	117
Al	Solid-propellant flames	LIF	High speed (5 kHz) LIF imaging of Al atoms allowed the study of their distribution in flames produced during combustion of aluminised solid propellants	118

analysed.<sup>96</sup> The insulation efficiency decreases with age because of environmental, electrical and mechanical stresses. A rapid, reliable and non-destructive method of analysis is therefore required to minimise time where the power is shut down. Both standard and remote LIBS experiments were undertaken. The standard LIBS setup involved laser pulses from a Q-switched Nd:YAG laser operating at 1064 nm exciting the sample and then light emitted travelling through a fibre optic to a Mechelle spectrometer equipped with an intensified CCD detector. The

remote LIBS system was basically the same but with a portable spectrometer. In pristine samples, there were distinct peaks for C, CN and Si. However, in worn insulators, other elements originating from their environment, *e.g.* Al, Ca, Fe Mg, Na and Ti were clearly detectable, with the signal being proportional to their age.

Fatunsin *et al.* estimated children's exposure to hazardous brominated flame retardants in plastic toys.<sup>97</sup> These authors used a portable XRF instrument that had first been tested on some

proprietary standards to ensure accuracy. The instrument was placed as close to the sample as possible with signal being measured for 60 s. The thickness of the material was corrected for if it was very thin. The LOD was  $5 \text{ mg kg}^{-1}$ . The XRF was used as a screening tool that identified whether or not a sample contained Br. Those that did underwent further analysis that involved an extraction followed by gas chromatography – mass spectrometry to identify and quantify individual Br-containing compounds. Although this is a very simple application, it does demonstrate how useful and quick portable XRF can be as a screening tool.

Another simple application was presented by Henn *et al.* who described an *online microwave-assisted solid sampling system for polymers* followed by flame furnace AAS detection for the determination of Hg in polymers.<sup>98</sup> Four polymers (polypropylene, polyethylene terephthalate, high density polyethylene and polyvinylchloride) were analysed. The system used was described in detail including a schematic diagram. The sample ( $3 \text{ mm} \times 3 \text{ mm}$ ) was mixed with cellulose wetted with ammonium nitrate solution, placed into the device, ignited in a stream of oxygen and then the Hg determined. The system was optimised with respect to the oxygen flow rate ( $0.6 \text{ L min}^{-1}$ ), mass of cellulose (20 mg), volume and concentration of ammonium nitrate solution ( $20 \mu\text{L}$  of  $6 \text{ mol L}^{-1}$ ), position in the system (just in front of the waveguide) and sample mass. A quartz T-piece on a burner head of an AAS instrument enabled detection. The design of this was also optimised, with one that had no holes and no slit in the under-side being optimal (gave the lowest characteristic mass). The flame conditions were also optimised. The method was validated through the analysis of the reference materials European Reference Material ERM EC 680K and ERM EC 681K low density polyethylene, with good agreement with certified values being obtained. The LOD was  $0.2 \text{ mg kg}^{-1}$ . It was concluded that the device was very successful and is portable and could therefore be employed with numerous spectrometers.

A paper by Sengupta *et al.* used *EDXRF and DC arc-OES for the determination of 22 analytes in neoprene gloves* that had been contaminated with radioactive materials.<sup>99</sup> Both the EDXRF and the DC arc-OES analyses were capable of direct analysis of solid samples. This was thought to be an advantage in that they do not require an acid digestion that would be required for ICP-OES analysis. There is therefore less chance of workers becoming contaminated with radioactive material. For the DC arc-OES analysis, the gloves were incinerated, homogenised, loaded onto electrodes and then excited using the arc. The two techniques had similar detection limits with the EDXRF values ranging between 20 and  $40 \text{ mg kg}^{-1}$  whereas the DC arc-OES had LOD of typically  $5\text{--}20 \text{ mg kg}^{-1}$  with a few analytes, *e.g.* B, Be and Cd being significantly better (*e.g.*  $0.1$  or  $0.2 \text{ mg kg}^{-1}$ ). There was a significant difference in precision though; with the DC arc-OES providing values of typically 15–25% RSD whereas the EDXRF had a precision of <10% RSD. Results for those analytes that were above the LOD for the two techniques were in good agreement, with differences rarely being greater than 10%.

### 3 Inorganic chemicals and materials

In continuation of the previous review period, papers detailing the development, or interesting application, of atomic spectrometry have been grouped into the following topic areas; Inorganic chemicals, fertilizers, forensic analysis, catalysts and building materials.

#### 3.1 Inorganic chemicals

Once again, the analysis of an eclectic assortment of matrix types was reported during the review period, examples of which are included in Table 2.

Several papers discussed the *analysis of edible salt*, an important topic because of its high consumption by the population where trace contamination could lead to unintentional bioaccumulation. Caridi *et al.* evaluated the concentrations of As, Cd, Cu, Hg and Pb as well as the anthropogenic  $^{137}\text{Cs}$  and natural  $^{40}\text{K}$  radioisotopes in nine samples of food salts using ICP-MS and High Purity Germanium (HPGe) Gamma Spectrometry.<sup>100</sup> Thankfully, all results obtained were under allowable levels, thus excluding the risk of toxic effects on humans. A simple sampling process of dipping a filter paper into aqueous solution of edible salt for determination of Ca and Mg by LIBS was reported.<sup>101</sup> Whilst samples were easy to collect, their presentation with consistent sample surface height was found to be critical to generating a persistent plasma. Reference signal from Na(I) and C(II) lines at 568 nm were also required for intensity normalization of the analyte Mg(II) and Ca(II) lines to counter the inhomogeneous distribution of the dry residues. The authors also reported the same protocol to determine Ca, K and Mg in edible sea salt products.<sup>102</sup> A means of direct analysis of salt solutions using LIBS was reported by Lin *et al.* (in Chinese).<sup>103</sup> Sample solutions were continuously pumped through a funnel held above a beaker to produce a thin stream of liquid that served as the point of analysis. Using this arrangement, Na was determined by internal standardisation of the Na I 589.0 nm and Na I 589.6 nm lines with the H I 656.2 nm line to give a LOD of  $19.54 \mu\text{g mL}^{-1}$ .

A precise analytical procedure of HPLC-ICP-MS was developed to rapidly determine the *iodine species of iodide and iodate at trace levels in high salt brine samples*.<sup>104</sup> Efficient separation was achieved within 8 minutes using a Dionex IonPac AS-14 anion exchange column with a  $100 \text{ mM} (\text{NH}_4)_2\text{CO}_3$  solution at  $\text{pH} = 10$  as mobile phase. Linear calibrations were obtained over  $1.0\text{--}100 \mu\text{g L}^{-1}$ , with detection limits of  $0.05 \mu\text{g L}^{-1}$  for iodate and  $0.20 \mu\text{g L}^{-1}$  for iodide.

Applications of the analysis of *zeolites and related materials* continues to be an area of substantial research. However, the procedures for their characterisation have quickly matured, leading to token details being mentioned in manuscripts. A number interesting papers utilising the absorptive power of zeolites to remove arsenic from natural<sup>105</sup> and deep well waters,<sup>106</sup> hexavalent chromium in wastewater<sup>107</sup> and mercury from flue gas<sup>108</sup> were reported. In each study, XRF was the preferred technique for characterising the elemental composition. The optimisation and validation of a thermal desorption

(TD)-AAS method for total Hg determination, without sample digestion, was reported for zeolites intended as dietary supplements.<sup>109</sup> The instrumental set-up was optimised to meet the LOD, accuracy and precision requirements as set out in accordance to EC 333/2007. Accuracy was assessed using six CRM materials with concentrations ranging between 0.22–99.8 mg kg<sup>-1</sup>, with excellent recovery at all levels. Furthermore, a detection limit of 0.45 µg kg<sup>-1</sup> was achieved using 100 mg of sample.

A paper by Camacho *et al.* detailed the *examination of the laser-induced plasma produced by a transversely excited atmospheric (TEA) high-powered CO<sub>2</sub> laser operating at 10.591 µm on zeolite-like potassium gallosilicate samples.*<sup>110</sup> The central efforts of this work focused on characterisation of the electron temperature, electron density and average expansion velocity for various plasma species based on the spatial and temporal study of 2D LIBS data. A noteworthy result of this study highlighted the ability to determine species in the early phase of the plasma, enabled by the use of a CO<sub>2</sub> laser with a high excitation wavelength. This resulted in a lower continuum background enabling the detection of species in higher ionization states or elements with short lifetimes such as oxygen.

Three papers discussed the *coupling of liquid chromatography with atomic spectrometric detectors* for the preconcentration and speciation of analytes. The first paper detailed the separation and preconcentration of 10 trace metal ions from high purity boric acid by using an online two-dimensional valve switching method coupled with ion chromatography-ICP-MS.<sup>111</sup> The system consisted of a sample loop, a Dionex MetPac CG-1 matrix capture column, iminodiacetic acid cationic chelating column and a Dionex IonPac CG10 ion chromatography column coupled with an ICP-MS instrument. The cationic chelating column retained the metal ions in the sample using its carboxyl functional groups to separate them from the boric acid matrix solution. These were then eluted with 1 M HNO<sub>3</sub> for separation by valency using ion chromatography followed by detection using ICP-MS. The method LODs were 0.001–0.023 µg L<sup>-1</sup> across the analytes and spike recoveries ranged between 83% and 110%. Shmakova *et al.* reported the use of HPLC-ICP-AES, amongst other techniques, to understand the incorporation of niobium into polytungstate macrocyclic structures.<sup>112</sup> Good separation and analyte stability were achieved using an eluent consisting of an acetate buffer with 0.04% tetrabutylammonium hydroxide ion-pair agent with an acetonitrile gradient profile. In order to eliminate plasma quenching the eluent was diluted in line with ultra-pure water prior to entering the spray chamber. Optimal conditions were achieved with an eluent flow rate of 0.18 mL min<sup>-1</sup> and stable plasma burning was observed even when acetonitrile reached 55% in the gradient profile. A method based on HPLC coupled with HG-AFS was proposed for the determination of arsenic and antimony redox couples (As(III) and As(V) as well as Sb(III) and Sb(V)) in highly corrosive copper electrolyte samples was reported by de las Torres *et al.*<sup>113</sup> Separation was achieved using a PRP X100 (100 mm × 4.1 mm × 10 µm particle size) column with a phosphate and tartrate mobile phase for As and Sb, respectively. Post-column derivatization for hydride generation was accomplished by adding NaBH<sub>4</sub> and HCl solutions by means of a peristaltic pump and the volatile species carried to

the AFS detector with Argon. The detection limits were 1.2, 2.3, 0.3 and 0.4 µg L<sup>-1</sup> for As(III), As(V), Sb(III) and Sb(V), respectively.

### 3.2 Fertilisers

Interest in the *combination of LIBS and chemometric data analysis* for sample classification is rapidly growing in multiple fields, and the analysis of fertilisers is no exception to this. In one example, LIBS in association with partial least squares regression was developed for the rapid determination of P in compound fertilisers.<sup>119</sup> Samples were milled and pressed into 25 mm pellets for analysis and LIBS spectra collected over the reduced wavelength range from 210 to 260 nm, which contains the most intense P emission lines. This was used to build a multivariate model from 36 training samples characterised using ICP-OES and validated using a further 11 test samples. Correlation between the LIBS predicted value and that determined by ICP-OES was 0.946, indicating good correlation between the two test methods. However, reference materials should be used to understand true accuracy. The same authors reported a similar study for the determination of N in ammonium phosphate fertilisers.<sup>120</sup> The correlation coefficient of the quaternary linear model was 0.981 but the maximum relative error of the validation samples was as high as 432%. Further examples include the rapid detection of P in compound fertilisers including Si as an independent variable,<sup>121</sup> the determination of K, N and P using support vector regression<sup>122</sup> and quantification of Al, C, Fe, P and Si in phosphate slurries.<sup>123</sup>

Away from LIBS, Machado *et al.* discussed a *strategy of internal standardisation to overcome the non-spectral matrix effects* caused by easily ionised elements on the determination of As, Cd and Pb in mineral fertilisers using ICP-OES.<sup>124</sup> Four elements (Bi, Ir, Sc and Y) were chosen as internal standards for investigation because of their physico-chemical properties being similar to those of the analytes. The accuracy and efficiency of the internal standards were evaluated through the analysis of CRM NIST 695 following microwave digestion with 6.0 mL HNO<sub>3</sub> and 2.0 mL of 30% H<sub>2</sub>O<sub>2</sub>. The most effective were found to be Y (360.1 nm) and Sc (424.7 nm) for As and Ir (215.8 nm) for Cd and for Pb; with respective recoveries of 101%, 94% and 99%. Whilst not the most progressive paper, it does reinforce the need for proper matrix control to less experienced analysts.

### 3.3 Forensic applications

The *statistical interrogation of data obtained from atomic spectrometric techniques for the rapid classification of gunshot residues* (GSR) featured significantly through the review period. The feasibility of a method of identification and discrimination of GSR from different calibre ammunition using TXRF and pattern recognition using principal component analysis (PCA) was discussed by Ferreira *et al.*<sup>125</sup> Swabs from a shooter's hands were extracted with 5% v/v nitric acid and solution deposited on a quartz disk for the determination of 14 elements: Al, Ba, Br, Ca, Cu, Fe, H, Mn, Ni, Pb, S, Sb, Sr and Zn. The method proved to be adequate for identification of one- and three-shot residue inorganic components from 0.40, 9 mm, 0.380, 0.38 and 0.308

calibres. Machine learning techniques, such as discriminant analysis, supported vector machines and partial least squares of Ba, Cu and Pb concentrations determined using TXRF was a means of identifying GSR on a shooter's skin.<sup>126</sup> The protocol was successfully validated following the analysis of 100 samples collected from numerous participants firing 9 mm ammunition. Machine learning algorithms were also reported for the classification of GSR samples based on their LIBS spectrochemical data.<sup>127</sup> Samples were collected from a shooter and a non-shooter's hands using the standard design carbon stub used by forensic practitioners and analysed directly. Small spot ablation was performed using a 266 nm, high power Q-switched Nd:YAG laser optimised for frequency, energy, spot size and number of shots using Box–Behnken experimental design. Data processing was performed on the signal-to-noise ratio of five elements; Sb (259.8 nm), Cu (324.7 nm), Al (396.1 nm), Pb (405.8 nm) and Ba (455.4 nm) with a high identification accuracy of 87–100% depending on the algorithm employed.

Handguns, with centrefire ammunition, are the firearms most commonly associated with crime. It is for this reason that GSR studies predominantly focus on the detection of the elements Ba, Pb and Sb, which are associated with the primer materials of this type of ammunition. However, interestingly, in Australia the predominant illicit firearms are small calibre, long rifles which use rimfire ammunition that does not contain antimony, allowing them to only be classified as 'consistent' with GSR under the ASTM guidelines. To overcome this, Seyfang *et al.* set out to establish a method based on the *characterisation of glass particles originating from ground glass fractionator in rimfire ammunition*.<sup>128</sup> Samples were collected on a standard GSR stub and the glass particle surface prepared using focussed ion beam to reveal the glassy surface free from contamination. Analysis using TOF-SIMS was performed using a Au<sup>+</sup> primary ion gun at 30 keV under a vacuum of  $5 \times 10^{-6}$  Pa. Several measurements were made by rastering a  $5 \times 5 \mu\text{m}$  area revealing unique fingerprints in the glass from different ammunition suppliers. Furthermore, the composition of glass fractionator was found to be stable during firing, which raised the possibility that chemical testing of the glass in GSR may be used to identify the ammunition from which the residue was derived.

### 3.4 Catalysts

The origin and nature of catalytic materials continues to be as varied as their application and, whilst it is encouraging to see an explosion in the number of papers pertaining to the sequestration and fixation of carbon dioxide, the application of atomic spectrometry in the field of catalysis has become somewhat mature. The ability to study catalytic materials under reaction-like conditions is invaluable to truly understanding its activity, selectivity and durability. It was therefore no surprise that this continues to be an area of research.

Kuzmenko *et al.* designed a von Hamos geometry wavelength dispersive spectrometer combined with an *in situ* reactor cell for the *speciation of S* using non-resonant S K $\alpha$  emission.<sup>129</sup> The cell, constructed with a 7  $\mu\text{m}$  Kapton film window, was equipped

with a heating element, thermocouples and gas supplies to allow feeding of reactive gases. The spectrometer operated at a 15 cm focusing radius, and was equipped with a curved Si(111) crystal and position sensitive detector, achieving an energy resolution of 0.56 eV at 2.3 keV. Installed at the SuperXAS beamline of the Swiss Light Source, the set up was used to study the S poisoning of SiO<sub>2</sub>-supported Ru nanoparticles performing carbon monoxide methanation.

X-Ray absorption spectroscopy, in particular XANES, is the technique of choice when characterising oxidation state and coordination environment of active species. Single particle XAS, together with XRF and XRD was used to understand the process of nickel poisoning of Fluid Cracking Catalysts.<sup>130</sup> Operando XAFS Imaging of the distribution and chemical states of Pt in the cathode catalysts of polymer membrane fuel cells was used to clearly visualise the degradation of the cathode during accelerated degradation test.<sup>131</sup> In both papers, a full account of the principle, analysis and data interpretation was presented. The technique of high energy resolution fluorescence detected (HERFD)-XAS was used to overcome the unique analytical interferences found during *in situ* studies of V-W/TiO<sub>2</sub> catalysts for the selective reduction of NO<sub>x</sub> using ammonia.<sup>132</sup> The group found it impossible to perform XAS measurements in transmission mode because of the low energy radiation at the V K edge (5465 eV), which was absorbed by the W in the catalyst. Conventional fluorescence measurements were also difficult because of the overlapping of V K $\alpha$ 1,2 with the K $\beta$ 1,3 lines of Ti, furthermore, the quartz window used for *in situ* cells absorbed ~35% of X-ray photons at the V K edge energy further hampering analysis. Ganzler *et al.* also utilized spatially resolved operando HERFD-XANES to reveal a crucial contribution of Pt–CeO<sub>2</sub> perimeter sites in overcoming CO self-inhibition during low temperature CO oxidation.<sup>133</sup>

Whilst not strictly operando, the *coupling of ICP-MS to electrochemical flow cells* provides a unique insight into electrocatalysis stability research. An interesting paper by Shkirskiy *et al.* discussed the influence of flow cell geometry, flow rate and coupling distance on overcoming challenges due to differing time scales of electrochemical and concentration transients.<sup>134</sup> Optimised conditions were used to determine the residence time distribution of the cell and improve understanding of Pt dissolution during cycling voltammetry.

A LIBS method with minimal sample preparation was used as means of investigating the *deactivation of Pd/C catalysts*, where leaching was the main deactivation mechanism.<sup>135</sup> Samples were dried, milled and pressed into pellets with a palmitic acid binder. The LIBS analysis was performed using a Q-switched Nd:YAG laser at 1064 nm with a pulse duration of 7 ns under an argon blanket to reduce the effects of atmospheric gases. Spectra, collected for four samples with varying reaction times, was normalised to the argon 763.57 nm emission peak to minimise effects of varying parameters such as intensity shift. Results were compared with those from the more established technique of ICP-MS following the removal of the carbon support by ashing and subsequent dissolution of palladium rich residues with aqua regia. Good agreement was obtained between the two methods. The authors claimed the main



Table 3 Applications of the atomic spectrometric analysis of building materials

Analytes	Matrix	Technique	Comments	Reference
Cl	Concrete	XRF	Plug samples from marine structures were spilt into 2 mm layers to allow depth profiling	150
Cl, S	Concrete	XRF	Samples submerged into Cl <sup>-</sup> and SO <sub>4</sub> <sup>2-</sup> rich baths were analysed to determine the inhibitory effects of Cl <sup>-</sup> ions on sulfate attack	151
Ca	Concrete	XRF	Comparison of Ca leaching by biogenic and sulfuric acids	152
Cl, S	Mortar	PIXE	2D mapping of Cl <sup>-</sup> and SO <sub>4</sub> <sup>2-</sup> ions diffusion in homemade mortar samples	153

advantage of the method was that it is non-destructive. Whilst LIBS analysis is minimally invasive and essentially non-destructive on a bulk scale, it cannot be regarded as such when materials are milled and pelletized prior to analysis. A similar study was also reported for the monitoring of V leaching from V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts during the gas phase dehydration of glycerol.<sup>136</sup> However, little was detailed regarding the preparation of the sample.

The high economic value of *platinum and associated PGMs* continues to drive the re-invention and fine-tuning of methods for their determination in catalytic convertors. Eskina *et al.* described the determination of Pd, Pt and Rh in spent catalysts using HR-CS-GFAAS following microwave digestion with 4 : 1 HCl and H<sub>2</sub>O<sub>2</sub>.<sup>137</sup> Results from the optimised method were comparable to those obtained using the established ICP-OES approach. The use of a handheld XRF was described as a fast means of determining Pd, Pt and Rh in finely ground catalysts.<sup>138</sup> The 40 kV incident X-ray source used allowed accurate and relatively precise determination from 200–6000 ppm in just 30 s. Omrani reported the use of ICP-MS/MS with ammonia reaction gas as a means of accurately determining Pd, Pt and Rh in spent catalysts.<sup>139</sup> A combination of on-mass analysis for <sup>105</sup>Pd and <sup>103</sup>Rh, and mass-shift reaction of <sup>194</sup>Pt to 228 amu, was used to eliminate potential isobaric interferences. The same study also measured the emission of PGMs from exhaust gases, collecting particulates on nitric acid washed quartz fibre filters. Concentrations were determined using the same instrumental set-up described, following microwave digestion with aqua regia.

An interesting paper reported the use of ICP-MS/MS as a screening reactor to monitor intermediate species formed during the iridium and ruthenium ion-catalysed gas-phase reaction of ethanol to butanol.<sup>140</sup> Metal ions of interest generated in the plasma were isolated using the first quadrupole mass filter and introduced into the collision-reaction cell with gaseous ethanol where reactions took place. The product ions and newly formed metal adducts were then immediately analysed *via* mass spectrometry allowing rapid assessment of the possible formation pathways.

### 3.5 Building materials

This year's review has seen several papers that utilised LIBS for the *analysis of cementitious materials*. Kapteina *et al.* discussed the application of LIBS for fast and reliable profiling of damaged reinforced concrete, highlighting its ability to increase information density whilst reducing analytical effort and cost compared with alternative instrumental techniques and to wet chemical analysis<sup>141</sup> (German). Calibration free LIBS for the determination of the major constituents, Al, Ca, Fe and Si, in cement brands from Pakistan was reported.<sup>142</sup> Quantification was based on plasma parameters determined from the emission spectrum, with the assumption that the plasma was optically thin and follows local thermodynamic equilibrium. The paper also provided a comprehensive protocol to test these assumptions. The deduced compositions using CF-LIBS were in agreement with results obtained by a range of techniques including PIXE, EDX, XRF and LA-TOF-MS. Jia *et al.* discussed the use of a flattop laser, rather than the standard Gaussian profile, for LIBS analysis of cement.<sup>143</sup> A nanosecond Q-switched Nd:YAG 1064 nm laser was transformed to a flattop profile with uniform intensity by introducing a beam shaping diffractive element next to the focus lens. This resulted in a more consistent ablation, more stable spectral intensity, and thus a better correlation calibration curve and lower LOD compared with the Gaussian profile laser.

With *chlorine penetration being one of the dominant damage processes of reinforced cement*, it is not surprising that developments in analytical procedures for the determination of Cl continue to feature. The critical Cl concentration at the phase boundary between reinforcing steel and mortar was evaluated using LIBS for accelerated corrosion tests in alkaline and carbonated mortars.<sup>144</sup> The commercially available instrument used achieved an LOD of 0.03 wt%. Quantitative detection of Cl in cement through the detection of CaCl molecular emission at 617.9 nm produced with microwave-assisted LIBS was reported as a means of reducing Cl LOD.<sup>145</sup> The paper described in detail the instrument set-up and optimisation, with ideal conditions including a minimum laser energy of 7.5 mJ with a 1.5 ms 600 W

microwave pulse, a 500–1000 ns gate-delay and a gate-width of 300  $\mu\text{s}$ . This yielded a LOD for 100 shot accumulation of  $47 \pm 7 \mu\text{g g}^{-1}$ , while for a single shot it was  $170 \pm 59 \mu\text{g g}^{-1}$ . Whilst this represents a noteworthy improvement in LOD, the authors acknowledged that the additional elements of the instrument increased its complexity and removed the advantage of standoff analysis associated with conventional LIBS. Dietz *et al.* also reported the use of the CaCl molecular emission as means of determining Cl concentrations using LIBS.<sup>146</sup> Mounting the sample on an X-Y stage, the 2D mapping of Cl was possible with a detection limit of 0.094 wt% and spatial resolution of 200  $\mu\text{m}$ . Further examples are included in Table 3.

A comparison of the suitability of multiple techniques for the determination of salinity in mineral building materials was reported.<sup>147</sup> The paper investigated both aqueous extractable methods with UV and IC, and direct solid analysis with WDXRF and SEM-EDS. Samples were soaked in 10% solutions of chloride and sulfate salts of Ca, K, Mg and Na, then recovered, dried and powdered for either extraction in water or pelletisation for analysis. Results indicated that methods based on solid phases (XRF and EDS) gave higher salinity values than those based on aqueous extracts (IC and UV) suggesting that salts partially bind within the mineral. This discrepancy was more pronounced for sulfate salts. Mijatovic *et al.* provided a detailed description of the validation of a pressed powder EDXRF procedure for the determination of 10 major elements (Al, Ca, Fe, K, Mg, Na, P, S, Si and Ti) and eight trace elements (As, Cr, Cu, Mn, Ni, Pb, Sr and Zn) in cement based composites.<sup>148</sup> The study examined the built-in calibration curves provided by the instrument manufacturer against 14 CRMs and 21 in-house reference materials with good correlation. A method was also reported for the determination of Ca in cementitious materials by ICP-OES as a means of estimating binder concentrations.<sup>149</sup> The HCl dissolution procedure was optimised for small samples sizes, whilst it was noted that the method was obviously not suitable for samples with calcareous or dolomitic aggregates.

### 3.6 Ceramics and refractories

In accordance with many other sections, the ceramics of cultural heritage origin have been moved into a separate section. This has therefore led to a significant decrease in the number of papers cited in the current section. However, the papers that do still qualify have covered several interesting topic areas, including LA in liquid followed by ICP-MS detection, slurry sampling followed by ETAAS detection and various X-ray-based characterisation techniques. Since ceramics are resistant to high temperatures and are notoriously difficult to dissolve, the techniques described have normally involved the direct analysis of solid materials.

Furuta and co-workers have produced two papers that have discussed different applications of LA in liquid with ICP-MS detection.<sup>154,155</sup> The paper by Hirosawa and Furuta used the technique to determine a suite of elements in a single crystal of gallium nitride.<sup>155</sup> A 340 mg crystal of material was inserted to a chamber and water added so that the depth between the water surface and the surface of the crystal was 3 mm. A Nd:YAG laser

was then fired at the crystal for a period of 70 minutes over an area of 4 mm<sup>2</sup>. The water containing the ablated material was then collected and analysed using dynamic light scattering to determine particle size and SEM-EDX for trace element determination. In addition, the suspension was also transferred to a container and nitric acid added. After dissolution on a hot-plate and dilution, the digest was analysed using ICP-MS. Since such an easy dissolution was possible is evidence that the ablated material had transformed from gallium nitride to gallium oxide. Preliminary results indicated that the crystal was not homogeneous. Therefore, the authors made four collections from the same crystal and then combined them before again splitting it into four aliquots for digestion. In addition, the analytical uncertainty was also poor. This was rectified by determining the Ga present in the ablated samples and then using that as an internal standard. The procedure was validated by the analysis of NIST 610, a standard glass sample, although the weight of material and the volume of water used as well as the dissolution procedure was different. The analytes Cd, Ge, Mg and Y were in the crystal at concentrations of between 0.1 and 2 mg kg<sup>-1</sup>. The paper by Fujiwara *et al.* used LA in liquid as a sampling method for silicon carbide prior to analysis using SF-ICP-MS.<sup>154</sup> Microwave dissolution using a mixture of nitric, hydrofluoric and sulfuric acids was used on the ablated material. External calibration was used for most analytes although isotope dilution (ID) was used for the determination of Ti. Again, relatively poor precision was observed for those analytes using external calibration, although expanded precision values were better than 10%. The ID methodology using a 10 ms measurement interval improved this to 3.4%. The full methodology was given as an easily understandable flow diagram in the paper. Method validation was achieved using NIST 610, 612 and 614 glasses and the National Metrology Institute of Japan ceramic samples NMIJ 8001-a and NMIJ 8002-a.

Two interesting papers have discussed *mechanistic aspects of processes that ceramic materials undergo*. One by Lee *et al.* used LIBS and XPS to investigate the short-term (10, 30 and 60 s) and long term (10, 30, 60 and 180 min), high temperature (900 °C) oxidation in air of aluminium chromium nitride coatings on tungsten carbide substrates.<sup>156</sup> The XPS was used to determine the chemical bonding states and concentrations of surface elements and the LIBS was used to obtain data on diffusion through the material and for surface mapping. Other techniques used for the characterisation were grazing incidence X-ray diffraction (GI-XRD) and focussed ion beam (FIB). The coating started changing colour within a few seconds of the oxidation starting and for the colour to be different over the whole surface within 10 minutes. The GI-XRD and XPS data indicated that aluminium and chromium oxides started forming after one minute and then after 10 minutes, Cr-W and Co-W oxides started forming. The N content decreased within the first few seconds of oxidation starting and had disappeared completely after 10 minutes. The O content showed the opposite trend. A paper by Hostasa *et al.* used LIBS to monitor the evaporation loss of SiO<sub>2</sub> from transparent YAG ceramics over the course of the fabrication process.<sup>157</sup> After milling and pressing, the samples containing silica over the concentration

range 0–0.275% were calcined in air at 600 °C and then sintered in a vacuum at 1735 °C for 16 hours. Finally, annealing occurred with two different methods being tested. In one annealing was at 1100 °C for 100 hours and the other at 1300 °C for one hour. The silica was added in two forms, silica soot and tetraethyl orthosilicate. During the analysis, 10 spectra were obtained from the same location to improve the signal to noise ratio and the signal at the Si line at 288.158 nm was ratioed to the Y line at 288.654 nm. The detection limit was 0.0017% silica (8 mg kg<sup>-1</sup> Si). More than 80% of the silica evaporated during the sintering stage under vacuum. This was attributed to the formation of SiO under a low partial pressure of oxygen.

A paper by Glinskaya *et al.* determined Al, Ca, Fe, Hf, Mg, Ti and Y in *yttrium stabilised zirconia* using ICP-OES following two different treatment methods.<sup>158</sup> Samples underwent either a stabilising firing or remained unburnt. Interestingly, the sample preparation method required differed markedly between the two treatments. The unburnt material dissolved in sulfuric acid whereas the burnt material had to be brought into solution *via* a fusion using either potassium pyrosulfate or potassium bifluoride. These reagents had to be used in large quantities and hence contributed significant contamination. In an attempt to overcome this problem, the authors optimised a microwave dissolution procedure. Parameters studied included the mixture of acids, the temperature, the heating rates and the hold time at the maximum temperature. Complete dissolution was achieved using a 2 : 1 mixture of hydrofluoric and sulfuric acids and with a stepwise increase in temperature where the sample was heated to 150 °C over 15 minutes, held there for 20 minutes and then raised to 220 °C over 15 minutes and maintained for a further 40 minutes. Partial method validation was achieved through the use of standard additions analysis.

A paper by Turner and Filella used a portable XRF instrument to *determine Sb in numerous types of household products*.<sup>159</sup> Included in this number are different types of paints, ceramicware usually used for cooking, toys *etc.* The Sb is usually added as an opacifier or as a colour fastener. Of the numerous samples analysed, a drinking glass enamel and a ceramicware enamel contained the pigment lead antimonate at a huge concentration of Sb of 62 800 mg kg<sup>-1</sup>. Other sample types had varying concentration ranges of Sb, but were typically 300–27 500 mg kg<sup>-1</sup>. Method validation was achieved through periodic analysis of the polymer disks supplied by the instrument manufacturer that had known Sb content. Analytical data for these samples were always within 15% of the certified value, which was deemed sufficiently accurate. The authors pointed out that there is a lack of understanding of the health implications of Sb and hence further studies on the toxicity and on the bio-accessibility, *i.e.* how much of the Sb can be leached from the material, is required.

*Slurry sampling followed by ETAAS* detection was used by Oreste *et al.* for the determination of Cd, Cr and Pb in ceramic tableware.<sup>160</sup> Sample was first crushed and milled using tungsten carbide balls in a fragmentation vessel. Sample (10 mg) with particle size of less than 25 µm was then mixed with nitric acid and Triton X-100 dispersant and sonicated in an ultrasonic

bath. The suspension was then analysed using ETAAS. Central composite design was used to optimise the sample preparation in terms of the concentrations of the nitric acid used to leach the ceramic and of the Triton X-100 and the sonication time used for the extraction. Instrumental operating conditions were optimised using standard pyrolysis/atomization curves for each analyte. The results from the slurry sampling ETAAS were compared with those obtained using an acid decomposition technique which involved the use of concentrated nitric and hydrofluoric acids and then placing it in a sonic bath at 40 °C for 2 hours. The digest was then diluted to 10 mL before analysis. Results from the two preparation methods were similar, as demonstrated by a paired *t*-test. The slurry sampling method provided precision values of 6.9, 2.1 and 4.1% RSD for Cd, Cr and Pb, respectively. These values are good considering the small sample mass used. Spike/recovery experiments yielded values of between 90 and 111% (*n* = 3). Concentrations in the ceramic samples were 0.04–184, 67–1395 and 42–5305 mg kg<sup>-1</sup> for Cd, Cr and Pb, respectively. A separate part of the study used dilute acetic acid to assess the leachability of the analytes. This is a standard test to determine the potential for the analytes to be leached into foodstuffs. The concentrations leached were 0.07–1.68, 0.1–5.0 and 0.6–46.3 mg kg<sup>-1</sup> for Cd, Cr and Pb, respectively. Although significantly lower than the “total” values, there is clearly a possibility that leaching into foodstuffs could occur.

### 3.7 Glasses

As with other sections, the analysis of glasses associated with cultural heritage have been moved to their own section. This has made the glass section smaller than usual. Many of the applications of the analysis of glass have involved the use of chemometric treatment of the analytical data. This was for either forensic purposes or for classification of materials prior to re-cycling. There have also been a few interesting applications, including one that used LIBS to measure the surface hardness.

As always, the *development of CRMs* is necessary since they can be used to help method validation and ensures that instrumental drift can be monitored. A paper by Wu *et al.* described the preparation and characterisation of three synthetic Andesite reference glass materials entitled ARM-1, ARM-2 and ARM-3.<sup>161</sup> They were made through the direct fusion at 1550–1600 °C of high purity oxide powders doped with analyte elements. The concentrations of the elements were all very similar and were nominally 500, 50 and 5 mg kg<sup>-1</sup>. The element that differed markedly to these concentrations was As, which had been added to the fusions in the form of arsenic III oxide to help complete de-gassing of the melts. This was therefore present at a concentration of 3500 mg kg<sup>-1</sup> in all of the samples. The materials were analysed using electron probe microanalysis (EPMA), XRF, ICP-OES, ICP-MS, LA-ICP-MS and LA-SF-ICP-MS; with data being contributed by 10 different laboratories. Method validation was achieved through successful analysis of the US Geological Survey (USGS) reference materials USGS NKT 1G and USGS TB-1G. Preliminary reference

and information values for 56 elements were obtained along with uncertainties which were typically in the range 1–20%. It was noted that some elements, *e.g.* Cr, Ni, Tl and V led to problems during the analysis and this was attributed to analytical limitations.

Four papers reported forensic applications of the analysis of glass.<sup>162–165</sup> In the first of these examples, by Sharma *et al.*, particle induced gamma ray emission (PIGE) and instrumental neutron activation analysis (INAA) were used for the determination of 18 major, minor and trace elements in soda-lime glass samples.<sup>162</sup> For the PIGE determination of the major elements (Al, Mg, Na and Si), 200 mg of powdered glass sample was mixed with 450 mg of cellulose containing lithium carbonate and then pelletised using a two ton hydraulic press. The reference materials USGS STM-1 and USGS G2 were prepared in the same way. The INAA determinations of the trace analytes required only 50–100 mg of sample. The four elements determined using PIGE were sufficient to determine whether or not a glass was of the soda-lime type whereas the other 14 analytes could be used to identify differences between glasses of the same type. Strangely, the authors did not explore this in greater depth by using any chemometric techniques. The paper by Park and Carriquiry gave an overview of the learning algorithms available that can evaluate forensic glass evidence.<sup>163</sup> The overview contained 46 references and gave a very lengthy description of the history of statistical analysis of glass, methods to compare the elemental composition of glasses, datasets used for training, testing and analysis, comparisons between different algorithms and a general discussion. It was good to note that this group are constructing a large glass database with enough information from both within and between glass samples to enable the computation of well-conditioned estimates of high dimensional covariance matrices. The research group is to make this database available to anyone working in the area. The concept was then expanded upon in a paper by Park and Tyner.<sup>164</sup> Here, they used their database to simulate different forensic scenarios. Two different classifiers (the standard American Society for Testing and Materials (ASTM) method and Random Forest) were compared in an attempt to elucidate why the learning algorithms out-perform traditional methods for classifying float glass. By analysing every step of the ASTM method, it was concluded that it was not optimal. The fourth paper was by Teklemariam and Gotera who used LIBS to analyse food glass containers and then cluster analysis to discriminate between them.<sup>165</sup> Eight NIST glass reference materials were used for verification purposes and 18 different types of glass (jars, float glass, bottles, bulbs, a tea cup, a laboratory beaker and an electronic display glass) were the test samples. A library of data comprising 47 wavelengths belonging to 12 different elements was obtained by repeat ( $n = 10$ ) analysis of NIST 1411. The same wavelengths were then monitored for the sample glasses with 10 shots at 10 different places on the sample being measured. Both univariate and multivariate calibration strategies were adopted. The univariate calibration utilised a simple ordinary least squares regression method where the LIBS emission intensity at each wavelength and its corresponding oxide concentration given for the NIST glass standards were

examined. A simple correlation between intensity and the oxide concentration was assumed. However, the correlation coefficients were extremely poor. The multivariate calibration strategy using partial least squares regression with data obtained from five of the NIST glass standards provided significantly better calibration data. Once confidence in the data had been obtained they were treated using hierarchical cluster analysis using Ward's method. This was employed to discriminate between the different types of glass. Clear discrimination between the different glass samples was obtained and this was further emphasised when the technique of "bootstrap" resampling of the data was employed.

Several other applications have been reported. A particularly interesting one was published by Momcilovic *et al.* who used LIBS as a tool for the determination of surface hardness of glass samples.<sup>166</sup> These authors used a transversely excited atmospheric pressure CO<sub>2</sub> laser (TEA CO<sub>2</sub>), which previous studies had shown offers some advantages over the Nd:YAG laser. The ratio of the signal of the Zr ion line at 355.66 nm to the Zr atom line at 360.12 nm was used to determine the hardness of the sample. This was because these lines were narrow, sharp and well resolved compared with some of the other signals and also provided good sensitivity. A Vickers Hardness test was run as a complementary technique. A plot of the Zr ionic/Zr atomic intensity ratio against the Vickers hardness gave a correlation of 0.998. An additional advantage of the technique was that it could be used for curved glass surfaces or surfaces of irregular shape, whereas the Vickers hardness test cannot.

Another paper that used a CO<sub>2</sub> laser for LIBS analysis was presented by Lehmann *et al.* who used it for the rapid determination of Pb in glass cullet as a means of classifying the glass prior to re-cycling.<sup>167</sup> Five glass samples were first analysed using XRF which identified that the Pb contents ranged between 1 and 25%. The authors then used two different LIBS setups. One was a standard setup using the CO<sub>2</sub> laser with an echelle spectrometer. A modification was made where the echelle spectrometer was replaced by a series of filters, a fast photodiode and an oscilloscope. A schematic diagram of both setups was provided. The first setup was used to identify the spectral regions required so that the correct filters could be used in setup 2. Two potential ranges were identified: between 360 and 370 nm and between 400 and 410 nm. Two strong K atom lines were observed in the second range and these were thought likely to cause interference. A mathematical correction factor was therefore devised. Once the system was optimised, the LOD for the first region was approximately 6 mg kg<sup>-1</sup> whereas the second region produced LOD that were approximately an order of magnitude lower. The system was compared with a commercial XRF sorting instrument capable of analysing glass fragments of between 3 and 60 mm with an accuracy of 98% for fragments over 16 mm and with a sample throughput of 28 tons per hour. The LIBS setup with the filters was capable of making an identification in 5 ms, had a LOD of 6% in the 360–370 nm region and 0.6% in the 400–410 nm region. Although these LOD are huge, it should be noted that a lead crystal glass may contain up to 30% Pb and hence the methodology is fit for purpose. Although these LOD are comparable with the XRF-based sorter,

it was hoped that the LOD could be improved further by utilisation of a higher efficiency photodiode.

Michaliszyn *et al.* developed a new method for the SI-traceable quantification of elemental contents in solid samples using LA-ICP-MS.<sup>168</sup> The LA unit and a conventional nebuliser system were joined *via* a Y-piece so that aqueous standards and laser ablated solid material could be introduced to the plasma simultaneously. A pseudo-standard additions methodology was therefore established in which the solid sample served as a reference with a matrix element *e.g.* Si in glass being used as an internal standard. The methodology was validated by analysing the materials NIST SRM 610 and NIST SRM 612 glasses for their Pb and Rb content. Good agreement with certified values was obtained. The method enabled SI traceability without recourse to matrix matching solid reference materials.

The final paper in this section was presented by Turner who analysed glass and enamels of consumer container bottles.<sup>169</sup> A portable XRF instrument was used for the analysis of the alcoholic beverage bottles. Concentrations of the analytes Cd, Cr and Pb in the glass was typically 1100, 3000 and 1100 mg kg<sup>-1</sup>, respectively. Although the values were very high, they were not regarded as being potentially toxic because they were not easily extractable. However, some of the enamels and paints on the bottles contained huge concentrations, *e.g.* a Cd concentration of 20 000 mg kg<sup>-1</sup> and a Pb concentration of 100 000 mg kg<sup>-1</sup>. A standard leaching test using 0.1 M acetic acid that simulates water percolating through landfill was used for the extraction. Analytical testing used ICP-MS against matrix matched standards. The leachates from these samples contained 3200 and 1200 µg L<sup>-1</sup> for Cd and Pb, respectively.

### 3.8 Nuclear materials

The properties of materials used in plasma facing materials for nuclear fusion remains a popular topic, with LIBS being the dominant measurement technique in this field. The properties of materials used in nuclear fission reactors is also a key area, including fuel composition and impurities, and resistance of materials to corrosion. Accurate and precise measurement of isotopic ratios of radionuclides using various mass spectrometric techniques has been applied to source attribution, with important implications for nuclear safeguards and contamination monitoring. Finally, the development of methods that contribute to safe and cost-effective decommissioning of nuclear sites is an ongoing motivation. This includes developing procedures for measurement of challenging radionuclides at trace levels, predominantly using mass spectrometric techniques, as well as supporting this through the development of reference materials to enable method validation.

**3.8.1 Fusion.** The international pursuit of improving nuclear fusion has resulted in continuing research into the properties of materials following long-term irradiation. The dominant technique in this field over the last few years has been LIBS, sometimes used in combination with other techniques. The purity, durability, integrity and structural changes of tungsten and tungsten-alloys in plasma-facing components was the focus of a number of studies in relation to safe and efficient

operation. The interaction of deuterium and tritium with materials was also studied extensively.

Given its ability to *undertake real-time, in situ, remote measurements in extreme environments*, LIBS remains a popular *technique* when investigating materials used fusion. A review by Li *et al.* compared remote LIBS configurations and the signal enhancement methods employed to improve spectral signal efficiency and intensity.<sup>170</sup> The review also discussed the recent applications of remote LIBS and its limitations in a range of fields.

Imran *et al.* used LIBS to measure elemental (W, Mo, Li, Na, Ca, Cr) and tile material (C, Si, Ti) *impurities deposited at different positions on the Experimental Advanced Superconducting Tokamak (EAST) divertor tile surface.*<sup>171</sup> The results suggested that high heat plasma interaction with plasma facing components led to Mo erosion from the first wall and W from the upper divertor, with non-uniform impurity deposition at different depths. The techniques of SEM with EDS were used to verify the tile composition and surface morphology. Another study outlined an *in situ* diagnostic for mapping the deposition distribution (IMap) on plasma facing components for assessing material deposition and fuel retention.<sup>172</sup> The IMap system was built using LIBS and was capable of remote scanning and automatic adjustment of lenses, mirrors and fibres to enable measurement of wall properties over a wide area. Hydrogen and deuterium, along with elements with emission lines between 380 and 850 nm could be identified, along with depth profiles and fuel retention. Shaw *et al.* described the combination of LIBS with laser ablation mass spectrometry (LIBS-LAMS) to quantify gas concentrations below a tungsten surface.<sup>173</sup> The sample was He ion implanted, before being exposed to various plasmas (He, deuterium or 90% deuterium/10% He plasmas). The combination of LIBS-LAMS measurement showed an increased near-surface deuterium concentration in samples exposed to He during mixed He/deuterium plasma exposure, but deuterium permeation below the W surface was reduced.

Castin *et al.* investigated *the impact of C impurities in tungsten under irradiation*, in particular the interactions with self-interstitial atoms.<sup>174</sup> Under several irradiation conditions, self-interstitial atom loops were observed, with SIMS used to demonstrate that the samples were likely contaminated with C during irradiation. An object kinetic Monte Carlo model was used to demonstrate that the evolution of the self-interstitial atom loops were likely due to C injection. In a separate study, Moon *et al.* determined C to be the main deposited element in the grooves of tungsten tiles following plasma operation.<sup>175</sup> The grooves are present to improve thermo-mechanical durability and integrity under high heat fluxes, and the impact of tile shaping and misalignment on fuel retention was studied. Carbon deposition modelling using the Monte Carlo neutral transport code 3D-GAPS showed different C concentrations at the groove entrance, dependent on the tile shaping. The highest carbon and deuterium densities were measured at the plasma-exposed side of the flat tile and aligned gap, with agreement between experimental and modelled deposition profiles.

Catarino *et al.* analysed *divertor tiles exposed to three successive plasma campaigns at Joint European Torus (JET),*<sup>176</sup> with the

samples providing a valuable resource for studying long-term plasma-material interactions. A range of ion beam analysis techniques, nuclear reaction analysis and X-ray emission were used to provide information on factors including tungsten erosion, fuel retention and Be deposition. Ibanez *et al.* used calibration-free LIBS to measure tungsten alloys containing Ta and Re.<sup>177</sup> Using ambient gas pressure of 0.1–10 Torr of He, Ne and Ar gas, accurate measurements of W-2 at% Ta was achieved, with the highest line intensities using Ar gas. For W–Re, results agreed well with the nominal Re concentration down to 0.5 at%, with further work required to reach the target detection limit of 0.2 at% Re expected in W–Re alloy at ITER. Calibration-free LIBS was also used by Almaviva *et al.* to measure metallic coatings (W–Al–deuterium) simulating fuel and eroded material-contaminated ITER divertor plasma facing components.<sup>178</sup> Calibration-free analysis showed good agreement with nominal concentrations, with clear W, Al and deuterium emission lines in the spectra. The measurements contribute to accurate measurement of the tritium inventory in plasma facing components.

Several studies focused on *fuel retention (deuterium and tritium) in fusion materials*. Hydrogen retention was measured on a tantalum sample using LIBS by Li *et al.*<sup>179</sup> Differences were found in the spatial and temporal resolutions of H and Ta plasmas due to the difference in atomic mass between the two elements, with H retention mainly on the sample surface. The results helped to understand the LIBS plasma dynamics and how this can be applied to *in situ* measurements. Jiang *et al.* developed an improved LIBS system to measure the deuterium and H content on W surfaces.<sup>180</sup> Several improvements were made over the previous LIBS design, including the laser profile and focus and the emission light collecting optics. The deuterium and H contents on tungsten samples were studied over timescales of seconds to hours, with measurements comparing favourably with thermal desorption spectroscopy and nuclear reaction analysis. Thermal desorption analysis was also used by Xu *et al.* as part of measuring deuterium plasma-driven permeation in ferritic steel alloy F82H with and without sputter-deposited W coatings.<sup>181</sup> Enhanced deuterium retention was measured in coated F82H, with SIMS used to show higher deuterium concentrations in tungsten coatings compared with in the F82H substrate. Deuterium permeation was also the focus of a study by Wang *et al.*<sup>182</sup> In a solid tritium breeding blanket,  $\text{Li}_4\text{SiO}_4$  is in high-temperature contact with a reduced activation ferritic/martensitic (RAFMs) steel which, over time, forms a corrosion layer. This was analysed using XRD, SIMS and TEM corrected for spherical aberration. These showed a three-layered corrosion product with inner layer  $\text{LiCrO}_2$  and mid-layer  $\text{LiFeO}_2$ . There was a decrease in deuterium permeability with an increase in corrosion period, which was proposed to be a cracking and re-oxidation process during corrosion, which offers a possible approach for preventing tritium permeation.

Despite the popularity of LIBS in this field, there were studies that focused on *alternative measurement approaches*. Lang *et al.* employed GD-OES as a depth profile technique to investigate deuterium (D) concentrations in dispersion-strengthened tungsten materials modified with 1–10 wt% TaC, TiC or

ZrC.<sup>183</sup> In a number of materials, deuterium was observed beyond the implantation depth following exposure, with increasing oxygen content correlating to decreased deuterium retention. Dispersion-strengthened W was also the focus of a study by Kim *et al.*, focusing on thermal and microstructural properties for materials fabricated by the Spark Plasma Sintering Process compared with those produced by commercial suppliers.<sup>184</sup> Chemical composition was determined using GD-MS, with thermal diffusivity and specific heat measurement used to derive thermal conductivity up to 900 °C. The addition of TiC and  $\text{Y}_2\text{CO}_3$  to tungsten fabricated by Spark Plasma Sintering improved microstructure stability against recrystallisation after high heat flux exposure, but the reduction in thermal conductivity with increasing content of the additive element had to be considered. *Time of flight mass spectrometry* was used by Wu *et al.* to investigate charge-state distribution and temporal evolution of multi-charged ions emitted from a Mo plasma, with the aim of improving LA diagnostics of plasma-wall interactions.<sup>185</sup> The study used TOF-MS at different laser power densities commensurate with those used in LIBS diagnostics in EAST tokomaks. The results showed that ion charge state increased with laser power density with a maximum charge state of 7, with the greater velocity of higher charged ions indicating that separation between different charges took place during plasma expansion. Lungu *et al.* developed and applied XRF methods for quality checking and characterisation of plasma facing components in relation to the need to develop erosion-resistant materials used in the reactor vessel.<sup>186</sup> The XRF was applied to the measurement of the thickness and uniformity of tungsten-based coatings, as well as studying the erosion pattern following plasma exposure. Instrument calibration was developed using a combination of theoretical, Monte Carlo simulation and standard sample measurements.

**3.8.2 Reactor materials.** The stable and radioactive impurities present in nuclear fuels and reprocessed material is of ongoing importance for safe and cost effective reactor operation, which also requires assessment of the properties of materials used in reactors, such as hardness or long term resistance to corrosion. A range of destructive and non-destructive measurement techniques were utilised, including ICP-MS, thermal ionisation mass spectrometry (TIMS), SIMS and XRF, with the properties of LIBS outlined in the fusion section also being of potential benefit.

Dhara and Misra prepared a review of the role of Total XRF (TXRF) for elemental determination and speciation studies of constituents *in nuclear fuel and related materials* (91 references).<sup>187</sup> The speed, simplicity and non-destructive nature of TXRF was highlighted as some of the advantages. These same advantages were highlighted by Bootharajan *et al.* for the XRF characterisation of spent fuel in a high dose reprocessing facility for advanced fuels in lead cells.<sup>188</sup> A hybrid K-edge/KXRF densitometer was developed and commissioned for this study, with validation using a series of U solutions, followed by measurement of mixed Th/U/Pu solutions. A separate study by Quemet *et al.* compared K-edge densitometry with isotope dilution TIMS for U determination in pellet samples.<sup>189</sup> The detection limit and uncertainties were lower using TIMS,

however, K-edge densitometry analysis time was shorter and generated less effluent. Pandey *et al.* employed WDXRF to determine trace U in plutonium dioxide powders.<sup>190</sup> Following pelletisation of the samples, U was measured at concentrations ranging from 100–1000  $\mu\text{g g}^{-1}$ , with a reproducibility of <5% RSD. In addition, good agreement between obtained using WDXRF and ICP-OES was also achieved. In a separate study by Pandey *et al.* used WDXRF to determine U in deeply depleted uranium dioxide.<sup>191</sup> A calibration plot was obtained from measurement of matrix-matched calibration standards, with a reproducibility of <0.05% for sintered pellets with U concentrations from 86.81–88.04%.

LIBS is another non-destructive technique used effectively in several studies. Wu *et al.* reviewed the feasibility of LIBS for the nuclear industry given its increasing use in the field (189 references).<sup>192</sup> The review covered applications including analysis of nuclear materials, steels and alloys, as well as current challenges and potential ways to overcome these. One such challenge identified by Li *et al.* was the weak plasma emission and spectral interferences for U, particularly in complex sample matrices.<sup>193</sup> To overcome this, LIBS combined with laser-induced fluorescence (LIBS-LIF) was proposed for the determination of U in ore samples with results being compared with those obtained using LIBS alone. Uranium ion lines were more suitable for determination than atomic lines, with improved sensitivity and detection limits achieved using LIBS-LIF compared with LIBS alone. Rollin *et al.* also investigated measurement of impurities in uranium using LIBS, focusing on the vacuum ultraviolet (VUV) range rather than the UV-visible range, where a large number of actinide emission lines makes trace element measurement challenging.<sup>194</sup> The study focused on C and V impurities in the VUV (below 200 nm) and UV range, with results suggesting that detection limits could be improved for non-metal impurities that have intense lines in the VUV. This is in agreement with results from non-nuclear studies. As well as impurity measurements, Galmed *et al.* used LIBS to detect the change in surface hardness of reactor wall vessels for different material matrices.<sup>195</sup> The plasma excitation temperature was used to measure the hardness of pure titanium and titanium alloys where hardness was changed by irradiation with different doses of 1 MeV C ions. A good relationship was found between the excitation temperature and Vickers hardness, with the sample matrix strongly influencing measurements.

*Destructive mass spectrometric techniques have also been applied extensively to the measurement of nuclear fuels and materials.* Cong *et al.* applied ICP-MS to determine 42 trace impurity elements in nuclear grade UF<sub>4</sub> based on standard addition calibrations.<sup>196</sup> Detection limits ranged from 0.4–72 ng g<sup>-1</sup> with recoveries of 92–111% and RSDs generally better than 10%. Validation of the method was achieved using a reference uranium oxide material, with the aim of applying the method to the quality control of UF<sub>4</sub> in a molten salt reactor. A study by Bradley *et al.* to determine rare earth elements (REE) and other trace impurities in uranium ore concentrates as an indicator of ore characteristics was undertaken using ICP-MS.<sup>197</sup> Isotope dilution mass spectrometry was favoured to improve uncertainties, with REE separated using high performance ion

chromatography prior to measurement to remove interferences. Jovanovic *et al.* determined trace elements in 20 uranium ore concentrates from eight locations using LA-ICP-MS.<sup>198</sup> The results compared favourably with solution-based ICP-MS and was used in combination with a machine-learning algorithm to assess the origin of the samples. The technique was therefore potentially suitable for National Nuclear Forensic Library applications. Trace impurities were also the focus of a comparative study between ICP-AES and DC arc carrier distillation in nuclear-grade BeO by Pathak *et al.*<sup>199</sup> The study focused on multiple metallic impurities, with both techniques deemed suitable for the application.

*Corrosion resistance was the focus of several publications.* X-ray based techniques were used by Kim *et al.* to assess the corrosion behaviour of Zr–Nb–Sn alloy after exposure to high temperature hydrogenated water.<sup>200</sup> Synchrotron scanning transmission X-ray microscopy showed the different electronic structures at the oxide/metal interface. X-ray absorption spectroscopy spectra suggested Zr suboxide could form above the oxide/metal interface, with a thicker suboxide layer formed at a higher dissolved H concentration. Several techniques were used by Banos *et al.* to measure surface corrosion on the surface of unirradiated uranium after reaction with water at various temperatures and timescales.<sup>201</sup> Analysis using focused ion beam (FIB), SIMS and XRD showed bulk UH<sub>3</sub> formation on the majority of the 10 samples examined, with a correlation found between UH<sub>3</sub> formation and a critical threshold headspace pressure. A compact LIBS system assessed hydride corrosion in four samples of depleted uranium charged with controlled H concentrations in a study by Garlea *et al.*<sup>202</sup> After the surface corrosion layer was removed, 100 laser pulses at five different sample locations provided in depth LIBS measurements, monitoring atomic emission signals from U, C, H and O. The H content matched the sample specification, with H-charged samples showing elevated O content due to rapid U and UH oxidation.

**3.8.3 Nuclear forensics and security.** Accurate and precise measurement of isotopic ratios is essential for determining the source of contamination, including illegally acquired nuclear materials and fallout following global weapons testing and nuclear accidents. Such measurements are also important for environmental monitoring following nuclear accidents and safeguarding nuclear materials. Mass spectrometric techniques continue to be popular for isotopic ratio measurements, specifically ICP-MS, TIMS and SIMS.

*Both MC-ICP-MS and TIMS instruments continue to be favoured for high precision isotopic ratios.* Eppich *et al.* focused on Pu isotopes in environmental swipe samples measured using MC-ICP-MS following digestion and chemical separation.<sup>203</sup> The method was validated using reference materials, with a precision of <1% achieved for <sup>240</sup>Pu/<sup>239</sup>Pu, <sup>241</sup>Pu/<sup>239</sup>Pu and <sup>242</sup>Pu/<sup>239</sup>Pu at a ratio of  $\geq 6.3 \times 10^{-2}$ . A <sup>239</sup>Pu detection limit of 0.10–0.58 fg was calculated, with an expanded uncertainty averaging 1.7% in swipe samples containing 0.32 fg and 10.5 fg total Pu. Varga *et al.* at JRC-Karlsruhe also used MC-ICP-MS to determine the U production age on particles collected on a swipe sample of enriched material that was seized in 2011.<sup>204</sup>

Samples were measured following nitric acid leaching, with a  $^{235}\text{U}$  composition of  $72.51 \pm 0.03$  wt% and a production date of December  $1992 \pm 1$  year, showing similarity with two other materials seized in Europe. Zhang *et al.* used TIMS for U isotopic measurement related to nuclear safeguard and forensic applications, with a new filament carburisation technique used to enhance sensitivity for ultra-trace measurement.<sup>205</sup> Compared with the classical filament method, the ionisation efficiency was improved by a factor of 10 to  $\sim 0.2\%$  for U. Filament carburisation and U loading was achieved in 10 minutes, with the method validated using picogram level certified reference materials, with  $^{235}\text{U}/^{238}\text{U}$  relative uncertainties of  $\sim 1\%$ .

For some *nuclear forensic studies*, SIMS was the preferred analytical technique. Kips *et al.* focused on the microscale isotopic heterogeneity in various fuel pellet fragments using NanoSIMS.<sup>206</sup> Microscale variations in U isotopic composition was determined in some fuel fragments, which would otherwise have been overlooked in macroscale measurements. In these samples, the  $^{235}\text{U}/^{238}\text{U}$  ranged from 0.0081–0.035, with the presence of  $^{236}\text{U}$  in one sample suggesting at least three U oxide powders of different composition were used in fuel pellet production. NanoSIMS was also used by Zirkparvar *et al.* to measure atomic  $^{235}\text{U}/^{238}\text{U}$  and molecular UO ratios from a range of compounds ( $\text{UO}_2$ ,  $\text{UO}_2\text{F}_2$ ,  $\text{UO}_3$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$ , and  $\text{UF}_4$ ) and silicates (NIST-610 glass and the Plesovice zircon reference materials).<sup>207</sup> The higher abundance of molecular secondary ions compared with atomic ions following sputtering with an oxygen primary ion beam, was the basis for assessing whether molecular isotopic ratios offered improved precision compared with atomic ratios. This was the case for  $\text{UO}_2$  and silicate reference materials where secondary ion production was internally consistent. It was not the case for other materials where production rates were variable. Irregular surface topography and/or molecular interferences were suggested as reasons for this variation.

Large geometry SIMS was used by Szakal *et al.* to conduct *age-dating measurements on single micrometre scale particles* using the  $^{230}\text{Th}/^{234}\text{U}$  radiochronometer.<sup>208</sup> Instrument optimisation steps were described, along with an option to simulate larger particles by combining individual measurements of single particles with low count rates and identical isotopic signatures to reduce uncertainties. A range of CRMs and real materials over the size range of 0.6–3.0  $\mu\text{m}$  and ages of 0–60 years were measured, with experimental results comparing well with predicted model ages. Bellucci *et al.* also used large geometry SIMS in combination with SEM to measure U and Pu isotopes simultaneously in a mixed hot particle recovered from the Thule accident in Greenland.<sup>209</sup> The particle was shown to have a single composition of weapons grade Pu, with the bulk of the particle having enriched U, with  $^{235}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  ratios of  $1.12 \pm 0.04$  and  $0.006 \pm 0.002$ , respectively. However, a small portion of the particle had  $^{235}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  ratios of  $0.11 \pm 0.04$  and  $0.001 \pm 0.002$ , respectively. This was potentially due to mixing of the particle with the environment or heterogeneous U enrichment from the weapons. The results showed the importance of spatially resolved measurement that may pick up on heterogeneity that bulk analysis misses.

Several studies focused on *measurement of actinide isotopes in materials released, or contaminated by, the Fukushima Daiichi Nuclear Power Plant accident*. Igarashi reported the first Pu isotope measurements in radioactive particles released during the accident to determine whether nuclear fuel radionuclides were present.<sup>210</sup> Radioactive particles from units 1, 2 and 3 were measured using ICP-MS, with Pu only detected in unit 1 materials at activities of  $1.70\text{--}7.06 \times 10^{-5}$  Bq for  $^{239+240}\text{Pu}$  and  $4.10\text{--}8.10 \times 10^{-3}$  Bq for  $^{241}\text{Pu}$ , with atom ratios consistent with ORIGEN (a computer code system for calculating the build-up, decay, and processing of radioactive materials) calculations and environmental measurements. The difference in results between samples showed the value in measuring Pu isotopes for monitoring particle formation processes. In a separate study, Jaegler *et al.* used a combination of  $\alpha$ -tracks detection, microscopic and mass spectrometric measurement to investigate the fate of actinide-bearing particles in environmental samples.<sup>211</sup> Detection using  $\alpha$ -tracks was a useful technique for localising and characterising particles based on a test on a road dust sample collected in the Fukushima contaminated region. Multiple techniques were also used by Martin *et al.* during the measurement of sub-mm particulate material from Fukushima power plant unit 1, to improve understanding of the accident and environmental legacy.<sup>212</sup> The combination of XRF with absorption contrast micro-focused X-ray tomography showed uranium particulates existing around the exterior of porous Si-based particles. This was confirmed to be  $\text{UO}_2$  reactor fuel following synchrotron radiation analysis and mass spectrometric measurement. The results have implications for reactor decommissioning and long-term environmental monitoring, as nuclear material was shown to exist outside of the reactors primary containment.

*Isotope ratio measurements were also successfully applied to dating of nuclear materials*. Christl *et al.* measured  $^{244}\text{Cm}/^{246}\text{Cm}$  and  $^{245}\text{Cm}/^{246}\text{Cm}$  using accelerator mass spectrometry (AMS) without yield tracer addition for dating fuels with a known irradiation history.<sup>213</sup> The results achieved a precision of 5 years with the authors acknowledging that this could be improved upon. The method was dependent on  $^{244}\text{Cm}$  decay and a constant  $^{245}\text{Cm}/^{246}\text{Cm}$  ratio post irradiation. Chen *et al.* developed a procedure using a  $^{231}\text{Pa}/^{235}\text{U}$  chronometer for ageing of U samples to better understand the source and suspected use of materials.<sup>214</sup> A  $^{233}\text{Pa}$  spike was chemically separated from a  $^{237}\text{Np}$  stock solution, with the chronometer applied to measurement of a certified reference material (CRM U100). The model age was older than previously published results based on a  $^{230}\text{Th}/^{234}\text{U}$  chronometer. Isotope measurements were undertaken using a high resolution ICP-MS instrument. In another study by Mathew *et al.*, four different plutonium CRMs were used to compare radio-chronometric ages.<sup>215</sup> An inter-comparison exercise assessed different facilities, mass spectrometric capabilities and chronometers ( $^{234}\text{U}/^{238}\text{Pu}$ ,  $^{235}\text{U}/^{239}\text{Pu}$ ,  $^{236}\text{U}/^{240}\text{Pu}$ ), with lower uncertainties in model ages achieved for laboratories set up for trace level analysis.

**3.8.4 Nuclear decommissioning.** Safe, cost effective decommissioning and accurate waste characterisation is of ongoing importance to the nuclear industry. The range of



radionuclides and sample matrices that must be characterised necessitates the development of robust, reproducible measurement techniques, supported in many cases by radiochemical separation and the development of CRMs for method validation.

An increasingly popular technique for measurement of *long-lived radionuclides* relevant to nuclear decommissioning is ICP-MS. Asai *et al.* employed LA-ICP-MS for the direct measurement of  $^{135}\text{Cs}$  in adsorbents, which had been used for decontamination of water at the Fukushima power plant.<sup>216</sup> A model Cs adsorbent was prepared, crushed and coated with a nitrocellulose-based curing agent to provide a thin, flat surface to facilitate stable LA sampling. A  $^{135}\text{Cs}/^{137}\text{Cs}$  isotopic ratio of  $0.41 \pm 0.02$  agreed with solution based ICP-MS, but only required <10 mg of sample. Warwick *et al.* discussed the applications of tandem ICP-MS/MS for radionuclide measurement, outlining the flexibility of the instrument setup for improved interference removal compared with alternative ICP-MS instrument designs.<sup>217</sup> The technique of ICP-MS/MS was also used by Xing *et al.* for trace U measurement in calcium fluoride sludge following lithium borate digestion and anion exchange chromatography separation.<sup>218</sup> The method was validated using spiked sludge samples, with minimum detectable activities of 0.15 mBq (0.65 pg), 0.67  $\mu\text{Bq}$  (8.38 pg) and 0.014 mBq (1.13 ng) for  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$ , respectively. The use of He as a collision gas was shown to improve U sensitivity compared with no gas, with potential benefits for other actinides. The same instrumentation was applied to the determination of  $^{238}\text{Pu}$  without prior separation, using  $\text{CO}_2$  and  $\text{H}_2$  gases to overcome the isobaric  $^{238}\text{U}$  interference.<sup>219</sup> The method was verified using IRMM-086 reference material, with quantification of  $0.25 \text{ pg mL}^{-1}$  with uncertainties <15% in the presence of  $0.5 \text{ ng mL}^{-1}$  U. Hou also used  $\text{CO}_2$  as a reaction gas in an ICP-MS/MS instrument for measurement of Pu isotopes, converting UH interferences to UO that did not overlap with the Pu signal.<sup>220</sup> A total U decontamination factor of  $10^{12}$  was achieved by combining reaction cell and radiochemical separation, enabling accurate measurement of  $<10^{-15} \text{ g g}^{-1}$  Pu.

*Thermal ionisation mass spectrometry was applied effectively to the low-level detection of radionuclides* that are considered difficult to measure using radiometric techniques. Dion *et al.* evaluated TIMS for isotopic Sr and Cs measurement in the presence of isobaric interferences ( $^{89}\text{Y}$  and  $^{90}\text{Zr}$  for  $^{89}\text{Sr}/^{90}\text{Sr}$ , and  $^{135}\text{Ba}$  and  $^{137}\text{Ba}$  for  $^{135}\text{Cs}/^{137}\text{Cs}$ ).<sup>221</sup> The decontamination factor for  $^{90}\text{Zr}$  was  $\geq 2 \times 10^8$ , compared with  $5 \times 10^6$  and  $8 \times 10^6$  for  $^{135}\text{Ba}$  and  $^{137}\text{Ba}$ , respectively. The Y decontamination factor was  $>5 \times 10^7$  but showed a temperature dependence as it sublimed from the filament. The stable background isotope concentration was increased to monitor chemical and instrumental response, and the method was validated using a thermal neutron irradiated enriched uranium foil, with good agreement compared with the published Evaluated Nuclear Data File results. The uncertainty of the isotopic ratio measurements with TIMS was a factor of 5–10 improved compared with these published values. Kavasi *et al.* focused on  $^{90}\text{Sr}$  measurement using TIMS following chemical separation from  $^{90}\text{Zr}$ .<sup>222</sup> The  $^{90}\text{Sr}/^{88}\text{Sr}$  abundance sensitivity was  $2.1 \times 10^{-10}$ , and the method was tested in an

IAEA proficiency test exercise. Tap water and milk samples with  $^{90}\text{Sr}$  reference values of  $2.2 \text{ fg g}^{-1}$  and  $19.5 \text{ fg g}^{-1}$  were tested, with  $^{90}\text{Sr}/^{88}\text{Sr}$  ratios of  $6.47 \times 10^{-8}$  and  $9.04 \times 10^{-9}$ . The method showed good accuracy and precision, with a relative bias of 4.2% and  $-2.1\%$  and a combined uncertainty of 4.1% and 7.6% for tap water and milk, respectively. This was the first known application of TIMS for  $^{90}\text{Sr}$  confirmed by an independent proficiency test.

Trinquier *et al.* investigated a prototype cavity source for improving the combined U ionisation and transmission efficiencies compared with conventional TIMS.<sup>223</sup> The combined efficiency was improved by a factor of 4–15 up to a maximum of 5.6%. The new source was tested on uranium reference standards in the 100 pg range bound to resin beads, with a relative external precision of 2% and accuracy of 0.4–0.9% for  $^{235}\text{U}/^{238}\text{U}$  ratios. Tang *et al.* also investigated improving ionisation efficiency, in this case using negative TIMS for trace measurement of  $^{99}\text{Tc}$ , noting the previous use of the technique for elements with relatively high ionisation potentials.<sup>224</sup> The ionisation efficiency was improved to >10% using platinum filaments and a barium hydroxide ionisation activator. The method was used to measure the isotopic abundance and concentration of  $^{97}\text{Tc}$  produced in the authors' laboratory. Maasen *et al.* also used TIMS for detecting sub-pg quantities of  $^{238}\text{Pu}$ .<sup>225</sup> Contamination from U was minimised by chemical separation prior to measurement, during loading using a resin bead loading procedure and a TIMS protocol that minimised U ionisation. The method offers complete Pu isotopic analysis using a single technique.

Another efficient technique for *determining minute amounts of long-lived radionuclides is AMS*, with several studies focusing on actinide measurement. Kazi *et al.* undertook tests to improve ionisation efficiency of  $\text{UO}^-$  during  $^{236}\text{U}$  determination.<sup>226</sup> The instrument used was not configured for reliable delivery of a  $\text{Cs}^+$  sputter beam when currents of >0.5 mA was used. To produce a steady stream of  $\text{UO}^-$ , currents closer to 1.5 mA are required. To overcome this, several powders were tested as binders to UO to form the sputter target, with Si and Ta + Si enhancing  $\text{UO}^-$  current production. Lopez-Lora *et al.* published two papers on the use of AMS for actinide measurement. The first used low energy (1 MV and below) AMS for measurement of  $^{237}\text{Np}$ , with  $^{242}\text{Pu}$  used as the normalisation isotope in the absence of a suitable Np tracer.<sup>227</sup> The study also investigated analysis of Pu isotopes and Np in the same cathode with traces of natural U, with quantification of  $1 \text{ fg } ^{237}\text{Np}$  and  $^{239}\text{Pu}$ , and  $0.1 \text{ fg } ^{240}\text{Pu}$ . The method was validated using an IAEA reference seawater (IAEA-443). The second study by the same author developed a radiochemical procedure for actinide extraction from <10 L seawater samples prior to measurement.<sup>228</sup>

*Certified Reference Materials* are critical for method validation and ensuring procedures are fit for purpose when characterising nuclear materials. The use of Pu reference materials was reviewed (172 references) by Wu *et al.* to produce datasets that allowed users to select a suitable material for method validation.<sup>229</sup> Essex *et al.* also focused on Pu, preparing an enriched  $^{244}\text{Pu}$  isotope dilution reference material.<sup>230</sup> The material minimises the spike corrections needed for accurate Pu

information from a single mass spectrometric measurement, and the material was characterised for traceable measurements of very small Pu quantities. This makes it relevant for applications including nuclear safeguards where measurements of <1 ng Pu are required. Essex *et al.* also characterised a  $^{231}\text{Pa}$  reference material, primarily for  $^{233}\text{Pa}$  tracer calibration produced for  $^{235}\text{U}/^{231}\text{Pa}$  model age measurements.<sup>231</sup> Isotope dilution mass spectrometry was performed on purified  $^{231}\text{Pa}$  using a  $^{233}\text{Pa}$  spike, which decayed to  $^{233}\text{U}$  before mass spectrometry measurement using a certified U assay. The material improved metrological traceability and the overall measurement uncertainty of model ages.

Robust, reproducible radiochemical separation procedures are often required for interference removal prior to measurement. In a study by Kazi *et al.*, a new method was developed to separate Am(III) from Cm(III) by selective oxidation of Am to Am(V) using  $\text{Na}_2\text{S}_2\text{O}_8$ , Ag(I), and NaOCl in 0.01 M  $\text{HNO}_3$ .<sup>232</sup> When loaded onto DGA resin, Cm(III) was selectively retained, with a separation factor of 110 prior to measurement of  $^{244}\text{Cm}$ ,  $^{245}\text{Cm}$  and  $^{246}\text{Cm}$  in spent fuel samples using AMS. Automated separation or coupling separation online with mass spectrometric measurements has been extensively proven as a rapid method compared with offline separation, with techniques including CE, HPLC, FIA and sequential injection analysis (SIA). Willberger *et al.* investigated the electrophoretic mobilities of actinides in different oxidation states by coupling CE with ICP-MS.<sup>233</sup> Acetic acid (1 M) was the chosen background electrolyte, with actinides prepared in 1 M HCl and 1 M  $\text{HClO}_4$ . The electrophoretic mobility for U–Pu was (III) > (VI) > (V) > (IV). Values for Cm and U were measured for the first time under the experimental conditions described, with the trends linked to the calculated species distribution of the actinides in 1 M acetic acid and the corresponding average effective charges. Two papers by Kolacinska *et al.* used SIA followed by ICP-MS for radionuclide separation and measurement. The first paper used diglycoamide (DGA-b) for  $^{239}\text{Pu}$  preconcentration and U separation, with a total analysis time of 45 minutes and a detection limit of  $88 \text{ mBq L}^{-1}$  from a 100 mL sample.<sup>234</sup> The second paper used the same SIA setup, with tetrahexyl diglycoamide (THDGA) used for  $^{239}\text{Pu}$  preconcentration and separation, achieving a similar detection limit of  $96 \text{ mBq L}^{-1}$ , with the method applied to nuclear reactor coolant and spent fuel pool water.

### 3.9 Electronic materials

**3.9.1 Wafers, thin films and multi-layer materials.** Some of the most popular techniques used for the analysis of thin films is SIMS or TOF-SIMS. Numerous papers have been published in this research area. Three papers by the same research group reported the use of *massive cluster SIMS* for the analysis of the homogeneity of photoacid generator<sup>235</sup> and photoresist films.<sup>236,237</sup> All three papers used  $\text{Au}_{400}^{4+}$  clusters for the analysis. The methodology was capable of determining the components of the materials with 10–20 nm lateral resolution and approximately 10 nm depth resolution. The samples were bombarded with a stream of particles, each of which is separated in time and space, and then the emitted ions were collected and

analysed using TOF-SIMS. In the paper by Hou *et al.* 1 000 000 individual particles were used, creating 1 000 000 mass spectra. This enabled identification of co-localised molecules at the nanoscale range. Approximately 85–95% of secondary ions indicated an origin of photoacid generator – photoacid generator co-emissions and 90% showed polymer – photoacid generator co-emission. This indicated that the photoacid generator molecules exist as small aggregates that are < 10 nm in size and that these aggregates are highly homogeneously distributed within the polymer matrix. A fourth paper used a dual beam system in which a primary beam of argon gas clusters ( $\text{Ar}_{2300}^+$ ) at an energy of 5 keV with secondary ion intensities measured using  $\text{Bi}_3^+$  at 25 keV to analyse organic layers.<sup>238</sup> Both beams were at  $45^\circ$  to the sample, but the bismuth beam was at a  $90^\circ$  azimuth to the argon gas cluster ion beam. The bismuth beam ion intensity was less than 0.2% of that of the gas cluster beam. Five methods of measuring the interface position were compared, with the theory behind each of them being discussed. Briefly, method one used the median interface position in the intensity profiles for the five lightest ions for  $15 \leq m/z \leq 150$ . Method two used extrapolation of the position for each ion to  $m/z = 0$  for ions with  $m/z \leq 150$ . Method three was the same as for method two but for  $m/z \leq 300$ . Method four used the extreme positions for all  $m/z \leq 100$ . A fifth method used pseudo-molecular ions to calculate the position. Comparison with the location identified using the matrix terms identified that the errors associated were: method four 10%, method three 12%, method one 14%, method two 17% and method five being by far the worst at 50%.

Michalowski has produced a series of papers that have *utilised SIMS for the depth-profiling analysis of thin films*.<sup>239–241</sup> In one, ultra-low impact energy (90–150 eV) SIMS was used to elucidate chemical states in annealed thin films of titanium and indium that had been deposited on silica.<sup>239</sup> The use of ultra-low energy primary ions ensure that the sputtering process is significantly different to that observed at normal energy (>1 keV). This is because they do not have sufficient energy to break strong covalent bonds. This means that it is possible to use it to obtain qualitative information about the types of bonds present in a sample. The procedure identified the formation of titanium and indium oxides, but in the case of the Ti, the silicide was also identified. The second paper used SIMS for investigating carbon grain formation in boron nitride epitaxial layers with atomic depth resolution.<sup>240</sup> When grown under a flow of argon, the films become contaminated with carbon in the form of clusters. Two types of growth of the boron nitride films were identified: 3D growth and self-terminated growth. The growth mode that occurs depended largely on the pressure within the reactor; with low pressure favouring 3D growth. In this mode, the carbon clusters appear in an organised way with the cluster in one boron nitride layer nucleating another in the successive layer. Eventually, a 3D carbon grain is formed. At high pressure, the self-terminated growth occurs and the carbon clusters are more chaotically arranged.

A gas co-injection system used in conjunction with a focussed ion beam TOF-SIMS analysis and with standard TOF-SIMS was reported in two papers by Priebe *et al.*<sup>242,243</sup> Although

having some advantages, focussed ion beams can also produce disadvantageous analytical artefacts. When used in conjunction with the gas co-injection system, these artefacts were minimised. In addition, the addition of certain gases can enhance the ionisation probability (and hence sensitivity) of analyses. In the study by Priebe *et al.*, the influence of water vapour and fluorine on the secondary ion signals and sputtering rates was studied.<sup>242</sup> The system was used for the depth-profile analysis of thin films (100 nm) of silver, copper, tungsten and zirconium. Samples were analysed using an ambient vacuum as well as in the presence of water vapour and fluorine. The highest increase in ionization probability was achieved for the copper thin film, which was increased by a factor of 10 by water vapour, whereas the fluorine increased it by a factor of 510. When sputtering rate was studied, it was the zirconium film that was most affected. The second paper discussed how the addition of fluorine enhanced spatial resolution of TOF-SIMS and had the added bonus of separating mass interference.<sup>243</sup> A compact high vacuum-compatible version of a TOF-SIMS instrument was integrated with a focussed ion beam system and this was used to analyse a multi-layered sample comprising 100 nm thick thin films of Cu, Zr and zirconium copper silver alloy. The signals arising from the secondary ions were enhanced by up to three orders of magnitude, which led to much higher spatial resolution. The quality of the images and the depth profiles were improved during a single measurement. This is not possible under standard vacuum conditions. Another advantage was that the addition of the fluorine enabled the interference from  $^{107}\text{Ag}^+$  on  $^{91}\text{Zr}^{16}\text{O}^+$  to be overcome. This was considered to be an important advance because the polyatomic interferences such as this are still a significant problem during SIMS or TOF-SIMS analyses.

The TOF-SIMS *three dimensional analysis of thin films deposited on high aspect ratio structures via atomic layer deposition and chemical vapour deposition* was discussed by Kia *et al.*<sup>244</sup> Two different kinds of high aspect ratio structures were used during the study. One studied the cobalt seed layer corrosion by copper electrolyte before and after copper electroplating. However, samples such as this where the copper may enter through the silica can cause severe problems with the analysis because of geometrical shadowing. This arises because of the  $45^\circ$  angle of the primary beam. The problem is discussed at length with the aid of diagrams in the paper. The second study introduced a new testing platform designed to eliminate these problems. Lateral high aspect ratio test chips were used to study the uniformity of silicon dopant concentration in atomic layer deposited hafnium oxide films. In contrast to the conventional vertical high aspect ratio structures, the lateral ones when used with three-dimensional TOF-SIMS analysis are unaffected by the sputter yield and topography.

A paper by Hofmann *et al.* also discussed *the problems associated with depth-profiling of multi-layers*.<sup>245</sup> Preferential sputtering effects are common among some techniques, *e.g.* SIMS and GD-OES. However, preferential sputtering can also affect other techniques, *e.g.* XPS and Auger electron spectroscopy that measure the residual surface. The depth resolution function can be affected by surface or interface roughness as

well as atomic mixing. The surface roughness has an effect of preferential sputtering which has an effect on XPS and Auger electron spectroscopy but no effect on SIMS profiling. Conversely, where there is atomic mixing, there is a strong effect on the depth resolution function which, in turn, affects the SIMS depth-profiling significantly whilst having only a moderate effect on the XPS or Auger results. The interface width, location and the layer thickness calculations are affected by preferential sputtering when depth-profiling is undertaken using XPS or Auger. However, the SIMS data are affected only if there is significant atomic mixing.

X-ray-based techniques have also been used for depth-profiling or surface analysis. *Reference-free grazing incidence XRF and X-ray reflectometry (XRR)* was used by Honicke *et al.* for the analysis and depth-dependent characterisation of ultra-thin layer stacks of alumina, hafnia and alumina that had been atomic layer deposited on silicon wafers.<sup>246</sup> The XRR characterisation was undertaken using a copper  $K_\alpha$  X-ray source. Since multiple layers, low density contrast materials or very thin layers that do not have pronounced angular minima, the data obtained require a full modelling. This was achieved using commercial software. However, the modelling uses the thickness, roughness and the density of each layer as parameters. This means that the number of parameters increases rapidly and the inter-parameter dependencies can confuse or falsify the modelling results. The authors therefore used a reference free method to help validate the XRR data. A modelling approach to the reference free GIXRF-XRR data was presented, with the overall result being a reduction in the number of free model parameters. Karki *et al.* prepared thin films of nickel-titanium using magnetron sputtering from separate titanium and nickel targets and then characterised them in terms of their composition, the depth distribution, stoichiometry and the molecular species present.<sup>247</sup> The thickness and density of the films were determined using XRR, the elemental depth profiles of Ni, O and Ti were determined using SIMS and Rutherford back-scattering spectrometry (RBS), the percentage atomic composition was determined using XRR and EDS, and XPS was used to determine which molecular species were present. There was good agreement between XPS and EDS results. The XPS also identified the presence of Ni-O bonds at the surface, which was in agreement with the SIMS results that found surface contamination by O was present in all samples. The thinner films (21.5–22.7 nm) also had O present throughout the body. However, thicker films (51.3–52.3 nm), although having the O contamination at the surface, did not have any in the bulk of the sample. Nolot *et al.* prepared some ultra-thin films of molybdenum sulfide on a silica film of 270 nm thickness on a silicon wafer and then characterised them using in-line WDXRF, GIXRF and in-line XPS.<sup>248</sup> The in-line WDXRF analysis utilised the fundamental parameter approach to elucidate the Mo and S stoichiometry because there were no readily available S standards. Results were within the uncertainty of that obtained using the reference-free GIXRF method. The WDXRF also provided the mass deposited per cycle. Szwedowski-Rammert *et al.* used laboratory-based GIXRF and grazing emission XRF (GEXRF) instruments for the analysis of multi-layer

structures.<sup>249</sup> A good discussion of the capabilities of the techniques was supplied along with easy to understand diagrams. The non-destructive nature of the techniques was emphasised as being one of their advantages. The differences between the two techniques was also highlighted. The experimental section demonstrated that quantitative, non-destructive depth-profile analysis was possible for a nickel-carbon multi-layer sample. The study also demonstrated the first sub-nanometer thickness characterisation of multi-layered samples.

Azuma and Kurokawa studied the *influence of a contamination layer on thickness evaluation of thin films calculated using XRR*.<sup>250</sup> A custom-made XRR spectrometer comprising a powerful X-ray generator, a rotating copper anode, a germanium (111) monochromator and a silicon avalanche photodiode detector was used to analyse a thermally oxidised silica thin film of 10 nm thickness on a silicon (100) substrate. The thin film was cleaned using UV and ozone before analysis. Data acquired were treated using the Parrat equation and a non-linear least squares curve-fitting technique was adopted to obtain the optimal values of the structural parameters. A structural model was also used to obtain theoretical data. The simulated dataset was run on the calculation model without allowing for contamination. The offset in the silica thickness was greatly affected by the contamination layer if its presence was ignored. It was concluded that the offset was independent of the thickness of the contamination layer, but that the density of it was far more significant. In addition, the contribution of the contamination layer to the thickness determination is dependent on the X-ray energy (the wavelength). This was not directly proportional to the X-ray energy though. Instead, it increased when a high contrast was used to obtain better sensitivity for the light elements.

*Lasers have also been used for the analysis of thin films.* Techniques such as LA-ICP-MS,<sup>251</sup> laser ablation of solids in liquids followed by ICP-OES determination (LASIL-ICP-OES<sup>252</sup> and LIBS<sup>253</sup>) have all been used during this review period. The paper by Weiss *et al.* used both LA-ICP-MS and LIBS for the direct analysis of solid transition metal boride-based materials.<sup>251</sup> Usually, certified materials matched as closely as possible to the sample type under investigation are required to obtain accurate results for these techniques. These authors circumvented this requirement by undertaking a dried droplet approach for the LIBS measurements. Here, a wafer was dipped in 2% hydrofluoric acid to remove the oxide layer and then 0.5  $\mu\text{L}$  aliquots of standards were pipetted onto the surface in grids of three samples per wafer and four replicates of each. They were then dried in a vacuum desiccator. For the LA-ICP-MS measurements, the authors adopted the microgroove approach, in which micro-grooves were laser ablated into the surface, filled with standard and then ablated into the ICP-MS instrument. Both of the procedures were described in full with the aid of diagrams. As a reference method, the sample was acid digested and analysed using ICP-OES. Both of the laser-based techniques were regarded as being rapid, but with the LA-ICP-MS generally providing the more accurate results for the evaluation of stoichiometry. Herzig *et al.* reported the use of LASIL-ICP-OES for the quantitative analysis of gadolinium

doped cerium oxide thin films.<sup>252</sup> The LASIL cell was a new design made of polyetherether ketone, a particularly inert polymer. This means that the liquid could be a dilute acid. As well as the material of manufacture, the configuration of the ablation cell was altered from previous ones, leading to a hugely decreased (by a factor of six) wash-out time. This lower time for the analyte to be present in the plasma actually improved the sensitivity because there is an increase of analyte in the plasma per unit of time. The LASIL could therefore be used in conjunction with ICP-OES rather than the usual ICP-MS. The paper described the new design at length. The results obtained using the new cell were compared with those obtained using SEM-EDS and were in good agreement. The film thicknesses analysed ranged between 220 and 14 nm. The SEM-EDS reached its limit at 110 nm, whereas the LASIL-ICP-OES method could analyse all of the films with good accuracy. Rapid micro-analysis of aluminium indium tin oxide thin films using LIBS with Nd:YAG 350 picosecond laser pulses was described by Liu *et al.*<sup>253</sup> The thin films had been deposited by radiofrequency magnetron sputtering. The plasma formed was thoroughly characterised in terms of temperature ( $5063 \pm 150$  K) and electron number density ( $4.6 \times 10^{16} \text{ cm}^{-3}$ ). A single laser shot created a crater of diameter  $46 \pm 1 \mu\text{m}$  and could therefore be regarded as being only partially non-destructive. An EDS analysis was also undertaken so that a comparison could be made. Results from the LIBS and EDS were in agreement.

One final application in this section used *GD-OES for quantitative depth-profiling* of copper indium gallium sulfur selenide (CIGS) thin films.<sup>254</sup> In this very theoretical study, the operating conditions were optimised and an algorithm devised to convert the measured properties (intensity of the emission lines against sputtering time) to more useful parameters such as molar fractions against depth profile. The authors provided the mathematics to fulfil this. The accuracy of the quantification method was tested using several samples. The bandgap energy profile of the material with optical measurements and the depth profile of Na was correlated with the measurements from open-circuit voltage of the corresponding devices. The quantification of the sample depth was validated by comparison with profilometry and XRF measurements.

**3.9.2 Solar cells.** Two reviews of different aspects of the analysis of perovskite solar cells have been published.<sup>255,256</sup> In the one by Harvey *et al.*,<sup>255</sup> the use of TOF-SIMS to investigate the effects of chemical gradients on the performance and reliability was reviewed, with 63 references being chosen from the literature. The review started by highlighting the advantages and disadvantages of the technique and compared its capabilities with those of complementary ones, *e.g.* XPS and AES. It was highlighted that it may be used for both inorganic and organic matrices and that it has superior lateral resolution (100 nm) and significantly improved detection limits compared with many of the other techniques. It then went on to describe the fundamentals of how it works and provided examples of applications in the areas of depth-profiling, imaging and 3D tomography. The other review, by Hidalgo *et al.*<sup>256</sup> cited 164 references and gave a very good comparison of tools that may be used for mapping and characterising perovskite solar cells. These tools

include various types of electron microscopy (SEM, TEM as well as energy dispersive X-ray detection and electron energy loss detection), AFM (including conductive AFM, Kelvin probe force microscopy and piezo force microscopy), synchrotron-based X-ray techniques and other spectroscopy techniques. A simple table summarised the capabilities of each, citing the information they give and their resolution. A section of text highlighted with figures, example results and the theory was then given for each of the techniques. Although a very long review, it does give an excellent overall view of the state of the art and gives an outlook on how their use may be expanded to give yet more information.

**3.9.3 Electronic equipment and devices.** There has been a significant number of *review or overview articles* in this research area published over this review period. An overview by van der Heide *et al.* cited only 19 references, but gave a decent overview of surface analysis in the semiconductor industry.<sup>257</sup> The paper concentrated on three main techniques: SIMS, XPS and AFM. A brief overview of the state of the art for each technique was given in individual sections that also gave relevant examples. The SIMS section discussed the advantages of the use of gas cluster ion beam (GCIB) primary beams. Previously, the primary ion beams tended to damage the surface of the sample, whereas the GCIB do not. This makes them particularly useful during the analysis of organic materials, *e.g.* thin films or photoresist materials. The use of Orbitrap instruments also improves resolution of standard TOF-SIMS instruments by a factor of 20. An additional advantage is the ability to perform MS/MS analyses, enabling molecular peak assignment – even for complex organic molecules. The introduction of higher energy monochromated photon sources into stand-alone lab-based XPS instruments was also discussed. Such instrumentation has enabled XPS sub-surface analysis, *i.e.* beyond the sputter front during depth-profiling. The latest advances in AFM, namely conductive probe atomic force microscopy was also discussed. A second paper by the same research group discussed achieving “reproducible data” and gave examples from the surface analysis of semiconductor materials.<sup>258</sup> In plants where there is high volume manufacturing, it is necessary to have long-term stability of data. The authors discussed the areas of potential problems, including the use of different instrumentation, sample variability, the understanding of the techniques used by different personnel, data processing protocols, *etc.* Examples were given for each of these. The problems were illustrated by the results of a round-robin test which varied widely. A third overview was presented by Wu *et al.* who discussed the recent progress in advanced characterisation methods for silicon-based lithium ion batteries.<sup>259</sup> The overview contained 114 references and advances in the characterisation techniques were summarized. The techniques discussed were split into two main sections: those capable of characterising chemical composition and those that characterise the morphology and crystal structure. Techniques discussed that fall into the first category were hard XPS (HAXPES), TOF-SIMS, XANES, synchrotron radiation photoelectron spectroscopy (SRPES) and nuclear magnetic resonance (NMR). Techniques that fall into the second category were SEM, TEM, scanning

transmission electron microscopy, X-ray tomography, *in situ* XRR, neutron radiography, *in situ* neutron reflectometry, *in situ* AFM, *in situ* XRD and *in situ* Raman. The capabilities of each of the techniques was described and examples of their use given. The review concluded with an extensive section on future prospects.

Two papers have summarised the *development of a reference material for electronic waste*.<sup>260,261</sup> The first<sup>260</sup> described the sample preparation, characterisation and chemometric evaluation of the data, whereas the second<sup>261</sup> discussed the homogeneity, stability, characterisation and uncertainty. Nearly five kg of printed circuit boards were collected, stripped of items such as fans and heat sinks, crushed and passed successively through a hammer mill, a knife mill and a vibrating cup mill. It was then homogenised and the particles of <233  $\mu\text{m}$  collected. After placing the material in 104 polypropylene bottles, residual moisture was determined from the contents of three random bottles. Five different acid dissolution procedures were then tested: aqua regia, inverse aqua regia, aqua regia diluted two-fold, concentrated nitric acid and nitric acid diluted two-fold plus hydrogen peroxide. Variables such as sample mass and reagent volumes were optimised using a full factorial design. All digestions were undertaken using microwave assistance. Analysis was performed using ICP-OES and instrumental neutron activation analysis (INAA). The analytical data obtained for 14 analytes were then subjected to PCA which identified the diluted aqua regia as being the best dissolution agent. Optimal conditions were to use 0.1 g of material and 10 mL of acid. A paired *t*-test was used to compare data obtained from ICP-OES and from INAA. Of the 14 analytes determined, only seven (Ag, Au, Cr, Fe, Sb, Sn and Zn) had data from the ICP-OES that coincided with the range found using INAA. The second paper used one way ANOVA at the 95% confidence level and linear regression to obtain the uncertainty contributions for between bottle homogeneity tests as well as short term and long term stability tests.<sup>261</sup>

The analysis of *different components of lithium ion batteries* has gained significant interest and several papers have used different analytical methods for the analysis. A paper by Stenzel *et al.* described the use of hydrophilic liquid interaction chromatography coupled with ICP-SF-MS for the quantification of organo (fluoro) phosphates which are decomposition products of lithium ion battery electrolytes.<sup>262</sup> The determination of such compounds is important because they resemble chemical warfare agents and, hence, are toxic. Separation was achieved using a strong anion exchange micro-column (1.9  $\mu\text{m}$  particles) with an isocratic eluent of 20 mM ammonium formate in 87% acetonitrile. Detection was at <sup>31</sup>P using medium resolution. An additional flow of oxygen was required to help decompose the organic matrix of the eluent even though the spray chamber was cooled to  $-5\text{ }^{\circ}\text{C}$ . Calibration using trimethyl phosphate covered the range 1–500  $\text{mg L}^{-1}$  for P and the LOD was 0.319  $\mu\text{g mL}^{-1}$ . A total of 16 different compounds were observed, although organic mass spectrometry was required for identification purposes.

Several papers have described the use of assorted *X-ray-based techniques for the analysis of lithium ion batteries* or their

components. Sato *et al.* used a polychromatic simultaneous WDXRF spectrometer to determine the valence of cathode materials in lithium ion batteries.<sup>263</sup> A schematic diagram of the instrument was given along with the explanation that the fluoresced X-rays pass through a slit, are dispersed off a flat crystal and are detected by different channels of the detector, which correspond to different energies. The performance of the instrument was improved by changing from the standard rhodium X-ray tube to a tungsten one, which extended the analyte list measurable from Cr, Fe and Mn to Co, Cu, Fe, Mn and Ni. The instrument was compact and had no moving parts in the optical system. It was therefore optimised for precision and signal rather than resolution. Different valence states of the analytes Co, Mn and Ni were determined using intensity ratios of different wavelengths. Analysis of the material NCM523 found that the valence change of the 3d transition elements during charging and discharging were 0.68 (from 2.90 to 3.58) for Ni, 0.19 (from 3.00 to 3.19) for Co and no change for Mn. From this, it was concluded that Ni was the element that contributed most to the redox process with Co making a smaller contribution. Another paper to report the analysis of cathodes in lithium ion batteries was presented by Banis *et al.*<sup>264</sup> It was shown previously that silicon doping substituted Si for P at sites of  $\text{LiFePO}_4$  and that this affected the performance of the battery. This study used XAS, XANES and XRF mapping as characterisation methods for understanding this process in samples that had been prepared using a melt-synthesis process. The XAS identified subtle changes in the local structure compared with  $\text{SiO}_2$  and amorphous glass phases formed as impurities in Si containing undoped samples. The study of Fe and P K-edges X-ray absorption spectra illustrated the effect of Si in the  $\text{LiFePO}_4$  structure in doped and impurity containing samples. The combination of the techniques enabled a better overview of the non-uniform nature of the ingot samples prepared.

A *semi-quantitative GD-OES depth-profiling study of the surface film formation and dissolution in Si/C anodes* of lithium ion batteries was presented by Richter *et al.*<sup>265</sup> As described previously, it is common to add silicon to the electrodes to increase the energy density of the lithium ion battery. Calibration standards containing graphite and 0.8 wt%, 11.1 wt%, 15.9 wt%, 21.5 wt%, 58.5 wt%, and 67.5 wt% Si were prepared. Another standard contained 100% Si. The method was validated using different pristine anodes with known Si content. Other silicon/carbon anodes from a commercially available cell were tested before contact with the electrolyte and after long-term cycling. Before contact, the Si content was uniform throughout the anode. However, after the long-term cycling, the concentration of Si peaked towards the surface. It was concluded that the Si dissolves in the electrolyte. The aging process was verified by interrupted GD-OES. In addition, Raman and ICP-OES both demonstrated the presence of the dissolved Si in the electrolyte.

The loss of performance of lithium ion batteries over time/number of cycles continues to be problematic. The *quantitative, spatially resolved post-mortem analysis of Li distribution and transition metal deposition on cycled electrodes* was reported by Lurenbaum *et al.* who used LA-ICP-OES for the task.<sup>266</sup> The laser used was a Nd:YAG operating at 213 nm and with a frequency of

10 Hz. The spot size was 150  $\mu\text{m}$  and the scan rate was 50  $\mu\text{m s}^{-1}$ . Calibration was against matrix matched standards and the wavelengths used were: 460.289 nm for Li (which is not the most sensitive line), 228.616 nm for Co, 257.611 nm for Mn and 341.476 nm for Ni. Detection limits were not terribly impressive, being 0.13, 0.03, 0.08 and 0.08% for Co, Li, Mn and Ni, respectively. However, the calibrations were excellent, with  $r^2$  being better than 0.99 for all analytes with an acceptable precision (<4% RSD). The authors stated that precision could potentially be improved through using an internal standard. However, this was to be undertaken in future work. The method was applied to graphite anodes and lithium metal oxide cathodes, in particular,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ .

The *analysis of ultra-pure materials* has also garnered interest. Reddy *et al.* developed a method whereby elemental impurities in ultra-pure (9N) germanium were determined using high resolution continuum source GFAAS or ICP-MS.<sup>267</sup> An acid dissolution of the sample was undertaken using quartz vessels that had been pre-cleaned for five hours using a mixture of hot 10% nitric and 10% hydrochloric acids. After rinsing with pure water, the vessels were further cleaned with acid vapour. Then, 10 g of sample was placed in a quartz vessel and heated to 250 °C. In a separate vessel, 50 g of manganese dioxide was mixed with 150 mL of concentrated hydrochloric acid and heated to 70 °C. A stream of argon passed the chlorine gas produced through two vessels of sulfuric acid to dry it and then into the vessel containing the sample. The germanium matrix boils away as the volatile compound germanium tetrachloride, which is trapped in a vessel of 20% sodium hydroxide. Once all of the germanium sample had volatilised, the vessel was cooled and the analytes dissolved in 200  $\mu\text{L}$  of sub-boiled hydrochloric and 200  $\mu\text{L}$  of sub-boiled nitric acids. After dilution to 3 mL, the digests were analysed. Sixty one analytes were recovered quantitatively. The method was therefore an extremely efficient way of matrix removal whilst also enabling a modest analyte pre-concentration. Therefore, the LOD obtained were impressive, typically being sub-ng  $\text{g}^{-1}$  and, in some cases, *e.g.* Be, REE *etc.*, being below 0.01 ng  $\text{g}^{-1}$ . Precision was also good, with RSD values ranging between 4 and 10%. Another example was presented by Dong *et al.* who determined trace elements in high purity quartz samples using ICP-OES and ICP-MS.<sup>268</sup> Sample (100 mg, of particle size < 74  $\mu\text{m}$ ) was mixed with ammonium hydrogen fluoride (400 mg) and 3 mL of nitric acid. The mixture was then heated at 200 °C for 2 h, cooled, mixed with 2 mL of 1 : 3 nitric acid and then heated at 250 °C until residue appeared. A further 2 mL of 1 : 3 nitric acid was added and then it was warmed until clear. Finally, it was diluted to 10 g using reverse aqua regia. Overall, a dilution factor of 100 was obtained. The mechanism of sample decomposition was investigated using XRD and thermogravimetric analysis which identified that sample was converted to  $(\text{NH}_4)_3\text{SiF}_6\text{NO}_3$  which, at 250 °C, decomposed completely, evaporating the silicon away. The resulting solution was analysed and approximately 40 analytes determined. The procedure was validated through the analysis of the CRMs GBW 07835, GBW 07836 and GBW 07837, with results in good agreement with certified values being obtained. The method had several advantages over existing

methods, including a smaller dilution factor, a shorter digestion time and the addition of relatively cheap and simple reagents. The overall result was that more analytes could be determined reliably. A final example of the analysis of ultra-pure materials was prepared by Gusel'nikova *et al.* who determined approximately 50 analytes in germanium dioxide.<sup>269</sup> The matrix was removed by placing sample (400 mg) into the recesses of a microwave bomb. Hydrochloric acid was added, ensuring that it did not come into contact with the sample. Microwave power was then applied and the hot acid fumes attacked the sample forming  $\text{GeCl}_4$ . In this way, any contaminants present in the acid do not come into contact with the sample, hence decreasing potential contamination. After the sample had been boiled away as  $\text{GeCl}_4$ , the residue was diluted with 0.5 M nitric acid that had previously been purified by sub-boiling distillation. Analysis was achieved using ICP-OES, yielding LOD in the range  $10^{-8}$  to  $10^{-5}$  wt%. Method validation was through spike/recovery experiments with recoveries typically being 80–120%.

Several papers have described *the analysis of electronic components or devices*. Two papers have reported the analysis of hard disk drives.<sup>270,271</sup> In the first of these examples, Castro *et al.* used and compared five different calibration strategies for the LIBS determination of B, Fe and some rare earth elements (REE) in the magnets from hard disk drives. The samples were heated in an oven at 500 °C for two hours to remove the magnetic field and then placed in a knife mill until the particle size was <500  $\mu\text{m}$ . The LIBS experimentation was undertaken using a Nd:YAG laser operating at 1064 nm and equipped with a spectrometer and a charge coupled device (CCD) detector. Two of the calibration strategies were multivariate (partial least squares and multiple linear regression) and the other three were univariate (multi-energy calibration, one point gravimetric standard addition and two-point calibration transfer). The authors explained in reasonable detail what each of these were. As well as the models being compared with each other, the data achieved were compared with those obtained following an acid dissolution and ICP-OES analysis. Both multivariate approaches provided reliable data (in the range 80–120% of expected values) for all analytes except Tb. This was attributed to matrix effects because the multivariate techniques can correct for interferences, but not matrix effects. The univariate approaches permitted corrections for matrix effects but it was emphasised that the appropriate selection of the blank and standard was mandatory. The standard error for the univariate methods ranged from 0.01 to 6%. It was concluded that all of the models could be used but that the standout one was the two-point calibration transfer. The other paper, also by Castro *et al.*, discussed the determination of Nd in hard disk drive magnets using wavelength dispersive XRF (WDXRF).<sup>271</sup> This was a very similar paper to the previous one, but on this occasion, only the three univariate calibration approaches were compared. The data were again compared with those obtained using an acid dissolution and ICP-OES analysis. It was noted that none of the models presented a perfect calibration, with some interferences occurring for all. However, given certain situations, each had advantages. These were: the identification of spectral interferences by multi-energy calibration, overcoming severe matrix

effects using one point gravimetric standard addition and use of a single point for calibration using two-point calibration transfer.

Two papers have discussed the analysis of *printed circuit boards originating from mobile phones*.<sup>272,273</sup> Erust *et al.* reported an intensified meso-acidophilic bacterial leaching of assorted analytes from waste printed circuit boards.<sup>272</sup> Plastic was removed from the samples which were then cut into pieces using a guillotine shear and then milled, first using a cutting mill and then an ultra-centrifugal mill. Pieces of between 250  $\mu\text{m}$  and 1 mm were obtained. Some of this then underwent an acid digestion using reverse aqua regia followed by ICP-OES analysis. This gave figures for the “total” concentration of analytes. Other sub-samples underwent the leaching procedure in which 2 g of sample was mixed with a mixture of iron-oxidising and sulfur-oxidising bacteria. The bacteria used were *Acidithiobacillus ferrooxidans* DSMZ 583, *Leptospirillum ferrooxidans* DSM 2705 and *Acidithiobacillus thiooxidans* DSMZ 9463 in a medium rich in phosphates, sulfates and iron and maintained at pH 1.8. The mixture was then incubated in a bioreactor at 30 °C whilst being stirred at 150 revolutions per minute for eight days. Sample (10 mL aliquots) were removed for analysis every two days. The leachable content was 55.9, 98.1, 79.5 and 66.9% of the “total” content for Al, Cu, Ni and Zn, respectively. The other paper, by Eskina *et al.* reported the digestion of electronic components in a mixture of hydrochloric acid and hydrogen peroxide in an autoclave at 220 °C.<sup>273</sup> The acid digests were then passed through one of two sorbents that had been made in-house using the Mannich reaction scheme for the thio-methylation of polyamines. One of the sorbents was used to retain the ecotoxicological elements and the other to retain the precious elements Au, Pd and Pt. The extraction process was optimised in terms of extraction time, weight of sorbent to volume of sample digest and the acidity of the digest. The remaining analytes in the digests were determined using continuum source graphite furnace atomic absorption spectrometry (CS-GFAAS). The ecotoxicological elements were retained from 0.1 M HCl with an efficiency of 96–100%. The precious metals could be quantitatively retained from a medium of 3.5 M HCl. The capacity and selectivity of the sorbents were also determined. The sorbent was then dissolved in nitric acid and the resulting solutions were also analysed using CS-GFAAS. The method was relatively straightforward and provided LODs of 0.00006 (for Cd) to 0.001  $\mu\text{g mL}^{-1}$  (for Pt).

Three papers have reported the use of LIBS for the *analysis of high voltage insulators*.<sup>96,274,275</sup> Surface pollution can lead to surface flashover voltage in wet weather such as rain or fog. This is considered to be a serious accident. Under normal circumstances, the power must be switched off while sampling and analysis occurs. Standoff analysis using LIBS is therefore hugely advantageous because it is quick and does not require an interruption to service. In the paper by Wang *et al.*, surface pollution was analysed in such a standoff way.<sup>274</sup> The power of the laser was altered and the higher the power, the greater the signal became along with a concomitant improvement in precision for some elements. However, the increased power also caused self-absorption for some elements and severe matrix

effects for others. The compromise laser energy of 80 mJ was chosen for further experiments. The effects of delay time and particles size and density were also determined during the optimisation. If the delay time was too long, the amount of Na ionised increased, hence leading to a decrease in signal at the wavelengths of 588.995 and 589.592 nm. A delay of 3  $\mu$ s was chosen as optimal. Similarly, a decrease in the particle size and an increase in the density of the sample both, improved the relative spectral intensities of the elements tested. The spectral intensities from 25 points on each sample were each divided by the background signal of the substrate, and the results were averaged. Results from the analysis of SEM-EDS were compared with those from LIBS. Several analytes, *e.g.* Mg and Na could be determined using LIBS, but not SEM-EDS. The paper by Kokkinaki *et al.* described how insulators can degrade because of electrical, mechanical and environmental stresses.<sup>96</sup> These workers used LIBS to analyse silicone rubber insulators that had been in service for up to 20 years on the Greek island of Crete. A total of eight insulators were analysed, seven of which had service and were suffering from varying degrees of pollution stress and the final one was in pristine condition. The authors used a Nd:YAG laser operating at 1064 nm and the light emitted from the plasma was transmitted along a fibre optic placed 1 cm from the insulator surface to a portable spectrometer that covered the wavelength range 300–600 nm. Similar experiments were also undertaken in the laboratory. The only difference in experimental setup was the use of a Mechelle spectrometer. The method developed identified some simple spectral indicators that reflect the extent of the chemical modification to the insulator surface. These indicators were the relative signals of C (as the CN molecular wavelength at 388.34 nm) and Si (at 390.58 nm). It was concluded that this approach was a rapid, reliable and simple method of analysis. Neettiyath *et al.* used vacuum UV-LIBS to determine S in thermally aged oil impregnated pressboard insulation material taken from high voltage transformers.<sup>275</sup> The authors described the experimental setup in detail giving a schematic diagram of the LIBS instrumentation. The LIBS was operated in a spatially resolved and temporally integrated mode with helium being used to confine the plasma formed and to increase the sensitivity of the S emission. The level of S increased with the age of the material.

### 3.10 Nanostructures

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

Two reviews and one perspective paper covering NP measurements have been published this year. The first of these covers the application of elemental speciation when applied to Ag nanoparticles and their dissolution products.<sup>276</sup> The review, citing 115 references, covers extraction procedures, which are mainly cloud point extraction (CPE) and solid phase extraction

(SPE) and applications involving capillary electrophoresis (CE), filed flow fractionation (FFF) and HPLC all coupled with ICP-MS as the detector. A brief section on sNP ICP-MS is also included. Much of the presented data is in a tabular format and includes the analyte(s), sample type and LOD values. The authors concluded that method accuracy needs to be improved although how this conclusion is made is not apparent as no method validation data is given for any of the articles cited. The second review is on the work of probing clusters and nanoparticles with synchrotron-based mass spectrometry and X-ray spectroscopy at the Lawrence Berkeley National Laboratory.<sup>277</sup> The review gives a brief description of the beamline and instrumentation, the use of vacuum UV molecular beam mass spectrometry to probe clusters in the gas phase, transitioning to a combined mass spectrometry and valence band photoelectron spectroscopy study of aqueous aerosols, and the development and implementation of soft X-ray velocity map imaging (VMI) of nanoparticles. The NP section deals mainly with aerosols of organic NPs and their reactions with a smaller portion covering core-shell Cu : SiO<sub>2</sub> NPs and compares the methodology with data acquired for aqueous CuSO<sub>4</sub> NPs. Good correlation was observed for spectra of these samples and those found in the literature. The authors set out future work directions which include the implementation of techniques such as X-ray photon correlation spectroscopy and resonant inelastic X-ray scattering to probe the photons, ions, and electrons that occur upon irradiation of X-rays in a liquid environment and incorporate mass spectrometry into studies to probe aqueous systems and nanoparticles in the soft X-ray region. The final paper covered here gives an overview of the investigating the natural nano-geochemical environment using recent advances in techniques for detecting NPs.<sup>278</sup> The paper covers electron microscopy, FFF-ICP-MS and sNP-ICP-MS as tools to provide information on processes involving naturally-occurring nanoparticles (NNPs). The authors suggest that applying 'nanoanalysis' on a single particle basis may lead to a more mechanistic understanding of particle formation and reactivity, global biogeochemical cycling, quantifying nanoparticle transport and impacts as they relate to hydrochemical and geochemical factors, and the possibly of differentiating engineered NPs from NNPs.

A number of studies covering investigations of data acquisition by sNP-ICP-MS have been published this year. One of these reports assessed the effect of the cell gas type used in a collision/reaction cell (CRC) on the peak width of the resulting data.<sup>279</sup> The influence of various CRC gases, gas flow rates, NP sizes and NP types was evaluated using Ag, Au, Fe and Pt NPs with both single and triple quadrupole ICP-MS instruments. The results showed that using a CRC produced a significant increase in the NP signal peak width (from 0.5 up to 6 ms). The effect was found to be greater as the cell gas relative atomic mass/relative molecular mass (RAM/RMM) increased. At a higher gas flow rate and/or for particles >100 nm  $\varnothing$ , the NP signal duration was also prolonged to a larger extent. For example, the use of NH<sub>3</sub> for Fe<sub>3</sub>O<sub>4</sub> NPs, detected as Fe(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> at  $m/z = 90$  amu, induced a significant peak broadening compared with that observed when using H<sub>2</sub> (6.10  $\pm$  1.60 *vs.* 0.94  $\pm$  0.49 ms). This extension of transit time was attributed to the collisions/interactions of



the ion cloud generated by a single NP event and precluded the detection of 50 nm Fe<sub>3</sub>O<sub>4</sub> NPs when using the NH<sub>3</sub> mass-shift approach. The authors concluded that the influence of a longer peak width on the accuracy of sNP-ICP-MS measurement data must be taken into account when using CRC to overcome polyatomic interferences and that to mitigate this potential detrimental effect light CRC gases and low gas flow rates should be used. It is now possible to use dwell times as short as 10 μs in sNP-ICP-MS. The effect of these shorter dwell times on the particle size detection limit (PS LOD) has been reported.<sup>280</sup> Decreasing dwell times below 100 μs did not lead to a statistically significant decrease in the PS LOD. For Ag NPs PS LOD was estimated to be 10–11 nm. When analysing samples of NPs close to the LOD, a low detection yield was observed. Only 5% of the number of NPs, estimated from the transport efficiency and particle number concentration, were detected whilst 20 nm NPs showed a 44% detection yield. Only for 30 nm NPs did the number of particles detected correspond to the theoretical value. Therefore, estimates of NP concentrations should be made with great caution at sizes approaching the PS LOD. In sNP-ICP-MS the use of a short dwell time to aid the detection of small nanoparticles can cause detector saturation for much larger particles and this has been evaluated this year.<sup>281</sup> In this work, the suitability of a traditional dead time correction (DTC) method applied to both ms and μs time-resolved (TR) spICP-MS was assessed. A custom data acquisition system was used to record the pulse counting signal at a sustained rate of  $2 \times 10^5$  samples per second. Model transients from microdroplets containing different concentrations of a thallium element standard were studied. The data were compared with the analysis of 11 Au NP suspensions covering a size range of 10–100 nm and introduced *via* regular solution nebulisation. Applying DTC to μs TR sNP-ICP-MS data allowed the increase of the maximum number of counts tolerated per particle or droplet four-to-fifteen-fold, resulting in a linear dynamic range of 10–60 instead of 10–40 nm AuNP. A cross-calibration between standard and attenuated sensitivity mode was established, further extending the linear dynamic range to 10–100 nm for Au NPs. The authors concluded that the findings support the theory of dead time related count losses being the main reason for nonlinear response in pulse counting sNP-ICP-MS but that the results also indicate that DTC can lead to slightly distorted particle size distributions. An alternative approach to extending the linear dynamic range is to monitor different isotopes of the element under study which is not possible with sNP-ICP-MS as data would be lost due to the fast scanning times involved (note that this is not the case for ICP-TOF-MS). However, combining sequential analysis of the same sample could be possible and this has been reported for Ti NPs whereby data for both <sup>47</sup>Ti and <sup>48</sup>Ti were acquired.<sup>282</sup> The linear range for <sup>48</sup>Ti was 30–400 nm, although detector saturation often occurred at a particle size of 250 nm or greater, whilst for <sup>47</sup>Ti it was 40–600 nm. The use of a desolvation device, coupled with SF-ICP-MS to reduce the PS LOD has also been reported.<sup>283</sup> For samples injected as a wet aerosol the PS LOD was 5 nm for Ag NPs and 19 nm for TiO<sub>2</sub> NPs. With a dry aerosol, the PS LOD values reduced to 3.5 nm for the Ag NPs and 12 nm for TiO<sub>2</sub> NPs. The method was applied

to detect TiO<sub>2</sub> NPs in sunscreen lotions, rainwaters, and swimming pool waters. Particle number amounts of Ti-containing NPs were between 27 and 193 μL<sup>-1</sup> in rainwater samples and similar values were found for public swimming pool waters. In sNP-ICP-TOF-MS the steady-state background ion signals follow a compound Poisson distribution that reflects noise contributions from Poisson-distributed arrival of ions and gain statistics of microchannel-plate-based ion detection. This compound Poisson distribution has been characterised with Monte Carlo simulations to establish net critical values as decision levels for the discrimination of discrete NPs in sp-ICP-TOF-MS analyses.<sup>284</sup> This approach was applied to the analysis of Au–Ag core–shell NPs and the results compared with conventional sigma-based NP-detection thresholds. Additionally, the separation of overlapping background and NP distributions was investigated by accurate modelling of the compound Poisson TOF-MS signal distribution. Accurate size measurements of 20 nm Au NPs that had a mean signal intensity of less than four counts was achieved.

The *baseline signal from electronic noise, sample carryover of dissolved elemental species in the sample affects the detection limits* achievable for NPs using sNP-ICP-MS. A study has been undertaken to produce a data processing procedure for the deconvolution of sNP-ICP-MS data when the baseline is large in magnitude. It was applied to quantify both the size distribution, 20 to 100 nm Ag NPs, and the concentration of dissolved silver ions (Ag<sup>+</sup> up to 7.5 mg L<sup>-1</sup>) in mixtures.<sup>285</sup> Poisson statistics were used to determine the thresholds to allow the identification of the beginning and end of NP signal events using an ICP-MS instrument with a μs time resolution data acquisition system in the presence of a significant background signal of up to 1 000 000 counts per second (cps). The critical level (false positive probability was set to 5%) and detection limit (false positive and false negative probabilities were set to 5%) based on Poisson distributions, were implemented to determine the thresholds. A range of different sets of NP ion cloud extraction conditions were tested to verify the calculated thresholds and to obtain optimal extraction conditions at different Ag<sup>+</sup> concentrations. The authors stated that the method can be universally applied for the detection of different elements with sNP-ICP-MS. This approach may prove beneficial for those workers in *e.g.* the ecotoxicology field, where samples from exposure studies contain both NPs and dissolved species of the analyte element. An alternative approach to baseline reduction is to separate out the dissolved and NP fractions in a sample which can be achieved using FFF with the dissolved species going to waste. This does of course limit the information available about a sample and precludes the determination of *e.g.* the ratio of free and particle bound nutrients or toxicologically relevant elemental species which are required for mass balance purposes. Thus, workers have constructed an interface to convert the discontinuous cross flow in FFF into a continuous flow to the ICP-MS instrument.<sup>286</sup> Two frit materials, ceramic and steel, were investigated to overcome the challenges of the interaction of dissolved elemental species with the frit and to improve recovery. The set up allowed a combined method to be developed which monitored both the dissolved fraction in the

cross flow and the particulate fractions in the detector flow. Comparison of the dissolved fraction data with those obtained from ultrafiltration of the samples under test, aqueous standards and environmental water samples, gave mean recoveries in the range of 87% to 120% for Ca, Mg and Si. In the case of Al and P the dissolved fraction was in the low  $\mu\text{g L}^{-1}$  range which resulted in elevated recoveries although still matching within confidence intervals. Asymmetric flow field-flow fractionation (AF4) coupled on-line with ICP-MS and molecular (fluorescence and UV) detection has been investigated as a powerful tool for the characterisation of bioinorganic nano-conjugates.<sup>287</sup> In this work biotin-antibody complexes bio-conjugated with streptavidin quantum dots (QDs-SA-b-Ab) were characterised after separation from the excess of the individual species used in the bio-conjugation reaction using a channel width of 500  $\mu\text{m}$ . The efficiency of the bio-conjugation process was estimated to be 86% for a 1 QDs-SA : 5 b-Ab bio-conjugation ratio. In addition, sample recovery of around 90% was achieved.

There are numerous methods used to determine particle size and particle number concentrations available to the analyst. The results of a European metrology project, InNanoPart, has developed methods for the measurement of particle size, concentration, agglomeration, surface chemistry and shell thickness.<sup>288</sup> Advancements made included being able to make SI traceable measurements of nanoparticle number concentration in liquids through small angle X-ray scattering (SAXS) and sNP-ICP-MS as reference methods with Au NPs of differing sizes, 10, 30 and 100 nm being the model analyte. Particles with a 5 nm diameter could not be detected by the reference methods and those of 250 and 500 nm exhibit a high degree of sedimentation so were not studied further. The paper contains a wealth of detail on the methodologies used and also covers the validation of a range of laboratory methods, including particle tracking analysis (PTA), dynamic light scattering (DLS), differential centrifugal sedimentation (DCS), ultraviolet visible spectroscopy (UV-vis) and electrospray-differential mobility analysis with a condensation particle counter (ES-DMA-CPC). In general, it was shown that reference methods agree on a number concentration values within their uncertainties, which were better than 10%. Additionally, for all measured samples, agreement of the nominal method with the reference methods could be verified. The laboratory methods showed a good degree of agreement with reference methods and nominal values, even though they provided much higher uncertainties. A separate study also compared a number of different methods, SEM, DLS, DMA, nanoparticle tracking analysis (NTA), and sNP-ICP-MS, for particle number concentration (PNC) measurements.<sup>289</sup> The analytes were monodisperse AuNPs of 30 or 60 nm  $\varnothing$  with different surface coatings (citrate, polyvinylpyrrolidone or branched polyethyleneimine). The two techniques that only measured the NP core size (sNP-ICP-MS and SEM), as opposed to the larger hydrodynamic diameter, yielded PNCs with the closest agreement (within 20% of each other), while PNCs among all techniques sometimes varied by a factor of 3. Positively charged AuNPs coated with branched polyethyleneimine yielded the most variable results. Deriving the PNC using the particle size distribution has several

advantages over using only the mean size based on these results. The size distributions measured by the different techniques were also used to model the AuNP concentration that would reach the cells in an *in vitro* toxicity experiment. A strong impact of the analytical technique on the modelled cellular AuNP concentration for some of the AuNPs was found. A systematic evaluation of flow field flow fractionation (FIFFF)-UV-ICP-MS and sNP-ICP-MS/MS has been undertaken and the results obtained compared with data DLS, NTA, TEM, membrane filtration, centrifugation and dialysis for the detection of iron oxide ( $\text{FeO}_x$ ) NPs.<sup>290</sup> Seven synthetic nano- and submicron  $\text{FeO}_x$  with different mineralogy and coating were prepared. The FIFFF was optimized for Fe recovery, yielding 70–90%. The FIFFF system could detect Fe-natural organic matter complexes <5 nm and organo-mineral  $\text{FeO}_x$  particles ranging in size from 5–300 nm. The sNP-ICP-MS method had a size detection limit for  $\text{FeO}_x$  of between 32 and 47 nm. The distribution of hydrodynamic diameters of goethite particles detected with FIFFF, NTA and DLS were similar but the values were twice as large as the Fe cores of particles detected using sNP-ICP-MS and TEM. Conventional fractionation by centrifugation and dialysis generally yielded similar fractions as FIFFF but membrane filtration overestimated the large size fractions. Single particle ICP-MS has also been evaluated and validated as a qualitative method for the assessment of the presence/absence of particles containing specific elements in a sample.<sup>291</sup> The binary response obtained allows the use sNP-ICP-MS as a screening tool for rapid classification of samples, which can be analysed further if required. A metrological treatment of sNP-ICP-MS as qualitative method was undertaken, providing solid criteria for identifying particle events and the presence of particle in the samples by using the critical value (or limit of decision) concept. Based on theoretical and experimental evidence, a critical value for identification of particle like events by using a 5 sigma criterion (where sigma is the standard deviation of the baseline) was proposed to eliminate or minimise the occurrence of false positives. A 2.33 sigma criterion, where sigma is the standard deviation of the number of particles counted in blanks was proposed for use to confirm the presence of particles larger than the minimum detectable size in a sample. Size critical values of 25–30 nm were obtained for metallic, spherical and solid particles of gold and silver and 50–80 nm for aluminium, whereas number concentration critical values of around  $10^5$  particles per L were achieved. Subsequently, the screening approach was applied to the detection of particles from approved metallic additives in foods which showed that some products labelled as containing NPs did not do so when subjected to the developed method.

A number of studies have used *LA-ICP-MS imaging for the detection of NP exposed tissues*. Three papers have been published by the same group of workers on the imaging of Ag NPs in collagen rich microstructures using LA coupled with either ICP-MS or ICP-TOF-MS. In the first paper of this series, high resolution LA-ICP-TOF-MS, with cellular spatial resolution, was used to assess the uptake of Ag NPs by fibroblast multicellular spheroids (MCS) of 20  $\mu\text{m}$  thickness.<sup>292</sup> A 193 nm laser was used with a 10  $\mu\text{m}$  spot size and the instrumental acquisition time

was 20 ms per replicate. Quantitative data were acquired for the Ag NPs and elemental distributions of Ag, Co, Cu, Fe, K, Mg, Mn, P and Zn. The LOD values obtained were at the femtogram level. Matrix-matched calibration standards were printed using a non-contact piezo-driven array spotter with an Ag NP suspension and multi-element standards. After incubation of the NPs with the MCS for 48 h the Ag NPs were only detected in the outer rim of the MCS and not in the core. The Ag NPs were inhomogeneously localised in the outer rim and co-localised with single-cell-like structures visualized by the Fe distribution. The quantitative value for the total mass of Ag NPs in a thin section obtained by the method agreed with that obtained using ICP-MS in liquid mode after acid digestion of the MCS sections. In the second paper in the series, MCSs were incubated with Ag NP suspensions,  $5 \mu\text{g mL}^{-1}$  for 24 h and LA-SF-ICP-MS (spot size  $8 \mu\text{m}$ , dwell time 2 ms) was used to quantitatively image the Ag NP and Br, Cu, P, and Zn distributions.<sup>293</sup> A calibration using a NP suspension was applied to convert the measured Ag intensity into the number of NPs present. The determined numbers of NPs in the MCS thin sections ranged from 30 to 7200 particles in an outer rim. The particle distribution was clearly correlated with the P and Zn present. The third paper reported on the penetration of different size and coated NPs into the MCS, with different incubation times, using LA-ICP-TOF-MS as a means of detection.<sup>294</sup> The MCS sections were exposed for up to 48 h to one of four types of Ag NPs (5, 20 or 50 nm  $\varnothing$  citrate coated, or 20 nm  $\varnothing$  polyvinylpyrrolidone coated). The results showed that the penetration pathway of the NPs was strongly related to steric networks formed by collagen fibrils, and that Ag NPs with a hydrodynamic diameter  $> 41 \text{ nm}$  were completely trapped in an outer rim of the MCSs. The impact of the NPs on essential elements (P, Fe, Cu, and Zn) in areas of Ag NP accumulation was also investigated. A linear increase at the sub-femtogram level in the total concentration of Cu in samples treated with small or large Ag NPs (5 or 50 nm  $\varnothing$ ) was observed. There is a wealth of information in the three papers and the ability of ICP-TOF-MS to simultaneously acquire both NP and dissolved elemental information is clearly demonstrated. A method for quantitative LA-ICP-MS/MS imaging of  $\text{FeO}_x$  NPs in gelatin microspheres containing  $\text{CaCO}_3$  crystals was reported.<sup>295</sup> The strong spectral overlap between the  $^{56}\text{Fe}$  signal and those of various Ar, Ca and O based polyatomic species was overcome a mixture of 1 : 9  $\text{NH}_3/\text{He}$  as the cell gas in mass-shift mode with the ions monitored being  $\text{Fe}(\text{NH}_3)_2^+$  and  $\text{CaNH}_3^+$ . The method was validated by using two CRMs, NIST SRM 1577 and 1577a bovine liver, which were solubilized by acid digestion. Gelatin droplet standards containing Fe were prepared on a high-purity single-side polished silicon wafer. High-resolution LA-ICP-MS/MS imaging revealed the mixed structure of the gelatin microspheres containing a high loading of  $\text{FeO}_x$  NPs ( $2.69 \pm 0.91 \text{ wt\% Fe}$ ) in the gelatin phase.

One possible *exposure route to NPs is through ingestion*. One study this year reported on this exposure route for Ag NPs and  $\text{AgNO}_3$  using a simulated human gastrointestinal *in vitro*

digestion model with a pH gradient ranging from 7 (mouth), to 5 (stomach), to 7 (intestine) to resemble the conditions upon food consumption.<sup>296</sup> Total Ag content was determined in the samples, after acidic digestion, using ICP-MS whilst the particle size, size distribution, and mass- and number-based concentrations in the samples was determined using sNP-ICP-MS. In addition to this Caco-2 and HT29-MTX cells were exposed to Ag NPs and  $\text{AgNO}_3$  that had previously been through the model digestive system. The results obtained showed that between 48 and 92% of the AgNPs dissolved during the digestion, with those with a citrate modified surface being more stable than those modified with lipoic acid. Cellular exposure to increasing concentrations of pristine or *in vitro* digested AgNPs resulted in a concentration dependent increase of total Ag and AgNPs content in the cellular fractions. The cellular concentrations were significantly lower following exposure to *in vitro* digestion AgNPs compared with the pristine AgNPs. Transport of silver as either total Ag or AgNPs was limited ( $<0.1\%$ ) following exposure to pristine and *in vitro* digestion AgNPs. The authors concluded that the surface chemistry of AgNPs and simulated digestion influence their dissolution properties and uptake/association with the Caco-2 HT29-MTX cell system, highlighting the need to take *in vitro* digestion into account when studying nanoparticle toxico-kinetics and toxico-dynamics in cellular *in vitro* model systems. Transformation of dissolved  $\text{AgNO}_3$  into Ag NPs after the digestion procedure was also observed during an extraction procedure using TMAH to solubilise cells exposed to either Ag NPs or  $\text{AgNO}_3$ .<sup>297</sup> In this work the aim was to develop single particle ICP-MS protocols for liver tissue from rainbow trout. A total of four different extractants were used: proteinase K or TMAH both with/without  $\text{CaCl}_2$ . Spike recovery tests in the proposed extractant solutions, using Ag NPs or  $\text{AgNO}_3$  were conducted and recoveries for the former were 95–105%. However, the TMAH alone caused  $\text{AgNO}_3$  to precipitate and was therefore not a suitable extractant. However, this effect was not observed when  $\text{CaCl}_2$  was added to the TMAH before use. The authors postulated that the cause of this apparent particulate signal with TMAH is likely to be precipitation as  $\text{Ag}_2\text{O}$  under the high pH conditions and that the addition of  $\text{CaCl}_2$  might drive dissolved  $\text{Ag}^+$  to form complexes with the  $\text{Cl}^-$  anion or perhaps with the TMAH, such as  $[\text{AgN}(\text{CH}_3)_4]^{2+}$ . Proteinase K, with or without  $\text{CaCl}_2$ , failed to completely digest the tissues. Silver NPs spiked onto liver tissues and analysed 24 h later, also showed no significant change in particle size distribution or particle mass concentration compared with those freshly spiked into solution without liver present. The particle number concentration fell significantly to around 80% of the freshly spiked Ag NP. Samples from an *in vivo* dietary study where fish were fed nominally  $100 \text{ mg kg}^{-1}$  Ag, as either  $\text{AgNO}_3$  or Ag NPs, were analysed to demonstrate the utility of the method. There was no significant difference between the particle number concentration, mean particle size or particle mass concentration between the *in vivo*  $\text{AgNO}_3$  and Ag NP treatment liver tissues. Biological samples often contain significant amounts of NaCl and the effect of this on the

accuracy of Ag NP size determinations by sNP-ICP-MS has been investigated.<sup>298</sup> Non-spectral interferences, such as the effect on transport efficiency from NaCl at a concentration of  $450 \text{ mg L}^{-1}$ , led to an under-evaluation of the diameter of Ag NPs by 7% whilst at  $4500 \text{ mg L}^{-1}$  the Ag NP diameter was under estimated by 28% when calibration standards were prepared in water. The effect of organic C was also investigated by preparing samples in 1, 2 and 5% v/v MeOH which gave signal enhancements of 8, 22 and 22%, respectively, again when compared to standards prepared in water, leading to an over estimation of the particle size. Whether this effect is due to improved sample transport or ionisation efficiency is not known but the latter has not been reported for Ag although it is a known effect for elements with a high first ionisation potential. The study emphasises the need to matrix match calibration standards to the samples.

*The increasing use of NPs* in many consumer products has led to their transport to the environment, often through wastewater treatment plants (WWTP). Hard X-ray fluorescence microscopy (XFM) and SEM have been employed to characterise and evaluate the morphological transformations of ZnO NPs in a simulated sewage sludge.<sup>299</sup> Synthetic ZnO nanorods (725 nm length and 140 nm in diameter) were incubated for 1 and 3 h in the presence of  $10 \text{ mg L}^{-1}$  humic acid as a relevant aqueous component of wastewater sludge (which does seem a bit questionable as humic acids are derived from soils and thus may not be representative of the organic component of real wastewater sludge). Results provided by the different techniques evidenced a significant decrease of ZnO NP concentration with time and the occurrence of ZnS as the predominant Zn compound. The presence of diffuse nanoparticles of ZnS,  $\text{Zn}_3(\text{PO}_4)_2$  and Zn adsorbed to Fe-oxhydroxides were also imaged. These types of studies are of special relevance to correctly assess the impact of NPs in the environment. The incidence and persistence of Ag NPs in the wastewater process has been studied using sNP-ICP-MS in influent and effluent samples, as well as reclaimed and backwash waters of an ultrafiltration (UF) system in a WWTP, showing a concentration of 13.5, 3.2, 0.5 and  $9.8 \text{ ng L}^{-1}$ , respectively, with relative standard deviations (RSDs)  $< 5\%$ .<sup>300</sup> The total Ag concentration (Ag NP and dissolved Ag) ranged from 40 to  $70 \text{ ng L}^{-1}$ . Most of the Ag NPs detected were below 100 nm in diameter. Biological and physical processes in the secondary treatment section of the WWTP removed 76% of the colloidal Ag fraction, while with the tertiary treatment (ultra-filtration) of the WWTP removed 96% of the colloidal fraction. The persistence of Ag NPs in various water matrixes, including a synthetic wastewater (SWW), was determined by spiking  $300 \text{ ng L}^{-1}$  of Ag NPs (40 nm) and monitoring the concentrations and size changes for 15 days. The persistence was found to be influent  $>$  effluent  $>$  reclaimed  $>$  SWW. The partial dissolution of Ag NPs in all waters was observed from time 0 h. The current concentrations in the outlet flows from the WWTP effluent and reclaimed waters were low. Product weathering and further environmental transformations can create composite particles (CPs) that may contain multiple NPs, a residual product matrix, such as a polymer, or

transformed/added surface coatings. An online and matrix-matched calibration method for the multiplexed analysis of NPs using ICP-TOF-MS has been developed.<sup>301</sup> In this work the NP mass is determined based on absolute sensitivities measured with microdroplet standards. As microdroplets are introduced along with NP-containing samples a matrix-matched calibration of element mass is performed. For accurate determination of the particle number concentration (PNC), a standard element, e.g. Cs, was spiked into NP containing samples. Then, based on absolute sensitivity from microdroplet signals the sample uptake rate into the plasma is directly determined. The online microdroplet method requires no external NP standards and a detailed explanation of the approach is given in the paper. The approach was used for the quantification of well-characterised NPs (Ag, Au and Pt) in different matrices, including phosphate-buffered saline, Triton-X surfactant, and effluent from a wastewater treatment plant. The results demonstrated accurate multiplexed quantification of spiked NPs in all matrices in terms of both the element mass and PNC suggesting the utility of the approach for quantification of NPs in challenging or not well-defined environmental matrices. For the WWTP effluent sample, endogenous and spiked NPs were quantified in a single run.

Analysis of samples for *NPs that form naturally in the environment* are also of interest this year. A methodology that used TEM, sNP-ICP-MS and FFF was developed to allow the investigation of metallic NPs associated with composite particles (CPs).<sup>302</sup> The study used these techniques and nanoplastic CPs consisting of a gold-polymer nanocomposite (polystyrene-block-poly(acrylic acid)) (Au-PS) as a model system. Metal NP size and particle number concentration was obtained using sNP-ICP-MS. Asymmetric flow field-flow fractionation (AF4) and centrifugal field-flow fractionation (CFFF) separated and sized the CPs 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 (gold-polystyrene) engineered NPs (from 1 to  $>8$ ) contained in the CPs. In particular, CFFF utilizing a carrier that was density-matched to the polymer, proved very successful in measuring multiple gold engineered NPs in the CPs. The authors concluded that the developed methodology could be applied to investigate NP properties in environmental systems. Wetlands and river floodplains are often very rich in natural organic matter (NOM). Strong binding of chalcophile metals like copper by NOM is expected to interfere with sulfide precipitation and is likely to affect the growth of these nanoparticles. To investigate this, experiments on the formation of copper sulfide nanoparticles ( $\text{Cu}_x\text{S}$  NPs) in anoxic solutions with varying Cu ( $50, 500 \text{ } \mu\text{mol L}^{-1}$ ) and sulfide ( $100, 1000 \text{ } \mu\text{mol L}^{-1}$ ) concentrations in the absence and presence of fulvic acid ( $0, 5, 50 \text{ mg C L}^{-1}$ ) were reported.<sup>303</sup> The size development of the  $\text{Cu}_x\text{S}$  NPs and their stability were tracked over 4 weeks using TEM and size exclusion chromatography (SEC)-ICP-MS. Additional dissolution experiments were also performed in closed containers in the absence and presence of  $\text{O}_2$  and fulvic acid over several months; providing

Table 4 Applications of nanomaterial characterisation and/or detection

Analyte	Technique	Comments	Reference
CuCoO <sub>2</sub> nanoplates	ICP-OES, SEM, TEM, XRD, XPS	Analytes prepared by solvothermal method at 140 °C for 24 hours using zeolitic imidazolate framework-67	305
CuO and hydrous FeOOH NPs	DLS, SEM, sNP-ICP-MS, XRD	The use of H <sub>2</sub> O <sub>2</sub> to narrow the size distribution and decrease the size of CuO and hydrous FeOOH NPs under conditions of high supersaturation	306
CdSe/ZnS core-shell quantum dots	TOF-SIMS, TEM, XRD	Method used to acquire 6 nm depth profiles distinguishing core and shell layer	307
CoTiO <sub>3</sub> and SiO <sub>2</sub> NPs	LIBS, SEM, XRF	Quantitative and qualitative data of the NPs composition	308
Au NPs	FFFF, ETAAS	Performance evaluation. Fractions eluted from FFFF collected and then analysed using ETAAS. Time for maximum absorbance increased as particle size increased	309
poly(tetrafluoroethylene)-poly(methyl methacrylate) (PTFE-PMMA) and poly(tetrafluoroethylene)-polystyrene (PTFE-PS) core-shell NPs	TOF-SIMS, SEM, XPS	Complete (PTFE-PMMA) and incomplete encapsulation (PTFE-PS) of the core by the shell material observed using TOF-SIMS	310
Al NPs embedded in a ZrCuAg matrix	TOF-SIMS	Chemical structure measurements revealed distinct Al signal segregation indicating a spatially resolved detection of single 10 s of nanometer particles and/or their agglomerates	311
Ag NPs in toothpaste	sNP-ICP-MS	Ag NPs extracted by sonication with 0.1% Triton X-100. Detection limits of particle size, number concentration and mass concentration were 23 nm, $3.9 \times 10^8$ particles per kg and 26 ng kg <sup>-1</sup> , respectively. Spike recoveries of 87–94%. Data obtained agreed with those of the NP manufacturer	312
TiO <sub>2</sub> NPs	FFFF-multi-angle light scattering (MALS), FFFF-ICP-MS	Combination of ultra-centrifugation and hexane washing, thermal destruction of the matrix, and surfactant assisted particle extraction. Recoveries > 90% and no particle agglomeration observed	74
Pd NPs	sNP-ICP-MS, SAXS, SEM, XRD,	Pd NPs synthesised through the reduction of PdCl <sub>2</sub> by tetraethylene glycol in the presence of KOH	313
InP nanowire	Nano-focused X-rays. Scanning transmission X-ray microscopy (STXM), XRF, scanning XRD, and X-ray beam induced current (XBIC)	The current from the nanowire was directly collected, allowing simultaneous combination of measurements giving information about morphology, elemental composition, crystal structure and charge collection	314
Li nanowires on Ti surfaces	LA-ICP-MS, SEM, XRD, XPS	Topographical and chemical characterisation revealed that the stable continuous nanowire network is composed of fine Li-based nanoparticles (~7 nm) and exhibits high surface wettability, high mechanical stability and a sustained release of Li <sup>+</sup> ions over 21 days at 37 °C under vigorous shaking in water, simulated body fluid and protein-containing fluids	315
ThO <sub>2</sub> NPs	HERFD-XANES	Observed that the first post-edge feature is very sensitive to the lowering of the number of coordinating atoms and therefore to the more exposed Th atoms at the surface of the NP. The sensitivity of the L3 edge high-energy resolution fluorescence detected (HERFD) XANES to low coordinated atoms at the surface stems from the hybridization of the <i>d</i> -density of states of Th with both O and Th neighbouring atoms	316
Pt nanoclusters	ICP-OES, SAXS	One-pot green synthesis method. Blue and green fluorescent, water-soluble, quantum yield of ~7.0%, ~9.5 ns lifetime using the multi-stimulus responsive intrinsically disordered protein Rec1-resilin	317
Cu NPs	Static and dynamic light scattering, TOF-SIMS	Demonstrated that soluble Cu but not particulate forms were associated with inhibition of bacterial growth	318
Porphyrin-armoured Au NPs	FT-IR, XPS	Molecular docking analysis revealed thermodynamically favourable interactions with specific amino acid residues of $\alpha$ -synuclein and thus influence the stability of the protein and its aggregation	319

Table 4 (Contd.)

Analyte	Technique	Comments	Reference
TiO <sub>2</sub> NPs	AF4-ICP-MS	Ionic strength has a considerable influence on the AFFF membrane zeta potential and hence, NP recovery during separation. Control of membrane zeta potential achieved by varying ionic strength to obtain the same electrostatic charge as the NPs. This minimised NP adsorption on the membrane	320
Au NPs	sNP-ICP-MS, SEM, TEM	Densities determined at low concentration with a 100 μs dwell time. Good agreement with the size measured by SEM and TEM. Linear function for diameters up to 100 nm while 250 and 400 nm particles required signal suppression due to signal saturation	321
Ag NPs	XANES, EXAFS	Oxidation of Ag NPs by MnO <sub>2</sub> detected. Initial fast oxidation to Ag <sup>+</sup> (0–10 min) followed by a slower reaction (>10 min) where Ag <sup>+</sup> was removed by adsorption on MnO <sub>2</sub> surfaces.	322
Ag NPs	XPS	Identification of the differences in the band-shape and energy peak position of photoemission spectra due to the particle dimension	323
Se NPs	FFFF, DLS, sNP-ICP-MS, TEM	FFFF always yielded the lower estimate of the hydrodynamic size than DLS data. The results obtained by SP-ICP-MS were consistent with the TEM data	324
<sup>57</sup> Fe labelled iron oxide NPs	MRI, sNP-ICP-MS	The use of isotopically labelled ( <sup>57</sup> Fe) iron oxide NPs to distinguish between administered and endogenous iron signals in MRI scans	325
CuFe <sub>2</sub> O <sub>4</sub> and CuZn <sub>1-x</sub> Fe <sub>2</sub> O <sub>4</sub> inverse spinels	LIBS	A new sampling strategy based on skimmer-like 3D printed cones that allows for thin dry nanoparticle aerosols to be formed <i>via</i> optical catapulting was introduced. Increase of the sampling throughput by facilitating stable atmospheric-pressure optical trapping of individual particles and spectroscopic chemical characterization within a short timeframe	326
ZnO NPs in powder form	sNP-microwave induced plasma (MIP)-OES	Direct NP introduction to the plasma <i>via</i> a dilution chamber with He as the carrier gas.	327

insights into the oxidative dissolution behaviour of Cu<sub>x</sub>S. The results showed the high colloidal stability of Cu<sub>x</sub>S NPs in anoxic environments irrespective of the NOM concentration. Median particle diameters ranged between a single digit and tens of nm, with an increase in particles size observed as the Cu and S concentrations rose. At low Cu and S concentrations, fulvic acid restricted particle growth by up to 25% compared with 'blank' suspensions and metal sulfide clusters smaller than 1 nm were detected. The Cu<sub>x</sub>S nanoparticles only dissolved when both fulvic acid and O<sub>2</sub> were present. Pore size measurements of ultrafiltration membranes, often used in the preparation of environmental samples to operationally define different fractions, can be a challenging task and a new approach using Au NPs has been developed.<sup>304</sup> Suspensions of mixtures of 20, 30, 40 and 60 nm Au NPs, 7 × 10<sup>7</sup> particles per mL for each nominal size, in SDS to minimize adsorption effects were subjected to UF. Subsequently, the particle size and number of Au NPs in feed and permeate suspensions was determined using sNP-ICP-MS. The cut-off size determined in this way was found to be in good agreement with the membranes' functional pore sizes or bubble point sizes measured by gas-liquid displacement porosimetry. However, significant differences between the functional pore sizes and

the manufacturers' removal ratings were observed. The sNP-ICP-MS set up allowed 20 nm Au NPs to be detected at concentrations as low as 50 particles per mL with a size resolution of 1 nm.

Table 4 shows other applications of nanomaterial characterisation and/or detection presented in the literature during the time period covered by this ASU.

## 4 Cultural heritage

Samples of cultural heritage/archaeological samples have been collected into their own section in this year's review rather than being spread amongst other sections. The analysis of such materials can achieve many things including elucidating provenance and trade routes, obtaining information on preparation techniques and detecting forgeries. Since all such samples are precious (not just in monetary terms), there has been a push over many years to use analysis techniques that cause no or, at worst, minimal damage. As such, X-ray-based techniques and laser-based techniques, *e.g.* LIBS or LA followed by atomic spectrometric detection, have proven very popular. Often, the data have been obtained by analytical scientists, but the paper is then written by an archaeologist or a historian. Therefore, there

is often a paucity of scientific detail in many of the papers. Therefore, most of the papers discussed in this section will appear in tabular form.

Several *review or overview articles* have appeared during this review period. A general review of instrumental techniques for architectural heritage materials was prepared by Zhao *et al.*<sup>328</sup> The review (with 325 references) covered numerous analytical techniques. These were split into six main sections, which were: imaging techniques (optical microscopy, AFM, SEM), traditional spectroscopic techniques (UV-Vis, FTIR, Raman, LIBS), thermal gravimetric analysis (thermogravimetry, differential thermal analysis and differential scanning calorimetry), X-ray-based techniques (XRD, XRF, XPS, XANES, EXAFS, *etc.*), ion beam techniques (PIGE and PIXE) and MS-based techniques (GC-MS, pyrolysis-GC-MS, MALDI-TOF-MS, TOF-SIMS and ICP-MS). A discussion of the relative merits of each was given in their own sub-sections. The one section that was lacking detail was that about ICP-MS. The assorted papers that used LA-ICP-MS or other related techniques was not really discussed. Nevertheless, it is still a good starting point for people interested in the analysis of cultural heritage materials. Many of the reviews concentrate on a particular technique rather than a specific sample type. An example was produced by Save *et al.* who reviewed (with 53 references) the use of portable XRF for large scale geochemical surveys of archaeological settlements and features.<sup>329</sup> The analysis of archaeological sites can give an indication of where exactly passed cultures were performing tasks, *e.g.* smelting *etc.* and so this paper is welcome. Other examples include papers by Zucchiatti<sup>330</sup> who reviewed (with 81 references) ion beam analysis for the study of cultural heritage materials and another by the Analytical Methods Committee who gave a brief overview of LIBS for the analysis of these materials.<sup>331</sup> This latter paper had only five references, but gives an overview of the concepts of LIBS and how it may be used for the analysis of assorted smaller objects as well as larger ones, *e.g.* monuments. A fuller review of the use of LIBS in archaeological science was presented by Ruan *et al.*<sup>332</sup> The review (with 163 references) gave examples published between 2011 and 2017 that had used LIBS to analyse metallic alloys, ceramics, glasses, painted artworks, historical buildings and biomaterials. There were also brief sections describing where LIBS was combined with other techniques, *e.g.* Raman and ICP-MS. A review paper by Ager *et al.* gave an overview of the work undertaken at the Centro Nacional de Aceleradores, Seville, Spain, that has focussed on the analysis of cultural heritage samples for several years.<sup>333</sup> The institute used to focus on ion beam analysis technologies, but more recently has concentrated on the use of portable XRF instrumentation. Numerous examples are given that demonstrate the applicability of the technique to jewellery, coins, paintings and ceramics. The advantages and disadvantages of the techniques are discussed along with methodologies, *e.g.* combining the techniques, of overcoming them. The review contained only 29 references, but is an interesting read. Tonazzini *et al.* discussed (with 118 references) the analytical and mathematical methods used for revealing hidden details in ancient manuscripts and paintings.<sup>334</sup> Analytical techniques discussed included multi-spectral

imaging, XRF, thermography, Raman and LIBS. The mathematical approaches included chemometric methods, *e.g.* PCA and its modifications (independent component analysis (ICA) and dependent component analysis (DCA)), Linear Discriminant Analysis (LDA), self-organising maps and blind source separation techniques. Other approaches discussed included pseudo-colour imaging and RGB imaging (where red, green and blue light is used in different proportions to produce a large number of colours). A section on future perspectives was also presented which discussed the potential of digital photography for this type of task. One last review of note was presented by Katsifas and Zachariadis who gave an overview (with over 80 references) of EDXRF spectrometry and complementary non-destructive analytical techniques in the archaeometric study of copper artefacts.<sup>335</sup>

Heginbotham *et al.* reported the results of an *inter-laboratory comparison using EDXRF* of copper alloys found in heritage materials.<sup>336</sup> A protocol was devised and five institutions participated using nine tube-based instruments of seven different types. When all participants used the same protocol, reproducibility improved by between 65 and 83%. This enabled 15 analytes to be reported consistently compared with only eight from a 2010 study. It was hoped that researchers in the area would use the protocol to collaborate more effectively and with greater confidence in their data.

Two papers have been published that reported the *development of new instrumentation designed specifically for the analysis of cultural heritage materials*. Shameem *et al.* reported the development of an echelle LIBS – Raman instrument that used a single nano-second, pulsed Nd:YAG laser operating at 532 nm and an intensified CCD as detector for both measurements.<sup>337</sup> The elimination of background and long-lived fluorescence signals which could mask the weak Raman signal were achieved by gating the CCD detector to extremely low time scales (ns). The different power densities for LIBS and Raman were achieved by changing the focal spot dimensions on the sample surface. The instrument was applied to the analysis of natural and artificial pigments in artworks and enabled the identification of the materials, provenance, state of conservation and helped elucidate degradation mechanisms. The authors concluded that their hybrid instrument was more compact, had greater stability and was more cost effective and technically more advanced than other, similar instruments. Another paper, by Santos *et al.*, characterised an instrument that was capable of undertaking energy dispersive XRD and XRF measurements simultaneously on the same spot on the sample surface.<sup>338</sup> The instrument was described in detail, in the paper. However, it had a conventional copper X-ray source and a single X-ray detector on a computer-controlled XY stage. There was a necessity to obtain several hundred spectra which lengthened the time required for analysis. However, this could be somewhat compensated for by using variable acquisition times, depending on the count rate obtained from individual samples. Data filtering and analysis was undertaken offline by using an algorithm written in the programming language Python. The results obtained from the instrument were sufficiently encouraging to

spur the authors into starting the development of a more compact and portable instrument.

A paper by Pospisilova *et al.* described the use of LA-ICP-MS to elucidate provenance of natural clay-based pigments in paintings.<sup>339</sup> An ArF laser operating at 193 nm and at  $3.7 \text{ J cm}^{-2}$  with a repetition rate of 10 Hz was used with a scan rate of  $20 \text{ } \mu\text{m s}^{-1}$ . The laser spot size was a critical parameter. If it was less than  $65 \text{ } \mu\text{m}$ , results were very poor. There was no marked improvement if the laser spot was increased from  $65 \text{ } \mu\text{m}$  to  $110 \text{ } \mu\text{m}$  and therefore a spot size of  $65 \text{ } \mu\text{m}$  was used throughout. Four CRMs were used: a silicate-based one (NIST 612 glass), a carbonate-based one (SARM 40) and two clay-based ones (GW 03101a and GBW 0303). These were pressed into pellets before LA-ICP-MS analysis. In addition to the use of CRMs, further method validation was undertaken by acid decomposition of some of the certified materials followed by ICP-OES determination, analysis by a second laboratory for the silicate content and by SEM-EDS. Having identified that same results were being obtained by all the techniques, the authors used the LA-ICP-MS system and SEM-EDS to analyse a painting entitled "portrait of a horse". Although complications could arise through the artist's use of dirty brushes, it was possible to differentiate between different ground preparatory layers. Historically, these layers were made of red clays from three different locations in Europe (Czech, Italian and German boles). This work proved that the clay used in the preparatory layer on this painting originated from Bavaria in Germany.

A paper by the same research group determined the influence of laser wavelength and laser energy on the depth-profiling of easel painting samples.<sup>340</sup> When undertaking such analyses, it is necessary to minimise the damage caused, hence the paper optimised the laser pulse parameters to obtain sufficient resolution whilst ensuring that crater size is minimised, there is no peripheral heat-induced damage to pigments, *etc.* Two different wavelengths were used. A Nd:YAG operating at 532 nm and 10 ns pulse duration and a Nd:YAG operating at 266 nm with a pulse duration of 5 ns. The effects of altering the laser power at each wavelength was also tested. In general, the lower wavelength provided better data. The laser power also had an effect, with the higher energy ones giving larger craters. An unsurprising finding was that the number of laser firings at a single spot should be optimised so as to cause least damage. One interesting finding was that F could be determined as CaF during depth-profile studies.

#### 4.1 Metallic artifacts of cultural heritage

The analysis of cultural heritage materials in the field of non-ferrous metals has received a significant amount of work during this review period. However, the papers that give very little scientific detail will not be covered in this review. Those papers that give a good description of the science or on how the analytical data are treated are summarised in Table 5. The same rationale has been applied to samples that are organic in nature, ceramics and glasses. Applications of the analysis of these are given in Tables 6–8, respectively.

#### 4.2 Cultural heritage samples of organic origin

For the cultural heritage field, the need for analytical techniques that can handle minute sample amounts and that are minimally destructive are still the main focus of developments. A micro-scalpel sampling method has been developed.<sup>355</sup> High precision controllers are utilised to maneuver the scalpel in all three dimensions at micrometre precision. In addition, the angles at which the scalpel meets the sample surface can be adjusted. This portable device allows the sampling of a minimal amount of material directly from a sample cross-section (width  $10\text{--}50 \text{ } \mu\text{m}$ ) and the overall sampling procedure takes approximately 10 min. This results in a very operator friendly device that minimises the destructive nature of this sampling technique. The developed device was utilised to analyse the paint layers ( $100\text{--}200 \text{ } \mu\text{m}$ ) of a mock sample containing of individual layers of lead white, titanium white, lead white, and lead-tin-yellow. The lead containing layers of this mock sample, as well as the paints used to create this, were analysed using multi-collector ICP-MS to determine the Pb isotope composition. The ratios obtained for the respective layers were indistinguishable from the pigments used to create them illustrating that no contamination between the layers was present.

A very common issue encountered when analysing paintings is that varnishes and binders can cover up emission from underlying paint layers. This is because signals measured in the nanosecond time scale often only reveal emission from the most fluorescent materials, *i.e.* binders and varnish. A multi-spectral time-gated photoluminescence imaging approach was utilised to overcome this.<sup>356</sup> It enabled the differentiation of luminescent pigments, based on their different emission spectra but also the lifetimes of these. Owing to the time gated detection it was possible to distinguish the fast-living (lifetime of nano- or picoseconds) from long-living emitters (lifetime of microseconds or milliseconds). Hence, trap state emission of semiconductor pigments could be recorded, which otherwise would have been covered by the intense fluorescence of the organic compounds. For this purpose, a Q-switched laser source ( $\lambda = 355 \text{ nm}$ , pulse energy  $700 \text{ } \mu\text{J}$ , pulse duration  $1.0 \text{ ns}$ , repetition rate  $100 \text{ Hz}$ ) was spectrally filtered by an excitation filter and coupled to a silica optical fibre (diameter  $600 \text{ } \mu\text{m}$ ). A uniform excitation over the field of view ( $10 \text{ cm}$ ) was achieved by projecting and magnifying the optical fibre head through a magnifying optical telescope. A time-gated intensified camera was utilised for detection, which was created by optically combining an image intensifier (temporal width adjustment from  $5 \text{ ns}$  to continuous mode) with a cooled monochrome digital camera and a  $50 \text{ mm}$  objective. Spectral resolution was achieved by using a filter wheel equipped with 10 band pass transmission filters ( $400\text{--}850 \text{ nm}$  spaced by  $50 \text{ nm}$ ). The developed set up could then be utilised to record nanosecond and microsecond emissions and was applied to the analysis of two Maimeri paintings (*Ana a tavola* and *Vista del Colosseo dai Giardini*). Emissions induced by the crystal defects in semiconductor pigments (microsecond timescale) were captured in addition to those at the nanosecond timescale.



Table 5 Applications of the analysis of cultural heritage materials that are non-ferrous in nature

Analytes	Matrix	Technique	Comments	Reference
Ag, Au, Cu and Pd	Gold artefacts from the Punic era stored in Cadiz, Spain	Portable XRF	A zinc filter was used to absorb the gold signal, enhancing the Pd signal (LOD without the filter = 0.17 wt%, LOD with filter = 0.07 wt%). However, to maintain an acceptable precision (<10% RSD) an increased analysis time to 600 s was required. Ternary plot of Ag, Au and Cu was prepared that also showed those samples containing Pd. Most samples had <2.5% Cu, indicating it was not added deliberately. Over 25% of samples had detectable Pd, indicating access to a Pd-containing gold source	341
Various	Archaic Athenian silver coins	EDXRF	Near surface analysis of 788 silver coins with the aim to separate different sources of the silver. Method validation through the analysis of 13 CRMs. Instrument drift checked through periodic analysis of one sample. Ternary diagrams plotted for Au–Cu–Pb and for Au–Bi–Pb. Analytes with concentrations > LOD had their data treated using PCA. The analytes Au, Cu and Pb accounted for 56% of the variation, although other analytes, e.g. Cr, Ni, Sn and V were also present in many samples. Nine types of coin analysed. Experimental data indicates very little re-cycling of the metals	342
Various (8)	56 bronze weapons of small and normal size from Chengdu, China.	MC-ICP-MS ICP-OES	A rare example of where sample was acid digested for analytes (ICP-OES) and Pb isotopes (MC-ICP-MS) to be determined. Most normal-sized weapons had the same Pb isotope ratios as the small weapons indicating the same ore origin. One weapon did not; indicating it had been imported. Metallographic analysis demonstrated flaws in the small weapons indicating they were ceremonial and produced only for burial. The normal-sized weapons usually had more Sn or Pb alloying elements than the small ones	343
Various (10)	Two bimetallic sword fragments from ancient China	Neutron diffraction Neutron resonance transmission imaging	The two techniques were used to characterise the presence and distribution of phases (neutron diffraction) and elements (neutron resonance transmission imaging) in the samples. The latter was possible because of a position-sensitive gas electron multiplier (n-GEM) detector. Spatial resolution was approximately 1 mm	344
Various	Glass flute components	Portable XRF ICP-OES ICP-MS	Portable XRF used to analyse keys, springs and other fittings of glass flutes. The reference material NIST 610 was used to validate p-XRF glass analysis. Eight alloys were used for metal analysis validation. Both ICP-OES and ICP-MS were used for validation purposes after glass and metallic reference materials had been acid digested. Metallic components comprised a silver–copper alloy for all visible metal pieces (for aesthetic purposes), bronze was used for components requiring more mechanical resistance and some steel parts used for some other smaller parts. The glass was of a potash-lime-silica type	345
Various	Metal layers on watch cases	LA-ICP-MS XRF, SEM	Laser operating at 193 nm and 4 ns pulse duration used for LA. Eight varied reference samples with defined layer depth and composition used for calibration/validation. Results of LA-ICP-MS compared with those from XRF. Layer thickness also determined using SEM	346
Various + Pb isotopes	Lead coins	MC-ICP-MS XRF	Between 10 and 50 µg of material taken from already damaged parts of the coins and then acid digested. Alternatively, cotton swabs taken and then leached into 1 M nitric acid. Binary plots of Cu against Sn, Cu against Ag and Sn against Sb as well as $^{208}\text{Pb}/^{206}\text{Pb}$ against $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ against $^{207}\text{Pb}/^{204}\text{Pb}$ . Clear groupings of coins observed. Three different origins of Pb observed throughout the time period investigated	347

Table 5 (Contd.)

Analytes	Matrix	Technique	Comments	Reference
Various	Historical copper alloy aquamanilia	Portable XRF; LIBS	Material composition of seven historical artefacts analysed using XRF and LIBS. Four figures were cast using quaternary and ternary copper alloys containing Zn at 17.5–23% and a mixture of Sn and Pb below 7%. Some samples identified to be copies made in the 18 <sup>th</sup> to 20 <sup>th</sup> centuries rather than being medieval. XRF and LIBS data were in reasonable agreement. Analytical data treated using PCA. However, the authors acknowledged that the procedure was not without problems that arose through many sources. A decent discussion was given as explanation	348
Various	Sasanian coins	LIBS	Depth-profiling using a variant of calibration-free LIBS to determine thickness and homogeneity of a mercury layer on the surface of a silver-based alloy. The variant was entitled “calibration-free inverse method”. A copper-based alloy was used as a standard since the method used did not require a standard matrix matched to the sample. The data obtained were in good agreement with those obtained previously using a destructive XRF method that required a cross section to be analysed	349
Various	Islamic oil lamps from 10 <sup>th</sup> to 13 <sup>th</sup> centuries	Portable XRF	Monte Carlo technique used in conjunction with p-XRF for analysis of lamps. Corrosion layers/patina <i>etc.</i> were not problematic as Monte Carlo procedure enables analysis of the bulk alloy without need for removal of surface layers. The technique is therefore completely non-destructive. The structure and composition of the surface layers were also determined	350
Various	Copper-based coins from Byzantine period	μ-XRF ICP-OES	Initial XRF analysis to identify elements other than copper present in the sample in a semi-quantitative manner. Micro-destructive technique then adopted. A tungsten carbide drill bit was used to drill through the edge of the coin towards the centre and sample removed was then acid digested prior to ICP-OES analysis. Analytical data pre-processed using column autoscaling and then interrogated using PCA. Temporal trends over 120 year period observed	351
Various	Spanish coins recovered from shipwrecks off Western Australia	LA-ICP-MS	Coins pre-cleaned using 10% nitric acid to remove concretion. Then LA-ICP-MS conducted, leaving a crater 50 μm wide and 75 μm deep. Although data collected was not fully quantitative, linear discrimination analysis (LDA) was used enabling coins of known provenance to be sorted into identifiable sub-groups. Then, 27 coins of unknown origin were analysed and their origin predicted from the LDA model	352
Various	Tarnish on Daguerreotypes	XRF XANES SEM-EDS	The XRF visualised the Cl and S on the surface whereas the XANES identified the primary components of the tarnish to be AgCl and Ag <sub>2</sub> S. However, Au <sub>2</sub> S, Au <sub>2</sub> SO <sub>4</sub> , HAuCl <sub>4</sub> and HgSO <sub>4</sub> also observed to be minor components	353
Various	Sagunto Ibero-Roman votive bronze statuettes	Portable XRF	Portable XRF instrument used in two modes: full contact with sample and at an angle. Full contact mode provided better precision. Accuracy of the analysis validated through analysis of the reference material BAS-CURM50.04-4, an alloy of copper, tin and lead (plus Fe, Ni and Sb). Twenty statuettes analysed. Analytical data treated using PCA. It was possible to differentiate the statues according to their smelting and manufacturing processes as well as their chronology	354

The analysis of *painting under-layers can help shed light on the processes involved in creating canvases* and generally gain a greater understanding of these under-layers and the

preparatory process. For this purpose, a computer-assisted thread-level canvas analysis algorithm was optimised to measure the spacing and angles of canvas threads.<sup>357</sup> The

Table 6 Applications of the analysis of organic cultural heritage samples

Analyte	Matrix	Technique	Comments	Reference
Multiple	Miniature portraits on ivory	High resolution XRR, MA-XRF, micro-XRD, environmental SEM-EDS incorporating water vapour in specimen chamber	MA-XRF visualised secondary interventions and gave rise to analytical information from all layers including the ivory itself. Micro-XRD was utilised to identify the phase composition as well as the crystal structure of the pigments. On one of the three portraits a thin degraded organic layer was identified by environmental SEM	359
Ca, Cu, Fe, Hg, K, Mn, Pb, Zn (as identified by XRF)	Canvas “the meeting of the pilgrims with the Pope” by Vittore Carpaccio	Vis-IR imaging, XRF	Integration of multispectral Vis-IR imaging with XRF spectrometry aimed at pigment mapping of large areas. After a multi-spectral scan of the canvas (380–2550 nm, special step of 250 $\mu\text{m}$ , bandwidth 20–30 nm for Vis range and 100 nm in NIR range), XRF spectrometry (Ag anode, maximum 50 kV, 40 mA) was performed on 47 selected spots with a spatial resolution of 3 mm using an acquisition time of 60 s. These could then be spatially referenced to the multi-spectral image cube. PCA was utilised to determine the effectiveness of the representation compared with the individual analysis of the two sets of data. Applying this method allowed the identification of defined clusters linked to different red pigments used	360
$^{14}\text{C}$	Painting	AMS as $\text{CO}_2$ following combustion	Radiocarbon dating utilised to identify post 1950 forgeries. The varnish had been removed prior to analysis of the organic binder (19 $\mu\text{g}$ carbon). The minute samples size was overcome by coupling an elemental analyser directly to the gas ion source of the AMS. The painting ( <i>Village Scene with Horse and Honn &amp; Company Factory</i> ) was signed May 5, 1866 AD. This could be refuted by the $^{14}\text{C}$ dating of the oil binder which matched the 20 <sup>th</sup> century nuclear period due to the access in $^{14}\text{C}$ . In addition, the seeds from which the oil was extracted were dated post 1950	361
Multiple	Rock paintings	pXRF	Analysis 35 figures in the north western part of the Erongo (Namibia) in black, white and red rock paintings. Excitation was achieved by a Rh anode providing a beam spot size of 1.2 mm. A fast Si drift detector with an active area of 25 $\text{mm}^2$ was utilised. Two different black and white pigments were identified. Iron oxide was used for red paintings	362
Multiple	Painting (floral painting)	LIF	A KrF excimer laser (248 nm) which is highly absorbed by coating materials was utilised for its selectivity and therefore the controlled cleaning process. The LIF was applied to monitor the cleaning process <i>in situ</i> as it utilised the same but attenuated laser beam at 0.005 $\text{J cm}^{-2}$ . The spectra of 300 single-laser shots were accumulated to assess the surface	363
Pigments with spectral range of 400–2500 nm	Chinese scroll paintings	XRF	An automated hyperspectral scanning system equipped with a two-dimensional horizontal scanning platform was developed. A line halogen lamp was designed to avoid heating effects. The hyperspectral camera, consisting of a visible and near IR (VNIR) imaging camera and a short wave IR (SWIR) camera, was utilised in line scanning mode. Scanning rate, illumination intensity and imaging rate were optimised to achieve a spatial resolution of 0.5 mm. The obtained data were linked to a reference library of the most common traditional Chinese pigments to identify those in the paintings. The developed system in combination with MA-XRF was applied to portrait of Bazalibudala Arhat and was able to identify most pigments and molecules of different vibrational overtones	364

algorithm identifies the individual thread trajectories based on X-radiographs that had previously been digitalised at a spatial resolution of 42.3  $\mu\text{m}$  per pixel. The centre-to-centre distances between threads and the thread angle relative to the X-axis at each point along its length can then be extracted. This was achieved by extracting the canvas features from the digital X-radiograph image based on the difference in optical thickness of the radiopaque ground layer (difference of thickness of threads and the space in between them). Following that, a Bayesian machine-learning model was trained and deployed to automatically detect thread centres based on the thickness differences. Finally, the response was used to trace each thread in the canvas which can be visualised in thread spacing and thread angle maps. This approach was applied to *Girl with a Pearl Earring* (Vermeer). The thread count of  $14.8 \pm 2.7$  threads per cm horizontally and  $14.6 \pm 3.6$  threads per cm vertically was comparable to previous Vermeer works and could indicate that this was a preferred choice of canvas. In addition, the results compared well with those obtained in a previous study within the stated uncertainty of the counting method. Thread angle maps highlighted deviations in thread angles, which showed wave-shaped distortions extending more than 5 cm into the picture plane. These are indicative of the points where the edges of the painting were laced onto a larger frame before applying the ground layer, so called primary cusping.

As was seen in last year's review, the challenge of handling large amounts of data produced by various spectroscopy

techniques remains a focus of the scientific community. To aid classification of Chinese red seal inks an orthogonal partial-least-squares discriminant analysis (OPLSDA) methodology was developed.<sup>358</sup> The aim was to sort ink samples based on their plume fluorescence spectra (250–750 nm). The developed approach maps training observations from wavelength, latent variable and class spaces. It illustrates the similarity of an unknown samples compared with results obtained for training samples and can calculate the class membership probability. It was shown that samples assigned a class membership probability of >80% were correctly sorted 99.5% of the time. The developed method was superior compared with an alternative classification approach in terms of sensitivity (98.9%), specificity (99.8) and false in-class rate. This is a very useful data processing approach for single Japanese ink samples and therefore mainly applicable to the analysis of documents or scriptures. It would be interesting to see if it would be possible to apply this approach to more complex samples, such as ink mixtures or inks from different geographical locations. Other examples of the application of atomic spectrometry to the analysis of organic materials are shown in Table 6.

#### 4.3 Ceramic materials of cultural heritage

See Table 7.

Table 7 Analysis of ceramics of cultural heritage

Analyte	Matrix	Technique	Comments	Reference
Various	Early bronze age pottery from Tigris valley (Turkey)	Polarised EDXRF XRD SEM-EDS Optical microscopy	Twelve samples analysed. The XRD demonstrated that a firing temperature of between 700 and 950 °C was used. Small amounts of each of six samples were ground into a powder for EDXRF analysis. Hierarchical cluster analysis used on data obtained from XRF. Two main groups of pottery identified: calcareous and non-calcareous. The cluster analysis of SEM-EDS data indicated three groups: the same as above plus an intermediate calcareous group. This intermediate was not one of the samples analysed using EDXRF	365
Various (29)	Late Roman period amphorae from Spain	XRD, XRF, optical microscopy	Portions of amphorae ground in a mill and then either fused into a glass pellet (0.3 g of sample + 6 g of lithium tetraborate) for major and minor elements or pressed into a pellet (5 g of sample + agglutinating agent at 200 kN) for trace elements. Cluster analysis and PCA of analytical data showed three clusters with two kilns being clearly identified and a third cluster being a mixture from two kilns. The XRD identified firing temperature ranges at each kiln	366
Various (13)	East Asian blue and white porcelain	Portable XRF, XRD	Discrimination attempted between Chinese and Japanese blue and white porcelains. A Corning A glass reference material was used as method validation. Although 13 analytes determined, only seven had data treated using PCA. The PCA analysis clearly segregated samples from the two Chinese kilns. The products from Japanese and Chinese kilns were largely separated, although a few samples confused the issue. This was attributed to the Co-based pigment being used in Japan in these samples having potentially been imported from China	367

Table 7 (Contd.)

Analyte	Matrix	Technique	Comments	Reference
Various	Catalan pottery	EDXRF	Provenance study of Catalan pottery undertaken from six different villages. Samples analysed using EDXRF with reference materials BAS BCS-315 and ECRM 776-1 firebrick being used as method validation. Analytical data treated using Supervised Machine learning algorithms and unsupervised methods. For the supervised methods, training sets of samples of known origin are required. The algorithms used were: weighted k nearest neighbour, Random Forest, artificial neural network, linear discriminant analysis (LDA) and general linear models. Unsupervised models included hierarchical cluster analysis, k-means and PCA. The unsupervised models failed to distinguish pottery from the different villages, whereas the supervised models succeeded; even though the villages were in close proximity to each other	368
Various	Pottery	LIBS	Pottery produced in Brazil differentiated from those from abroad using LIBS followed by chemometric analysis of the data. Chemometric tools used were: PCA to first screen the data and then LDA and soft independent modelling of class analogy (SIMCA). The Brazilian pottery was identified as having higher Ca content. Three datasets investigated for both LDA and SIMCA: total spectrum, spectral bands and maximum intensities. SIMCA proved unreliable with most samples not being distinguishable for all three data sets. However, LDA was more successful, with 100% of test samples being identified correctly when using the total spectrum, decreasing to 86.7% being correctly assigned when using maximum intensities	369
Various (Al, Ca, Fe, Mg and Si)	Chinese ceramics from different dynasties	LIBS	The LIBS operating conditions were optimised carefully prior to the study. Analytical data were pre-processed (mean centering yielded best performance although other methods, <i>e.g.</i> no pre-processing, normalising, regularising, Savitzky–Golay smoothing, first order derivative and second order derivative, also performed well). The results of this underwent a generalised sequential backward selection system which was described in full with the aid of a schematic diagram. The aim of this was to select the assessment criteria. These were: accuracy, sensitivity and specificity. The output from this was then inserted to Random Forest. The whole process proved to be successful in differentiating different dynasty ceramics	370
Various	Ancient Chinese ceramics	EDXRF	Several algorithms used on the analytical data (Random Forest, Adaboost, k-nearest neighbour and support vector machine. Of these, the Random Forest provided best classification (96.41% on the “leave one out” cross validation). Mahalanobis distance also calculated for each sample. Celadons classified according to provenance	371
Various	Archaeological ceramics from South India	EDXRF XRD FT-IR SEM-EDS	Samples were finely powdered in an agate mortar and pestle and then pressed into pellets for analysis. Analytical data treated using cluster analysis, PCA and factor analysis. Three PCA groupings of elements were identified. Group 1 had Na, Fe, Ge, Ti, Mn, Te & Ca, group 2 contained Al, Zn and K and group 3 contained Si, O, Sr and Mg. Cluster analysis identified three clusters, meaning that even in only eight samples, there were three distinct groupings	372
Various (11)	Algerian archaeological pottery	Portable XRF	Samples (44) from five sites underwent p-XRF analysis from at least two different points on the sample. Cluster analysis of the data indicated two groups of samples, although the distinction was not absolutely clear because one source of clay seemed to be used throughout. However, there was a difference in the lead glaze used which enabled tentative distinction	373
Various (11)	Ancient ceramics	LIBS	The laser wavelength was 1064 nm, the pulse width was 6 ns, the laser operating frequency was 5 Hz, and the laser pulse energy was set to 120 mJ. Analytical data analysed using PCA and kernel PCA (KPCA). A back propagation neural network was then also applied to both methods. The KPCA could distinguish the samples of different origin better than PCA alone. When the back propagation was used, the KPCA had a recognition rate of 99.38% for samples from different regions and 95.83% from similar regions. The equivalent PCA values were 96.25% and 85%. The method enabled quick, accurate on site measurement and identification	374

#### 4.4 Glass materials of cultural heritage

As always, there has been interest in the analysis of glasses of cultural heritage. However, this remains a relatively small

section compared with the other sample types. Again, most papers concentrate on causing minimal damage during the actual analysis and then use chemometric techniques to try and

Table 8 Analysis of glasses of cultural heritage origin

Analyte	Sample	Technique	Comments	Reference
Various	European glass beads found in Angola	Portable XRF LA-ICP-MS Variable pressure SEM-EDS $\mu$ -Raman	Samples analysed using p-XRF to gain semi-quantitative data to identify samples to be analysed using LA-ICP-MS. The LA-ICP-MS analysis was undertaken at 4–12 spots on the beads. Calibration was against NIST 612 glass, which was also used periodically to determine the amount of drift. Ternary diagrams of Na <sub>2</sub> O, MgO + K <sub>2</sub> O and CaO identified four clear classes of glass: natron-soda lime, plant ash soda-lime, mixed soda-potash and forest plant ash potash-lime. Different elements found to be associated with the different colours, <i>e.g.</i> Co was associated with As, Ni and Zn in blue beads. The trace elements, especially rare earth elements (REE) helped with provenance studies	375
Various	European glass beads found in Angola	Portable XRF LA-ICP-MS Variable pressure SEM-EDS $\mu$ -Raman	Very similar study to the one above	376
Various	Reverse glass paintings	XRF	Multiple analysis sites (3) per sample. Analytical data treated using hierarchical cluster analysis and PCA. Both techniques identified three sub-groups when the whole spectrum between 2 and 16 keV was analysed. When only a partial spectrum was analysed (between 3 and 4 keV), the same three groups were identified: group 1 samples contained huge concentrations of Pb; group 2 comprised Pb (but at a lower concentration than group 1) and Sr. The third group contained low concentrations of Pb and Sr	377
Various (58 isotopes)	Glass from late second to early 5 <sup>th</sup> century	LA-ICP-MS $\mu$ -XRF	A successful study to find provenance and chronology of glass samples, but also to identify the extent of glass re-cycling. Small fragments of glass were mounted in epoxy blocks and polished before analysis using an excimer laser operating at 193 nm, 5 mJ and at a repetition rate of Hz. Craters with diameter of between 60 and 100 $\mu$ m and a depth dependant on ablation time, but typically 150 $\mu$ m were produced. Method validation achieved using Corning A and NIST 612 reference glasses. Data interrogated using PCA. Nine sub-groups were identified: Sb-only, two different groups of Mn-only, four groups of mixed Mn-Sb, high iron, manganese and titanium and a last group that had no de-colouring agent	378
Various (33)	Glass from 11 sites in Southern Italy	LA-ICP-MS Electron microprobe analysis (EMPA) XRD SEM-EDS	Samples (61) analysed dating from 22 <sup>nd</sup> to 6 <sup>th</sup> century BCE. A Nd:YAG laser operating at 266 nm used for analysis. NIST 612 used for method validation. The combination of the four analytical techniques enabled the raw materials and manufacturing techniques to be identified as well as giving a chronology. Numerous glass types also identified, including plant ash glass, mixed alkali and natron	379
Various	57 glass samples from 40 beads from Poland covering approximately 800–250 BCE	LA-ICP-MS	NIST 610 and Corning glasses B and D used for method validation and drift correction. Three replicate single ablation measurements at random points measured for each sample. Precision was typically <5% RSD for major elements and <10% for minor and trace ones. Of the 57 pieces analysed, 5 were high magnesium glass (prepared using halophyte plant ash) and 52 were low magnesium glass (prepared using mineral soda, <i>e.g.</i> natron). Some evidence of semi-finished products transported to European workshops where they were coloured and/or opacified	380
Various	Glass from a mosaic in a Roman Villa in Spain	LA-ICP-MS SEM-EDS XRPD	Laser operating at 193 nm used. Method validation achieved using NIST 612 and Corning A and B. An array of statistical methods used: nonparametric two-tailed Mann-Whitney U-test, for pairwise comparison as well as a Kruskal-Wallis test, followed by a <i>post hoc</i> Dunn's multiple comparison test, and Welch's analysis of variance (ANOVA) with a Games-Howell <i>post hoc</i> test (for multiple comparisons) as well as PCA. The tesserae were almost exclusively Mn and Sb base glass, indicating recycling was common-place. A subset of red, green and orange tesserae had distinct base-glass characteristics and could originate from Egypt	381

Table 8 (Contd.)

Analyte	Sample	Technique	Comments	Reference
Various (58)	Roman glass from Alicante, Spain	LA-ICP-MS	Analysis of 60 samples from 4 <sup>th</sup> and 5 <sup>th</sup> century BCE. NIST 610 and 612 as well as Corning B, C and D used for calibration and method validation/drift control <i>etc.</i> Statistical comparison with glasses of known origin in the literature indicated that the glasses had been imported from eastern Mediterranean, probably Egypt. Two main sub-classes identified: high iron magnesium and titanium a and high iron magnesium and titanium b. This was potentially a result of geopolitical changes with time	382
Various	Stained glass windows	Macro-XRF	Thought to be the first application of such a technique to stained glass. Completely non-destructive method. A description of the instrument was given in the paper. The study concluded that it was possible to assess the structural integrity of the window; distinguish groups of glass panes with a similar composition and outliers within the same panel; differentiate glass paints, especially modern ones and to document glass alteration	383
Various	Late bronze age glass beads	LA-ICP-MS	Glass beads (37) on string of beads were analysed. NIST 610 and 612 used for calibration. Corning A was used once before and once after each run to check for drift. Beads were soda lime-silicate, however, two distinct groups were identified. These were: high and low magnesium (as shown by a biplot of MgO against CaO). Two samples were outliers – possibly because they came from a different batch or source. The glasses were identified as probably coming from Mesopotamia rather than Egypt.	384
Various	Glass beads from lower Nubia, Sudan	LA-ICP-MS	A Nd:YAG laser operating at 213 nm was used. NIST 610 and Corning glasses used for calibration and validation. Precision was between 1 and 5% RSD for major elements and between 1 and 10% for trace elements. Four main glass types identified: Low-alumina soda-lime glass, high alumina glass, plant ash soda-lime glass and mixed alkali glass. A small subset was identified as being mineral soda-high alumina. Most glasses originated from eastern Mediterranean. However, the mineral soda – high alumina sub-set originated in Sri Lanka or South India	385
Various	Glass from the Celtic Oppidum of Trisov, Czech Republic	LA-ICP-MS SEM-EDS	Samples embedded in epoxy resin and polished before analysis using a 213 nm laser yielding a spot size of 65 $\mu\text{m}$ , with a repetition rate of 10 Hz and power of 8 J $\text{cm}^{-2}$ . Corning glasses A and B used to monitor accuracy and precision. Glasses were identified as being of natron type similar to that originating from Syria	386

elucidate provenance or sample preparation methods. It was noted that the majority of the glass applications tended to have greater quality control, *i.e.* reference or certified reference materials were usually analysed. This is far less common during the analysis of ceramics, possibly because of the lack of suitable materials.

## Glossary of terms

2D	two dimensional
3D	three dimensional
AAS	atomic absorption spectrometry
AES	Auger electron spectrometry
AF4	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
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
DRC	dynamic reaction cell
EAST	experimental advanced superconducting tokamak
EDS	energy dispersive spectrometry
EDXRD	energy dispersive X-ray diffraction

EDXRF	energy dispersive X-ray fluorescence	MIP	microwave induced plasma
ELM	extreme learning machine	MIP-AES	microwave plasma atomic emission spectrometry
EPMA	electron probe microanalysis	MS	mass spectrometry
ESI-MS	electrospray ionisation mass spectrometry	NAA	neutron activation analysis
ETAAS	electrothermal atomic absorption spectrometry	NAAR	neutron activation autoradiography
ET	electrothermal vaporisation	Nd:YAG	neodymium doped-yttrium aluminium garnet
EXAFS	extended X-ray absorption fine structure	ND	neutron diffraction
FAAS	flame atomic absorption spectrometry	NEXAFS	near edge X-ray fine structure
FFFF	flow field flow fractionation	NIST	National Institute of Standards and Technology
FI	flow injection	NMR	nuclear magnetic resonance
FIB	focused ion beam	NRA	nuclear reaction analysis
FI-CVG	flow injection chemical vapour generation	OES	optical emission spectrometry
FTIR	Fourier transform infrared	PBS	phosphate buffered saline
FWHM	full width at half maximum	PCA	principal component analysis
GC	gas chromatography	PCR	principal component regression
GD-MS	glow discharge mass spectrometry	PET	polyethylene terephthalate
GD-OES	glow discharge optical emission spectrometry	PGAA	prompt gamma neutron activation analysis
GI-SAXS	grazing incidence small angle X-ray scattering	PGM	platinum group metals
GIXRD	grazing incidence X-ray diffraction	PIGE	particle induced gamma ray emission
GIXRF	grazing incidence X-ray fluorescence	PIXE	particle-induced X-ray emission
HG	hydride generation	PLS	partial least squares
HPLC	high performance liquid chromatography	PLS-DA	partial least squares discriminant analysis
HR-CS-	high resolution continuum source atomic	PLSR	partial least squares regression
AAS	absorption spectrometry	ppb	parts per billion
IAEA	International Atomic Energy Agency	ppm	parts per million
IBA	ion beam analysis	RAFM	reduced activation ferritic/martensitic
ICA	independent component analysis	RBS	Rutherford backscattering spectrometry
ICP	inductively coupled plasma	RDA	regularised discriminant analysis
ICP-MS	inductively coupled plasma mass spectrometry	REE	rare earth elements
ICP-OES	inductively coupled plasma optical emission spectrometry	rf	radiofrequency
ICP-QMS	inductively coupled plasma quadrupole mass spectrometry	RIMS	resonance ionisation mass spectrometry
ICP-TOF-	inductively coupled plasma time-of-flight mass	RMSECV	root mean square error of cross validation
MS	spectrometry	RSD	relative standard deviation
ID	isotope dilution	SEC	size exclusion chromatography
IL-	ionic liquid-dispersive liquid-liquid	SEM	scanning electron microscopy
DLLME	microextraction	SEM-EDS	scanning electron microscopy-energy dispersive spectrometry
IP	Institute of Petroleum	SF	sector field
IRMS	isotope ratio mass spectrometry	SIA	sequential injection analysis
ISO	International Organisation for Standardisation	SIBS	spark induced breakdown spectrometry
JET	Joint European Torus	SIMCA	soft independent modelling of class analogy
K-SVM-	k-fold support vector machine recursive feature	SIMS	secondary ion mass spectrometry
RFE	elimination	SNR	signal to noise ratio
LA	laser ablation	SP	single particle
LASIL	laser ablation of sample in liquid	SR	synchrotron radiation
LC	liquid chromatography	SRM	standard reference material
LDA	linear discriminant analysis	SXRF	synchrotron X-ray fluorescence
LIBS	laser induced breakdown spectrometry	SVR	support vector regression
LIBS-	laser induced breakdown spectrometry-laser	STXM	scanning transmission X-ray microscopy
LAMS	ablation mass spectrometry	TEM	transmission electron microscopy
LIF	laser induced fluorescence	TGA	thermogravimetic analysis
LIPS	laser induced plasma spectroscopy	TIMS	thermal ionisation mass spectrometry
LOD	limit of detection	TOF	time of flight
LOQ	limit of quantification	T-PGAA	time-resolved prompt gamma activation analysis
MALDI-	matrix-assisted laser desorption ionisation time-of-	TPR	temperature programmed reduction
TOF	flight	TXRF	total reflection X-ray fluorescence
MALS	multi-angle light scattering	UOP	universal oil products standards
MC	multicollector	USGS	United States Geological Survey
		UV-VIS	ultraviolet-visible



VUV	vacuum ultraviolet
WDXRF	wavelength dispersive X-ray fluorescence
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

## Conflicts of interest

There are no conflicts to declare.

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