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

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

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This update covers the literature published between approximately June 2021 and May 2022 and is the latest part of a series of annual reviews. It is designed to provide the reader with an overview of the current state of the art with respect to the atomic spectrometric analysis of various metals, chemicals and materials. These materials

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include ferrous and non-ferrous metals, glasses, polymers, ceramics, engineered nanostructures, fuels, nuclear materials, building materials, catalysts and electronic components. Also included is the analysis of forensic samples such as explosives and gunshot residue. It is not a comprehensive review of all papers that have used an atomic spectrometric technique. Instead, it includes only those papers that have some novelty through making an advance in either knowledge or the application of atomic spectrometry. Those papers that maximise the information gleaned from analytical data, *e.g.* the provenance of cultural heritage or forensic samples, through the use of chemometric analysis will also be included.

1   Introduction

This is the latest review covering the topic of advances in the analysis of metals, chemicals and materials. It follows on from last year's review[1] and is part of the Atomic Spectrometry Updates series.[2–6]

This year's review period has seen a significant upturn in the number of relevant papers. Increases in number for most sections were noted. An especially large increase was observed for the forensic sections. It was therefore decided to devote a section to forensic applications rather than have several sub-sections spread throughout the review. Since the ideal scenario is to leave the sample as undamaged as possible so that it may be used in the future, most of the forensic applications used non-destructive techniques such as assorted X-ray-based techniques or minimally damaging ones, *e.g.* LA or LIBS. This is common to cultural heritage samples too. Another aspect common to many sections is the significant use of chemometric packages to aid classification/identification. The fuels section was again noted for significant re-invention of wheels or the lack of validation for many papers. The analysis of nanostructures has become commonplace over the last few years. This has largely moved on from the method development of single particle ICP-MS to real-life applications and encompasses more than just engineered nanoparticles. Applications involving nano-polymers, single cell analysis and even single virus analysis have been presented.

1.1   Reviews of instrumental techniques

The ever-increasing popularity of laser induced breakdown spectroscopy (LIBS) has continued over this review period. This is because it is so versatile and can be used on virtually any sample type, both solid and liquid, with no or little sample preparation, causing minimal damage. It can also be used in standoff mode, *i.e.* it can analyse dangerous or unpleasant materials, *e.g.* explosives or nuclear materials from a safe distance. It may also be used in unpleasant working conditions, *e.g.* at the production sites at foundries where extreme temperatures are found. This "in-line" or "at-line" ability has the potential to save time, effort and money and is therefore very attractive. There are still a few problems associated with it, *e.g.* the difficulty in calibrating samples at different temperatures or different sample types, the analysis of uneven or rough surfaces, *etc.*, but intense research has been on-going to resolve these issues. Since the *popularity of*

LIBS has been rising over the last 10 years, it has started to attract useful review papers. An example was by Pedarnig *et al.* who produced a review (with 484 references) of elemental analysis of industrial materials by in-line LIBS.[7] As well as a brief introduction and theoretical overview, the review provided numerous examples of the analysis of materials including assorted alloys (ferrous, not-ferrous, scrap metal and metal melts), glass, fertilizers, foods, coals and other fuels, batteries and other electrical and electronic material (plus electronic waste materials), nuclear materials, papers, pharmaceuticals, wood and refractory materials. The review is a good perspective of the current state of the art for on-line LIBS analysis. Another example was presented by Goncalves *et al.* who reviewed the advances made in the last few years of LIBS analyses in environmental systems.[8] This review contained 85 references and focussed on environmental samples, *e.g.* soils, rocks *etc.*, but there were useful sections for lubricating oils and electronic wastes. A further review, by Zhang *et al.* containing 71 references discussed "remote LIBS applications".[9] Although written in Chinese, the papers cited are often in English and could be of use to the reader.

Li *et al.* reviewed (with 149 refs) *artificial neural network-based chemometrics applied during LIBS analysis*.[10] The authors discussed the different types of artificial neural network, how they are formed, trained and evaluated, what each type can do, made a comparison with other types and gave their limitations. Since these networks are so frequently used for LIBS analyses to enable identification of different glasses, polymers, alloys *etc.*, then this review is a very helpful contribution and is a good place to start for anyone new to the area and with limited knowledge of the subject.

One other LIBS review of note is worthy of mention. This was presented (with 86 references) by Xu *et al.* and was on the subject of *molecular emission from LIBS*.[11] Topics discussed included molecules of organic origin, *e.g.* –OH, –CH, –NH, –CN and C_2 and molecules formed to facilitate the determination of halides, *e.g.* CaF, CaCl, SrCl, *etc.* The review covers quantification of inorganic analytes as well as identification/classification of materials *e.g.* polymers and explosives.

Techniques other than LIBS have also been reviewed. A review with 185 references by Francischini and Arruda was entitled "when a picture is worth a thousand words: molecular and elemental imaging applied to environmental analysis: a review".[12] A useful table presented the advantages, disadvantages and resolution capabilities of: matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS), secondary ion mass spectrometry (SIMS), desorption electrospray ionization mass spectrometry (DESI-MS), Raman, LA-ICP-MS, LIBS and synchrotron XRF. Each of these techniques was also discussed in separate sections of the review giving a brief theory and applications. The majority of the applications were of environmental origin, but also included were nanoparticles and micro-plastics.

2   Metals

2.1   Ferrous metals

As usual, this has been an area of intense research activity, with much of it focussed on the use of LIBS. In previous review

periods, much of the interest in LIBS was focussed on calibration improvements. This has not been the case during this review period. Instead, the application of LIBS to the targeted analysis of inclusions and other applications such as underwater analysis, on-line analysis, *etc.* have become more popular. This section will describe these new LIBS applications as well as new areas of analysis using established techniques such as ICP-OES, ICPO-MS and AAS.

An interesting overview of the *determination of Si in stainless steels* using ICP-OES was presented by Franciscono and Rollet.[13] Since the samples need extremely harsh acidic conditions for dissolution, the Si may polymerise or form aggregates. Both of these species may not pass through the nebuliser/spray chamber assembly in a representative way, *i.e.* they may be discriminated against, hence yielding an apparent lower concentration than expected. This study investigated the experimental requirements necessary to prevent this from happening. Samples of several reference materials were dissolved using hydrochloric acid of varying concentration (12 M, 9 M or 6 M) with the addition of a few drops of hydrogen peroxide. Other parameters tested were the effects of filtration, dilution and aging of the digest. Higher concentrations of Si and higher concentrations of hydrochloric acid exacerbated the problems. The particles slowly dissolved with time, but too slowly to be useful analytically. It was concluded that the best dissolution procedure for each sample type should be elucidated rather than simply using a compromise.

Two papers have discussed the *effects of sample temperature on the LIBS analyses* of steels.[14,15] In the paper by Lin *et al.* the spectral intensity of both ions and atoms were reported to increase with increasing temperature.[14] However, the temperature of the plasma formed hardly changed (14 709 K and 14 227 K at 1432 °C (the melting point of the steel) and at 20 °C, respectively). It was noted that both the correlation coefficients and the root mean square error of prediction (RMSEP) for C (193.03 nm), Cr (205.56 nm), Mn (293.31 nm) and Si (288.16 nm) improved at 1432 °C compared with those at 20 °C. Although the correlation coefficients were better, the improvement was only marginal, *e.g.* from 0.9577 to 0.9832 for the Cr. However, the RMSEP improvement was significant for all four analytes, with the value for Cr improving from 1.24% to 0.27%. It was concluded that controlling the temperature of the smelting process aids the stability of the LIBS analysis. The other paper, by Chang *et al.*, described how the accuracy of the analysis decreases if the temperature of the sample is different to that at which the calibration model was produced.[15] Inevitably, it is impractical to produce a calibration for every temperature. Instead, these authors used Functioning Data Analysis (FDA) to produce a non-linear trend line using a calibration prepared at 20 °C as the input and elemental concentration as the output of a least squares support vector machine (SVM). This is a mathematical algorithm that is a set of supervised learning methods used for classification, regression and outlier detection. The model was built using nine reference material samples, of which five were used at room temperature to make the calibration model and at six elevated temperatures to construct the conversion model. The other four samples were used at three elevated temperatures and acted as "test" samples. Using these models, the spectra obtained at any temperature may easily be converted into the equivalent mapping at room temperature and hence input to the conversion model to obtain accurate concentration data. Using the methodology the relative error typically improved by an order of magnitude compared with data obtained when not using the models.

Another paper discussed *how LIBS data can be affected severely when the sample surface is uneven*.[16] These authors described how Bessel beams may be used to overcome the problem. Bessel beams are non-diffracting beams that have the advantage of extended linear focus, hence the laser beam has uniform fluence distribution. The authors discussed how a Bessel beam is produced from a Guassian beam and described the experimental setup. An alloyed steel tube and slanting steel pieces were used as samples. A total of 50 shots in different places on the samples were made which, on the curved surface of the 22 mm diameter tube, represented a change in measurement distance of 3 mm. The accuracy and stability of the measurements were determined through the correlation coefficient, the root mean square errors of cross validation (RMSECV) and the average RSD. The data obtained using the Bessel beams were significantly improved over those obtained using Guassian beams, with the average RSD for Mn improving from 24.78% to 10.12%. Similarly, the R^2 values improved from 0.933 to 0.956.

Several papers have continued to discuss *ways of improving accuracy of LIBS analyses through the use of multivariate regression methods or other statistical means*. Unfortunately, fiber-optic LIBS suffers from increased spectral interferences, matrix effects and self-absorption effects because the laser fluence is limited by optical fiber loss and attenuation. Chen *et al.* attempted to overcome these problems by comparing two linear models: Partial Least Squares (PLS) and Sparse Partial Least Squares (SPLS) as well as the non-linear model Support Vector Machine (SVM) during the fiber-optic-LIBS analysis of pig iron.[17] Of the three models tested, the SVM provided the best results, with coefficients of determination for the predicted concentration against the certified concentration for Cr, Mn, Ni and Ti being 0.9849, 0.9705, 0.9882 and 0.9837, respectively. The respective root mean squared errors of prediction were 0.0185%, 0.0982%, 0.0179% and 0.0178%. The conclusion was that SVM offers significant advantages in terms of accuracy when using fiber-optic LIBS. Another example was described by Yang *et al.* who took a different approach.[18] These authors stated that errors can be caused by noise, weak signals, self-absorption, matrix effects and the instability of the shot-to-shot signals. They used spectral pre-processing in the form of empirical mode decomposition to correct for the noise component, hence facilitating the analysis when weak signals are obtained. The empirical mode decomposition is a data-adaptive multi-resolution technique to decompose a signal into physically meaningful components. It can be used to analyse non-linear and non-stationary signals by separating them into components at different resolutions and reduces noise by refining the wavelet-scaling coefficients. The overall effect is that baseline signals are smooth and convergent. Its

performance was favourable when compared with other de-noising methods. The method was applied to the determination of Cr in austenitic stainless steels, resulting in improved correlation coefficients of calibration, reduced root mean square error values and the average relative error of the predicted Cr concentration decreased from 10.46% to 3.858%. It was again concluded that the methodology could be routinely used to improve the accuracy of LIBS analyses.

According to Deng *et al.* the accuracy of *single sample calibration LIBS can be severely undermined by self-absorption effects* which destroy the linear relationship between signal intensity and concentration.[19] They therefore developed a method of self-absorption correction. This was achieved by collecting spectra from the test and calibration samples under the same experimental conditions and then selecting one spectral line for each element or oxide. The shapes of the selected lines as well as the H_α line were then extracted for curve fitting through the Lorentz function, enabling the full width at half maximum (FWHM) of each line to be calculated. The relative self-absorption coefficient, K, may then be calculated and applied for the correction. A comparison of single sample calibration with and without this self-absorption correction was made during the analysis of alloy and iron ore samples. Using the self-absorption correction methodology for the alloys, the RMSEP decreased from 0.83% to 0.40% and the average relative error decreased from 13.75% to 4.06%. The results for the pressed ore samples were less impressive, but still offered a significant improvement; with RMSEP decreasing from 4.77% to 2.34% and average relative error improving from 90.48% to 14.60%. The method was simple, had good universality and does not require information such as the Stark half-width parameter. Consequently, the authors envisage it having great use for single sample calibration LIBS.

Song *et al.* developed a random forest-assisted artificial neural network model to improve the accuracy of Cr and V determinations in low alloy steel samples.[20] Several Fe wavelengths covering the entire spectrum were chosen as internal standards. The standardized spectral variables were then input to the RF-ANN with the calibration samples being used to first train and then verify the algorithm. The LIBS data obtained from certified steel samples using the random forest-artificial neural network methodology were compared with those obtained using a calibration curve and were far superior. The RMSECV for Cr and V were reduced from 0.060 and 0.042 using a calibration curve to 0.021 and 0.007, representing improvements of nearly three and six-fold, respectively. Additional advantages of the random forest methodology were that it used a large amount of spectral information and it used filters to remove redundant data thereby enabling a rapid training speed for the artificial neural network.

Two papers by the same research group have discussed the application of long-short, double pulse *LIBS* to the determination of Mn in underwater steel samples.[21,22] In the first example, by Cui *et al.*, it was emphasised that underwater LIBS suffers from numerous problems including self-absorption effects, weak signal intensity and low lifetime of the signal. These could all be overcome using Fraunhofer-type lines. During this experiment, the LIBS parameters were set so that the long pulse was of 30 μs duration and at a power of 100 mJ whereas the short pulse was of 7 ns with a power of 25 mJ. There was an inter-pulse delay of 15 μs, *i.e.* the short pulse was fired half way through the long pulse. Ten certified steel materials (YSBS451073-2013, YSBS37207-2015 and eight others from the 2015 series) were used as samples and these were submerged in deionised water such that the gap between them and the surface of the water was 100 mm. Measurement of the Mn was at 403.307 nm. This was used to calculate the optical density of the plasma formed. The optical density values and the certified Mn concentrations were used to construct a linear calibration curve ($R^2 = 0.9843$). Two of the certified materials were then used as test samples, with results indicating that the relative error of prediction was better than 10%. Overall, it was concluded that the use of Fraunhofer lines would be of great benefit to underwater LIBS measurements. The other paper by that group compared the long-short double pulse version of LIBS with conventional single pulse LIBS.[22] The long-short double pulse version gave a better stability and this was attributed to the long pulse causing a cavitation bubble without a plasma and then the short pulse creating a plasma within the bubble. The LIBS parameters of intra-pulse delay time, long pulse width and delay time were optimised. Results indicated that plasma stability and spectral signal intensity were greatly improved using a long pulse width of 80 μs and an intra-pulse delay time of 70 μs. A linear calibration ($R^2 = 0.9842$) was obtained when measuring five steel samples with differing Mn content.

Several papers have used LIBS for the *rapid classification of scrap metal samples*, enabling their efficient re-cycling. Among these papers was one by Brooks and Gaustad who discussed the use and reliability of handheld XRF and handheld LIBS analysers in a scrapyard setting.[23] They noted that prior to the advent of these instruments, experts had to rely on years of experience and tools such as magnets, files, grinding wheels and acids to distinguish between different metals. These handheld instruments make the classification easier and enable non-experts to make the classification. The authors did note that the best results were obtained on flat, clean samples and that real life samples of irregular shape were not classified as successfully. However, the results were encouraging and on-going work should improve classification further. It should be noted though that plated or materials could still be mis-classified. In another paper, Yuan *et al.* input the data obtained from 51 pre-selected wavelengths using fiber-optic LIBS into principal component analysis (PCA) combined with SVM to produce a model capable of distinguishing between 14 types of steel.[24] The classification success of the PCA-SVM model increased with an increase in the number of principal components, reaching 100% success after 13. Using SVM only, a maximum classification success rate of 95% was achieved. The combined PCA-SVM model therefore enabled a rapid classification method using portable instrumentation that could be applied in real time at scrap centres. Data from LIBS together with a decision tree-based algorithm was developed and its use in the circular economy (*i.e.* zero waste) discussed by Moros *et al.*[25] This machine learning methodology enabled the classification of 10

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different classes of materials (*e.g.* alumina, silica and magnesium oxide-based materials) through the emission intensities and emission intensity ratios of analytes such as Al, C (through CN–), Mg, Si and Zr. After "training" of the model using known samples, it was applied to real samples. Although correct classification was achieved in only 75% of samples, it was noted that with pre-cleaning and other sample treatments, the classification success rate could be higher. The authors were pleased with these initial results and considered that the methodology could be useful for the iron and steel industry, which are the main users of refractory materials.

The analysis of *inclusions (the number, size, distribution and composition) in iron and steels* is vital in ensuring the materials are fit for purpose. A paper by Imashuku and Wagatsuma reviewed (with 66 refs) three emission spectrometric techniques, namely cathodoluminescence, X-ray excited optical luminescence (XEOL) and LIBS that have been used for such an analysis.[26] The review provides a convenient table summarising the abilities of each of the techniques along with their attributes and drawbacks and then gives individual sections on each technique. It was concluded that LIBS offers the best opportunity for on-line analysis because it does not require a vacuum or any sample pretreatment. The lateral resolution of cathodoluminescence is superior to that of LIBS and also provides information of the chemical species present. The XEOL provides similar information to cathodoluminescence but, like LIBS, also operates under ambient conditions. The review would certainly be of interest to somebody working in the area. Inclusions are usually small (often <50 μm) and so analysing them needs tools that are capable high spatial resolution, ensuring that the surrounding matrix does not confound the results. Laser-based techniques are capable of the task, but care must be taken to ensure that the resulting crater is not too large. A paper by Wang *et al.* discussed the use of microchip-LIBS to undertake the analysis of inclusion size in ductile iron and hence determine the grade of the material.[27] A microchip laser operating at 1064 nm, with an energy of 80 μJ and a pulse width of 550 ps was used to create craters of 10 μm diameter over a 1 mm^2 area of sample. The optical system was described in full, with detection using a CCD. Sample was placed on a stage which was moved at a rate of 50 μm s^{-1} and the laser operated at a frequency of 10 Hz, enabling the craters to overlap. When the laser hit an inclusion the spectrum obtained was significantly different from the surrounding iron matrix because both Mg and Ti were observed at 285.2 nm and 334.9 nm, respectively. Since the craters overlapped, it was therefore possible to determine the size of the spherical inclusions. Results obtained using LIBS were comparable to those obtained using conventional scanning under a metallographic microscope. Although deemed successful, the methodology was slow; taking 67 minutes to cover an area of 1 mm^2. Work is on-going to try and improve the speed of analysis so that it may routinely be used in the workplace.

One of the advantages of LIBS is that it may be used remotely or in a standoff fashion. This means that it may be used in areas where working conditions may be unpleasant or dangerous. A paper by Li and Guan discussed *the real-time monitoring of laser cleaning of a commercial 444 type ferritic hot-rolled stainless steel* using LIBS.[28] The cleaning process was undertaken using a 1064 nm laser operating at 55 kHz and a pulse duration of 24 ns. The power was varied between 20 and 90% of full power in an attempt to optimise the system. The area to be cleaned was flushed with 5 L min^{-1} argon to prevent re-oxidation. Detection of light emitted was through a commercial optical spectrum analyser. The relative intensity ratio of the Fe signal at 520.9 nm and the Cr at 589.2 nm was used to estimate the extent of cleaning. When the oxide layer had not been removed, the Cr signal far exceeded that of the Fe. However, when the oxide layer was removed, the Fe signal increased suddenly and significantly. The authors recommended that the relative intensity ratio of Fe/Cr should be kept small to prevent over-cleaning from occurring. To ensure this, the laser power had to be monitored closely. The cleaned surface was bright and very smooth – as determined using an optical micrograph.

The *determination of C in steel* has long been of interest because it dictates the hardness and weldability. Two papers of interest have been prepared in this review period. The first, by Zehra *et al.* used vacuum UV LIBS with a line plasma rather than a conventional point plasma.[29] The optical system required for this was discussed at length. The system was optimised with special care being taken to optimise the focal length between the cylindrical lens and the sample target (2.5 mm). The C was determined at 97.7 nm. A calibration curve was established by analysing six certified reference materials (CRM Fe 1/1, 11CM 5078, 108 BS XAAS, CRM 12 B 1767, IARM-206A 206A and CRM 12X 15252) containing C concentrations of between 50 and 940 mg kg^{-1}. Using the optimised setup, the LOD was ∼50 mg kg^{-1}, representing an improvement by a factor of six compared with those obtained using a conventional point plasma. However, when compared with data obtained in previous studies, one of which yielded a LOD of 1.2 mg kg^{-1}, the LOD obtained in this study was less impressive. The authors explained that direct comparison with previous studies is not possible because the detection system used in this study was old and no longer operated at peak performance. The authors thought that, had a new spectrometer and collection optics been used, a far better LOD would have been obtained. A second paper also described the determination of C in steels.[30] This paper described the employment of a genetic algorithm (an algorithm that will keep evolving until a suitable fitness level is reached) with back propagation artificial neural network and double pulse LIBS for the determination of C at 193.09 nm as well as the concomitant analytes Cr, Fe, Mn and Si. Using the ratios of C/Fe, Cr/Fe, Mn/Fe and Si/Fe, the algorithm successfully managed the determination of C with better accuracy than either a traditional calibration curve or with the univariate back propagation artificial neural network alone. This was evidenced by the average relative error of prediction being 8.29% compared with over 14% for the other two methods.

Two papers have reported the *analysis of the interface region between steel and aluminium.* This is important because it is necessary to determine if there is any diffusion of metals between layers. The first paper, by Holub *et al.*, used LIBS for the task.[31] Two halves of a cylinder were connected with one half

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being the aluminium and the other steel. No glue or other form of fusing was used. The whole cylinder was sealed together by silica on the outer boundary. A LIBS instrument then took spectra across the join and the Fe/Al ratio determined. The data were then fed into PCA, self-organizing maps and standard data metrics. For the PCA analysis, the data treated using Euclidian and Manhattan treatments were compared with the expected ratio. Both treatments were in good agreement with expected values, with the Euclidian treatment perhaps being marginally better. The first principal component could easily distinguish between the aluminium and steel layers. The data obtained from the self-organizing maps software was also very encouraging. Future work was to be focussed on a bigger variety of samples as well as applying the procedure developed to heterogeneous samples. The other paper to examine the boundary between aluminium and steel was presented by Paudel *et al.*, who used slow flow direct current glow discharge-mass spectrometry (GD-MS).[32] The "slow flow" refers to the discharge gas flow rate and is sometimes used as a description of several instrument types. The instrument used determined Cr and Ni across the layers. These analytes originated in the steel and could, potentially diffuse into the aluminium layer. A heat-treated (at 400 °C for 30 min) and non-heat-treated sample were analysed and the results compared. Both analytes were shown to be enriched at the interface, especially in the heat-treated sample. This phenomenon was studied further using electron probe microanalysis (EPMA) and scanning electron microscopy with energy dispersive spectrometry (SEM-EDS). The Cr had a particularly high concentration in the aluminium layer. It was concluded that the experiment had increased our knowledge of the mechanisms that govern the growth and formation of intermetallic phases and could therefore help in the optimisation of the manufacturing process of the joints.

Kuptsov *et al.* have continued their work *using a two-jet arc plasma*, this time extending its use to both spark sampling of solid materials and calibration using solutions.[33] Minimal changes to operating conditions were required, although a slight adjustment to the injection gas flow was necessary to prevent the liquid calibrants from condensing and flowing away from the analyser. Once the conditions had been optimised, coefficients of relative sensitivity factors were used to construct calibration curves. These were calculated using the spectral lines of analytes and an internal standard which was a matrix element (iron in the case of steel samples and copper in the case of copper samples). Analysis of three certified steel materials for the analytes Cr, Cu, Mn, Mo, Ni and Si yielded results that, in general, were in good agreement with certified values with most results differing by no more than 15%. The worst result was achieved for Si in the material GSO 130-3, where the result of $0.18 \pm 0.01\%$ did not compare favourably with the certified value of 0.145%. Despite this anomaly, the authors concluded that the technique provided results with good accuracy and reproducibility.

A paper by Aboura and Moore discussed the *nano-SIMS analysis of the 300 series austenitic stainless steels* and of precipitation hardened nickel-based alloys for H and D content.[34] The analysis is well known to be challenging and the paper records many artefacts that can confound the results, with many of these artefacts not having been recorded previously. Confounding artefacts include: D outgassing during analysis and D contamination in the analysis chamber. Methods attempted for the mitigation of the effects include: changing beam current, changing raster size, the use of an energy slit, *etc.* The conclusions are too lengthy to list here, but are presented in the paper along with recommendations for best practice.

Aidene *et al.* asked the intriguing question "Does chemometrics work for matrix effects correction in X-ray fluorescence analysis".[35] These authors used EDXRF to analyse two sets of samples: 46 carbon and alloy steel reference materials and 68 samples of iron, manganese, chromium and other ores, of which 41 were reference materials. Once analytical data had been acquired, they were processed in numerous ways with a comparison made between the conventional ways (ordinary least squares, fundamental parameters and intensity correction) and chemometric algorithms (partial least squares, K nearest neighbour (KNN) regression and ANN). The efficiency of the assorted models were evaluated by calculating the root mean squared error of calibration and validation as well as R^2 (Pearson's correlation coefficient for the measured *vs.* predicted plots in calibration and validation). Since the large number of samples had very broad concentration ranges, significant matrix effects were observed, meaning that ordinary least squares treatment was incapable of making adequate corrections. A little surprisingly, the best performing treatment was that of conventional intensity correction. The authors did point out that the chemometric methods also offered satisfactory precision (but inferior to the intensity correction), but the accuracy obtained was very dependent on sample type/interferences present. For instance, the partial least squares method was adequate for compensating for simple line overlap, but could not compensate for non-linear matrix effects. Instead, the non-linear algorithms of KNN and ANN were superior for this purpose. However, they suffered the drawback of needing significant numbers of samples to train the models. The paper was interesting and was a timely reminder that chemometric methods are not a magic bullet and cannot compensate for everything.

Finally in this section are two papers that have analysed *steel powders used for additive manufacturing (3D printing)*. The paper by Guo *et al.* used LIBS for the rapid analysis of synthetic steel powder (made by mixing varying proportions of high purity iron and manganese powders).[36] Samples were analysed in three different ways: pressed pellets (already used for soils, sediments *etc.*), adsorption band (where the sample is sprayed onto the surface of a tape containing a conductive adhesive), and loose powders. The adsorption band method uses simpler tools, is more easily automated and is more rapid than the pressed pellet methodology. The powder method was not conducive to LIBS measurements, with extremely irreproducible results being produced. The LIBS intensities for Mn (at 403.307 nm) and Fe (at 404.581 nm) were used to calculate intensity ratios. For the pressed pellets the calibration curve of intensity ratio

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against Mn content yielded a regression of 0.910, which was far inferior to the 0.998 obtained using the adsorption band. In addition, the error bars were significantly wider for the pressed pellet samples (>20% RSD compared with ~6% RSD for the adsorption band) and the signal intensities were a factor of 3–4 greater for the adsorption band method. The obvious conclusion was that the adsorption band methodology is the best for this type of analysis. The other paper to analyse steels used for 3D printing was by Li *et al.*, who used micro-beam XRF for the task of determining the analytes Cr, Cu, Mn, Mo, Ni and Si and then used LIBS to corroborate the data.[37] Samples were prepared by mixing two types of alloy powder: SS431 and 316L stainless steel *via* a high precision, multi-channel coaxial feeding nozzle and a laser beam focussed to melt the mixture into a cladded layer. Poly-capillary X-ray optics were used to obtain high spatial resolution with a spot size of 20 μm. Calibration was through the use of certified reference materials (2012-316L and GSB03-208-6-2006) with similar composition to the samples. The results of the μ-XRF and LIBS were in good agreement, but the μ-XRF method had the advantage of better resolution and, hence, could give more information regarding the elemental distribution. Analysis of these materials is important because when the proportions of the two starting powders are altered during the preparation to form a gradient stainless steel, cracks appeared in the martensite–austenite transformation region when the Ni content reached between 6.5 and 8.5%.

2.2 Non-ferrous materials

This has again been a busy area of research and, in common with the Ferrous metals section, the most popular area of research has been LIBS. However, there has also been a good selection of other techniques employed and these will all be discussed in this section. A forensic application relevant to this section has been placed in the inorganic forensic section (Section 5.4) of the review,[38] The reader is referred there for more details.

2.2.1 New reference materials. *Reference materials are still the best way of ensuring quality data* are obtained and so it is always good when new ones are developed. A paper by Yamani *et al.* described the preparation and certification of three new aluminium alloy reference materials (NIS-CRM067 to NIS-CRM069).[39] During preparation, the samples were cast into bars with a diameter of 40 mm and then sliced into pieces 30 mm in length. The ends of the samples were then polished smooth. Once prepared by the Egyptian National Institute of Standards, the materials were sent to several independent laboratories for analysis. The methods of sample preparation and analysis varied between laboratories, with a microwave dissolution method and a wet preparation method being used along with different analytical techniques such as XRF, ICP-OES, AAS and AES. The paper then went through the statistical processing and certification of the materials. Another paper describing the preparation of standards was presented by Martinuzzi *et al.* who developed a robust and cost-effective protocol to fabricate calibration standards for the thickness determination of metal

coatings using XRF.[40] As the authors pointed out, XRF is the most commonly used technique for this because it is non-destructive, robust and easy to use. The primary standards are expensive, may not be readily available and have a limited shelf-life. The method developed involved the electroplating of Ni onto brass plates (10 cm × 7.5 cm × 0.25 mm) for four discrete times ranging between 2 and 26 minutes. The thickness of the coating was then measured by cutting the plate in half and analysing it using light microscopy and SEM. The coatings for the four different plating times were 1.2, 3.9, 7.8 and 15.6 μm thick, representing a plating rate of 0.6 μm min^{-1} under the conditions specified. Each plating was undertaken in triplicate so that an estimate of reproducibility could be made. Precision was better than 5%. The materials were then used for the determination thickness of coating in certified standards. The results were in very good agreement with certified values when the in-house standards were used for calibration and were significantly better than the data produced when no standardisation was used.

2.2.2 Reviews. Magnesium alloys are increasingly popular as both structural materials and medical implants. A review by Zeller-Plumhoff *et al.* discussed (with 189 refs) synchrotron radiation micro-computed tomography and nano-tomography as well as complementary techniques such as XRD, small angle X-ray scattering (SAXS), XRF and diffraction tomography for the analysis of such materials.[41] The review discussed what synchrotron means and then described the methods used for the analysis. Also reviewed was the analysis of the materials at all stages of their life, *i.e.* from development, through to corrosion studies. Each stage had its own section in the review, as did the analysis of different magnesium-based alloys (Mg–Al, Mg–Y Mg–Zn, and Mg-rare earth element alloys). The outlook provided stated that future work would focus mainly on the biological aspects *e.g.* the effects that cells have on the degradation *in vivo*. The review would certainly be of interest to somebody new to this area of research.

2.2.3 Copper and copper-based alloys. The analysis of copper and copper-based alloys *e.g.* brass and bronze has, as usual, attracted significant research attention. Much of the more interesting work has employed LIBS, but other techniques are also popular. One example, by Kuptsov *et al.* used a *two-jet arc plasma with spark sampling and calibration using solutions*.[33] Both steel and copper samples were analysed, so this paper was discussed in Section 2.1. The reader is referred there for more detail.

As mentioned previously, many of the papers used LIBS for the analysis and some of these are still reporting methods to try and *improve the accuracy of the analysis*. An example was presented by Xu *et al.* who optimized a combined atomic and ionic line algorithm to give high spectral stability and quantitative accuracy during the LIBS analysis of bronze and soil samples.[42] The theory of the algorithm was presented in the paper and then it was applied as a simulation first and then to the determination of Fe and Mn in the samples. For the analysis of the bronze sample, the algorithm improved the RSD obtained from 7–15% when using atomic and ionic lines individually to 5–8% for when they were combined. In addition, a small

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improvement in the R^2 of the calibration curves was also achieved, with values improving from 0.982 and 0.992 to 0.991 and 0.996 for Mn and Fe, respectively. The root mean square error of cross validation (RMSECV) values also demonstrated a minor improvement. Similar improvements were also observed for the soil samples leading the authors to conclude that the algorithm could help commercialization of LIBS. In a paper packed with theory and mathematics, Deng *et al.* attempted to improve the accuracy of single sample calibration LIBS using self-absorption correction.[19] Unfortunately, self-absorption effects are known to destroy the linearity of calibration graphs in LIBS, so relying on only one calibrant can lead to serious error. These authors therefore corrected for this using a method that did not rely on complicated preparatory information. Instead, they used intensity ratios of spectral lines of differing sensitivity to determine the extent of self-absorption, producing a self-absorption coefficient (K). They tested the methodology during the analysis of aluminium bronze and pressed ore samples. Compared with standard single sample calibration LIBS, the modified version provided greatly improved results with the root mean square error of prediction (RMSEP) and average relative error (ARE) decreasing from 0.83 wt% and 13.75% to 0.4 wt% and 4.08% for the aluminium-bronze samples. Results of the pressed ore samples were even more impressive, with RMSEP and ARE decreasing from 4.77 wt% and 90.48% to 2.34 wt% and 14.60% when the self-absorption was corrected for. The large improvement led the authors to conclude that this was a big step forward in the use of single sample calibration-LIBS. A paper by Ahmed *et al.* discussed the use of calibration-free LIBS for the analysis of iron–copper alloys.[43] The authors first calculated the plasma temperature using select lines of Cu and Fe (ensuring that the lines chosen were not subject to self-absorption or poor sensitivity) and then used a Boltzmann plot for the calculation. These yielded results of 8400 K $\pm$ 1000 using the Cu(I) lines and 8700 K $\pm$ 1000 using the Fe(I) lines. They then calculated the electron number density using the Stark broadened line profile, obtaining a result of 2.2 $\times$ 10^{16} cm^{-3}. These values could then be applied to help calculate the concentrations of analytes found in the sample, yielding results of 23.85 $\pm$ 5% for Fe and 76 $\pm$ 5% for Cu. The methodology was validated through the analysis of the same sample using ICP-MS. No details were given, but presumably, some sort of an acid dissolution was required prior to this analysis. The results of the ICP-MS analysis were in excellent agreement with those obtained using LIBS, leading the authors to conclude that the simple, rapid and reliable LIBS method could be used to obtain accurate data.

An interesting LIBS application by Myakalwar *et al.* used *LIBS to monitor the molten phase desulfurization process of blister copper*.[44] The on-line or standoff use of LIBS is one of its main advantages over many other techniques because it does not require the analyst to get close to hazardous or unpleasant environments. The desulfurization process occurs when oxygen is passed through the molten sample (at 1270 °C) and the S removed as SO_2. The paper described the LIBS setup in detail, giving schematics to aid comprehension. A high energy laser pulse (270 mJ) at 10 Hz was used for the excitation and the Cu, O

and S emissions at 351.06 nm (picked to avoid self-absorption), 777.34 nm and 921.29 nm, respectively were used for the analysis of both molten and gaseous phases. Once the data had been obtained, they underwent chemometric analysis (hierarchical cluster analysis) and the best 50 spectra out of 200 taken per time point were averaged, giving a mean spectrum. In this way, the LIBS was capable of determining the exact point that all of the S had been removed and so the desulfurization process could be stopped before oxidation of the copper occurred. The efficiency of the desulfurization process could therefore be optimized because of the LIBS measurements, saving time and expense.

The matter of *"crosstalk" and its measurement using LIBS* was discussed by Meinhardt *et al.*[45] Crosstalk is the interaction between a surface layer, *e.g.* an oxide layer and the substrate below when a laser is attempting to remove it. The paper discussed how this interaction may occur and gave three possibilities. These were: (1) direct interaction between the laser beam and surface layer, (2) indirect interaction between the expanding plasma originating from the substrate and the surface layer at the crater walls and recasting layers being present after the ablation step and (3) contaminating the substrate material underneath surface layer. The authors set up a study in which a brass substrate had a layer of stainless steel of thickness 500 μm placed on top. In most cases, this was glued, but for a few experiments it was clamped. The LIBS data indicated that the latter two methods had the greatest effect on the LIBS measurements. However, these effects could be minimized by utilizing a two-stage ablation sequence in which a circular trench is first ablated in the surface layer (to approximately its entire depth) and then a second laser pulse aimed at the centre of the trench is used for the LIBS measurement.

Two papers have reported the use of *glow discharge (GD) as a means of analysing copper and copper alloys*; with one by Hoffmann *et al.* using GD-OES and the other, by Phukphatthanachai *et al.* using GD-MS (and LA-ICP-MS).[46,47] In the paper by Hoffmann, a matrix independent calibration GD-OES method was developed to determine O in copper, aluminium and magnesium and some of their oxides.[46] The samples were hot pressed prior to analysis. The atomic lines of O at 130 nm and at 777 nm were used for the determination with the conditions used for the DC discharge being 700 V, 20 mA and with a 4 mm anode. The detection system comprised a 750 mm Rowland circle with photomultiplier tubes or a 400 mm Rowland circle with a CCD. The emission yield of O at 130 nm was heavily dependent on the matrix. The line shift effect was also significant at this wavelength. However, these problems were not the case for the 777 nm line, where the same emission yield was obtained for all the matrices and line shift did not occur. In addition, for both detection systems, the signal at 777 nm was greater than at 130 nm. An FeO layer was then prepared and characterized using Rutherford Backscattering Spectrometry (RBS), XRD and GD-OES. The results obtained for this using the method developed were not so good because it showed an enhanced emission yield at 777 nm (*i.e.* it deviated from the matrix independent calibration), although it was similar to the emission yield of the Al at 130 nm. These initial results were still

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encouraging though. Future work is to include the analysis of more samples, the use of other O wavelengths (although the one at 844.636 nm is beyond the sensitive region of the monochromator/PMT assembly), calibration at a constant pressure along with changing the impedance. The paper by Phukphatthanachai *et al.* reported the determination of S in copper and copper alloys.[47] These workers characterized some materials using isotope dilution mass spectrometry (IDMS) and then used these as calibrants for GD-MS and LA-ICP-MS. Several calibration strategies were attempted for both techniques with validation being achieved with reference materials other than those used for calibration. For both techniques, all except one of the calibration strategies provided data that were in excellent agreement with certified values. The exception was the matrix cross type calibration that provided marginally worse data. When matrix matched calibrants were used and for a S concentration range of 25–1300 mg kg^{-1} the GD-MS analysis provided significantly better relative expanded uncertainty values (3 to 7%) compared with LA-ICP-MS (11 to 33%). However, for the matrix cross type calibration, the relative expanded uncertainty for the GD-MS increased to at least 12% and to at least 54% for LA-ICP-MS.

A new *technique entitled X-ray and Particle Induced Fluorescence (XPIF) spectrometry*, which is a combination of laser-based XRF and PIXE was described by Boivin *et al.* who then applied it to the analysis of brass, bronze and stainless steel samples.[48] The methodology was described extensively in the paper. Briefly, an extremely intense laser source (multi-hundred TW laser system) interacted with the solid sample, accelerated protons and produced X-rays characteristic of the elements that were present in the sample. These intensities were input to an iterative MATLAB algorithm that enabled calculation of X-ray yields *etc.* It automatically generated a characteristic emission X-ray spectrum from the image of photons hits on a CCD X-ray camera, detected and assigned the Kα and Kβ peaks with elements and computed the integrated yield from the peaks. Through an iterative process, they then found the mass ratios which optimized the fit between the experimental yields and the simulated yields. As a validation step, they tested three homogeneous metallic multi-element samples using XPIF and a reference commercial EDX spectrometer. The X-ray yield from each of the characteristic wavelengths was then related to the mass fraction of that element in the sample. The instrument was capable of switching from laser driven PIXE to laser-driven XRF or even using both simultaneously. Results obtained using XPIF from the samples were compared with those obtained using a conventional EDXRF analysis and were within the error bars. The new technique has two main advantages over existing methods: no previous knowledge of the sample composition is required and it has a higher yield than laser-driven PIXE without X-rays. On-going work will look to increase the repetition rate so that smaller fluctuations occur which, hopefully, will result in a reduction of uncertainties and an increase in accuracy.

2.2.4 Aluminium and aluminium-based alloys. In common with the analysis of other metal types, LIBS has been the analytical method of choice by many workers for the analysis of aluminium and its alloys with *attempts to improve accuracy* being a popular area of study. This is exemplified in a paper by Dai *et al.* who used LIBS combined with Least Absolute Shrinkage and Selection Operator (LASSO) to select the spectral features followed by Least Squares Support Vector Machine (LSSVM) for regression.[49] This enabled a multivariate quantitative analysis model to be established for the analytes Cu, Fe, Mg and Ni. The performance of the model was compared with a more traditional univariate linear calibration and partial least squares regression. The LIBS–LASSO–LSSVM proved to be superior, yielding R^2 values of better than 0.99 for all analytes, improved RMSEC and RMSEP values and average relative errors of 5.76, 3.20, 3.49 and 5.49% for Cu, Fe, Mg and Ni, respectively. The better performance was attributed to the LASSO–LSSVM being able to eliminate errors arising from self-absorption and noise originating from the emission source. The LASSO had the added advantage of reducing the risk of over-fitting the data because it identifies the main spectral features. It was concluded that the combination of methods is a rapid, accurate and feasible way of analysing alloys. Another paper by the same research group improved the accuracy of the Fe determination in aluminium alloy using millisecond LIBS under spatial confinement followed by SVM to aid regression.[50] Spatial confinement apparently leads to spectral enhancement of the ms-LIBS by a factor of 2–2.5, depending on the Fe wavelength used. Using the LIBS system under confinement and the SVM significantly improved accuracy and repeatability (in terms of RMSEC, RMSEP, R^2 and ARE). This was achieved through a concomitant decrease in matrix effects.

A paper by Shabbir *et al.* reported *methodology to account for the errors experienced during the LIBS analysis of irregular shaped sample surfaces*.[51] Unfortunately, such errors are common and can seriously affect the analysis of, for example, scrap metal. Consequently, the authors developed a method that used 20 reference materials. The samples were cut and then a saw was used on one half of the cut surface, roughening it with 1 mm trenches, mimicking irregular-shaped scrap metal. The other half of the surface was smooth. Then LIBS analysis was undertaken on both halves using the same conditions before the emission intensities were treated with a complex series of chemometric packages. The first step was a univariate regression, then multivariate regression with machine learning and finally, multivariate regression with transfer learning. The first two steps were used for training calibration models with the spectra obtained with the smooth half of the sample surface. The irregular surface data were then used with the calibration models to identify and quantify physical effects (*i.e.* assess the prediction performance of the calibration models). The third part of the chemometric treatment was then used to transfer the data from the first two steps to software that could learn from any disparities arising from the irregular surface. Results were compared with those obtained using a simple internal standard and with other chemometric techniques, *e.g.* a machine-learning -based multivariate regression, and were a significant improvement. For the analytes Fe, Mg, Si and Zn, the average relative error of calibration was 2.3% and average relative error of prediction was 16.3%.

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The technique of LIBS is generally regarded as being minimally damaging to samples. However, if improved sensitivity is required, single shot LIBS must increase power and hence cause a bigger crater, increasing sample damage. Many studies have therefore used double pulse LIBS with a second laser beam fired orthogonally so as not to cause further sample damage. A new method entitled "*target enhanced orthogonal double pulse LIBS using a dielectric target* was reported by Jiang *et al.*[52] In this study, the second laser fired orthogonally was aimed at a target compound (in this case potassium hydrogen carbonate) and the plasma produced from this excited the plume of material from the sample caused by the first laser beam. Potassium hydrogen carbonate was chosen as the dielectric target so as not to cause interfering wavelengths from a metallic target. The setup was applied to the determination of Al, Cr, Cu, Mn and Si in aluminium alloy and led to an increase in sensitivity by a factor of between eight and 15 (depending on the analyte and the energy of the second laser) when compared with conventional orthogonal double pulse LIBS. The method seemed ideal for causing minimal damage whilst improving sensitivity of the analysis.

Xu *et al.* used a fibre-laser-based LIBS instrument to determine Cu, Mg and Mn in aluminium alloys.[53] A fibre laser is a fibre optic doped with a rare earth element that acts as the gain element for the laser. The laser had a high repetition rate and a low pulse energy. The laser spot overlap, non-overlapping ablation area, scan speed and single pulse energy were studied in detail. A linear function between the intensity and the non-overlapping ablation area was observed. The function between the spectral intensity, single point pulse number and scan speed was also demonstrated. After complete optimization, the performance of the system was evaluated. The R^2 values for all three analytes were >0.998, the average RSD was better than 5% and the RMSECV values were 0.0103 wt%, 0.0384 wt% and 0.0295 wt% for Cu, Mg and Mn, respectively. Overall, it was concluded that the method offered a stable, rapid and accurate way of analysing alloys.

An "*at production line*" *application of LIBS* was described by Leosson *et al.* who used it to monitor the Ti concentration and the phase transformations occurring in molten Ti–Al alloy.[54] Such on-line applications are of course, hugely beneficial in that they can help identify end points of reactions, saving time and money for industry by enabling adjustments to preparation procedures to be made in real time *etc.* At temperatures above the liquidus of the material, the Ti concentration was constant, but below the liquidus the concentration obeyed that expected from the phase diagram. This was an encouraging sign since it indicated that the LIBS was capable of measuring the Ti concentration in the molten material accurately. The LIBS measurements also demonstrated that the Al$_3$Ti phase forms and dissolves in only a few minutes when the melt temperature is decreased or increased. It was concluded that LIBS enabled the accurate monitoring of the chemical composition of the liquid phase identifying the formation of solid precipitates in real time.

2.2.5 Other non-ferrous materials. Numerous other non-ferrous materials have been analysed using varying techniques during this review period. The *most common non-ferrous materials to be analysed were gold and silver*. An example, by Narlagiri and Soma used LIBS followed by data input to PCA to reduce the number of dimensions before the output of this was fed into a new regression for quantification.[55] The new regression was a multi-output regression with shallow neural networks that uses two nodes at the output layer. These nodes calculate the composition of one element each. The model was trained using three bimetallic materials: Au20–Ag80, Au50–Ag50 and Au80–Ag20. In addition, LIBS spectra from aluminium, copper and bronze were also collected to simulate Au0–Ag0. Once trained, the model was applied successfully to materials containing Au30–Ag70, with an error of <10%. It was predicted that, in the future, such a model could be applied to the analysis of multi-component systems.

Two papers have discussed the measurement of the *thickness of organic layers on sterling silver*[56] *and the thickness of an actual gold layer on silver, copper, iron or lead*.[57] In the paper by Porcinai and Heginbotham, organic layers of known thickness and of several commonly used protective coatings (Zapon nitrocellulose lacquer and the acrylic resins Paraloid B72 and Paraloid B44) were used as calibrants for the XRF analysis.[56] The method worked through the amount of fluorescence attenuated from the metal substrate below the organic layers. The thicker the organic layer, the greater the attenuation. Once the calibration had been established, coupons of sterling silver were painted or sprayed with assorted polymers at different concentrations and dissolved in different solvents. The XRF analysis of the resulting coupons found that the coatings were of uneven thickness, especially for the brushed samples. The accuracy of the thickness measurement was calculated by means of a semi-empirical approach and the results indicated that thickness could be estimated with an uncertainty of ±5%. Sabbarese *et al.* used a handheld XRF instrument to determine the thickness of gold layers covering four metals.[57] This was achieved by first covering the metals with different thicknesses of gold so that a calibration curve could be established. This was accomplished in three ways: a ratio of the most intense lines of the covered element, a ratio of the intensity between two lines (one from each layer) and a partial least squares method. All three methods allowed successful calibration and subsequent determination of the thickness of the gold layer.

Kuptsov *et al.* determined *impurities in solid tellurium using ETV sample introduction to the two jest arc plasma-OES system they had developed* previously.[58] Sample (25 mg) was inserted to the ETV device and then the optimized temperature program run (drying at 95 °C for 50 s, ash/charring at 1050 °C for 60 s and then vaporization at 2400 °C for 15 s). The general idea was to remove as much tellurium as possible during the ash stage so that the analytes could be determined interference-free during vaporization into the plasma system. Up to 17 analytes could be determined simultaneously, with LOD ranging from 0.02–50 ng g^{-1}, which represented a 2–50 fold improvement on those obtained using a dissolution procedure followed by ICP-OES analysis. Method validation was through the use of the alternative technique but also spike/recovery experiments.

Several other interesting papers have been presented during this review period. These are summarised in Table 1, below.

Table 1 Applications of the analysis of non-ferrous metals

Analyte	Matrix	Method	Remarks	Reference
Au	Gold layers on brass	Portable XRF	Thickness of gold plating layers on a brass substrate were determined. A calibration curve was constructed using Au and brass reference materials and intensity ratios of the signals from peaks in both the gold layer and brass substrate. A calibration was also performed using partial least squares. Results from the two calibration methods were in good agreement	59
Various	Scrap metal	LIBS	The LIBS analysis of scrap metals is hindered by contamination, *e.g.* paint and by uneven surfaces. This study developed a hardware module that identified the shape and colour of the scrap and then transmitted this information as well as the best position to undertake analysis to a LIBS module. This then identified which type of metal was present in each piece of scrap. The number of data points for the identification were then minimised using PCA to accelerate the process. The optimized process had 24.5% better accuracy than an un-optimized system	60
Various	Scrap metal	LIBS	An automated system was developed that uses LIBS data to classify scrap waste without having to come into contact with it. The system is durable and controllable, even at high speed	61
Various (Al, Ca, Cr, Cu, Fe, Mg, Na, Ni, and Sn)	Damaged Chinese coins	LIBS	Many Chinese coins of different denomination are of similar shape and size. If they are damaged, discriminating between them can be problematic. A LIBS method was developed where the emission intensity data obtained were input to KNN for classification. The success rate for the four different denominations tested was 100%	62
Various (Bi, Pb and Sn)	Bismuth brass	LA-spark induced breakdown spectroscopy (SIBS)	High repetition rate (5 kHz) fibre laser used for LA-SIBS with detection using a fibre-optic spectrometer and CCD. Plasma temperature and electron number density measurements indicated plasma was in local thermal equilibrium. Detection limits were 25.5, 64.2 and 316.5 ppm for Bi, Pb and Sn, respectively. The method developed reportedly had several advantages over LIBS including: fast spectral data collection and low background continuum	63
Various (Cd, Co, Cu, Mn and Pb)	Zirconium and zirconium–niobium alloys	ICP-OES	A matrix separation and preconcentration method was developed that used a strong cation exchange resin ($\sim$0.4 g) in a micro-column. Elution of analytes was in 1% diethyle netriaminepentaacetic acid. The method was free from spectral interferences. It was validated by comparing data obtained with those obtained using Japanese Industrial Standards as reference methods and by spike/recovery experiments	64
Various (Ca, Fe, K, Ni and Zn)	Copper	TXRF; ICP-OES	Copper matrix was separated from analytes electrochemically. A "bottom up" approach was taken to measure the combined uncertainty of the results. Results obtained using TXRF were validated through analysis using ICP-OES, with the Student's *t*-test identifying no significant difference between the techniques	65

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3 Organic chemical and materials

3.1 Organic chemicals

3.1.1 Pharmaceutical and cosmetic samples. There has been a large number or papers that have fallen under this category during this review period. However, they are on very disparate subject matters, with no one subject being the focus of attention. Similarly, no one analytical method has been the focus. The use of LIBS continues to increase, but it is by no means the only area of interest.

The introduction of organic solvents to ICP-MS instruments is well known to be problematic because they can extinguish the plasma at high concentration, build up soot deposits on cones after prolonged use at lower concentration and generally cause plasma instability. A paper by Sanchez *et al.* discussed the *introduction of ethanol-based samples to an ICP-MS system via a total sample consumption system combined with a high sample matrix introduction system.*[66] Parameters such as the temperature of the introduction system, the injector bore of the torch, ion lens settings, plasma sampling zone and the gas flow through the high matrix introduction system were studied systematically. Sample uptake by the total sample consumption system was set at 25 $\mu L min^{-1}$. Optimal results, in terms of minimizing matrix effects, were obtained when using a 2.5 mm injector bore, a temperature of 300 °C, a nebuliser gas flow of 0.4 $L min^{-1}$, a dilution gas flow of 0.56 $L min^{-1}$ and a slightly elevated (by 5 V) extraction lens setting. The sampling zone was not a critical factor when the large bore injector was used. However, for narrower bore injectors, good results could be obtained, but the sampling zone had to be optimized very carefully. Once optimized, the system was applied to the determination of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Rb, Sr, V and Zn in bioethanol samples (diluted 1 : 1 with water) and alcoholic beverages. The authors noted that during the optimization, it was necessary to minimize interferences rather than optimize sample signal. Spiking experiments yielded recoveries of between 80 and 115% without the necessity of using an internal standard. It was hypothesised that had an internal standard been used, recovery may have improved further.

The determination of ^{13}C is not an easy analysis because it constitutes only 1.1% of natural C. Zakon *et al.* developed a method by which ^{13}C could be determined in organic compounds (1,2-dibromoethane, 2-chloroethylbenzene and naphthalene) using GC-MC-ICP-MS.[67] The analytes were transferred from the GC instrument through *via* a heated transfer line with the column reaching the tip of the injector of the torch.[67] Measurements were made in low resolution mode (resolution of ~300) and the instrument was tuned on the background signals of ^{12}C and ^{13}C (or possibly $H^{12}C$) originating from atmospheric CO_2 or impurities in the argon gas. Operating in low resolution mode cannot separate the ^{13}C from $H^{12}C$. This is possible in medium or high resolution modes, but the concomitant drop in sensitivity (>90%) precludes this. Since the analytes were introduced to a "dry" plasma (*i.e.* no H other than that originating in the target compounds was present), it was assumed that the formation of $H^{12}C$ would be minimal. The entrance valve to the MS had to remain shut for four minutes after injection to ensure that the C originating in the solvent (dichloromethane) did not overload the Faraday cup detectors. Once the solvent front had safely passed, the valve was opened to allow the analytes in the organic samples to be determined. Precision over the concentration range 0.2–0.6 nM C was 0.3 or 0.4‰, degrading to 1‰ at lower concentration. The method was validated through comparison with data obtained using GC-isotope ratio mass spectrometry (GC-IRMS). Results were in good agreement, although the precision for the GC-MC-ICP-MS was poorer. Nevertheless, it was concluded that the method was capable of obtaining accurate and precise data and could be an alternative to the conventional GC-IRMS.

Elemental detection of fluorochemicals is not easy because of the excessively high excitation energy/ionization potential of F. However, this problem has been tackled by White *et al.* who used *nanospray induced chemical ionization in the afterglow of an ICP for the determination of F-containing compounds.*[68] Formation of BaF compounds in the plasma itself is not very efficient, leading to poor sensitivity. However, using the afterglow region and sodium or barium acetate solutions (1 mM) introduced *via* nanospray, the HF formed in the plasma can be transformed into BaF prior to determination using mass spectrometry. The samples of 10 F-containing materials were introduced through a regular LC pump using a 50 : 50 water acetonitrile mixture as eluent. Sample (20 μL) was injected and then, after atomization in the plasma the ions went through a specially constructed interface (schematic shown as well as a good description), reacts with either the Na or the Ba introduced *via* the nanospray and then detected using MS. The sensitivity was excellent, offering 280 counts per second per ppb of F, which was two orders of magnitude greater than conventional ICP-MS. A LOD for F of 8–11 $ng mL^{-1}$ was achieved when measuring BaF^+.

A paper by Zhao *et al.* discussed the use of *laser induced filament breakdown spectroscopy for the study of aliphatic nitro-alkanes.*[69] The instrument was made in-house and comprised a Ti:sapphire laser operating at a power of 3.3 mJ per pulse, at a wavelength of 800 nm, for a period of 65 fs and with a frequency of 1 kHz, a quartz vessel in which sample is introduced and where it is turned into an excited "filament", optics and a Czerny–Turner spectrometer equipped with an intensified CCD. The setup was used to monitor the CN and C_2 formation as well as measuring the filament features such as length, diameter and temperature. The C_2 converted to CN through a single atom substitution reaction which predominantly took place at the cooler ends of the filament rather than the hotter middle. The time integrated intensities of CN and C_2 as well as the length and diameter of the filament could be used to identify which of the samples was which.

An interesting on-line application of LIBS was reported by ShangGuan *et al.* who used it to *monitor the progress of laser paint removal.*[70] The use of lasers to remove paint is more environmentally friendly than the use of chemical strippers and is more easily automated. However, monitoring the extent of the reaction is necessary to optimize the process, ensuring that residues are not left and that the base material is not unnecessarily damaged by excessive ablation. The Fe and Zn lines

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were monitored in real time and the data passed to the chemometric tool of K nearest neighbour (KNN) to evaluate and automatically calculate the extent of cleaning. The classification accuracy of distinguishing different levels of cleaning was 100%.

Steganography is the practise of concealing a message within another message or an object. A paper by Yin used *LIBS coupled with a non-negative least squares machine learning algorithm to study steganography*.[71] Regular inks and those same inks with Ag or Cu dissolved in them at different concentration were used to construct a message and then LIBS was used to identify and decode the hidden message. The paper was exceptionally short on experimental detail (no LIBS parameters or instrumentation were discussed). However, the subject area is fascinating and is yet another example of the use of LIBS.

Several other *relatively simple applications have also been described*. These have employed several different analytical tools. An example by Dib *et al.* determined P in biochar-based fertilizers using spark induced LIBS.[72] Three types of biochar were prepared: ground eucalyptus leaves and branches, banana fibre and peanut shells. Each type of biomass (3 g) was mixed with 100 mL of 270 mg L^{-1} P solution and then shaken for 24 h at 25 °C. After pyrolysis, the materials were pressed to form pellets which were then analysed using a spark discharge (to improve sensitivity and stability) followed by LIBS analysis. Calibration was achieved by using matrix matched standards, *i.e.* using some eucalyptus-based biochar with differing amounts of added P. Results obtained using this system were compared with those obtained following the dissolution of 100 mg of sample and P determination using a high resolution continuum source FAAS system. A Student's *t*-test indicated that there were no significant differences between the results obtained using the two techniques. However, the result for the peanut shell biochar was $1.85 \pm 0.16\%$ for the SD-LIBS but only $0.98 \pm 0.21\%$ for the FAAS. To this author, despite what the statistics may say, this looks like a problem. However, the method developed was certainly rapid, simple, left no chemical residues and, with further investigation, could potentially be used as a quality control measure for biochar production.

An paper by Reddy *et al.* discussed the use of ETAAS to determine a suite of analytes (20) in high purity (7N) semiconductor grade chemicals such as triethylborate, tetraethyl orthosilicate and trimethyl phosphate.[73] The first problem encountered was that the autosampler cups that are made of polystyrene were attacked by these chemicals. Therefore, replacements made from PTFE had to be manufactured. Then, a complex temperature program involving four drying stages was required. Normally, these authors use three drying stages, but a fourth was introduced to prevent the oxygen originating from water attacking the graphite tubes at elevated temperature. Since no suitable CRMs exist, spike and recovery experiments were used for method validation. The effect of sample storage container type was also studied, with perfluoroalkoxy and polypropylene both being tested. The polypropylene led to elevated levels of some of the analytes, *e.g.* Al, Ca and Fe, but not necessarily for all three sample types. Some elements, *e.g.* Sn, were significantly above the recommended limit for both

container types. The Sn was hypothesised to perhaps originate from catalyst residues in the plastics. It was concluded that packing, transport and storage of these chemicals needs to be done with great care to prevent contamination.

A third application was by Qu *et al.* who used a combination of LIBS and single particle aerosol mass spectrometry in both positive and negative modes to analyse Tibetan incense samples on-line.[74] Both the ash and the smoke were analysed using LIBS whereas just the smoke was analysed using the single particle aerosol mass spectrometry. The LIBS data showed that although a few elements were present in the smoke (Ca and Sr), the majority of the analytes remained in the ash (Ba, Ca, Fe, Mg, Mn, Si and Sr). The mass spectrometry also identified Ca and Sr in the smoke but, in addition, also identified Cr, Fe and Mg. Although Pb was not detected in the smoke of untreated samples, some samples were soaked in a lead solution and dried before burning. Under these conditions, the mass spectrometry technique could identify individual Pb isotopes. This, the authors thought, could possibly extend its use analytically. The data from the untreated samples were input to PCA and clear groupings of Tibetan incense, mosquito repellent incense and temple incense were identified using bi-plots of the first two principal components.

3.1.2 Analysis of pharmaceutical materials. The analysis of impurities in pharmaceutical materials is an expanding topic area. According to Pinheiro and Nobrega, this is because of a revision of the United States pharmacopoeia that now includes chapters describing sample preparation and two analytical techniques; namely ICP-OES and ICP-MS.[75] This *overview paper* contains 99 references and summarises the sample preparation methods used for the determination of elemental impurities in medicines. The review is conveniently split into sections that include: dilution in aqueous or organic medium, extraction techniques, microwave-induced combustion and wet digestion methods (including microwave-assisted methods). Tables are used to good effect and summarise the data nicely. The review is a good starting point for anyone new to the area and is a good source of reference for more experienced workers.

A paper entitled "*Tutorial and spreadsheet for the evaluation of instrumental quantification uncertainty by the linear weighted regression model*: determination of elemental impurities in nasal spray by ICP-MS" was presented by Pluhacek *et al.*[76] There is nothing terribly novel about the chemistry in this paper, with samples simply being diluted and acidified prior to analysis. Method validation was through spike/recovery experiments for the analytes As, Cd, Co, Hg, Ni, Pb and V. Despite the lack of novelty in the actual analysis stage, the tutorial is a worthwhile contribution because it is a good example of how to determine uncertainty and is therefore useful from the metrics perspective.

The development of a *LA dielectric barrier discharge -optical emission spectrometric method for the direct determination of Cl and S in pharmaceutical samples* was reported by Ding *et al.*[77] A continuous wave IR laser operating at 808 nm was used to volatilize the analytes from the condensed surface and then a dielectric barrier discharge operating using an alternating

voltage of 10 kV and at a frequency of 25 kHz was used to excite the analytes further. The Cl and S were measured in commercial tablets of the drugs sulfadiazine and chloramphenicol. The dynamic range extended between 0.5 and 20%, R^2 was only 0.93 and LOD were reported to be at the mg kg^{-1} range. Although the linearity was not great, the sensitivity was sufficient for the analysis. The method was quick, the results of the commercial tablets were in agreement with expected values and the method could be used on-line because minimal sample preparation was necessary. Since LA is a very localised analysis, there was also the possibility that it could be applied to homogeneity studies of the pills.

Two papers by Pinheiro *et al.* described the dispersive liquid–liquid microextraction (DLLME) of analytes in pharmaceutical samples prior to ICP-OES analysis.[78,79] In the first example, the DLLME process involved extracting the analytes (Cd, Co, Hg, Ni, Pb and V) from the 10-fold diluted drugs into a deep eutectic solvent formed by mixing DL-menthol (2 M) with decanoic acid (1 M) at 60 °C.[78] The extraction procedure was optimized using Plackett–Burman design to identify significant factors followed by a central composite design to determine the optimal values for those factors that were significant. In this paper, there were seven parameters to be optimized. These were (with their respective minima and maxima): deep eutectic solvent volume (50 and 100 mL); sample pH (2 and 4); 8-hydroxyquinoline concentration (0.50 and 1.0% m/v); extraction time (1 and 3 min); centrifugation time (2 and 4 min); centrifuge speed (2000 and 3000 rpm) and ionic strength, NaCl concentration (0 and 5% m/v). Unfortunately, each analyte had a different set of optimal conditions. Therefore, a compromise set were used. These conditions were: sample pH of 3.4, 8-HQ concentration of 1.0% m/v, 70 mL of DES as extractant solvent, vortex time of 3 min, centrifugation time of 4 min and centrifugation speed of 3000 rpm. Since 8 mL of the 10-fold diluted drug was treated and the extraction volume of deep eutectic solvent was 70 μL, large preconcentration factors resulted (between 22 and 86, depending on the analyte). Linearity of standards was at least 0.9982 for all analytes. Spike/recovery experiments were undertaken with recoveries of between 90 and 109% being obtained. Precision was also acceptable with RSD values of <6% being obtained. The other paper was very similar in design, but fewer analytes were determined, (Cd, Hg and Pb).[79] Again, seven parameters were optimized and once optimized, the procedure yielded a performance very similar to the previous paper.

A *HPLC-ICP-MS method of determining the contaminant sodium hexachloroplatinate in carboplatin* was reported by Li *et al.*[80] Standard samples of the two species were first separated on a PRP-X100 anion exchange column using a mobile phase of 50 mM dihydrogen phosphate at pH 5.5. Once the retention times of the species had been determined, a four-way valve switching system was placed between the column and the ICP-MS sample introduction system. In that way very high concentrations of carboplatin could be directed to waste, ensuring that an excessively high Pt background did not exist for the detection of low concentrations of hexachloroplatinate. The linear range for the target species was 1–100 μg L^{-1} and the LOD was 0.1 μg

L^{-1}. Precision was 2.7–3.4% RSD and recoveries from spiked samples were 90–98.8%.

A simple and rapid method for determining *thimerosal (also known as thiomersal) in vaccines* was developed by de Oliveira *et al.*[81] It is added as a preservative, but being an organomercury compound, is toxic. The method of detection was cold vapour-atomic fluorescence spectrometry. There was therefore the requirement to transform the thiomersal into inorganic Hg so that the cold vapour generation efficiency could be maximized. To this end, the authors tested four different oxidation systems: (1) potassium bromide/potassium bromate; (2) potassium permanganate; (3) potassium iodide/potassium iodate and (4) sodium sulfide/potassium permanganate. Only systems (1) and (2) yielded quantitative oxidation. Spike/recovery experiments demonstrated a lack of matrix interferences, with recoveries being 80.1–106% for oxidant (1) and marginally better for oxidant (2) (92.5–101%). The system developed was then applied to the determination of thiomersal in five different vaccines with varying thiomersal concentration. Results were comparable to those obtained using a microwave assisted digestion followed by CV-AFS. The method developed was simple, rapid, reliable and accurate.

Zhu *et al.* developed a method that met the requirements of the US pharmacopoeia which was capable of *determining 31 analytes in calcium carbonate mineral medicines*.[82] The samples (0.025 g) were dissolved in 1.25 mL of a 4 : 1 mixture of nitric and hydrochloric acids. After dissolution, the digests were diluted to 25 mL. Higher weights of material were attempted to be used but resulted in interferences from the calcium matrix. Analysis was achieved using ICP-MS with an assortment of internal standards introduced as a mixture on-line rather than being spiked into individual samples. The internal standards used were ^{45}Sc for those elements with a mass up to and including ^{59}Co, ^{72}Ge for the analytes ^{62}Ni to ^{95}Mo, ^{125}Te for ^{101}Ru to ^{137}Ba, ^{175}Lu for the analytes ^{189}Os to ^{197}Au and ^{209}Bi for analytes with a higher mass. Any polyatomic interferences were removed through the introduction of helium at a flow rate of 5 mL min^{-1} into the collision/reaction chamber. Calibration standards were matrix matched with the relevant proportions of the acids in water and the concentrations for the analytes were 20%, 50%, 100%, 150% and 200% of the maximum concentrations allowed (once the dilution factors had been taken into account). Although a relatively simple analysis, the method has to conform to the requirements of the pharmacopoeias and so much of the paper was spent discussing exhaustive validation of the methodology.

3.1.3 Cosmetics and personal care products. This has been a relatively quiet area of research during this review period. Those papers that have been published cover numerous analytes but three have concentrated on measuring nanoparticles (and ions) in the cosmetics.

A paper by Zawisza *et al.* described a method for the *determination of Au and Au nanoparticles in assorted face creams, serums, cream masks, sun creams and pad masks*.[83] A nanocomposite of aluminium-magnesium double hydroxide/graphene oxide nanocomposite was made in house and characterized using XRD, Raman and SEM-EDS. Using

solutions and suspensions of Au and Au nanoparticles, it was found that when the sample was at pH 1–5 the Au nanoparticles were retained in only 5 min with an efficiency of 100%. When the pH was 1–2, both Au ions and Au nanoparticles could be retained. The method therefore enabled a pseudo-speciation to be achieved, depending on the pH used. The maximum sorption capacity was 12 mg Au per g of material. Once retained, the material was dried and then analysed using EDXRF. The LOD was 0.06 ng mL^{-1}, precision was ~4% RSD and recoveries were better than 90%. A test of the effects of concomitant ions was made. The presence of Fe^{III} decreased Au recovery to only 70% even when a 1 : 1 ratio of Fe^{III} : Au was used. However, the recovery was then stable at 70% when higher concentrations of Fe^{III} were present. Other concomitants, *e.g.* Ca, Cl, Cr, Cu, K, Mn, Ti, Zn and species such as phosphates, sulfates and vanadates had minimal effect. For the samples 0.25 g was dissolved using aqua regia with microwave assistance and then diluted to 25 mL. After adjusting the pH to 2, 1 mg of the composite was added to retain the Au. Since an aqua regia extract was used, the Au nanoparticles in the cosmetics were dissolved and so total Au was determined. Since 0.25 g of sample was used and the Au then extracted onto 1 mg of nanocomposite, a significant enrichment factor was obtained. Despite this, the Au in several of the samples could not be detected. This was despite the fact that the product clearly stated that Au was present. The conclusion therefore was that the method was successful for determining total Au in these products and could identify those products that were advertising the presence of Au falsely.

Silver nanoparticles were extracted from cosmetic samples and analysed using single particle (SP)-ICP-MS in a paper by Kantorova *et al.*[84] The stability and extraction efficiency of the nanoparticles were tested using several extraction media. A solution of 0.1% v/v methanol in water was the optimum. A ratio of 5 mL of methanol solution for 0.05 g of material was used with an extraction time (using sonication) of 25 min. Significant levels of ions were present in the extract and so the particle size LOD for the SP-ICP-MS was 33 nm. The concentration limit was 5280 particles per mL of extract, corresponding to 528 000 particles per g of the original sample. Five samples of commercially available cosmetics were analysed using the optimised methodology. Silver nanoparticles were found in three of them. These authors also used TEM to analyse all of the samples. Silver nanoparticles below the size LOD of the SP-ICP-MS were found for the other samples. The total Ag content in the samples was also determined and ranged in concentration between 0.45 and 20 μg g^{-1}, with the Ag nanoparticles comprising 0.02–1.9% of the total Ag content.

Another paper to determine and to *discriminate between Ag ions and Ag nanoparticles in consumer products* was presented by Gruszka *et al.* who used ETAAS followed by chemometric treatment of the data.[85] The method was based on the kinetics of atomization being different between the two species with the nanoparticles taking slightly longer to give a signal. However, there is significant overlap between the signal of ions and that of nanoparticles. The authors therefore resorted to the use of chemometrics to deconvolute the two signals when they were in admixture. Standard samples of citrate stabilized nanoparticles

with mean diameter 10 ± 4 nm, 20 ± 4 nm, 40 ± 4 nm and 60 ± 8 nm were used to collect data for the model and a further set of standards used to test it. Data were input to Soft Independent Modelling of Class Analogy (SIMCA). This had limited success in deconvoluting the samples, with a success rate of 25–60% being achieved. Data were then inserted to partial least squares regression (PLSR) which had more success. The method developed was applied to the determination of Ag nanoparticles and Ag ions in personal care products. The sum of the two was close to the expected total.

Calibration-free LIBS and AAS were used by Jamali et al. to determine analytes in the eye cosmetic Kohl.[86] As is the norm for calibration-free LIBS, the electron temperature and electron number density were calculated and then concentrations of analytes calculated. For the LIBS analysis, 3 g of wax and 10 g of kohl were mixed using a swing mill and then pressed into a pellet ready for analysis. For AAS measurements, 1 g of kohl was digested using 20 mL of nitric acid and 10 mL of hydrochloric acid. The mixture was placed on a hotplate and evaporated until 2–3 mL was left. This was then filtered and diluted to 100 mL. The results obtained from the two techniques for several elements were in pretty good agreement. As an example, the AAS result for Pb was 0.527% which was in reasonable agreement with the LIBS result of 0.456%. The results for Fe were in even better agreement (0.127 and 0.124% for AAS and LIBS, respectively).

There have also been some *forensic applications* of the analysis of organic materials. These have been placed in Section 5.3. The reader is referred there for more details.

3.2 Fuels and lubricants

This year there seems to have been a reduction in the numbers of papers in this topic, possibly indicative of fossil fuels being seen in a negative environmental light and affecting the research in this area. There was, however, a small increase in papers on alternative fuels and 'bio' fuels. Coal is still a very strong contributor particularly from China with most papers focussing on modelling to improve data quality from LIBS analyses. A number of papers were very simplistic, including nothing new and novel and researchers in this field are urged to investigate industry standard methods prior to undertaking any method development in this area.

3.2.1 Petroleum products – gasoline, diesel, gasohol and exhaust particulates. Only two papers were of note in this section this year and contributions were generally low in this area. The first by Sorouraddin *et al.* described a method for the *determination of Pb in gasoline using GF-AAS by micro extraction using a deep eutectic solvent.*[87] In this method gasoline was extracted using ethanol and nitric acid and mixed with acetate buffer. The deep eutectic solvent consisting of methanol, mandelic acid and glycolic acid was then used to complex the Pb^{II}. The mixture was centrifuged and the top phase separated for analysis using GF-AAS. The LOD achieved using this method was 1.6 ng L^{-1} and the LOQ 5 ng L^{-1}. This method seems a little over-complicated, however it may be useful where expense is an issue and more complex elemental instrumentation is not available.

The second paper in this section by Martinez *et al.* used *ICP-MS and a high temperature total consumption sample introduction system (hTISIS) for the analysis of fuels, biofuels and their feedstock*.[88] Samples were diluted with xylene prior to analysis. Temperature, collision/reaction gas type and flow rate were varied in order to obtain the highest signal to background ratio for each element. Compared with a conventional sample introduction system the hTISIS operating at 300 °C yielded lower LOD for 22 of the 24 elements investigated. The exceptions were Mg and Na. This approach could provide a robust method for use in routine laboratories.

3.2.2 Coal, peat and other solid fuels. Coal, despite the environmental issues around its use, is still a strong contributor to this section with five papers of note this year and one review. The review containing 102 references by Liu *et al.* covered the topic *of LIBS for coal analysis*.[89] It gave an overview of LIBS within the industry at this time and the current limitations and potential developing trends for this topic.

The first paper in this section by Hommel *et al.* looked into *the continuous measurement of K and S by ETV-ICP-OES to investigate high temperature coal conversion processes*.[90] To estimate the fouling, slagging and corrosion potential of a coal during thermal carbon conversion processes, it is necessary to determine the behaviour of elements such as K and S. This study investigated the element release in oxygen-containing atmospheres at varying concentrations.

A paper by Yu *et al.* compared the *matrix effects of LIBS analysis of coal particle flow compared with coal pellets*.[91] The particle flow analysis of seven coal samples was compared with conventional pellet analysis. By analysing and comparing the data the particle flow achieved a more consistent signal and the matrix effects were reduced compared with the pellet analysis. The results of plasma morphology and flame evolution indicated that particle flow analysis alleviates the laser thermal effect reducing the influence of the pyrolysis of volatiles on carbon atom distribution in the plasma. This makes particle flow analysis ideal for on-line, *in situ* measurements.

A paper by Lu *et al.* described a method for the *quantitative determination of Ca, Na and V in petroleum coke using LIBS with a binder*.[92] In this paper a stearic acid binder was used, and the sample pressed into pellets. It was found that 30% stearic acid produced the best signal stability and the fewest matrix effects. Limits of detection achieved using this method were 0.51 mg kg^{-1} for Ca, 0.41 mg kg^{-1} for Na and 1.19 mg kg^{-1} for V.

The next contribution, by Petrovic *et al.*, investigated the *applicability of LIBS based on an infrared transversally excited atmospheric CO_2 pulsed laser for quantitative determination of inorganic elements in lignite coals*.[93] Calibration standards were prepared by mixing and pelleting an appropriate amount of rock reference material and graphite. Calibration curves were produced for Al, Ca, Fe, Mg and Si. The spectral intensities of analytical lines were normalized by the C spectral line to compensate for shot-to-shot fluctuations. The obtained calibration curves had good linearity over a wide range of concentrations with correlation coefficients in the range of 0.955–0.993, depending on the element. Limits of detection varied from 2.4 to 25 ppm for metals and 61 ppm for Si. These limits

are low enough to control the coal combustion processes in power plants.

An interesting paper submitted by Samanta *et al.* described the application of an *external particle induced gamma emission (PIGE) method for the quantification of light elements in coal, bottom ash and coke*.[94] An accelerator-based nuclear technique, PIGE is capable of quantifying low *z* elements (Li to S) using a low energy proton beam. The beam was collimated using a Ta collimator and the proton beam of 5 MeV was reduced to 3.5 MeV at the target. Targets were placed in front of the collimated beam and a high purity Ge detector placed 90° to the beam direction. Detection limits for B and F were 2 mg kg^{-1} and 90 mg kg^{-1}, respectively.

3.2.3 Oils – crude oil lubricants. Contributions for this section appear to have increased this year but unfortunately at the cost of quality. Many papers focus on various types of emulsion breaking sample preparation techniques however many are lacking analytical rigour, including detection limits and use of CRMs or samples with known concentrations for validation.

The first paper in this section, by Henn *et al.*, described a *microwave digestion method for the Mg, Pb and Sr isotopic analysis of crude oil*.[95] This method was compared with the ASTM D4807 method of decomposition. Column chromatographic protocols for target element isolation were fine-tuned for each analyte to ensure quantitative yields. No statistical difference was observed between the results for Mg and Sr isotope ratios obtained using both sample preparation methods. However, Pb was not recovered using the ASTM D4807 protocol. The Brazilian crude oil samples analysed were within the isotopic range observed for seawater and the deposit bedrock, suggesting that the method developed can be considered as a promising tool to decipher the formation history of oil reservoirs.

The next paper in this section was by Chacon-Patino *et al.* who aimed to extend previous studies to *characterize volatile and non-volatile Ni and V distributions by selective separation of n-heptane asphaltenes obtained from two Venezuelan heavy crude oils and the NIST Standard Reference Material (SRM) 8505*.[96] Asphaltenes were separated by extrography, *i.e.*, adsorption on SiO_2 and subsequent extraction with acetone, heptol (*n*-heptane/toluene 1 : 1 vol), and a mixture of toluene, THF and methanol. The results suggested that their solubility and aggregation strongly correlate to a higher hydrogen deficiency and increased heteroatom levels. High temperature gas chromatography coupled with ICP-MS showed that Ni and V compounds have boiling points of at least 566 °C. Quantification of the V-content below 704 °C for the Venezuelan crude 1 indicated that the acetone fraction contained a large amount of distillable V (similar to 62% wt). These results suggest that the extrography method is useful to produce fractions enriched with asphaltene species. Understanding Ni and V concentrations in asphaltene fractions has significant commercial importance as they are potential feedstocks as a precursor of carbonised materials such as carbon fibres.

Mohsen *et al.* submitted a paper describing the *synthesis of ionic imprinted polymers to determine V^{IV} in crude oil*.[97] Various

monomers were studied to obtain the largest adsorption capacity for V. These polymers were packed into SPE cartridges, the sample passed through, and the polymers then digested in sulfuric and nitric acids. Determination of V was achieved using AAS. The LOD for this method was 5 ng mL^{-1} and determination of V in crude and fuel oils of known V concentration agreed between 98 and 101% of accepted concentration.

Two papers describing methods of asphaltene analysis using gel permeation chromatography (GPC) were of interest this year. Asphaltene molecular composition and structure is important in petroleum chemistry however molecular characterization is hampered by aggregation. The first paper on this subject, by Acevedo *et al.*, investigated *nanoparticles and asphaltenes, interactions and their consequences using a quartz crystal resonator and GPC-ICP-HR-MS*.[98] In this study asphaltenes in toluene solutions were treated with biogenic SiO$_2$ nanoparticles and analysed. Deposition processes were followed using the quartz crystal resonator and the results showed nanoparticles effectively remove the largest aggregates. Molecular weight profiles were produced by analysis of S and V using GPC-ICP-HR-MS.

The second paper on this subject was by Zheng *et al.* who tracked *changes in asphaltene nanoaggregate size distributions as a function of Ag$^+$ complexation via GPC-ICP-MS*.[99] Atmospheric residue was analysed with and without the addition of silver triflate to disrupt aggregates that exist in the whole sample. The results suggested that silver triflate had very little effect on the S containing species but disrupts high molecular weight material to liberate V and Ni which then elute in the low molecular weight region.

3.2.4 Alternative fuels. Three papers and a review were of interest in this section this year. The number of papers on this subject had increased, however many were of little interest just describing standard methods for analysis for a set of collected bio-fuels and lacked analytical rigour.

A review article, by Martinez *et al.*, containing 180 references on the subject of *multi-elemental analysis of renewable fuel feedstock* has been published this year.[100] The use of oils and fats, mainly from non-edible or used sources, microalgae, plastic wastes and lignocellulosic residues are increasingly used as feedstock. Quality control of these materials involves the quantification of trace elements because their presence, even at trace levels, can lead to environmental concerns and may impact the performance of combustion engines. In order to circumvent these problems, accurate and sensitive analytical techniques are required to control the level of these elements. This paper reviews the different analytical tools used to undertake this type of analysis. The review focussed mainly on ICP techniques and sample preparation procedures *e.g.*, direct dilution, emulsification, extraction, and matrix decomposition. It provides an overview of analysis in this field at this time.

Garcia-Montoto *et al.* looked *at P speciation of fatty acid-based feedstocks and fast pyrolysis biocrudes using GPC-ICP-HR-MS*.[101] Renewable feedstocks, such as lignocellulosic fast pyrolysis oils, vegetable oil and animal fats, are becoming a viable alternative to petroleum for transportation fuels. However, the presence of P-containing compounds, mainly from phospholipids, in these feedstocks is known to poison and deactivate hydrotreating

catalysts during fuel production. In this work, GPC-ICP-HR-MS was used to analyse feedstocks including unprocessed soybean oil, animal fat and pyrolysis oils from red oak and milorganite to identify P species. The results showed the presence of a wide range of different P compounds. Analyses of a vegetable oil and two animal fats show different fingerprints based on the molecular weight of each of the samples, highlighting the structural differences among their corresponding P-containing compounds. While the presence of low-molecular-weight species, such as phospholipids, was expected, several high-molecular-weight species (MW > 10 000 Da) were found, suggesting that high-molecular-weight micelles or liposomes might have been formed due to the high concentration of phospholipids in these samples.

The second paper in this section, by Calbry-Muzyka *et al.*, compared *on-line and off-line measurements of organic Si compounds at an industrial biogas fed, solid oxide fuel cell plant*.[102] Online measurements of total Si were carried out using a nondispersive infrared sensor. Different sampling methods, including chemical adsorption, liquid quenching and solid-phase adsorption were used at six biogas sampling points. Organic Si compounds in the samples were determined by off-line methods including GC-FID and GC-ICP-MS. The online analyser's performance was satisfactory in both untreated biogas and in clean biogas where <0.1 mg m^{-3} of siloxanes were detected.

Finally, a paper by Wang *et al.* discussed the LIBS analysis of *ammonium dinitramide-based propellants that are used as fuels for thrusters for space propulsion*.[103] A heating sampler was developed to produce a premixed sample with a known mixture ratio. This was connected to a chamber that had been designed to simulate the space propulsion environment. The LIBS was used to measure emission intensities of the analytes H (at 656.3 nm), N (at 746.8 nm) and O (at 777 nm) as well as the Ar (at 738.4 nm) that was the inert gas atmosphere. Emission ratios of H/Ar, O/Ar and N/Ar were utilized successfully as a diagnostic tool to obtain the distribution of the propellant in the inert atmosphere. The authors concluded that the LIBS-based results provided fundamental data for the on-line measurement of ammonium dinitramide-based thrusters and that this may pave the way into LIBS analysis of energetic ionic liquids.

3.3 Polymers and composites

This has been a surprisingly busy area of research during this review period. Many of the applications have focussed on two main subject areas: the sorting of polymers for recycling and the analysis of microplastics. For the former, LIBS has found significant use. This is especially true now that portable/hand-held LIBS instruments are available commercially.

3.3.1 Reviews. *Five reviews have been published covering different aspects of this subject* area during this review period. One of the reviews, by Zeng *et al.*, covered (with 129 refs) the use of LIBS analysis of plastic materials.[104] This area has received increasing interest over several years now and so this review is timely. The review is conveniently split into sections and makes good use of easily referenced tables. Section headings include:

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instruments, analysis methods (including ratio methods for C/H *etc.*, statistical methods employed, chemometric tools employed), applications including on-line methods and a conclusions and future perspective. The biggest section is that describing the use of chemometric tools. Although the review does not discuss the theory of each of the methods, it does give examples of the packages used. These include: principal component analysis (PCA), soft independent modelling of class analogy (SIMCA), artificial neural networks, random forest, partial least squares, support vector machines (SVM), least absolute shrinkage and selection operator (LASSO) and several others. The review is well written and would be of interest to workers in the field. A similar sort of review by Neo *et al.* focussed on the chemometric techniques used to interrogate IR, Raman and LIBS data for sorting plastics in the recycling industry.[105] This review contained 155 references and covered topics such as: PCA, linear discriminant analysis (LDA), Partial Least Squares (PLS), K-nearest neighbour (KNN), SVM, random forests, neural networks and k-means clustering. A brief explanation of each was provided and then their use with IR, Raman and LIBS discussed in separate sections. Tabulation is used to good effect enabling the reader to easily identify which plastics have been identified, with what accuracy *etc.* A review by Kutralam-Muniasamy *et al.* overviewed microplastic pollution, methods used for analysis, transfer risk of metals to organisms and calls for relevant standardization.[106] The overview has 55 references and also relies heavily on well-tabulated data. It covers current methods of extraction (combinations of different acids under different conditions), detection and quantification of metals (the different instrumental techniques used), challenges, quality control and quality assurance. Since large discrepancies in results can occur through relatively small changes in experimental protocol, the review calls for standardized methods to be used. The fourth review (80 refs) was presented by Velimirovic *et al.* and was entitled "Mass spectrometry as a powerful analytical tool for the characterization of indoor airborne microplastics and nanoplastics".[107] The review defined what these particles are, gave a brief overview of where each particle size may end up in the body and then devoted the majority of its pages to analytical challenges, sample collection and preparation strategies, and mass-spectrometry-based methods for particles characterization. These included single particle ICP-MS as well as varying forms of organic mass spectrometry, such as pyrolysis-GC-MS, MALDI-TOF-MS, liquid chromatography-high resolution mass spectrometry, thermal extraction/desorption GC-MS and direct analysis in real time mass spectrometry. In its future perspective section, this review also calls for standardized methods as well as optimized methods of sample collection and extraction. The fifth review was presented by Prasad *et al.*[108] and discussed the TOF-SIMS analysis of polymer surfaces (59 refs). In the introduction, the review sets out the history of TOF-SIMS and describes its advantages over other surface techniques such as Auger electron spectroscopy and XPS. A theoretical section then covers the formation and extraction of secondary ions and another section describes sample preparations steps. Much of the rest of the review is split into sections covering individual polymer types. A good section on the limitations and challenges faced by TOF-SIMS and future perspectives round off the review.

3.3.2 Analysis of micro- and nanoparticles. This has been a popular area of research. It is known or has long been suspected that micro- and nanoparticles of polymers in the environment can act as sinks for toxic trace elements and other organic materials. Atomic spectrometry can be used to identify the plastics, determine which metals are associated with them, determine whether or not they are released from the particles once inside an organism *etc.* As well as the reviews described in the previous section, numerous applications have been described and these will be discussed below. It is important to differentiate between engineered nanomaterials discussed in Section 4.9 and those micro- and nanoparticles of plastic that have been formed by weathering or degradation of larger plastic bodies. It is the latter that are discussed in this section.

A method for the counting of nanoplastic particles in environmental waters was reported by Lai *et al.* who used single nanoparticle (sNP) ICP-MS technology that has been developed over the last few years.[109] The method involved the destruction of natural inorganic nanoparticles using nitric and hydrofluoric acids at pH 2, cloud point extraction of the nano-polymers using Triton X45 and some sodium chloride solution (not required for seawater samples), labelling of the polymer materials with Au, sucrose density gradient centrifugation to separate the labelled polymers from Au nanoparticles and then detection using SP-ICP-MS. The procedure was optimized ensuring that the Au was attached to numerous polymer types (polystyrene, polyethylene, polyethyleneterephthalate, polyvinyl chloride and polymethylmethacrylate). Although the method could not differentiate between different polymers, it could give an estimate of the total polymer particle number concentration and the particle size distribution. The developed method was applied to river, lake, sea and waters discharged from a wastewater treatment plant. The particle number LOD was 4.6×10^8 L^{-1} based on 269 nm diameter spherical polystyrene nanoparticles. Spike and recovery experiments indicated recoveries between 72.9 and 92.8%, depending on the polymer type and matrix. This is a good example of where a rather theoretical and "dry" subject such as nanoparticle analysis can be applied to real world problems.

The *labelling of nano-plastics with metal probes so that they be measured more easily* has been studied by Marigliano *et al.*[110] Polymers usually contain C and H (and some may also contain O or N) and therefore are not readily detectable using ICP-MS. Labelling them with a metal therefore facilitates their determination. This paper discussed three strategies whereby metals are attached to the plastics: labelling with metal ions, labelling with hydrophobic organometallic compounds and labelling with metal nanoparticles. The relative merits and drawbacks of each of the strategies were discussed, with examples of each given. Labelling with ions always has the possibility that insufficient of them will attach to the polymer surface or that too many ions remain in solution making it difficult to differentiate between dissolved ions and nano-polymer-attached ions. These problems are not encountered with nanoparticles, since separating free nanoparticles from those attached to the

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polymer is relatively straightforward and well-documented. The authors concluded that labelling either with hydrophobic organometallic compounds or with metals nanoparticles were the most promising strategies, with Au nanoparticles perhaps being the best option of all.

Several other quite exciting applications have been presented in this review period. Sommer *et al.* used *LIBS to identify microplastic litter*.[111] A Q-switched Nd:YAG laser operating at 532 nm and with a frequency of 10 Hz and energy of 200 mJ was used for the measurements, with detection achieved using a spectrometer equipped with an intensified CCD. Reference pieces of assorted polymers were used to "calibrate" the system. Measurements were made for C at 247.8 nm, for H at 486.14 nm and 656.29 nm, for N at 746.8 nm and for O at 777.3 nm. In addition, molecular bands for C_2, CH, CN, OH and CO were also monitored. Analytical data were input to PCA to aid the identification. The method proved to be very successful and was capable of distinguishing between polymer microparticles and other naturally occurring particles. In addition, it was able to differentiate between different polymer types. The method was extremely rapid (~1 s per measurement), portable, could be used for depth profiling (by analysing the same spot with successive laser firings) and offered great hope for studies held *in situ*.

Another paper that reported the identification of microplastics was presented by Feng *et al.*, who developed a *rapid SIMS method to identify and spatially map the polymers in Paramecia* (a type of unicellular organism).[112] Paramecia were exposed to six types of micro-polymers (polymethyl methacrylate, polyvinyl chloride, polypropylene, polyethylene terephthalate, polyglycidyl methacrylate and polyamide) that were in the diameter range 1–50 μm and at a concentration of 50 mg L^{-1} for 24 h. The resulting paramecia were then analysed using TOF-SIMS employing a Bi^{3+} ion primary beam at a power of 30 keV over a 300 × 300 $μm^2$ area. For 3D work, the sample was sputtered using an argon beam prior to analysis using the Bi^{3+}. Each of the different polymers produced a different mass spectrum, enabling identification to be made, even when no sample preparation was required. Each micropolymer type produced at least two fragments that led to a positive identification – even when a mixture of polymers was present. The resolution was slightly better than 700 nm meaning that a polymethylmethacrylate microparticle of 2 μm diameter and weighing ~4.6 pg may easily be detected. This is clearly an impressive result and the technique holds a great deal of promise for the future.

Another paper with an environmental bent was prepared by Liu *et al.* who developed a method of quantifying the dynamics of the UV aging process of polystyrene microplastics.[113] Given the enormous amount of plastic entering the environment and that this experiences degradation through UV irradiation, it is vital to see how it weathers, at what speed and what it weathers into. These authors therefore obtained polystyrene particles with a maximum diameter of 5 μm and made a 10 mg L^{-1} suspension with them. A 36 W UV light then irradiated the suspensions for set time periods (0, 3, 6 and 12 h). After each period, single particle ICP-MS was used monitoring the ^{13}C

signal to identify the particle size distribution. The results were compared with those obtained using SEM and were in broad agreement. Both techniques identified that the average particle size reduced almost straight away. Interestingly, the particle number concentration did not alter much during the first 12 hours, indicating that secondary particles were not formed. However, secondary particles did begin to form after 12 hours, with the total particle concentration reaching a maximum after 20 hours and having almost three times the number of particles than at the start.

A paper by Teramoto and Kim described the *development of a temporally and spatially resolved ICP-OES instrument* capable of measuring the size distribution of plastics.[114] Suspensions of polystyrene particles of 1.5 μm and 3 μm were prepared and introduced to the instrument using a monodisperse micro-droplet dispenser operating at high frequency (400 Hz). The ICP torch was inverted so that gravity could aid the stability of the sample introduction. A high speed camera operating with a double monochromator was used to detect the particles. A full description will not be given here, because it is not really an application of polymer analysis. However, it was capable of clearly separating the 1.5 and 3 μm particles and could be a powerful tool for such environmental analyses.

3.3.3 Sorting of polymers for recycling. The *recycling of polymers is of ever-increasing importance but classifying them is an analytical challenge*. Some of the coloured (or black) polymers cannot be analysed using IR and most polymers have similar components, *i.e.* C and H, with a few also having N and O. The reader is directed to Section 3.3.1 for a review by Neo *et al.* entitled "A review on chemometric techniques with infrared, Raman and laser-induced breakdown spectroscopy for sorting plastic waste in the recycling industry" which is relevant to this section.[105] It is known that LIBS can be used to differentiate between some polymers but often the spectra are very similar. A paper by Gajarska *et al.* used LIBS to obtain data and then treated the analytical data with a suite of chemometric tools (PCA, K-Nearest Neighbour (KNN), Hierarchical Cluster Analysis and Random Forest) and, in doing so, managed to differentiate between 20 different polymer types.[115] The LIBS parameters of gate delay, atmosphere (argon or air) and laser energy were optimised for the determination of C, C_2, Cl, CN, H, O and Si. Since such a large number of polymers were being tested, using different operating parameters and for different analytes, a huge number of variables resulted. This was simplified by forming "cluster purity" obtained using KNN. The best resolution for the 20 polymers was obtained using the shortest gate delay (0.1 μs) at the highest laser energy (3 mJ) and in an argon atmosphere. However, there was still significant overlap of some clusters. The authors therefore undertook a second optimization, this time of the spectral variables with the greatest relevance for polymer identification. When both optimizations were used, PCA and hierarchical cluster analysis could classify the 20 virgin materials which is among the greatest number reported thus far. In addition, polymers containing additives could also be identified, meaning that the method could potentially be used for real scrap samples.

The other paper in this section was presented by Liu *et al.* who used *LIBS analysis followed by chemometric methods to sort 20 types of polymer*.[116] Initially, only SVM was used to process the LIBS data, with half of it being used to train the model and the other half to test it. The method was very successful with 99.9% of the samples identified correctly. However, since the number of variables was so high, it took a long time for the processing (the modelling time was nearly two hours and the prediction time was 11.96 s). It is clearly unrealistic for such a slow process to be used in the "real world". Consequently, the authors employed PCA to decrease the number of variables. When 13 principal components were used prior to input to SVM, the identification rate dropped very marginally to 99.80%, but the time required for processing decreased dramatically such that the processing time was 1.44 s, modelling time was 12.16 s and the prediction time was only 0.02 s. This method is rapid and accurate and could feasibly be used for sorting at a recycling plant.

3.3.4 Other applications of the analysis of polymers.
A paper by Makino and Nakazato described the rapid determination of trace elements (Br, Cd, Cr, Hg and Pb) with an acceptable degree of accuracy in different polymer types using LA-ICP-MS and ^{13}C as an internal standard.[117] Numerous CRMs of several different polymer type were analysed; two of which were used for calibration (the ones with the lowest and highest concentration for each element) and the others as samples. The materials included EC680 and EC681 (polyethylene), NMIJ8103a (acrylonitrile butadiene styrene), NMIJ8123a (polyvinyl chloride), NMIJ8133a (polypropylene), JSAC0631 and JSAC0632 (polyester). The C content was measured using a CHN analyser and ranged from 45.620% to 85.543%. A Ti–sapphire laser operating at 266 nm was used to ablate the samples and the optimized fluence was 8 J cm^{-2}. Calibration regression coefficients when the internal standard was not used were respectable (0.8067–0.9980). However, when the ^{13}C was used, the regressions improved to 0.9556–0.9993. The worst performing analyte on both occasions was the Cd. Analysis of the other CRMs yielded data that agreed with certified values to within 30%. Precision was variable with RSD values ranging from 3 to 60%. The poorer values for precision were ascribed to inhomogeneity in the sample.

A relatively simple method of determining *Cd and Pb in food contact polymers* was described by Henn *et al.*[118] The microwave-assisted solid sampling method of sample introduction to flame furnace AAS used few chemicals and hence minimized waste and was therefore better for the environment. Sample was weighed into a quartz boat containing a cellulose pellet (mass 20 mg for Cd and 10 mg for Pb) and then soaked in 20 μL of 6 mol L^{-1} ammonium nitrate. The boat was inserted into the introduction device and microwave heated in the presence of oxygen (0.6 L min^{-1}). The analytes released were passed through a quartz transfer tube into a quartz tube placed on an AAS instrument's burner head. Calibration was achieved through aqueous standards being placed on the cellulose pellet and combusted in the same way as the samples. Limits of quantification were 1.7 mg kg^{-1} for Cd and 4.6 mg kg^{-1} for Pb. The accuracy of the method was demonstrated through the

analysis of CRMs (BCR 60, DOLT-4 and TORT-2) and through a conventional microwave digestion followed by ICP-MS determination. Results were in good agreement with certified values and many were also in agreement with the alternative method. This was especially true for the analysis of polypropylene. Analysis of HDPE, however, resulted in data only just over half that obtained using the full microwave digestion. This was attributed to additives in the polymer preventing it from combusting efficiently. The method clearly achieves its goal of producing less waste, but the inability to analyse all polymer types is somewhat worrying.

An interesting application was presented by Breuckmann *et al.* who determined *C, H, N and O in plastics using the WDXRF Rayleigh and Compton scattering spectra from a rhodium source* and partial least squares regression.[119] The method was applied to 84 polymer samples, some of which were thermoplastics and others thermoset plastics (*e.g.* polyurethane, epoxy resins and polyester resins). The PLS model was trained using 56 of the samples and the other 28 samples were used for validation. The method for model development was described in the paper. The results obtained were compared with those obtained using a standard elemental analyser and, for C, H and O were in good agreement. This is remarkable since H does not usually offer an XRF signal. The results for N were less accurate. This was thought possibly to be because fewer polymers contain N. The method was very encouraging though and the authors thought that it could be used equally successfully with EDXRF instruments, including the portable/handheld ones and be applied to other organic rich materials, *e.g.* soils.

The determination of F in polymers suffers from poor emission sensitivity because it is so hard to excite. Weiss *et al.* applied LIBS to the analysis of fluoropolymers enabling F to be determined.[120] This was achieved using molecular LIBS rather than the conventional atomic LIBS. A layer of copper foil or of calcium acetate was placed over the sample. As the LIBS laser ablated the sample, the F released interacts with the copper or calcium coating forming CuF or CaF. It is the emission originating from these molecules that is quantified. For the CaF, measurement was in the region of 531 nm and for CuF it was at 493 nm. The F line at 685.6 nm was also monitored for comparison. The linearity and sensitivity were tested by mixing different proportions of PTFE powder (3 μm) with cellulose powder (20 μm) and then pressing into a pellet. A range of pellets with an F content of between 0.6 and 14.5% w/w was obtained. After the layer of Cu or Ca was added, the analysis was undertaken. The LOD for the CuF was marginally better than for CaF (160 μg g^{-1} compared with 240 μg g^{-1}) and the R^2 was also better (0.99 compared with 0.95). When determining the F directly at 685.6 nm, the laser energy had to be much higher (6 mJ compared with the 1.6 mJ for both of the molecular bands). This yielded a LOD similar to that for CuF, but with a poorer R^2 value (0.94). The authors noted that although the LOD was similar, the higher energy laser shot required would do much more damage to the sample and would not be applicable to thermally sensitive materials. Since it is possible to undertake a raster across the surface, the method developed is therefore

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also capable of mapping the surface of the polymers to determine the homogeneity.

Epoxy nanocomposites have been the subject of study by Babu *et al.*[121] Aged epoxy micro-nanocomposites were classified using LIBS analysis followed by PCA and an Artificial Neural Network (ANN) data treatment. Material was aged in two ways: gamma irradiation using a ^{60}Co source at a dosage rate of 600 Gy h^{-1} and water aging by placing sample in distilled water at room temperature and at 90 °C until the weight gain remained unchanged. The LIBS intensities of two Zr lines were used to calculate the plasma temperature and it is this parameter along with the size of the crater that was used to assess the aging state of the material. The plasma temperature decreased and the crater size increased with increased aging, implying that the surface is softer. Data were then input to PCA to reduce the number of data points. Plots of PC1 *vs.* PC2 *vs.* PC3 for gamma irradiation-aged samples clearly identified those samples that were virgin, had been irradiated to a dose of 4 kGy and those at a dose of 8 kGy. Similar plots for the water-aged samples could also clearly discriminate between virgin material and those samples that had been aged at room temperature and those aged at 90 °C. Discrimination between the methods of aging could also be achieved. Application of an artificial neural network to the data led to even better classification than that achieved using PCA. The clear conclusion was that LIBS may indeed be used to classify the method and extent of aging of these materials.

There are *two forensic applications* of polymer analysis.[122,123] These are discussed in more detail in the forensic section and will therefore not be discussed further here. The reader is referred to Section 5.2 for more details for these papers.

4   Inorganic materials

As usual, there are a huge number of relevant papers for these sections. It should be noted that the review this year has a slightly different structure in that all of the forensic applications have been placed in one section (Section 5). Readers looking for applications regarding the analysis of gunshot residue, explosives and other materials should refer to that section.

4.1   Catalysts

As usual, this has been a very busy area of research, but little of it was research into the atomic spectrometry aspect. There are therefore, relatively few papers to be reviewed out of the many hundreds in the subject area. Papers that report a new catalyst and then simply characterize it using XRF or ICP-OES will not be reviewed as the atomic spectrometry is very routine – even if the catalyst is not. To improve the understanding of catalysts and to design better materials, it is crucial to study them during their catalytic active states. Therefore, what will be reviewed are those papers that use atomic spectrometry to elucidate catalytic mechanisms and therefore help optimize the manufacture or operating conditions. Papers that report the use of on-line atomic spectrometry will also be reviewed for the same

reason. Operando spectroscopy (an analytical methodology wherein the spectroscopic characterization of materials undergoing reaction is coupled simultaneously with measurement of catalytic activity and selectivity) is therefore among the more novel aspects of these papers.

A paper by Pishgar *et al. reviewed, with 246 references, in situ analytical techniques for the investigation of material stability and interface dynamics in electrocatalytic and photoelectrochemical applications*.[124] Methods discussed included: *in situ* UV-vis, ambient pressure X-ray photoelectron spectroscopy, *in situ* Raman, on-line ICP-MS, differential electrochemical mass spectrometry and varying types of microscopy. The advantages, disadvantages and capabilities of each were discussed.

Czioska *et al.* investigated the *Ir–Ir interaction in iridium oxide during the oxygen evolution reaction at high potentials using operando spectroscopy*, in this case, XAS.[125] Both calcined and uncalcined iridium dioxide nanoparticles were tested in an operando spectro-electrochemical cell. *In situ* XAS analysis of the material under different applied potentials indicated strong structural changes when changing the potential. The XAS data were then treated using principal component analysis (PCA) and FEFF9 (a software package for treating X-ray data). It was found that oxygen vacancies and lower oxidation states of Ir were formed at higher potentials. This meant that the model for the oxygen evolution reaction had to be modified. At potentials above 1.5 V stronger Ir–Ir interactions were observed especially in the calcined iridium dioxide samples. The atomic spectroscopy therefore provided insights at the most fundamental levels for this catalyst system.

Laboratory scale *XAS was employed by Huang et al. for the in situ analysis of a palladium catalyst on a compact inverse-Compton scattering X-ray beamline*.[126] Although XAS is one of the most powerful techniques for catalyst analysis, it suffers the drawback of having X-ray tubes that have a limited spectral flux density. This restricts them to *ex situ* or *in situ* experiments conducted over a large time scale, especially for X-ray energies above 15 keV. This paper discussed the use of a compact synchrotron facility based on inverse Compton X-ray scattering. It possesses a brilliant, low-divergence, energy-tuneable X-ray beam making it well suited for XAS techniques, especially for *in situ* experiments. The catalyst studied was a hydrogen-treated palladium/carbon type that exhibited significantly better decarboxylation activity than a bare palladium metal/carbon catalyst. A series of X-ray absorption near-edge structures (XANES) at the Pd K-edge (24.4 keV) was made, with spectral quality being equivalent to those from a synchrotron but with less than five minutes per spectrum being required. These enabled the authors to identify that the formation of alpha-phase palladium hydride may be the reason for the enhanced performance of the hydrogen-pre-treated Pd/C catalyst.

The *development of a system to enable the use of a commercially available gas-cell chip assembly within an X-ray nanoprobe beamline* was reported by Parker *et al.*[127] Its *in situ* capability was demonstrated by investigating the redox behaviour of supported platinum nanoparticles on ceria under typical lean and rich diesel-exhaust conditions. Excitingly, the setup allowed complementary techniques such as *in situ* transmission

electron microscopy and X-ray nanoprobe studies to be used under identical conditions. This has a major advantage compared with other systems because the same cell can be used since it is easily transferred between instruments. Therefore, the same catalyst particles can be studied under identical conditions of gas flow, pressure and temperature using multiple techniques.

In recent years *platinum-based bimetallic alloys have been investigated as an alternative to bare platinum cathode catalysts for proton-exchange membrane fuel cells* to improve their cost-effectiveness.[128] However, they have a reduced stability, which is poorly understood at a fundamental level. It is necessary to elucidate the entire chain of interconnected degradation mechanisms to formulate a comprehensive model of catalyst degradation that will help interpret bimetallic alloy behaviour. Bogar *et al.* combined *in situ* ICP-MS with *in situ* grazing-incidence small-angle X-ray scattering and *ex situ* SEM to study the morphological evolution of Pt_xNi_{100-x} model catalysts with Ni contents ranging from 0 to 75% that were undergoing potentio-dynamic cycling to two different upper potentials. It was therefore mimicking the different operational conditions of a proton-exchange membrane fuel cell. Analysis of the results enabled the authors to develop a methodology to distinguish the influence of Ni dissolution, particle coalescence and Ostwald ripening on particle size distribution and interparticle distance. They could also prepare time-dependent interplay maps to highlight the timeframe in which these phenomena occur. When 1.0 V was used as the upper potential, Ni dissolution was the prevalent force in morphological change. However, at 1.3 V, the Ni dissolution is rapidly overcome by particle coalescence at first and then by Ostwald ripening in the later stages of the investigated time range. The effects were more rapid with increasing Ni concentration.

Iridium catalysts are well known to be the best catalysts in acidic medium for the oxygen evolution reaction because of their stability and relatively high activity.[129] However, iridium is a scarce and expensive metal and so alternatives are sought. One possibility is to disperse the iridium in titanium dioxide, forming a mixture. However, the extent to which the performance of the mixture can be optimized is unknown. These authors used a scanning flow cell connected to an ICP-MS instrument to examine the activity and stability for the oxygen evolution reaction of a series of oxidized Ir–Ti thin films covering the composition range from 20–70% Ir. Irrespective of the composition, the Ir dissolution rate was below that of thermally prepared iridium dioxide. In addition, mixtures containing at least 50% Ir had a comparable activity to iridium dioxide. The superior performance was also investigated using XPS and atom probe tomography. Although this application is not strictly operando, the flow cell did enable a real time monitoring of Ir dissolution.

A similar approach was taken by Dukic *et al.* who used an *electrochemical flow cell connected to an ICP-MS instrument to monitor the time- and potential-resolved dissolution of carbon-supported intermetallic Pt-alloy electrocatalysts used for the oxygen evolution reaction*.[130] An in-house designed high-temperature disk electrode was also used in the study. The C

dissolution obeyed the Arrhenius law and its dissolved concentration increased exponentially with increasing temperature. Unexpectedly, the Pt dissolution also increased with increasing temperature. This, combined with the dissolution attributed to the rising potential governs the stability of the Pt. In addition, for the Pt alloy electrocatalysts, the Pt dissolution will also affect the dissolution of the other alloying material. Interestingly, the re-deposition rate of Pt also increases with temperature and, in the past, this has led to the mechanistic interpretation of the temperature-dependent kinetics related to the stability of Pt being confounded.

Two papers of interest *have employed LIBS for the analysis of catalysts*. One by Jolivet *et al.* reported the impregnation of alumina with nickel nitrate in the presence of citric acid.[131] The wet material was then sampled, cut in half and analysed using LIBS over different maturation times (between 30 s and 23 hours). The LIBS system was described in full, with a Nd:YAG laser operating at 1064 nm, at an energy of 1.5 mJ and at a repetition rate of 100 Hz. Sample was put on a motorized XYZ translation stage and with the assistance of a 15-fold magnification, the laser target area was highlighted. The translation stage moved in steps of 15 μm and the crater created was less than 15 μm in diameter. Light emitted was transmitted *via* fibre optics to two Czerny–Turner spectrometers, each equipped with a CCD. Results obtained using the system were compared with those obtained using the conventional techniques Raman and magnetic resonance imaging. Using LIBS, the analysis time was shortened by a factor of 30 and the low detection limits and its multi-elemental capabilities provided valuable information to understand the phenomena occurring during catalyst impregnation. The conclusion was that LIBS imaging has huge potential as a unique characterization technique capable of simultaneously monitoring the distribution of the metallic precursor, organic additive and support impurities. The other paper to use LIBS was by Burnette *et al.*[132] These authors studied the iridium-based catalysts used in monopropellant thrusters which have been used for decades to manoeuvre spacecraft. Unfortunately, the degradation or loss of the catalyst is known to limit their lifetime. Thus far, no method has been available to monitor the health of these iridium-based catalysts *in situ*. They therefore used a LIBS system to quantify iridium in the gas phase by thermally vaporizing various organometallic iridium compounds with known concentrations within a test cell and then monitoring the resulting iridium signal from optical emission lines that had no interfering lines in the region. The LIBS system employed a pulsed Nd:YAG laser operating at 355 nm with a repetition rate of 10 Hz and with an 11 ns pulse duration. Typically, 75 ± 5 mJ per pulse of laser light was focused down by a planar-convex lens to a spot size of 10 μm. Light emitted from the sample was transmitted through a fibre optic to a Czerny–Turner spectrometer equipped with an intensified CCD. The test cell was interesting. It was a Pyrex cell consisting of a six-way cross. The laser entered and exited through transparent windows along one axis of the test cell. The collection optics were aligned perpendicular to the laser path to collect the light emitted from the laser spark. The other ports were to allow hot gas to escape and to allow a thermocouple to

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be inserted. Detection limits depended on the method used to calculate them and the Ir compound used, but was as low as 6.21 μmol L^{-1}. This was the first time that gas phase Ir was detected using LIBS. Work is on-going in an attempt to improve the LOD further.

A paper entitled "Characterization of Electronic Properties of Titanium Atom in Heterogeneous Ziegler–Natta Catalyst Analysed by Soft X-ray Emission Spectrometry" was presented by Saito *et al.*[133] *Soft X-ray Emission Spectrometry was applied for the first time to the characterization of a heterogeneous Ziegler–Natta catalyst*, which comprised titanium tetrachloride and dibutylphthalate supported on magnesium chloride. The high energy resolution capability of the technique made it possible to detect and quantify the outermost shell orbit signals of L alpha at 452 eV and L beta at 458 eV of the Ti atom. These were assigned to Ti species interacting with dibutylphthalate and magnesium chloride, respectively. From the correlation between the signal intensity ratios and the catalytic performances, it was determined that Ti species interacting with the magnesium chloride provided the active sited for propylene polymerization.

4.2 Building materials

Building materials are analysed using atomic spectrometry to determine degradation pathways and mechanisms, to determine what is leached from them under environmental conditions and for quality control. Although the papers are not numerous, some are quite interesting.

Huang *et al. reviewed, with the aid of 64 references, the analysis of waste containing building materials*.[134] These materials may contain cement-based materials, gypsum and geopolymers. The review is split into solid phase analysis techniques, *e.g.* X-ray-based methods and destructive methods, *e.g.* those requiring an extraction (*e.g.* AAS). Similarly, the review is split into those techniques capable of analysing crystalline phases (*e.g.* XRD) and those able to analyse amorphous phases, *e.g.* XAFS. Other techniques capable of elucidating molecular structure and neighbouring environments, such as magic angle spinning (MAS)-NMR and FTIR were also reviewed.

A review entitled "Provenancing of cement using elemental analyses and isotope techniques – the state-of-the-art and future perspectives" was presented by Kazlagic *et al.*[135] The review contained 124 references and covered topics such as major elemental fingerprinting and isotope ratios. The techniques used for the analysis and the chemometric tools used were also discussed.

The transport of sulfate, chloride, acids and carbon dioxide through the pore structure of concretes usually causes damage. Attempts made to measure the extent of this usually require a bore to be cut through materials like concrete and then mechanical slicing of layers to allow the analysis. Decker *et al.* used LA-ICP-MS for the analysis of hardened cement paste, with a focus on the ablation mechanisms of a frequently used 213 nm quintupled Nd:YAG ns laser operating on the multiphase system in comparison with amorphous and well-characterized NIST 612 glass.[136] Aspects investigated included

energy-signal considerations, crater evaluations after multiple shots using different energy densities and the morphology of aerosol particulates captured on filters. A linear energy to analyte signal behaviour was observed over the range 2–6 J cm^{-2}. It was noted though that the mechanism of ablation was different to that observed in samples such as glass or brass, with the bottom of the craters having a strange "knobby structure". The same effect was observed after heating the material to 550 °C, so the presence of water was ruled out as a cause.

A paper by Abramson *et al.* employed X-ray emission spectroscopy for precise characterization of the S redox state in cementitious materials and, in particular, cementitious waste forms.[137] Cementitious waste forms are containers used to retain radionuclides and so it is important to identify their reductive capacity because many of the contents, *e.g.* pertechnetates (Tc^{VII}) are less soluble if reduced to Tc^{IV}. The authors state that the conventional way of determining the S oxidation states in cements is destructive because it relies on the wet chemical methodology of acid digestion in the presence of cerium(IV) followed by titration and colorimetric determination. Not only is this destructive, it is also time-consuming and labour intensive. These authors devised a non-destructive method using a high resolution benchtop instrument. Since the materials under investigation are not homogeneous, the instrumental method also has the advantage of being able to map the surface to find S hotspots. The S Kα wavelength around 2305–2310 eV was used to obtain spectra from the prepared cementitious pellets and sulfide and sulfate reference compounds. A doublet was observed, with each peak corresponding to a S species. Armed with sufficient knowledge of the sample composition, it is possible to quantify the S contribution to the cementitious waste form's total reduction capacity.

Another technique capable of spatial-resolution during analysis is LIBS. Langroudi *et al.* used *LIBS for the automated distinction between cement paste and aggregate*.[138] The harmful transport effects take place almost exclusively in the cement paste phase and therefore relevant limit values linked to harmful element contents are specified in relation to the cement mass. However, when concrete from an existing structure is analysed, information regarding the cement and aggregate content is often not available meaning that assumptions have to be made when converting the element content determined in the sample to that based on the cement content in the sample. Inevitably, this will lead to errors. The method reported in this paper prepared model samples and then used LIBS to obtain analytical data and then a machine learning algorithm to identify the cement and aggregate composition. Some of the samples prepared were used to "train" the algorithm while others were used as test samples. The analytes determined were: C, Ca, H and O, with the O data being used for internal normalization. Five machine learning algorithms were tested: Logistic Regression, Decision Tree Classification, Ridge Classifier, Random Forest Classifier and K-Nearest Neighbour (KNN), with the KNN proving to be most applicable. The algorithm was then incorporated into the LIBS system and tested on a real sample core. The authors predicted that a similar approach

could be adopted to numerous other inhomogeneous sample types.

There is no doubting that portable XRF has some advantages over other techniques in that it can be used in the field, *i.e.* there is no necessity to collect samples (causing damage to the bulk material) and returning it to the laboratory for analysis. Although it may not be as accurate as some laboratory-based instruments, it is still very capable of producing reliable data. Chinchon-Paya *et al.* used *portable XRF for the determination of chlorides and sulfates on the surfaces of concrete*.[139] Concrete prisms were made containing different amounts of sodium chloride and sodium sulfate. Monte Carlo simulations were undertaken to establish the minimum number of random analyses required for the mean value to be within an acceptable range of error. In order for the errors to be less than 10% in 95% of cases, it was necessary to perform six analyses for quantifying sulfate and eight for chloride. Since the method is essentially a surface analysis method, the effects of aggregate were minimal. Once optimized, the analyses were quick and reliable.

4.3 Fertilizers

There have been very few papers of relevance to this section during this review period, with only two contributions being of any note. Wu *et al.* developed a *self-absorption correction method for determining K in potash fertilizers using LIBS*.[140] The problem arises because potassium-containing compounds can represent 90% or more of the fertilizer and since LIBS is a direct analysis technique, *i.e.* sample digestion is not required, then a simple dilution is not feasible. Even the use of less sensitive wavelengths is not capable of compensating for such high concentrations. During the study, LIBS spectra were recorded from 27 potash samples collected from a factory that contained different K concentrations (as the compounds) over the range 90 to 97 wt%. The data from the K wavelengths at 404.4 nm and 693.9 nm were input to a machine learning algorithm to first "train" and then validate it. The algorithm corrected the self-absorption adequately and the authors hoped that it could be combined with LIBS for quality control purposes at production sites.

The other paper of interest was prepared by Singh *et al.* who determined *U in diammonium phosphate-based fertilizers using X-ray and gamma-ray techniques*.[141] There was a concern that any U present in the fertilizers could potentially contaminate the groundwater and so these workers undertook a study to determine the extent of this. Surprisingly, about 30% of the fertilizer samples collected from various places in Punjab State, India, contained between 100 and 200 mg kg^{-1} U, whereas the rest had <50 mg kg^{-1}. The conclusion was that in a waterlogged area such as Punjab, the contribution of U from fertilizers to groundwater was significant.

4.4 Other inorganic applications

The determination of Zr isotopic information is an increasingly popular area of geological/environmental analytical chemistry because it offers the possibility of tracing the history of magmatic differentiation as well as the formation and evolution of crustal reservoirs. It is useful therefore, that a new *Isotopic standard, NRC Zirc-1, has been prepared and is available commercially*.[142] The material was systematically calibrated relative to the existing commonly used standard IPGP-Zr through a collaborative approach between two different laboratories. These used the sample-standard bracketing and double spike methods of analysis for ICP-MS detection. In addition, the Zr isotopic composition of the certified reference materials BHVO-2 and AGV-2, as well as the Allende chondrite, was reported to ensure the robustness of the data and allow for future inter-laboratory data comparison. Results from the two laboratories were in good agreement.

The analysis of brines is important for many industrial processes. A paper by Zhang *et al.* reported a LIBS method for the determination of Mg and Na in brines.[143] In liquid samples the laser energy is reduced by the water with the consequence of decreasing plasma life and emission intensity. These workers circumvented that problem by placing the diluted sample (0.7 mL) on a filter paper, drying at 80 °C for 5 min and then analysing. The analysis was undertaken at seven different locations on the spot to ensure representativeness. The operating parameters were optimized, including the gate width (7 μs), delay time (the time between when the analytes start emitting and the measurement) (2.5 μs) and focal length (10.3 cm). Under the optimal conditions, the LOD were 7.98 and 10.57 mg L^{-1} for Na and Mg, respectively and both calibrations had R^2 values greater than 0.99. Data obtained for the analysis of six brine samples were in good agreement with those obtained using ICP-OES and recoveries of a spike of 200 mg L^{-1} ranged between 91.64 and 107.35%. The method developed was simple and rapid with low sample consumption and requiring no chemical reagents.

During their synthesis, ionic liquids often have the remnants of the starting anion left in them. This is often chloride. Vereycken *et al.* reported a method *whereby Cl in ionic liquids was determined using WDXRF*.[144] These researchers used the ionic liquid Aliquat 336 (I) as the sample for which the method was optimised because it is has the heaviest matrix and a very low Cl content. However, several other analogues were used as test samples, *e.g.* the Br$^-$, NO$_3^-$ and SCN$^-$. Several operating parameters were optimized. These included: the mask size and the collimator. For increased sensitivity, a large mask size was required, but this size could be decreased if sufficient analyte was present to ensure that radiation from the edge of the cup was removed. An added bonus was that the smaller 8 mm mask allowed the use of a smaller sample cup, enabling a smaller volume of sample to be used (2 mL). The 34 mm mask required the use of the 10 mL sample cups. The Cl Kα line was used to construct calibration curves. Detection limits ranged from 191 ppm Cl in undiluted A336 (I) to 42 ppm in 70% A336(SCN) in diisobutylketone. The method developed has a straightforward calibration procedure, required minimal sample preparation steps and was applicable to nearly the entire range of chloride concentrations.

The analysis of strong bases using ICP instrumentation can be problematic because they can have a very high dissolved solid loading which can block torch injectors (or coat ICP-MS

sample cones) and can damage glassware by de-vitrifying it. A paper by Patidar *et al.* reported how they overcame these problems *enabling analytes to be determined in caustic soda*.[145] The solid sodium hydroxide was first dissolved in water to make a 2.5 M solution (10%) and then diluted a further 10-fold. This was then neutralized using 2.5 M nitric acid and spiked with the internal standards Be, Ga, Gd, Sc, Tl and Y (all at 100 μg L^{-1}). Standards were prepared in a solution of high purity sodium nitrate to match the matrix in the samples. Standards and samples were then analysed using an ICP-MS instrument equipped with an argon gas dilution accessory – a commercial accessory that can be used to dilute samples once nebulised, enabling the analysis of much higher dissolved solids than would normally be advisable. A suite of 12 analytes were determined and spiking experiments using a concentration of 30 μg L^{-1} yielded recoveries of 94.6–103.3%.

Contaminants *(REE, PGM, I, S, Th, Tl and U) were determined in germanium and germanium oxide using ICP-OES* by Guselnikova and Tsygankova.[146] After an acid dissolution, the germanium matrix was removed with an efficiency of 99.99% by volatilization as the compound germanium tetrachloride. Optimal results were obtained using internal standards, with different analytes requiring a different internal standard. The REE, PGM and I required Be at 234.861 nm, Th, Tl, and U yielded optimal data using the Dy 353.170 nm line and the S required no internal standard. Detection limits were 10^{-7}–10^{-6} wt% which, for ICP-OES detection, is very respectable.

High purity hafnium is used for many industrial processes. However, it is obtained through the purification of zirconium-based materials and hence often has Zr present as a contaminant. A TXRF method for analysing materials throughout the various steps of the recovery process of hafnium nitrate as well as the end product was presented by Joshi *et al.*[147] The starting material was the aqueous zirconium nitrate raffinate which then underwent mixing and solvent extraction with a mixed alkylphosphine oxide, followed by hydroxide precipitation, filtration and then calcination at 650 °C; which resulted in the formation of hafnium oxide. For the TXRF analysis, standards of 10 μg mL^{-1} of both Hf and Zr were prepared and spiked with 10 μg mL^{-1} Ti as an internal standard. This was chosen because the Ti Kα X-ray line does not have any interference from Hf Lα and Zr Kα analytical lines. An aliquot (10 μL) of the standard solutions was then pipetted onto a clean quartz sample support and presented for TXRF analysis. A similar protocol occurred for the liquid samples. Solid samples were analysed directly, using relative sensitivity values for correction. Detection limits for Hf and Zr were 130 and 22 ng mL^{-1}, respectively. Results were compared with those obtained using ICP-OES and were in agreement. The TXRF method had the advantage of being able to analyse the solid materials directly hence saving time, money and reagents.

An interesting application was presented by de Higuera *et al.* who *determined analytes (Al, Ba, Cd, Cr, Cu, Fe, Sr, and Ti) in sparkler candles*.[148] These materials sparkle when lit and could potentially spread toxic elements over the foodstuffs in which they are inserted. The study investigated the concentrations of the analytes in the used and unused commercially available candles as well as the surface on which they were ignited. A Box–Behnken optimization was undertaken for the digestion of the materials, revealing that 5 mol L^{-1} nitric acid at 80 °C for 35 min was optimal. Analysis was undertaken using MIP-OES. In the unignited candles, the three major analytes were Ba (at a concentration of between 16.73 and 26.00% m/m), Fe (0.31 to 21.41% m/m) and Al (0.37–7.95% m/m). The other analytes were present at the mg kg^{-1} range, albeit some of them being >1000 mg kg^{-1}. Spike/recovery experiments yielded results of 82–118% and precision was better than 20%. Although the precision and recovery data are somewhat variable, they were sufficiently good for the authors to conclude that these candles present a health risk if used incorrectly.

4.5 Ceramics and refractories

This has been a relatively quiet area of research during this review period. Those readers looking for the analysis of archaeological ceramics are referred to Section 6.3. The current section will focus on the analysis of industrial or biomedical ceramics. As with many other sections, analysis using LIBS has garnered some of the more interesting work.

Hydroxyapatite is widely used for biomedical applications because it has similar composition and crystal structure to human bone. It has therefore found widespread use as coatings for prosthetics because it can promote bone integration. A paper by Gomes *et al.* used the one sample calibration version of LIBS for *the rapid stoichiometric analysis (i.e. the Ca : P ratio) of hydroxyapatite targets*.[149] As usual for this type of study, the plasma temperature and electron number density were calculated prior to the actual analysis. When results were obtained for the samples, they were compared with those obtained using calibration free LIBS and with those using XRF and AAS. The results were very similar with those from XRF and AAS and were a significant improvement on those obtained using calibration-free LIBS. The method had the advantage over AAS in that no sample preparation was required prior to analysis. In common with XRF, the LIBS was rapid and non-destructive but had the advantage of being cheaper and easily automated.

Three papers have reported attempts to *improve the accuracy of LIBS measurements during the analysis of ceramic materials*. In two by Kumar *et al.* LIBS was used for the stoichiometric analysis of ceria co-doped with samarium and gadolinium (an electrolyte in solid oxide fuel cells).[150,151] In one, prior to the LIBS analysis, the synthesised powders were mixed with a cellulose binder (at a ratio of 4 : 1), milled and then pressed at 10 tons to produce a pellet.[150] Since the material comprised three rare earth elements, a plethora of emission lines was observed. This confounded the analysis until the LIBS output was treated using partial least squares regression (PLSR). The paper gave a good description of how the PLSR was used to extract the Sm and Gd data from the overwhelming signal arising from the cerium matrix. The performance of the PLSR was improved further by smoothing the LIBS data using a moving average. Again, the paper described this process thoroughly and clearly. The overall effect was that root mean square error was as little as 0.24 mol%. It was concluded that LIBS measurements in

conjunction with the statistical analysis provided a rapid and reliable method that would be useful during the preparation and recycling of solid oxide fuel cells. Another paper that used a statistical method to improve accuracy of LIBS analysis was presented by Lv et al.,[152] who used it followed by data treatment using an autoencoder neural network to analyse ceramic raw materials. The authors stressed that use of an artificial neural network is potentially a good way to overcome matrix effects but can suffer the drawback of "overfitting". They therefore developed a model that combined linear regression and the sparse and under-complete (SUAC) autoencoder neural network. This was capable of performing non-linear feature extraction and dimension reduction; i.e. it reduces the amount of information required for the calculations from 8188 to 32 pieces. A model was therefore constructed using these two algorithms in conjunction with back propagation neural network (BPNN). Since the combination of linear regression and SUAC reduces the number of data points so significantly by removing redundant data, the BPNN can formulate the model with greatly reduced risk of overfitting. As a result, the RMSE values obtained for Al and Si using LR-SUAC-BPNN are significantly lower than for other methods, e.g. LR-partial least squares (PLS), LR-SUAC-PLS and no algorithm used, indicating it had the best quantitative analysis performance.

Another paper to have analysed cerium oxide was presented by Korotkova et al.[153] The work used both ICP-OES and ICP-MS to determine a suite of analytes including other REE, Co, Cr, Cu, Fe, Mn, Ni and V. The ICP-MS operating conditions of nebulizer gas flow, sample uptake rate, plasma sampling depth and extraction lens voltage enabled "robust" plasma conditions to be achieved, facilitating a high dissolved solids loading to be introduced. Detection limits for the two techniques spanned 10^{-7}–10^{-4} wt%.

Both microwave induced plasma (MIP)-OES and LIBS were employed by Oreste et al. for the multi-elemental determination in ceramic tableware.[154] The MIP-OES was used as a "bulk" analysis tool, i.e. to determine the total concentration of elements. This was achieved following an ultra-sound assisted dissolution using a mixture of hydrofluoric and nitric acids. The results were comparable to those obtained following two other sample preparation methods found in the literature. The data for the analytes Al, Ca, K, Mg and Na, were then input to Principal Component Analysis (PCA) which identified three groups of materials. One was for Brazilian samples, another was for imported samples and the largest group was a mixture of both. The group containing the Brazilian samples had, by far, the highest concentrations. The authors then used LIBS in an attempt to identify where a suite (16) of elements were located in the ceramic, i.e. whether it was in the ceramic body, the glaze, paintwork etc. This was therefore a much more localised investigation. It was noted that most of the elements originated in the paintwork. It was noted that many of the more toxic elements (Cd, Co, Cr, Cu, Mn, Pb and Zn) were found only on the outer-most surfaces, which obviously has ramifications for health if they are leached into food or beverages to be consumed. The study was a nice example of how different techniques can be used to obtain complementary information from the same samples.

Novel methods of analysing alumina have featured in three research papers during this review period.[155–157] In the first of these papers, Ikeda et al. used microwave enhanced LIBS that employed a helical coil with a 2.45 GHz semiconductor microwave.[155] The theory is that the LIBS laser ablates the sample and then a microwave discharge operating at a frequency of 10 Hz excites the ablated matter causing it to emit light characteristic of its components which is then transmitted via a fibre optic to a detector. Several parameters were optimised including: the antenna angle from the laser beam (60° achieved maximum signal enhancement) and the microwave antenna type (the optimized version here gave an electric field strength ~100 times that of previous antenna designs). The paper was interesting, but not really analytical. It described the instrumentation rather than any data obtained using it. The paper by Li et al. described the effects of a curved surface of a sample, i.e. an alumina tube, on the accuracy and precision of LA-ICP-MS data.[156] Considerable effort was expended in optimising the LA conditions. Spot size (100 μm), laser fluence (2.5 J cm^{-2}), repetition rate (no fixed optimum chosen because it depended on the scan speed and washout time), washout time (1.5–2.5 s), helium flow rate (1000 mL min^{-1}) and scan speed (200 μm s^{-1}) were chosen as well as the ICP-MS parameter of dwell time (10 ms). The authors provided a decent explanation as to why these parameters were chosen, highlighting potential errors if they were deviated from significantly. The methodology was applied to the mapping of La in the alumina tube. Results indicated that the La was not uniformly distributed. It also demonstrated that for a tube with outer diameter of 0.68 cm (as used in this experiment), the optimal range the laser should fire from was less than 1 mm. After 10 shots had been made, the tube had to be manually turned so that a new "flat" surface was exposed. The third paper, by Busam et al. described the analysis of solid alumina and sapphire using silicon and indium as secondary cathodes employing slow-flow DC-GD-MS.[157] The mask designs and GD conditions were optimised in terms of the best signal ratio and absolute intensity. The discharge conditions were found to be the most significant factor in the relative sensitivity factors of the analytes. Similar concentrations for many of the analytes in alumina were obtained using the two mask materials. The exception was for Nb, where the concentration was 84 ppb when an indium mask was used, but only 5.74 ppb when a silicon one was. For an indium mask, the LOD in alumina ranged from 0.40 (for V) to 2.3 ppb (for Mo). The results using a silicon mask were not so encouraging for the analysis of alumina. However, analysis of the sapphire showed the opposite trend, with silicon proving to be the better mask material.

Methods for the preparation of boron nitride[158] and of boron carbide[159] prior to analysis have been reported. These papers are welcome, because ceramics are notoriously difficult to bring into solution. Sio et al. described fusion methods utilising either lithium hydroxide or sodium hydroxide (depending on whether Li and Na are included in the list of analytes) for the digestion of boron nitride powders of three different grain size.[158] The lithium hydroxide fusion required 100 mg of sample

and 400 mg of flux. They were mixed together in a vitreous carbon crucible and then fused at 500 °C for one hour. After cooling, the samples were dissolved in water and very dilute hydrofluoric acid (except for when Si was to be determined). They also developed a column chromatography method for the removal of Si from the fluxes, thereby facilitating its determination. The fusion using sodium hydroxide was a modification of that for the lithium hydroxide. Detection limits were determined using procedural blanks and, for 57 of the 58 analytes studied, were less than 20 μg g^{-1}. The exception was for Si, which had a LOD of 312 μg g^{-1}. This was not problematic though, because the Si content in the powders was significantly higher than this. Method validation was through analysis of the NIST reference waters 1640a and 1643f. Yuan *et al.* developed a slurry technique for the determination of a suite of 10 elements using TXRF.[159] The dispersant polyacrylateamine was used at different concentrations to ensure that aggregation did not occur. A slurry concentration of 10 mg mL^{-1} was suitable. Results from the TXRF analysis were compared with those obtained using ICP-OES following a high pressure digestion and were in good agreement. Results of spike and recovery experiments were a little variable for the TXRF analysis with values ranging from 83 and 115%.

An environmentally friendly method of sample preparation was described by Senger *et al.* for the determination of W in silicon carbide samples.[160] The method, termed pyrohydrolysis, occurred when sample (20 mg) was mixed with 50% hydrogen peroxide (1.2 mL) and oxygen at a flow rate of 0.1 L min^{-1} at a temperature of 1000 °C for one hour. The process converted the WC into volatile W species which were extracted and collected in water. Using these optimized conditions followed by ICP-MS analysis, the concentration value of W obtained was in close agreement with the data obtained using a sodium bicarbonate fusion. The method offered an environmentally friendly method of sample decomposition, with the only waste products being water and oxygen.

4.6 Glass

There has been a significant rise in the number of research papers discussing the analysis of glass. Many of these have a forensic application have therefore been placed in Section 5.1. The reader is referred there for more information.

Other applications have, however, been provided. A paper by Liu *et al.* reported the *preparation of reference materials*.[161] This paper discussed the preparation of four quartz and zircon Si isotopic reference materials for use for accurate and precise measurements using SIMS. One was a fused glass quartz glass, one a natural quartz and the other two natural zircons. Repeat measurements using SIMS indicated that the materials are more homogeneous with respect to the Si isotope ratios (spot to spot uncertainty being in the range 0.090–0.102 parts per thousand) compared with the existing NIST 8546 (poorer than 0.160 parts per thousand). The samples were also analysed using multi-collector (MC)-ICP-MS following sample dissolution using a sodium hydroxide fusion so that delta ^{30}Si values could be calculated. The reference material NIST 610 was used

as a comparative material. The NIST 610 was considered to be homogeneous at the micron scale for Si isotopes but is not suitable for use during SIMS analysis. No SIMS matrix effects between the fused quartz glass and the natural quartz were observed. This indicates that the material may be used as a homogeneous reference material for SIMS Si determination in natural quartz samples.

A paper by Hommel *et al.* used *ETV as a means of sample introduction to an ICP-OES* instrument for the determination of 27 analytes in soda-lime glass.[162] The material, a candidate reference material with the code BAM-S005c, was crushed to a particle size of <100 μm and then inserted to the ETV apparatus. A gaseous matrix modifier (trifluoromethane) was used at a flow rate of 2.3 mL min^{-1} to help volatilise the material completely to the ICP. Calibration was achieved through the use of aqueous standards, with no significant matrix effects being noted. Alternatively, certified glass samples (NIST 610, 612 and 614) were also used for calibration as a means of extra validation. Other parameters optimized included the length and diameter of the plastic transfer tube, the inner and by-pass argon flow rates, the ETV temperature program, the use of graphite grit to help position the sample in the ETV boats and the inner diameter of the ICP torch injector tube. The presence of the trifluoromethane was critical in enabling the analytes to be determined simultaneously, otherwise the strong carbide forming elements, *e.g.* Mo, V, *etc.* were not volatilised quantitatively or reproducibly. Two of the 16 laboratories participating in the certification exercise used this method. Others used a conventional liquid nebulisation approach. The solid sampling approach provided better accuracy and precision than most other methods, even though a sample mass of typically 0.2–0.6 mg was used. The methodology was both rapid and reliable and the authors thought it could possibly also be applied to the analysis of other glass types, *e.g.* borosilicate.

Nano-SIMS determination of REE in silicate glass and zircon was reported by Shi *et al.*[163] A 2 nA O$^-$ primary beam was used to produce a 7–8 μm diameter crater and the secondary positive ions produced analysed. A multi-collector system was employed utilising a resolution of 9400 at 10% peak height to ensure that the heavier REE were separated spectrally from the lighter REE oxides. This was verified through the analysis of NIST 610, where no interference was observed. An internal standard of ^{30}Si was also determined. Based on the results of the NIST 610, the individual sensitivities ranged between 3 cps ppm^{-1} nA^{-1} (for Lu) to 13 cps ppm^{-1} nA^{-1} (for Eu). Reproducibility was 18% at the 2 sigma level which, although not great, was considered adequate. What was encouraging was that the secondary ion yield for the zircons were virtually identical to those obtained in the glass, making calibration between the two sets of samples easier.

A *simple TXRF method of glass analysis that was capable of multi-elemental analysis, that consumed low amounts of reagents and did not require a calibration curve* was presented by Costa *et al.*[164] These authors used central composite design (a statistical method often used to optimize parameters) to optimize the sample grinding procedure, with optimal values being 1 g of sample, grinding in a ball mill for 6 min and at an impact

frequency of 23 Hz. Once the optimal parameters had been established, 10 mg of ground sample was placed in a tube and 990 μL of aqueous 1.0% v/v Triton X-114 solution added. This was followed by the addition of 10 μL of 50 mg L^{-1} Ga solution as an internal standard and then the solution was vortex mixed for 30 s. An aliquot (10 μL) was removed, placed in a quartz glass sample carrier and then dried for 5 min using IR radiation. The residue was then analysed using TXRF. Results obtained using the method were validated using NIST 612 glass reference material. The accuracy of the results was somewhat mixed, with values of the certified values ranging from 41.9% (for Ba) to 120.5% (for Cr). For some elements though (*e.g.* Cu, Ni, Rb and Zn), very respectable results of 93–102.5% were achieved. Despite the varied results, application of principal component analysis (PCA) to the analytical data enabled a clear differentiation to be made between glasses from the screens of four different mobile phone manufacturers.

A paper describing a method to analyse car windshield glasses was presented by Martinez-Lopez *et al.* who used μ-XRF, LIBS and LA-ICP-MS for the task.[165] The three techniques were used to *assess the homogeneity of the glass*. This was achieved by first separating the inner from the outer panes of glass. Fragments (100) from the panes were then isolated and analysed. The LA-ICP-MS yielded the most precise data, with an RSD of <5% for most analytes in a single pane. The other two methods had precision values closer to 10% RSD for most analytes. All three techniques demonstrated that the panes were relatively homogeneous, but the LA-ICP-MS had better repeatability and reproducibility.

4.7 Nuclear materials

Characterisation of materials used for fusion remains a popular topic, with *in situ* measurement techniques such as LIBS proving to be a popular and valuable tool. The safe operation of nuclear reactors, including early indicators of potential fuel failure and accidents, is extremely important and has also been a popular area of research. Additionally, assessing impurities in fuel samples was also a popular topic, as well as tools to ensure the safe operation of reactors. Determining the composition and source of nuclear materials through isotopic ratio measurements remains an important area, with mass spectrometric techniques (ICP-MS and TIMS) frequently used as analytical approaches. The ongoing importance of reference materials to underpin and validate novel measurement techniques was addressed, including the continuing drive to develop rapid radioanalytical procedures for detection of more challenging radionuclides, with mass spectrometry again a popular technique.

4.7.1 Nuclear fusion. The measurement of the properties of materials used in nuclear fusion reactor designs is a common topic, along with assessment of measurement techniques in fusion reactor conditions, most commonly LIBS.

A set of *divertor tiles containing* a 0.2–0.4 μm Mo interlayer and 5–10 μm C layer on top was installed in Wendelstein 7-X and analysed for erosion and deposition following exposure to around 40 minutes of plasma in the standard magnetic divertor configuration over one year.[166] Vertical erosion and deposition patterns were assessed for the first time using picosecond LIBS. The position of peak erosion was identified (total 15×10^{19} C atoms per cm^2) due to plasma fuel (H, He) and impurity (O, C) ion impact. Wood *et al.* demonstrated quantitative isotopic determination of Li in Li hydroxide monohydrate in a 40 mTorr Ar environment using *in situ* LIBS and chemometrics.[167] Three chemometric analysis techniques were applied, with Li determined in minutes to one hour for 3–85% enrichment levels. The study also showed the first isotope-specific self-absorption of atomic emission in a laser produced plasma.

The *radiation dose effects on fibre-optic LIBS using a ceramic micro-laser* was assessed by Tamura *et al.*, focusing on the impact of 0–10 kGy h^{-1} dose rates on laser operation properties when measuring Zr metal.[168] Whilst the signal reduced with increased dose (mainly due to pulse energy reduction), useful spectra were obtained at the maximum dose rate, suggesting the system is applicable to remote elemental analysis in harsh environments.

Threshold Ionisation Mass Spectrometry was used by Bisson *et al.* to analyse D and He outgassing post-discharge in the full tungsten tokamak WEST.[169] Results included the presentation of the Threshold Ionisation Mass Spectrometry calibration method and consideration for uncertainties due to rapid pressure variations. The He outgassing was significantly faster than D, which may be related to different retention and outgassing from W and W-coated graphite plasma facing components. Walker used a combination of Threshold Ionisation Mass Spectrometry and Ultra-High Resolution Mass Spectrometry for characterisation of species used in fusion reactions.[170] Conventional mass spectrometry struggles with this because of mass interferences, for example with D$_2$ and He at mass 4. Selective ionisation of species combined with generation of a 'zone H' stability zone using ultra-high resolution improved sensitivity by a factor of over 100 compared with the Threshold Ionisation Mass Spectrometry method alone.

Lithium, sodium and NaK liquid metals are candidate heat transfer mediums installed in the irradiation capsule of advanced fusion neutron sources.[171] In this work, Hosaka *et al.* undertook *corrosion tests at temperatures of up to 823 K to assess compatibility of these liquid metal materials with the steel materials F82H and 316L*. The technique of TOF-SIMS was used to discover that the liquid Li caused depletion of C, Cr and Fe from steel, and Na and K corrosion occurred because of Na diffusion into the steel matrix and through surface oxidation.

4.7.2 Reactor operation and safety. The properties of fuels used in nuclear reactors is key for safe and efficient operation, as is accurately quantifying elements that can indicate unsafe reactor conditions and potential accident scenarios.

There is a drive for novel reactor designs to deliver improved safety, performance and economy. This includes early monitoring of potential fuel failure, for example through monitoring of Xe in gas cooled fast reactors using He as the primary coolant.[172] Single pulse LIBS was used, achieving a detection limit of 0.2 μmol mol^{-1} for 10^4 laser shots, offering promise for online monitoring of fuel integrity and development of a compact system within the primary He cooling loop.

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The *thermal behaviour of Xe along with Cs was assessed in uranium dioxide pellets* in relation to Xe monitoring in fuel rod behaviour during reactor operation, and Cs in cases of release following a nuclear accident.[173] This paper, by Panetier *et al.*, reported the implantation of stable Cs and Xe into the pellets at a depth of around 140 mm below the surface, followed by annealing under reduced atmosphere at temperatures corresponding to reactor operation and during an accident (1000 °C and 1600 °C, respectively). Migration of the Cs was investigated using SIMS whereas the TEM was used to investigate the uranium dioxide microstructure before and after annealing. Differences in Cs behaviour compared with Xe was assigned to different growth kinetics of bubbles at higher temperatures, corresponding to availability of thermal vacancies in the pellets and different atomic abilities for thermal resolution. A study by the same authors implanted Cs and Mo into uranium dioxide with assessment using the same techniques and temperatures, to assess the effect of Mo on Cs behaviour.[174] The Mo was more mobile in the presence of Cs, possibly because of more material vacancies being present through Cs implantation. The formation of Mo precipitates hindered Cs bubble migration, whilst the Cs release percentage remained similar when implanted alone and with Mo.

Assessment of fuel and reactor material impurities to satisfy regulatory requirements was the focus of several studies. Antonov *et al.* employed dc arc AES for direct measurement of Cl impurities in nuclear-grade graphite and graphite foils.[175] The evaporation and excitation of dc arc AES of Cl from standards and graphite samples were assessed, with a total procedural time (including sample preparation) of ten minutes and a detection limit of $0.8~\mu g~g^{-1}$. Fletcher *et al.* used ICP-MS/MS to assess P and S in uranium ore concentrates to improve understanding of fuel source, production, history and intended use.[176] The ICP-MS/MS setup allowed for improved removal of interferences affecting P and S, with concentrations measured compared with pyrohydrolysis and previously reported results.

The *composition of UF_6 (the primary material for U enrichment in light water reactors) was assessed using LIBS in relation to safeguards and non-proliferation*.[177] A cell was designed that was compatible with UF_6 physiochemical properties, compatible with a LIBS laser and portable so that it could be used for safeguarding purposes. The cell produced was gas tight, compatible with UF_6 and withstood long laser exposure. Sanyal *et al.* used micro-focused XRF to assess the homogeneity of U and Th fuel pellets prepared *via* different routes.[178] The technique was capable of mapping U in each spot on the fuel pellet with concentrations of 2–50% with respect to Th. The instrument's small footprint enabled the installation in a glovebox that would allow Pu pellet measurement.

Weilert *et al.* produced two studies *on diffusion of various elements in IG-110 graphite*. The first focused on Ag and migration of Pd, with a diffusion cell designed to simulate reactor conditions coupled to ICP-MS to assess time-release diffusion measurements.[179] Diffusivities of Ag and Pd were calculated. In the second study, Eu diffusion was assessed, related to its interest in gas reactor safety analysis.[180] The study was built upon no previous measurement of diffusion coefficients in the

literature, with this study using time-release methods as described. The results can be used for helping with predictive modelling in graphite reactors.

4.7.3 Isotopic ratio measurements. Accurate and precise isotopic ratios is a critical capability for assessing the source of contamination, with applications including monitoring fallout following nuclear accidents and identifying the source of illegally acquired nuclear materials.

Beaumais *et al.* focused on the assessment of $^{144}Ce/^{238}U$ in spent nuclear fuel.[181] This is because ^{144}Ce is a significant contributor to decay heat from spent fuel less than ten years after reactor discharge. A double spike isotope dilution TIMS approach was developed, focusing on chemical separation of isobaric ^{144}Nd and preparation of an in-house natural $Ce/^{233}U$ double spike. In mixed oxide fuel, a relative expanded uncertainty of approximately 1% ($k = 2$) was achieved, with $^{144}Ce/^{238}U$ values of 35×10^{-6} to 59×10^{-6} measured. Thermal ionisation mass spectrometry with an ATONA amplifier upgrade was used by Reinhard *et al.* for measuring $^{143}Nd/^{144}Nd$ isotope ratios from starting materials with mass of only 100 pg.[182] Compared with the previous setup, the external measurement reproducibility was improved by a factor of three, with an external measurement uncertainty of 23 ppm, contributing to measurement of smaller samples for geological and forensic applications.

The technique of TIMS was also the focus of a study by Louis-Jean *et al.* to achieve *high precision Sm isotopic analysis of nuclear materials*, focusing on a Pt activator as a new loading method.[183] Aliquots of 1–20 ng were loaded onto a single Re filament using a static non-evaporation technique. Applications for nuclear samples and monitoring neutron irradiation exposure, as well as geological samples were envisaged. The $^{240}Pu/^{239}Pu$ ratio was measured by Quemet using TIMS in dissolution residues of a spent fuel solution.[184] Repeatability of better than 83 ppm was achieved in each aliquot, with interpretation of the kinetic evolution that could not be reached by conventional direct concentration measurement.

A compact TIMS instrument was developed and tested for U isotopic ratio measurements.[185] The new instrument had a smaller magnetic sector compared with conventional instruments, with a sensitivity for U of 1 ion for 500 atoms, an abundance sensitivity of 50 ppm at $m/z = 237$, peak flatness of 3200 ppm and $^{235}U/^{238}U$ precision of 0.05% for the U200 standard. A combination of TIMS and ICP-MS was used for assessing a new synthesised $(Th–Np)O_2$ mixed oxide powder.[186] Using ID-TIMS and a total evaporation method, the expanded uncertainty for the Th mass fraction was <1%, with the main contribution coming from the spike mass fraction uncertainty. The expected uncertainty for Np was 1.8% and was measured using ICP-MS because of the lack of spike solutions for ID-TIMS. The powder stoichiometry was determined to be $Th_{0.836(50)}Np_{0.5164(50)}O_2$, with potential to extend the study to complex samples and in-house reference material characterisation.

Accelerator mass spectrometry (AMS) was applied by Johansen *et al.* to Pu *isotopic ratio measurements to distinguish between fallout from the Fukushima reactor incident and the nuclear*

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weapon detonated at Nagasaki through measurement of soils and biota.[187] The $^{241}Pu/^{239}Pu$ ratios were preferred to $^{240}Pu/^{239}Pu$ as the latter could not distinguish between most 2016 environmental samples and Fukushima contamination. The contribution of new Pu from Fukushima was assessed in samples including soil, earthworms and wild boar. It was determined that Pu from the Nagasaki detonation will be distinguishable in the environment for longer than that arising from Fukushima.

Isotopic ratio measurement was also effectively applied to age determination of single U particles for safeguard purposes.[188] Following chemical separation, $^{230}Th/^{234}U$ was measured using a single collector ICP-MS instrument along with a ^{233}U reference material containing ^{229}Th progeny. The purification ages of two certified materials (U-850 and U-100) were determined, with good agreement with the reference age of 61 years. Raiwa *et al.* obtained isotopic information on Am, Pu and U in 10 µm hot particles from the Chernobyl exclusion zone using spatially resolved resonant laser secondary neutral mass spectrometry.[189] The technique is capable of quasi-non-destructive analysis, can achieve multi-element measurement in short periods without laser adjustment, and achieves good suppression of isobaric interferences and high spatial resolution without extensive chemical separation. The U isotopic heterogeneity of fuel pellets was assessed by Rush *et al.* using extreme ultraviolet laser ablation and ionisation time of flight mass spectrometry.[190] The $^{235}U/^{238}U$ could be assessed in 100 nm pellets made by blending of two isotopically distinct feedstocks, with a wider heterogeneity due to incomplete blending. The results were in agreement with those obtained using nano-SIMS, with the TOF-MS technique showing promise for assessing sub-microscale chemical modification.

4.7.4 Reference materials and standards. Reference standards and materials are critical for ensuring validation of measurement of unknown materials. As analytical techniques improve, it is important to support this by providing reference sources of sufficient precision.

Dasgupta *et al.* developed an *in-house graphite reference material for the determination of B in nuclear grade graphite*.[191] Quantification was achieved using a charged particle activation analysis technique, with a detection limit of 1.4 mg kg^{-1} and a material that can be used to support measurement of unknown graphite samples. In a study by Scott *et al.*, Li/Be reference standards were prepared gravimetrically and assessed using MC-ICP-MS to enable measurement of Li/Be ratios in Li_2BeF_4, which is used for cooling of high temperature nuclear reactors.[192] More precise and accurate measurements were achieved using MC-ICP-MS compared with traditional concentration measurements of FLiBe.

Venchiarutti *et al.* characterised the U content and *isotopic composition in micrometre sized particles with the aim of certifying a candidate reference material*.[193] The amount of U per particle was determined by optical microscopy combined with ID-TIMS, and verified by MC-ICP-MS, with good agreement being obtained between the two techniques. The material was certified for U amount per particle and isotopic composition following a proficiency test exercise (NUSIMEP-9). An IDMS approach was

used by Hasozbek *et al.* to assess the U isotopic composition in certified materials U-CRM 112A and U-CRM 149.[194] A statistical approach was presented to simulate the range of $^{235}U/^{238}U$ ratios with regards to expanded uncertainty budgets. In another study, U and Pu quality control samples for IDMS were developed from two CRMs at JRC Geel in line with ISO 17025 and ISO 17034.[195] The materials CRM 126 (^{239}Pu) and CRM 116-A (^{235}U) were first cleaned to remove any surface oxide layer and then dissolved in 6 M HCl (for Pu) and 8 M HNO_3 (for U). The materials were then diluted to give a U concentration of 3 mg g^{-1} and a Pu concentration of between 1.5 and 2 mg g^{-1}. Aliquots of each were then bottled ready for use. The ^{235}U and ^{239}Pu values were assigned from gravimetric preparation and verified by IDMS, with a wider inter-calibration and characterisation campaign including proficiency testing exercises.

The production of several *new reference materials based on naturally occurring radioactive material* was described by Lee *et al.*[196] Zirconium silicate, bauxite and phosphogypsum were characterised using XRF and then measured by nine radioanalytical laboratories, with values assigned for Th and U isotopes in all materials, as well as ^{226}Ra for phosphogypsum. In another study, Jakopic *et al.* developed an ^{243}Am spiked CRM for mass spectrometry, with certified values for the ^{243}Am amount and $^{241}Am/^{243}Am$ ratio.[197] Values were confirmed using alpha spectrometry, defined solid angle alpha spectrometry and high resolution gamma spectrometry, with further validation through an inter-laboratory comparison exercise.

4.7.5 Difficult-to-measure radionuclides and stable elements. Waste characterisation and decommissioning of nuclear sites requires the measurement of a range of radionuclides in varied and complex matrices. This necessitates the development of robust and reproducible chemical separation combined with sensitive mass spectrometric and/or decay counting techniques.

Removal of Pb as a potential interference for Pu measurement using ICP-MS was the focus of a paper by Fan *et al.*[198] Sr-resin was investigated for Pb/Pu separation, with the optimised conditions (including different oxidation states) achieving a Pb removal factor of 2.2×10^5 and a 90% Pu recovery. The procedure was applied to the measurement of spiked matrix solutions. Plutonium was also the focus of a study by Kim *et al.*, who utilised gamma spectroscopy and TIMS without chemical separation for Pu assay in pure plutonium and uranium-plutonium mixed solutions from a reprocessing site in Japan.[199] The relative bias of <0.01% allows this approach to be used as a support or alternative to traditional IDMS and K-edge densitometry without compromising accuracy and precision.

Llopart-Babot *et al.* investigated combined measurement of ^{36}Cl and ^{129}I in concrete and graphite from a Belgian reactor undergoing decommissioning.[200] Pyrolysis was combined with chemical separation, with final measurement by liquid scintillation counting. Recovery through the procedure was assessed by determining stable Cl and I using ion chromatography and ICP-MS, respectively. Shibahara *et al.* used TIMS for evaluating the nuclear data of ^{135}Cs.[201] Additive agents were tested for the impact of Cs ionisation to achieve an intense and stable beam, with silicotungstic acid having the most impact while also

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showing the largest polyatomic interference. The optimised method was tested on two radioactive Cs samples.

LIBS was used to detect lanthanides (La, Ce, Pr, Nd and Sm) in an aqueous actinide matrix, with results presented for detection limit, accuracy, precision, calibration plot and results on identifying non-overlapping peaks.[202] An in-house designed sample cell was used to analyse samples of <1 mL, which is advantageous for reducing sample usage and analyst exposure.

Measurement of ^{107}Pd transmutation was considered by Miyake *et al.* due to the importance of Pd for industrial use and it being a target element for recycling of spent fuel.[203] Various reaction paths and cross sections were considered, with implanted samples irradiated with deuterons for several days. Using ICP-MS for measurement of ^{107}Pd and ^{105}Pd/^{107}Pd and ^{106}Pd/^{107}Pd ratios yielded data with good agreement with calculated values. Gamma spectrometry revealed the production of ^{105}Ag and ^{106}Ag.

With regards to nuclear decommissioning, ^{90}Sr is recognised as a radionuclide of significant interest. Yanagisawa *et al.* successfully measured pg L^{-1} levels of ^{90}Sr combining solid phase extraction with ICP-MS with isotope dilution for stable Sr isotopic ratios (^{86}Sr/^{88}Sr).[204] A combination of solid phase extraction and Dynamic Reaction cell separation achieved isobaric ^{90}Zr removal of 5.7×10^{-9} (Sr/Zr), with a ^{90}Sr LOD of 1.1 pg L^{-1} for a 10 mL injection volume. The method was validated using a water sample from the contaminated water storage tank at the Fukushima site, with good agreement between the data obtained using the technique described and from conventional methods.

4.8 Electronic materials

Although a considerable amount of research has been made into electronic materials, especially lithium ion batteries (plus alternatives), solar cells and other thin films, the number of papers reporting advances in atomic spectrometry have remained relatively few. These will be discussed over the next three sub-sections.

4.8.1 Wafers, thin films and multi-layer materials. Many of the analytical techniques used for this type of analysis are very specialised for surface analysis or, in some cases, capable of obtaining depth-profile data. Techniques such as SIMS, TOF-SIMS, RBS and X-ray-based techniques are therefore prevalent rather than the more normal atomic spectrometry techniques of ICP-OES/-MS, AAS, *etc.*

A paper by Kubala-Kukus *et al. described a plethora of low angle X-ray techniques* including: total reflection X-ray fluorescence (TXRF), grazing emission X-ray fluorescence (GEXRF), grazing incidence X-ray fluorescence (GIXRF), X-ray reflectometry (XRR) and total reflection X-ray photoelectron spectroscopy (TRXPS).[205] The paper is not a review. Instead it is more of a list of techniques available at the Institute of Physics of the Jan Kochanowski University in Kielce, or the collaborations they have made with other institutions. However, each of the techniques is discussed in individual sections, highlighting their differences, applications, capabilities and limitations. Although the overview is not limited to electronic materials, these are

often the techniques of choice for such analyses and this paper summarises the techniques nicely.

The capability of *isotope-dilution (ID)-ICP-MS, Rutherford Backscattering Spectroscopy (RBS) and Medium Energy Ion Scattering Spectroscopy (MEIS) for the analysis of silver – copper (Ag$_x$-Cu$_{1-x}$) thin films* was demonstrated by Kim *et al.*[206] Two sets of five thin films of different mole fractions were prepared by ion beam sputter deposition onto silicon wafers. Nominally, the films ranged from Ag$_{0.14}$Cu$_{0.86}$ to Ag$_{0.72}$Cu$_{0.28}$. One set of films were relatively thick (100 nm) while the other set were thin (10 nm). The thick films were analysed using ID-ICP-MS and RBS whereas the thin films were analysed using ID-ICP-MS and MEIS. Full uncertainty budgets were calculated for each technique. The results for the analysis of the thick films using ID-ICP-MS and RBS were in extremely close agreement. Plotting the data against each other yielded a slope of 0.996 m *i.e.* the data were within 0.4% difference. Results obtained using ID-ICP-MS and MEIS for the thin films were also impressive, with agreement to within 1% being obtained. For instance, for the film of nominal composition Ag$_{0.14}$Cu$_{0.86}$ the ICP-MS results (as a mole fraction) were Ag = 13.4 ± 0.3 and Cu was 86.6 ± 0.3 compared with the MEIS results of 13.3 ± 1.3 and 86.7 ± 1.3 for Ag and Cu, respectively. It can be seen that the ID-ICP-MS method was far more precise; a trend also shown with the other films. The analysis of the thick films yielded an improved precision for the ID-ICP-MS data. The RBS also showed impressive precision but was a factor of three – five times worse. The overall conclusion was that all three techniques could be used to determine the composition of thin films reliably and could therefore be used to characterize certified materials.

Analysis using TOF-SIMS is well known to be excellent at measuring analytes within 2 nm of the surface of a sample. However, interpreting the mass spectra can be complicated. Machine learning methods have been devised to help the process, but the generation of descriptors, *i.e.* what to include and what to exclude can be time-consuming and can potentially limit their versatility and practicality. Lang *et al.* developed a method whereby the *generation of descriptors was not required for TOF-SIMS spectra to be processed into images by the convolutional neural network.*[207] The authors applied the methodology to the analysis of thin films of different silane coupling agents, sometimes in admixture. The convolutional neural network outperformed the descriptor-based approach. In addition, it exhibited a high degree of automation and versatility and could have the potential to solve challenging issues.

Depth-profiling is always a popular area of research, with greater resolution, better sensitivity, fewer interferences *etc.* being sought. This next section describes those papers that have contributed to improving depth-profiling studies. Two papers have used *SIMS employing gas cluster primary ion beams* to analyse thin (20–50 nm) extreme ultraviolet photoresist films[208] and organic thin films.[209] The use of gas cluster primary ion beams causes less sputter damage to organic-based films. In the first example, Spampinato *et al.* used two SIMS instruments to analyse the photoresists.[208] One instrument was a conventional TOF-SIMS instrument whereas the other was equipped with an Orbitrap mass analyser with MS/MS capability meaning that

greater mass resolution could be achieved. The operating conditions for both instruments were kept as close as possible so that data could be compared. For instance, both used a sputter beam of Ar_{2000}^+. The Orbitrap-based instrument had approximately 20 times the resolution of the standard instrument as well as having improved mass accuracy (a few ppm) and this proved crucial for the analysis. The standard TOF-SIMS instrument suffered serious problems associated with mass spectra and depth-profiles exhibiting severe molecular (isobaric) interferences, whereas the Orbitrap-based instrument did not. The second paper, by Muramoto and Graham, also used a 20 keV Ar gas cluster beam for sputtering and a Bi_3^+ beam for analysis.[209] Both ion sources struck the sample at an angle of 45°, with a typical cycle comprising one scan of analysis, 10 scans of sputtering and 2 s of charge compensation. Three thin film types were analysed: gelatin, pullulan and polyethylene terephthalate (PET). Using SEM and a profilometer to analyse the topography of the craters a linear depth increase was observed with the increase of ion dose. For thicker films (>10 μm), the craters became distorted, with pillar-like structures forming which affected the linearity of the sputter yield and the depth resolution. To reduce this problem, a step-wise rotation of the sample was employed. Although the problem was reduced significantly, "blisters" appeared which still hampered depth-resolution measurements.

Other workers have also employed TOF-SIMS for depth-profiling studies. Kubo *et al.* used a *combination of soft X-ray photoelectron spectroscopy (XPS) employing Ar^+ sputtering and TOF-SIMS employing Cs^+ sputtering* to monitor the changes in the chemical state of Cr during deposition on a polyimide substrate.[210] Depth resolution at the nanoscale was achieved. Evidence from both techniques indicated that there was preferential O sputtering. Samples were therefore re-analysed using cross-sectional electron energy loss spectroscopy and non-destructive hard XPS. As a result, the depth profiles of Cr, Cr_2O, Cr_2O_3, $Cr(OH)_3$ and CrO_3 in the chromium thin film were determined. At greater depth, the concentrations of Cr_2O_3, $Cr(OH)_3$ and CrO_3 decreased and Cr and Cr_2O increased. This was attributed to the sputtering by Cs^+ and Ar^+. The results were thought to be useful for optimizing the chromium/polyimide fabrication process, which is important because it is one of the most important components in flexible electronics.

Mabrouk *et al.* used *TOF-SIMS with low energy Cs^+ ions for sputtering during the depth-profiling of polymethylmethacrylate thin films*.[211] The effects of the molecular weight of the material, the film thickness and the beam energy on the sputtering yield were determined. The sputtering yield decreased as the molecular weight increased until a threshold was reached, at which point it remained fairly constant. Sputtering yield increased logarithmically with increasing primary ion beam energy over the range 250–1000 eV. Depth-profiling was undertaken using dual beams, one of Cs^+ for sputtering and the other of 15 keV Bi_3^+ for analysis of the centre of the crater created by the sputtering. Negative secondary ions were measured. Preliminary experiments were also undertaken for the analysis of low molecular weight thin films (4 kg mol^{-1}). Similar trends were observed as when an argon gas cluster beam

had been used, but the effects were much smaller. This led the authors to conclude that the low energy Cs^+ primary beam had great potential for the analysis of dense, very thin films. Further work in this area was envisaged.

Another study to use TOF-SIMS to analyse thin films was presented by Ekar *et al.*[212] These researchers also used a dual beam approach employing 1 keV Cs^+ and 1 keV O_2^+ as the sputter beams and analysed using a Bi^+ primary ion beam. *Depth-profile analysis of metal, metal oxide and alloy multi-layers in atmospheres containing hydrogen, acetylene, carbon monoxide and oxygen* was performed. The samples (FeAgNi) and (CrTiAl) were multilayer structures of Fe_2O_3/Fe/Ag/Ni/NiO and Cr_2O_3/Cr/Ti/TiO_2/Al_2O_3/Al, respectively. The negative secondary ions formed by the samples in the presence of the flooding gases were monitored. A systematic comparison and evaluation of the TOF-SIMS depth profiles was performed regarding the matrix effect, ionization probability, chemical sensitivity, sputtering rate and depth resolution. The presence of acetylene, carbon monoxide and oxygen had some benefits over analysis in a vacuum, but only in specific cases. Since the sputtering rate decreases in the presence of the gases, a much longer time is required for a depth-profile to be acquired. In contrast, the addition of hydrogen did not reduce the sputtering rate and demonstrated improved results (reduced matrix effects) for the sample depth-profile analysis. A further improvement was observed by normalizing the signals. The different layers of the samples could clearly be identified. Further work was to be undertaken analysing the topography of the craters produced in the hydrogen atmosphere.

Techniques other than TOF-SIMS have also been used to obtain depth-profile data. *Glow discharge (GD)-OES has been used by Bouttemy et al. for the characterization of buried interfaces*.[213] These authors used a combination of pulsed radio-frequency (RF)-GD-OES and XPS to analyse the buried layers, taking advantage of the relatively rapid profiling rate of the GD-OES and then using XPS to analyse the bottom of the GD crater. The samples used were n-type indium phosphide with a S doping level of 1.6×10^{18} and of 364 μm thickness. However, there was a problem in that the reliability of the XPS data was compromised by a perturbed layer on the surface of the crater, which is not representative of the initial sample. The authors therefore used hard X-ray photoelectron spectroscopy (HAXPES), which offered the possibility of probing this layer in a different manner to the normal soft XPS. The soft XPS used Al Kα emitting at 1.49 keV whereas the HAXPES used Ga Kα emitting at 9.25 keV as the source and it is this greater energy that enabled HAXPES to undertake chemical state analysis at a higher sampling depth (50 nm, so approximately three times greater). This enabled analysis below the perturbed layer. Using both XPS and HAXPES, it was possible to discover that the perturbed layer was approximately 10 nm deep, identify the composition of this layer as well as the composition of the bulk material below it.

Wang *et al.* used direct current (DC)-GD-MS for the depth profile analysis of molybdenum disulfide films deposited on aluminium and steel substrates.[214] The operating conditions were optimized so that a flat-bottomed crater was produced and

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to ensure that sufficient analyte signal intensity was obtained. The optimum conditions included a discharge current of between 1 and 1.5 mA and a discharge pressure of 4.7 mPa. The resolution of the depth profiles was dependent on the substrate and were 0.55 μm for the film on the aluminium and 0.70 μm for that on the steel. The interface between the substrate and the film was measured to be at a depth of 4.46 μm for the film on the aluminium and 4.55 μm for that on the steel. These values were in reasonable agreement with those obtained using field emission scanning electron microscopy (FESEM) which were 4.85 μm and 5.45 μm, respectively. These researchers then used a steel CRM to "validate" the data. Good agreement with certified values was obtained (±12% of certified values), but this is not really a relevant material to analyse when the samples are thin films.

Titanium electrodes and titanium oxide films play an important role in state-of-the-art electronic devices. It is therefore important that they be fully characterized to enable optimal performance. In a paper by Leani *et al.* titanium oxide thin films were deposited on titanium substrates using electroformation with varying anodic potential values and with differing electrolyte compositions.[215] The oxidation state of the Ti at different depths was measured using energy dispersive inelastic X-ray scattering (EDIXS) under grazing incidence conditions. The spectra obtained were treated using multivariate statistical methods. The results indicated a well-defined distribution of titanium oxides in the (+3) state as compared with the standard (+4) state. This was in good agreement with predictions. The conclusion was that GI-EDIXS can provide valuable information from nanolayers of technological materials.

A *calibration-free, real-time organic film thickness monitoring technique using reflected XRF and Compton scattering measurements* was devised by Park *et al.*[216] The new simple, non-contact and non-destructive real-time film thickness measurement technique proposed to use the simulation of a field process dealing with thin flexible organic films and demonstrated its utility by setting up a bench-top X-ray thickness measurement system. The use of X-ray fluorescence and Compton scattering X-ray radiation reflectance signals for analytes of low z from films in close contact with a roller produced accurate thickness measurements. For thick films (>1 mm), the Compton scattering method should be used. For very thin films the fluorescence should be used because it has a signal 4.6 times higher than that of the Compton scattering. There is a region in the middle though, where both fluorescence and scattering can contribute. For films of thickness in that region, the analyst must decide which of the techniques to use. Correlation between thickness and signal intensity was excellent for both techniques over the range 0–0.5 mm, with R^2 values of 0.997 and 0.999 for fluorescence and Compton scattering, respectively. The experimental setup was discussed in the paper. The method is potentially of use for the on-line measurement of organic thin films during preparation.

Ruthenium and carbon thin films are used in multilayer monochromators over the range 8–20 keV. In a study by Kiranjot *et al.* the use of this material was explored for X-ray waveguide applications in the hard X-ray region.[217] The thickness of each Ru–C–Ru layer was optimized so that maximum intensity enhancement was achieved. The samples were prepared by using ion beam sputtering and were characterized using X-ray reflectivity (XRR) and GIXRF. The raw data obtained using XRR were subject to several mathematical models: Parratt recursive formalism, Motofit (an algorithm that uses the Abeles matrix/Parratt recursion and least squares fitting) and a method to try and model the roughness. The layer thickness, roughness and densities obtained from GIXRF-XRR analyses were then used to recalculate field intensity inside the stack. A deviation of 10% in depth from the optimum in the top cladding layer and of 5% in the guiding layer as well as the presence of a 1 nm thick top layer resulted in a significant deterioration of the field intensity. This demonstrated the control required during manufacture which could be facilitated by atomic spectrometry.

4.8.2 Solar cells. The development of new solar cells is still a very popular subject area of research. However, the advances in the atomic spectrometry have been less prolific during this review period.

A comparison of data obtained using a *commercial LIBS instrument and one made in-house was given for the analysis of p-type solar cells* by Benelmouaz *et al.*[218] The compact commercial instrument was operated at 1064 nm as was the laboratory instrument that was equipped with an echelle spectrometer. Both instruments were optimized to obtain the best signal to noise ratio. Interestingly, the morphology of the craters produced by the two instruments was different indicating a different way of interacting with the sample. During the depth-profiling analysis, both systems produced a crater approximately 0.2 μm deep per laser shot. However, the commercial system produced a top hat-shaped crater, *i.e.* one with vertical sides and a flat bottom which is ideal. The laboratory-made instrument produced a Gaussian-shaped crater which is far from ideal. Eight analytes (Ag, Al, Ca, H, K, Mg, Na and Si) were determined, with only the laboratory made system being able to determine Mg. This was attributed to the commercial instrument having poorer sensitivity in the UV region whereas the lab-based instrument had poorer sensitivity in the near IR region. The origin of these contaminants was identified as were their diffusion characteristics through the material. In general, the results obtained using the two systems were in agreement.

The *degradation mechanism of solution-processed organic light emitting diodes* was studied by Lee *et al.* who used TOF-SIMS and XPS in a sputtering depth-profile study.[219] The system under investigation was the poly(3,4-ethylenedioxythiophene):sodium polystyrene sulfonate. The TOF-SIMS analysis employed an Ar_{1500}^+ (2.5 keV and 0.5 nA) gas cluster ion beam for sputtering the sample and a Bi_3^+ beam (25 keV and 0.12 pA) for the analysis. Positive ion spectra were internally mass calibrated by using the CH_3^+, $C_2H_3^+$, $C_3H_5^+$, and $C_4H_7^+$ peaks. The XPS analysis employed an argon gas cluster ion beam to sputter the sample before the S 2p state was analysed. The studies identified that the device operation induced migration of the poly(3,4-ethylenedioxythiophene) in the poly(3,4-ethylenedioxythiophene):sodium polystyrene sulfonate layer towards the interface between the hole transport layer and the emissive layer. This had the effect of lowering the hole injection

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efficiency and shifting the carrier recombination zone toward the interface. An accumulation of excitons and hole polarons then induce quenching that results in molecular breakdown and device degradation. The TOF-SIMS data supported the hypothesis by identifying that molecular decomposition occurs only in the emissive layer after device operation.

The rapid determination of the *elemental composition of methylammonium lead iodide thin films using calibration-free LIBS* was reported by Wang *et al.*[220] The distribution of Pb/C over the films were determined and local elemental inhomogeneity and stoichiometric ratio deviation was identified. Calibration curves were constructed by putting liquid standards on the thin films prior to LIBS analysis. These calibrations had a root mean square error (R^2) of at least 0.99. From the calibrations, LOD for C, H, N and Pb were calculated, with values of 36.15, 39.54, 1.76 and 13.51 ppm, respectively being obtained. These represented the lowest LOD yet obtained.

4.8.3 Electronic components. A review paper by Lin *et al.* entitled "*Advanced in situ characterization of nanocomposite electrodes for sodium ion batteries – a short review*" that contained 80 references was presented.[221] Sodium ion batteries are becoming increasingly popular because sodium is more plentiful than lithium used in the current lithium ion batteries. However, there are problems associated with their use, such as poor cycling life, low energy density and they can have serious side reactions. Nanocomposite electrodes have the advantage of high structural stability and excellent conductivity. For the best possible performance, a good understanding of the structural and kinetic processes occurring during the charging discharging process is required. This is assisted by using *in situ* analysis techniques and these have been summarised in this review paper. A lengthy section on TEM, another for XED, a third for Raman and another for XAS were presented. In the XAS section, the authors split the subject into X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The two are related, but offer different information based on the energy position of the edge. The XANES is sensitive to the chemical bonding, whereas EXAFS depends on the atomic arrangement around the absorber. The review discussed the mechanical/chemical changes as well as the phase transitions occurring during the sodiation/de-sodiation processes.

Several papers have discussed the *analysis of waste or end of life electronic materials*. A paper by Van Yken *et al.* compared numerous methods for the analysis of waste printed circuit boards.[222] This included any pre-processing methods (*e.g.* ashing, smelting or no pre-processing), acid decomposition method (nitric acid, aqua regia and hydrofluoric acid, sulfuric acid and hydrogen peroxide (piranha solution) and a microwave assisted digestion) and the measurement technique (XRF or ICP-OES). The full methodology for each was given in the paper. Unsurprisingly, the accuracy and precision of the resulting data depended on the methodology adopted. Smelting in the presence of borax at 1350 °C led to losses of volatile analytes (especially Zn and, to a lesser extent, Cu) and was quickly discarded as a means of pre-processing. The ashing at 500 °C was however, a viable process. Some acid dissolution processes resulted in an insoluble residue that could only be brought into solution using a fusion technique. This extra step, although largely successful, adds to the time and hence cost of the analysis. The most successful analytical protocol involved the use of aqua regia and hydrofluoric acid in a microwave digester at elevated pressure (30 bar) and at 180 °C, followed by ICP-OES analysis. Particle size also had an influence. Smaller particles were more homogeneous, but more difficult to obtain (requiring more grinding *etc.*). The authors called for the production of a suitable certified reference material so that the accuracy of this challenging analysis can be determined.

The recycling of materials can be very lucrative, however, the measurement of analytes such as *rare earth elements (REE) can be troublesome using ICP-OES because their emission spectra are extremely line-rich* and the elements tend to interfere with each other. However, ICP-OES is usually chosen as the means of analysis because it is cheaper than ICP-MS. A paper by Patil *et al.* studied these interferences in complex electronic waste feeds.[223] These authors used 27 wavelengths recommended by the ICP-OES software for nine REE and then chose 445 line positions adjacent to them that originate from non-REE concomitants. The net intensity measured at each line position was calculated by subtracting the raw intensity of the blank sample (1% nitric acid solution) measured at the same wavelength. Two dimensional diagrams were constructed that mapped the interferences. An interference correction algorithm was prepared and then tested on waste from fluorescent lamps that contain over 50 elements. The approach used measured intensities of the analyte and interfering elements at different wavelengths and is independent of the analyte concentrations. It was more effective than the calculated intensities with conventional instrument software or interference correction that have difficulty correcting for interferences in complex samples such as e-waste. It was thought that the algorithm could be used for any type of e-waste.

Chemical inspection of electronic waste was achieved using data obtained using LIBS, LA-ICP-MS and μ-XRF by Andrade *et al.*[224] Both univariate and multivariate chemometric tools were used for calibration purposes for LIBS and μ-XRF. The univariate method involved plotting the ICP-OES reference value (x axis) against the value obtained using LIBS or XRF (y axis) and creating a linear model. The multivariate methods involved the use of partial least squares regression to combine the auto-scaled analytical signals from both techniques and reference concentrations determined using ICP-OES. Data obtained using LIBS, LA-ICP-OES and μ-XRF were input to PCA for calculation using the auto-scaled data. The score values were arranged to build the maps of scores and associated with its corresponding loading vector (*i.e.* to provide spectral information). In general, the univariate calibration approach failed, with very poor correlation coefficients and standard error of calibration values being obtained. The multivariate calibration approach was more successful. The overall approach of data fusion and chemometric analysis was a powerful alternative to obtaining data from such samples and enabled the authors to build regression models with better statistical parameters such as lower percent errors, better accuracy and reliability.

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Inverse production is where a conveyor belt of end of life material is sorted and select parts (the most valuable materials) are retained and recycled. This has been discussed by Noll *et al.* who developed a *fully automated LIBS system for the sorting and selection process for materials such as printed circuit boards from assorted mobile phones and servers*.[225] Schematics of the process were presented, with the LIBS system employing a Q-switched Nd:YAG laser, operating at 1064 nm, 100 mJ and at a frequency of 100 Hz. The sample was on a translation stage and the spectrometer was of the Paschen–Runge design, with eight CCD around the 500 mm Rowland circle. The spectral range was 234–545 nm. A 500 mm × 500 mm circuit board could be analysed for the important analytes Ag, Au, Cu, Nb, Nd, Pd, Ta and W in <30 s. The instrument was capable of both 2D and 3D analysis (*i.e.* it was capable of looking beneath any coating). The authors claimed this to be a world first and that they had high hopes for its use in the inverse production line industry.

The *analysis of batteries or battery components* has also been a productive area of research. Two papers by Fu *et al.* have used ICP-MS/MS to determine analytes in lithium hexa-fluorophosphate[226] and magnesium bis(tri-fluoromethanesulfonyl)imide.[227] In the first of these papers, polyatomic interferences were eliminated during the determination of 18 analytes in lithium hexafluorophosphate (an important electrolyte in lithium ion batteries) through the use of reaction gas mixtures in the reaction/collision cell.[226] Two operating modes were used. In simple ICP-MS/MS, the reaction cell gas was hydrogen and oxygen (2 mL min^{-1} and 0.3 mL min^{-1}, respectively) or hydrogen, helium and ammonia. These mixtures helped overcome the presence of argide ions. The mixture including the ammonia yielded marginally better results, with sensitivity increasing slightly and background equivalent concentrations decreasing slightly. The other method involved mass shift, *i.e.* where a component of the reaction gas adds to the analyte so that the effective mass determined is analyte + reaction gas. This was used for analytes such as Cu, Ni and Zn. For this, the addition of helium and ammonia was compared with the addition of ammonia, helium and hydrogen. Again, the three component mixture had a better effect on interference removal whilst simultaneously increasing sensitivity. Since no suitable reference material is available, results were compared with those obtained using a sector field (SF)-ICP-MS instrument. For the SF-ICP-MS measurements, the resolution was set for each analyte to ensure interference free measurements. Therefore, low resolution was used for: Ag, Ba, Cd, Pb and Sb; medium resolution was used for Al, Co, Cu, Mg, Mn, Na, Ni, Ti, V and Zn and high resolution was used for Cr, Fe and K. For 17 of the 18 analytes determined, there was no significant difference between the two sets of data; the exception being Fe. For the triple quad instrument methods, recoveries of spiked samples were in the range 92.4–108% and precision was typically 5–6%. The other paper[227] was similar in structure but differed in that it measured only 13 analytes in the different matrix and also compared nitrous oxide with oxygen and ammonia/helium as a reaction gas. The nitrous oxide donated O better than oxygen alone and hence results for most analytes were significantly improved compared with the introduction of oxygen alone. All analytes had a lower LOD when nitrous oxide was used, but some had a better sensitivity when oxygen was added (*e.g.* V). When compared with the addition of helium/ammonia, the results for nitrous oxide were mixed. In general, similar LOD were obtained, but the sensitivity of detection was improved for some analytes and seriously degraded for others. Spike/recovery experiments were again used yielding recoveries of 92.5–107%. Precision using the nitrous oxide was typically 2–5.3% RSD.

Two papers by Kroger *et al.* used *single particle ICP-OES measurements to determine microparticles in lithium ion batteries*.[228,229] In the first, a lithium transition metal oxide mixture Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ cathode material (known as NCM111) was analysed. The powder (200 µg) was injected into the top of an s-shaped gravitational counter flow classifier that had been made in house and argon introduced at the bottom. The argon flow continued through the classifier, exiting at the top and entering, *via* a chamber with an extra argon gas flow, an ICP-OES instrument where Li and Mn were determined. This on-line system therefore enabled the particles to be separated according to their size distribution, with smaller particles reaching the plasma first. The authors noted that prior to introduction, the particles had to be agitated on a laboratory shaker to avoid agglomeration. The gas flow through the classifier was optimised and results indicated that at higher gas flow (20 mL min^{-1}), the fraction of particle size < 1.2 µm was 60 ± 8%. This compared with a value of 81 ± 5% for a flow rate of 3 mL min^{-1}. The difference was attributed to the higher flow rate transporting larger particles much more efficiently. The plasma power and the makeup gas flow were also optimised. The particle size LOD was approximately 0.5 µm. Results were compared with those obtained using SEM and were in good agreement. Although particles as large as 10 µm could be separated, a problem with incomplete evaporation/excitation once in the plasma occurred. The method was therefore effectively limited to particles of <2 µm. In the other paper, a similar material (NCM 532, Li(Ni$_{0.5}$Co$_{0.3}$Mn$_{0.2}$)O$_2$) was studied to try and obtain insights into the state-of-charge distribution of the battery electrodes.[229] This could be achieved by measuring the Li content of individual cathode active material particles, which enabled a statistically viable elucidation of the mesoscale state-of-charge distribution between different particles. Results obtained were compared with those obtained using TOF-SIMS. Both techniques identified a persistent mesoscale heterogeneity of the electrode upon delithiation at slow rates and extensive relaxation times. The paper highlighted the necessity of analysis at the mesoscale for such materials.

Another paper to analyse NCM111 was presented by Winckelmann *et al.* who *used a commercial high resolution AAS instrument combined with machine learning data processing for isotope ratio amount analysis of Li*.[230] There is a shift in wavelength of approximately 15 pm around the Li wavelength of 670.8 nm for different isotopes and this small, but separable, difference was exploited to obtain isotope data. The cathode material was obtained, separated into five-subsamples of ~100 mg each and dissolved in aqua regia. The Li was then

extracted quantitatively using AG-50W-X8 exchange resin. Prior to the isotope ratio measurements, the total Li was determined using ICP-OES. As an alternative method, the samples were also analysed using multi-collector ICP-MS. For the HR-CS-ETAAS measurements, sample (10 μL of 25 μg L^{-1}) was used with an optimized temperature program and the reactive gas 1% tri-fluoromethane in argon to prevent the formation of lithium carbides and, hence, carry over/memory effects between samples. Analytical data were exported and input to the machine learning algorithm called XGBoost. This was first calibrated using materials with ^{6}Li amount fractions ranging from 0.06 to 0.99 mol mol^{-1} (as measured previously using MC-ICP-MS). The machine learning model was tested using two certified reference materials: IRMM-016 and LSVEC (a lithium carbonate material with certified C, Li and O isotope ratios). Results were in good agreement with certified values, with residual bias being only −1.8 parts per thousand. Precision ranged between 1.9 and 6.2 parts per thousand. The methodology was then applied to the candidate BAM reference material NCM111, using both the matrix separation method and without purification. Both sets of data were metrologically compatible with each other.

A calibration-free LIBS method was reported by Pamu et al. for the analysis of assorted lithium ion battery cathode materials.[231] This is a continuation of previous work and so the paper refers to previous papers for the LIBS setup and much of the theory. However, the method was used successfully for the determination of the ratios of the major electrode materials (Ni, Co and Mn) as well as some of the dopants, e.g. Cr and Mo. Materials were prepared by sol gel synthesis and included LiNi$_{0.5}$Mn$_{0.5}$O$_2$, LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$, LiNi$_{0.317}$Mn$_{0.317}$Co$_{0.317}$Cr$_{0.05}$O$_2$ and others. The LIBS methodology was rapid and was capable of characterizing the materials accurately, with results being in good agreement with the nominal values.

Diaz and Hahn used LIBS to characterise products released from lithium ion battery cells at thermal runaway conditions.[232] Commercial AAA-sized 3.7 V, 350 mA h lithium ion batteries were placed in a heating chamber and heated to 165 °C to induce thermal decomposition (this starts at 143 °C) in a nitrogen atmosphere. Any gases emitted over a 40 minute period were then analysed on-line using LIBS which employed a Nd:YAG laser, optics, a chamber in which the LIBS analysis occurred and a spectrometer equipped with an intensified CCD. The analytes of interest were: Al, C, Co, Cu, F, H, Li and P; however, emissions from Al, Co, and Cu were not found and only short-lived emissions from Na were detected. Emission from the batteries was not uniform. Although C and H were produced throughout the process, other analytes such as F, Li, Na and P were detected at different and irregular times. This was, according to the authors, indicative of analyte bearing particles being emitted from the battery. The authors also developed a calibration scheme for total C. The work is still at an early stage and modifications to the experimental protocol are to be expected to gain maximum information, improve sensitivity, accuracy etc.

As batteries age, they experience capacity fading and cycle reduction. The effects can be monitored using electrochemical methods, but the underlying causes cannot. Zech et al. used XRF and NEXAFS to study the physical causes of battery degradation.[233] The amount (XRF) and the oxidation state (NEXAFS) of Mn liberated from the cathode and coated onto the anode was determined. For the XRF analyses, an approach with no need for reference samples for quantitative elemental speciation was applied. This reference- or reference sample-free XRF is based upon radiometric and dimensional knowledge of all instrumental and experimental parameters as well good knowledge of X-ray fundamental parameters and helps overcome the lack of certified materials. A total of 50 full battery cycles with elevated cut off voltage were applied and the amount of Mn deposited on the anode was 1.6 parts per thousand. This led to a decrease in capacity of 12.5%. The NEXAFS analysis of the Mn L- and K-edges of the deposits enabled the study of the oxidation state. Furthermore, by applying different excitation energies, different depths of the deposits were investigated. The Mn was present as the divalent and tetra-valent forms, with the tetra-valent form being present solely in the anode bulk rather than the deposits. The understanding of the degradation process will help the prevention of it in future lithium ion batteries.

The analysis of high purity quartz has featured in two papers. In one by Busam et al. the solid, fused high purity quartz was analysed using direct current GD-MS employing indium of 7N purity as a secondary cathode.[234] Quartz is a non-conducting material and can therefore present problems during analysis. In this method, a secondary cathode is sputtered onto the sample during the discharge. These sputtered ions on the sample then attract some plasma and re-sputter the cathode material as well as some sample material. The secondary cathode material is also known as "masking material". In this way, non-conducting samples can be determined reliably and with much higher sensitivity. The operating conditions had to be optimized because the successful deposition on the sample depends on the pressure used (too high means the sample is completely coated, too low leads to poor deposition and an unstable discharge). The deposition success then dictates the voltage and current to be used. The relative sensitivity factors were calculated with respect to Si = 1 and to Fe = 1. Both sets were in agreement to within a factor of two with previously published data. Under the conditions used (current = 0.3 mA, voltage = 1.5 kV, Ar flow = 0.17 standard cubic centimetres per minute and pressure = 4.9 × 10^{-5} mbar) they were adequate for the task. Using the Faraday cup detectors for determining the analytes at higher concentration and the ion counters for the lower concentration analytes meant that a sample could be analysed in 10 min. Detection limits were at the ppb range which were better than those reported previously when a tantalum mask was used. The other paper to report the analysis of high purity quartz was presented by Devi et al.[235] These authors presented a "bottom-up approach of uncertainty evaluation" for the TXRF analysis of the material whilst participating in a proficiency testing program. The material was first dissolved using hydrofluoric and nitric acids to evaporate the Si as the tetrafluoride. After repeated treatments with nitric acid, the analytes Ca, Fe, K and Ti were determined using TXRF

employing the internal standard (Ga) method. The z-score, zeta-score and quality control sample analysis data revealed the accuracy of the data. The relative sensitivity of the instrument for the analyte with respect to the internal standard provided the highest contribution to the uncertainty. The LOD were: 0.95, 0.30, 1.86 and 0.94 mg kg^{-1} for Ca, Fe, K and Ti, respectively.

Two papers have discussed the *LIBS analysis of outdoor insulators for high power transmission lines*. Contaminants such as aluminium phosphate, glucose and others are hygroscopic, *i.e.* they absorb water, and can therefore cause flashovers even at relatively low humidity. The paper by Qin *et al.* used LIBS to analyse the aluminium phosphate contamination.[236] The moisture content in the aluminium phosphate also affected the LIBS signal. Using the atomic signal of P and over a discrete humidity range, the emission intensities from the spectral lines were normalized. This reduced the effect of the moisture content on the LIBS signal significantly. This standoff analysis is very rapid and has the advantage of not needing to shut the power off. The other paper was by Homma *et al.* who reported the LIBS analysis of high voltage silicone rubber insulators.[237] These materials also degrade over time in the field and so a method of measuring this would save time and money. A remote LIBS system was developed that could be used for the task. The system was described in full in the paper, but essentially, it had a Nd:YAG laser operating at 532 nm, assorted optics, a telescope system to collect the emitted light and a spectrometer/detector. Field aged insulators were compared with pristine ones with the LIBS system also undertaking depth-profiling analysis, *i.e.* it ablated the same spot sequentially. The emission intensity ratio of Si to Al was used as a measure of degradation, with the ratio decreasing by approximately 30% at the degraded surface compared with the bulk. A significant decrease in Si occurred up to a depth of 300 μm compared with pristine insulators. These results were confirmed by SEM-EDS measurements. The conclusion again was that LIBS was potentially a very good technique for monitoring degradation of the insulators and its on-line/standoff capability makes it safe, rapid and has the important advantage of not requiring the power to be shut down.

Contamination control during the production of silicon wafers is obviously an exceptionally important matter. A paper by Lim *et al.* used LA-ICP-MS to image metal ions and nanoparticles on structured silicon surfaces.[238] A silicon wafer was prepared and then an array of 8 × 8 pillars of dimensions 250 μm wide and 300 μm tall were attached. Each pillar had a well in the upper-most surface of dimensions 200 μm wide and 30 μm deep. This was produced using the Bosch process (etching using SF$_6$). This was capable of accepting 4.3 nL of aqueous solution introduced through a capillary tip. The aqueous solution contained either ions (Co, Cu, Si and Zn) at a concentration of 10 μg mL^{-1} or nanoparticles (copper indium sulfide/zinc sulfide quantum dots) of two different particle size ranges (4–7 nm and 15–19 nm). The droplets were allowed to dry naturally prior to analysis. The drying mechanism was studied extensively, with evaporation not occurring at the same rate throughout the process. The LA-ICP-MS data showed that for the ions all analytes except Si collected at the intersection of the wall and the bottom of the well, *i.e.* they migrated radially across the droplet as it dried, forming a ring. The smaller nanoparticles showed the same trend, but with the ring being slightly less pronounced. The smaller nanoparticles therefore acted in a similar way to the ions. The larger nanoparticles did not behave this way. These were distributed randomly demonstrating that particle size affects the distribution. Extrapolating their results to those for the cleaning solutions used on a full-sized wafer enabled the authors to deduce that similar conclusions could be made. The study was thought to assist in the control of contaminants during wafer manufacture.

Analyses undertaken using LIBS are fast and require little or no sample pre-treatment. However, the accuracy of the data can be questionable because signal is very matrix dependent and rough or uneven surfaces can also lead to inaccuracy. Many workers have therefore used an assortment of statistical methods to try and correct for these problems. Davari and Mukherjee have added to this list by using a *one dimensional convolutional neural network and a least absolute shrinkage and selection operator (LASSO) models for LIBS data analysis*.[239] The paper gives a decent description of how the models work and then applied them to LIBS data obtained while determining O impurities in the interstitial layers of Czochralski crystals. The analysis chamber was filled with 6 L min^{-1} He and 2 L min^{-1} Ar (these optimal conditions had been established in a previous study) and the O was measured at 777.19 nm. Using intensity data alone led to poor accuracy. However, once the algorithms had been trained, the predicted concentrations matched the expected concentrations much more closely over the range tested (0–16 ppm).

4.9 Engineered nanostructures

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

4.9.1 Topical reviews. A number of *reviews covering NP measurements* have been published this year. The first of these (380 references), by Huang *et al.*, covered the use of mass spectrometry for the multi-dimensional characterisation of natural and synthetic nanomaterials (NMs).[240] The techniques covered, ES-MS, FT-ICR-MS, ICP-MS, MALDI-MS and SIMS, show the range required to be able fully to characterise nanomaterials in applications such as bulk and surface composition, size, stability, source tracing and the distribution and fate in the environment and organisms. Probably the most popular single technique for NP detection and characterisation is single nanoparticle (sNP) ICP-MS and the analytical applications of this technique, with 308 references, were recently reviewed by Bolea *et al.*[241] The paper gives a brief introduction to the technique, defines the various measurands normally determined and also has a useful section on method validation, in which the authors pointed out that methods for calculating the LOD

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values for particle size and particle number concentration are varied and have yet to be agreed upon. The review then covers a number of different application areas, sample preparation and also the coupling of various separation techniques, including CE, FFF and different modes of chromatography, complementary techniques such as TEM, and finally immuno-assays and biomolecule quantification. The authors concluded that although sNP-ICP-MS is becoming a mature technique, progress to this level is currently hampered by the lack of vali-dated methods and the traceability of their results, which is due to the lack of matrix reference materials. A separate review, by Resano *et al.* (216 references) covered the underlying concepts behind single event-ICP-MS, which is needed to fully under-stand its potential, and also highlights key application areas, (sNP-ICP-MS or single cell-ICP-MS) and also the emerging area of micro/nanoplastic detection.[242] The review gave a compre-hensive guide to the principles of short transient signal measurements, the steps needed to undertake these analyses, the calculations involved and the progress in sNP and single cell ICP-MS since their inception. Again, the authors also noted the lack of available CRMs for method validation. Each of these reviews are recommended reading for practitioners new to the field or those wishing to update their knowledge.

In sNP-ICP-MS the baseline signal from dissolved or 'ionic' forms of the element(s) under study is one of the governing factors, with plasma instability and detector noise also contributing, for the obtainable LOD. It is therefore becoming increasingly common for a separation technique to be used to reduce the baseline signal during sNP-ICP-MS measurements and Lespes *et al.* have reviewed the use of FFF for NP charac-terisation.[243] The review (78 references) covered the theory of FFF, with the objective being to link the retention of nanoscale analytes and the characteristics of these analytes involved in their separation as well as method performance. The coupling of the various detectors used, *e.g.* dynamic light scattering (DLS), multi-angle light scattering (MALS), ICP-MS and UV as well as the various applications reported in the literature were reviewed. A prediction of the future trends that may arise was also presented. The authors concluded that FFF is a versatile technique for NP characterisation when combined with the various detectors discussed and can be used to elicit both NP size and chemical information and has the potential to provide a metrological solution for NP characterisation. A second review (103 references) in this area by Bai *et al.* dealt explicitly with the use of flow field-flow fractionation (F4) prior to ICP-MS for NP detection in environmental samples.[244] The review covered the basic theory of F4-ICP-MS, recent advances in its application to environmental samples and the characterisation of corona-coated NPs. The authors concluded that it is still not possible to differentiate between naturally occurring and engineered nanomaterials (ENMs) in environmental samples, that a combination of analytical techniques, which could include *e.g.* FT-ICR-MS, are required to investigate surface bound components of NPs and that large injection volumes could be used to allow ecotoxicological studies of NPs to be conducted at environmentally relevant NP concentrations.

Laycock *et al.* have systematically reviewed (159 references) the *determination of metallic NPs in biological samples using sNP-ICP-MS*, covering the entire process from sample collection to analysis.[245] The review showed that most research has been conducted on a limited range of engineered nanomaterials (*e.g.*, Ag and TiO_2) and that there is a lack of information for some important tissue types (*e.g.*, reproductive organs, skin and fatty endocrine organs). The authors also reported that the impor-tance of storage on particle stability, *e.g.* agglomeration, is often overlooked and that few studies assess the impact of the extraction reagents used on the formation of NPs by trans-formation of endogenous 'ionic' forms of the target analyte into new particulates. It was also stated that a 'one size fits all' extraction protocol, which would be attractive from a regulatory perspective, that is applicable to all possible types of engineered nanomaterial and biological matrices, does not seem practical. Alkaline-based extractions would appear to show greater promise for wide applicability to animal tissues, whilst enzy-matic based approaches have a role, especially for plant tissues. It was also reported that, as noted earlier in this section, there is a lack of consistency in the particle metrics reported and how they are determined (*e.g.* size limit of detection, and propor-tions of recovery), which makes comparison between studies more difficult. The paper ended with a series of recommenda-tions with the aim of establishing standardised protocols for regulatory use, an internationally agreed nomenclature, that suitable CRMs need to be produced along with the use of control samples during the analytical procedure.

Since there is often a high background level encountered, C is not usually detected using ICP-MS, although there are a few published papers on the topic. Therefore, an alternative for *the determination of plastic NPs is to label them with metals*, allowing the assessment of their distribution and uptake during eco-toxicological studies. A perspectives paper on this topic was produced by *Marigliano et al.*[110] Three different labelling strat-egies, the use of metal ions, hydrophobic organometallic compounds and NPs, for the detection of polystyrene (PS) nanoplastics by sNP-ICP-MS were presented and discussed. The advantages and disadvantages of each strategy were high-lighted. The addition of metal ions to the particle surface proved of limited use because of insufficient adsorption hence low sensitivity and a high baseline from unadsorbed ions whilst the use of an organometallic Pb compound proved laborious with regard to sample preparation. Labelling with metal NPs was considered to be a promising tool for the detection and quantification of nanoplastics in aqueous matrices using SP-ICP-MS. The authors concluded that this approach needs further development, particularly with regard to the effects of naturally occurring organic matter and colloids in environ-mental samples but could allow the detection of carbon-based ENMs in these sample types.

The use of *laser and X-ray based techniques is routinely used for the characterisation of NPs* during the production process and of the final products and the use of XPS for assessing the composition, thickness, and homogeneity of the coating of core–shell NPs has been the subject of a review article.[246] The review (86 references) focussed on four examples: CdSe/CdS

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quantum dots with a thick coating and a small core; NaYF4-based upconverting nanoparticles with a large Yb-doped core and a thin Er-doped coating; and two types of polymer nanoparticles with a poly(tetrafluoroethylene) core with either a poly(methyl methacrylate) or polystyrene coating. A theory section was included and the modelling of the XPS background for the investigation of the coating is discussed along with the use of hard-energy X-ray sources and a discussion about the sources of uncertainty for the determination of the thickness of the particle coatings. An overview of the analytical methods used for analysis and quantification of surface bound functional groups (FGs) on NPS, with emphasis on bioanalytically relevant FGs such as proteins, peptides, and oligonucleotides has been authored by Geissler *et al.*[247] The analytical techniques reviewed (with 259 references) included electrochemical titration methods, optical assays, NMR and vibrational spectroscopies, X-ray based and thermal analysis methods. The final review reported on here concerned the use of laser and plasma spectroscopy during NP production.[248] The review (600 references) gave details of various different NP production methods including flame, LA and electrical discharge synthesis and further techniques where laser-NP or plasma-NP interactions occur such as LIBS, LA-ICP-MS, sNP-ICP-MS and DLS.

4.9.2 Interlaboratory studies. There have been two reports on *interlaboratory studies concerning NPs* this year. The first of these was by Minelli *et al.* and described the outcome of the measurement of particle number concentration of 30 nm Au NPs and was conducted under the Versailles Project on Advanced Materials and Standards (VAMAS).[249] A total of 50 laboratories participated, with 74 different measurement reports submitted, and the methods used were particle tracking analysis (PTA), sNP-ICP-MS, UV-Vis spectroscopy, centrifugal liquid sedimentation and small angle X-ray scattering (SAXS). The study provided quantitative data allowing the repeatability and reproducibility of these methods, which followed a common measurement protocol, to be evaluated. It was found that the population-averaging methods, CLS, SAXS and UV-Vis exhibited a high measurement repeatability and reproducibility, with the between-lab variability being 2.6%, 11% and 1.4% respectively. However, the authors stated that the results may be significantly biased for reasons including inaccurate material properties, the values of which are used to compute the number concentration. Particle-counting method results (PTA and sNP-ICP-MS) were less reproducible than the population-averaging methods, with measured between-lab variability of 68% and 46% for PTA and spICP-MS, respectively. The paper gave a wealth of detail on the techniques used, analytical results and the interpretation thereof and is well worth reading. In sNP-ICP-MS the accurate knowledge of the transport efficiency of the sample to the plasma is fundamental for the correct determination of both particle number concentration and size and an interlaboratory study on this topic was published by Geiss *et al.* in the period covered by this review.[250] The transport efficiency was systematically determined on three different days with six carefully characterised Au NP suspensions in seven European and US laboratories using different ICP-MS instruments and sNP-ICP-MS software. Two methods for quantifying transport efficiency: particle size and particle frequency, were evaluated in the study. The resulting transport efficiencies did not deviate much under ideal conditions. The particle frequency method however systematically resulted in lower transport efficiencies. The extent of this difference (0–300% rel. difference) depended largely on the choice and storage conditions of the nanoparticle suspensions used for the determination. The particle size method is recommended when the principal measurement objective is particle size. If the main aim of the measurement is the determination of the particle number concentration, the particle frequency approach could be preferred as it might better account for particle losses in the sample introduction system.

4.9.3 sNP-ICP-MS fundamental studies. This section covers *research into the fundamental aspects of sNP-ICP-MS* and one example of this is research covered in two papers into the occurrence of spikes in the time scan from very dilute NP suspensions.[251] The researchers show that, at the very limit of dilution, there is a one-to-one correspondence between the spikes present in a time scan and the points of discontinuity of the outcome of a homogeneous Poisson process and that this relationship underlies the random nature of the sp-ICP-MS time scan. The difference between the number of nanoparticles having entered the plasma of the instrument and the number of detectable spikes in the time scan increases in a strongly nonlinear fashion with the particle number concentration. This counting bias is attributed to particle event coincidences in the time scan and the authors show that the counting bias is related to a stochastic process that models the spike occurrences in the time scan which turns out to be amenable to analytical methods and yields universal predictions. It was also established that the stochastic processes describing the nanoparticle arrivals in the plasma and the time sequence of spikes in the time scan are fully identical, thus helping to place on firmer grounds a frequently made hypothesis regarding the Poissonian character of the sNP-ICP-MS time scan. Monte Carlo simulations and experiments with gold nanoparticle dispersions, for the full spectrum of particle number concentration values tested were also undertaken to confirm the theoretical observations. Data processing in sNP-ICP-MS is either by software provided by the instrument manufacturers or independently developed spreadsheets, such as that provided by RIKILT in the Netherlands, or software programs such as that developed in Sweden. An addition to this tool bag, an open-source Python-based SP/SC ICP-MS data processing platform with an interactive graphical user interface was described by Lockwood *et al.* in a recent paper.[252] The program allows the analysis of large data sets, uses efficient and transparent algorithms and Gaussian and Poisson-based data filtering enables fit for purpose thresholding of particle signals from background noise. The software can also be used for LA-sNP-ICP-MS and other data sets that contain drifting or variable backgrounds. Signals from ICP-MS of single particles or single cells recorded with multiple data points can be integrated and several distinct calibration and processing pathways are available for use to determine particle masses, sizes, and number concentrations, or to calculate intracellular concentrations. Statistical parameters including

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means, medians, ionic background levels and LOD values are also calculated by the software. The paper presents the theory of the calculations and gives examples involving TiO_2 NPs in surface water, microplastic particles in soil and the C content across individual cells.

A paper by Donahue *et al.* demonstrated the feasibility of dual analyte quadrupole SP-ICP-MS to quantify chemical transformations and reaction kinetics at the sNP level *in situ* for bimetallic NPs.[253] The work required optimisation of the collision cell parameters, quadrupole mass analyser settling time and the detector dwell time and full details of this is given in the ESI discussion. A discussion on the theory of quantifying paired and unpaired isotope events was also included and three isotope systems were chosen for simultaneous detection ^{175}Lu and ^{140}Ce, ^{175}Lu and ^{153}Eu and ^{175}Lu and ^{165}Ho with each element pair being contained in doped polymer beads. Under optimal conditions, with the dual analyte sNP-ICP-MS approach, 97% of the detected beads were positive for each isotope for all three pairs of isotopes. Following this, 100 nm Ag NPs were analysed and >95% of detected events were positive for both silver isotopes at nanoparticle concentrations of 1×10^5 Ag NPs per mL whilst for a 1 : 1 mixture of Ag and Au NPs the detected particle events were, as expected, unpaired. Further experiments involved real time monitoring to quantify the chemical composition and reaction kinetics of individual Ag/Au bimetallic NPs. This allowed the individual bimetallic nanoparticle mass and chemical composition changes during two different chemical reactions: (i) nanoparticle etching and (ii) element deposition on nanoparticles to be determined at a rate of 300+ NPs per min. In addition, the results were corroborated by ICP-TOF-MS and X-ray EDS/SEM. The paper and supplementary information provide a wealth of information which fully describes all of the analyses undertaken.

4.9.4   Cerium. When conducting *in vivo* investigations with CeO_2 NPs, one challenge is to *separate the NPs from any ionic Ce present prior to sample analysis*. An analytical approach in which ultrafiltration was used to fractionate ionic and NP Ce species followed by measurement using sNP-ICP-MS was described by Huang *et al.*[254] Two sample pre-treatment methods, alkaline and enzymatic were evaluated and the results showed that the enzymatic pre-treatment was more efficient in extracting ionic Ce or CeO_2 NPs from animal tissues than the alkaline method. The results obtained also showed that the properties/states of all ionic and Ce species were well preserved. Recoveries of both species were over 85% and the size distribution of the extracted CeO_2 NPs was comparable to that of the original material used. The enzymatic approach was then applied to investigate the bioaccumulation and biotransformation of CeO_2 NPs in mice and it is reported that the thymus acts as a "holding station" in CeO_2 NP translocation *in vivo* and that CeO_2 NP biotransformation was organ-specific. A paper evaluating different filter materials used for the extraction and quantification of Ce NPs from natural waters was published by Jreije *et al.*[255] A fuller description is the work is given in the section covering Ag NPs. For CeO_2 NPs, recoveries for the polypropylene membrane were 60% in rainwater and 75% in river water. Membrane pre-conditioning with mono-, di- or tri-valent metal salts or

a commercially available 21 element solution increased NP recoveries to over 80%. The authors concluded that NP retention on the filters was attributable to particle aggregation and that a mass balance approach should be adopted when quantifying NPs in natural water samples.

4.9.5   Gold. Gold NPs are usually analysed as they can be *used as a calibrant in sNP-ICP-MS or are uptaken by cells* when used as a drug delivery agent. Workers at NIST have undertaken a rigorous assessment of the capabilities of sNP-ICP-MS for assessing the particle number concentration of Au NP suspensions of different sizes (30, 60 and 100 nm) and coatings (citrate, branched polyethylenimine, polyethylene glycol, polyvinylpyrrolidone).[256] Calibration of the ICP-MS instrument was by using NIST SRM8013 NPs and a comprehensive estimation of the expanded uncertainty for particle number concentration determination was carried out. The mean particle size or the particle size distribution obtained by different reference sizing techniques was first assessed for NIST AuNP RM 8012, nominal diameter 30 nm followed by that for the coated NPs under study ($n = 1$). Regardless of NP size or coating, a good agreement, of between 90 and 110% relative, between the sNP-ICP-MS direct determination of particle number concentration and reported particle number concentration was obtained for all of the suspensions studied only when reliable in-house Au mass fractions and thorough mean particle size determinations were included in the calculation of the derived particle number concentrations. The use of the particle size distribution over the mean size to derive particle number concentrations resulted in larger differences for materials with a low contribution (<2%) of smaller NPs (30 nm), materials with a higher polydispersity (100 nm), or materials with two distinct subpopulations of particles (60 nm), regardless of NP coating. The major contribution to the expanded uncertainty for the particle number concentration direct values was due to the variability in the number of observed particle events for the sample and the calibration standard. The paper, which is one of few published which considers an uncertainty budget for sNP-ICP-MS measurements, contains a wealth of information on the entire process and should be read by all practitioners in the field. Using flow injection (FI) for sample introduction in sNP-ICP-MS simplifies the determination of NP mass concentration by eliminating the requirements to measure the sample uptake rate and the transport efficiency. As the inherent sample in FI degrades the sensitivity and LOD of the measurement an alternative approach, mono-segmented flow analysis can be used. This involves the injection of a discrete volume of sample into a pocket of air within the carrier fluid which minimises sample dispersion and can also improves sample throughput. Experiments using this approach for the determination of 50 nm Au NPs were reported by Williams and Beauchemin.[257] Sample transport efficiency increased from 6.3% (FI-sNP-ICP-MS) to 8.4% using mono-segmented flow analysis -sNP-ICP-MS) and this factor, in combination with the square-wave shape of the MSFA peak, improved the sensitivity of the measurements. The Au NP particle size was measured with 0.6% RSD although the particle size LOD increased from 13 nm (for FI) to 38 nm.

Single-cell inductively coupled plasma mass spectrometry has been introduced for the analysis of intracellular essential elements and nanoparticles (NPs) at the single cell level although it can be a challenge to produce accurate and reliable results. A report by Liu *et al.* detailed the use of a high-efficiency sample introduction system, comprising a micro-concentric nebuliser, a low-volume single pass spray chamber with a make-up gas port, and a syringe pump to achieve single cell-ICP-MS.[258] The transport efficiency of single cells was 12% with the optimal number of cells in suspension to achieve this value being approximately 10^5 mL^{-1}. HepG2 cells were incubated with AuNPs, at 0.1, 0.5, and 1 μmol L^{-1}, prior to analysis using the system. The mass of Au in the cells measured using single cell-ICP-MS was in statistical agreement with the mass determined by conventional ICP-MS analysis after an acidic digestion procedure. An alternative approach to single cell-ICP-MS for analysing cell contents is to use SIMS, which has been described by workers at NIST.[259] The SIMS instrument was operated in image depth profiling mode to visualise, identify and characterise the biodistribution of Au NPs ingested by nematodes in both the lateral and depth dimensions. Conventional and sNP-ICP-MS were also used to determine the mean Au NP particle number within the nematodes, which ranged from 2 to 36 NPs depending on the size of Au NP the organisms were exposed to. The complementary data from the SIMS image depth profiling and the sNP-ICP-MS studies provided a complete view of the uptake, translocation and size distribution of ingested NPs within *Caenorhabditis elegans*. The paper gave a detailed discussion of the use of SIMS for this type of work and also of the sNP-ICP-MS work.

The detection and quantification *of Au NPs and Au ions in cosmetics marketed in Brazil* by sNP-ICP-MS has been covered this year.[260] The LOD$_{size}$ for pure Au NPs was found to be 22 nm whilst the LOD$_{particle\ concentration}$ was 10^6 particles per g. Three different extraction reagents were evaluated: 1% dimethyl sulfoxide (DMSO) solution, 10% tetramethylammonium hydroxide (TMAH) solution and deionized water with the best results obtained using the last. The recovery of dissolved Au and Au NPs from standard solutions/suspensions was 98% and 109%, respectively and a 'bottom up' approach was adopted for estimating the measurement uncertainty. Most of the cosmetics analysed contained quantifiable amounts of dissolved gold (<0.005 to 2.1 μg g^{-1}) and four contained quantifiable amounts of Au NPs, with the range being <LOD to 9.3×10^8 particles per g and the expanded uncertainties ($k = 2$) appear to range from 1 to 10% relative.

The translocation of Au nanoparticles across the gastrointestinal barrier along with related biological effects using an *in vitro* 3D-triple co-culture cell model has also been reported this year, with details given in the section on silver NPs which are also part of the study.[261]

Three studies reported *the use of laser ablation (LA) for detecting the signals from Au NPs*. Firstly, Metarapi *et al.*, used LA-sNP-ICP-MS to study Au NP degradation upon laser ablation in order to provide selection guidelines for the optimal laser fluence required for LA-NP work.[262] Gelatine was used as a sample matrix to mimic biological tissues and Au NPs of known size,

and with a size distribution of <5%, were used to monitor the measured NP size with changing laser fluence. Using the developed LA-NP sizing protocol, which is discussed in the paper, it was found that a fluence of >1 J cm^{-2} has the potential to degrade NPs, which the authors suggest is suitable for biological samples, where the fluence is generally required to be <1 J cm^{-2} but problems may occur for matrices, such as sediments, which typically require higher fluence values. One possible problem with FFF separations is the loss of particles in the fractionation devices. A combination of ICP-MS and LA-ICP-MS was used by Kriegel *et al.* to investigate this for hollow fibre flow field flow fractionation.[263] Recovery rates for 15 nm Au NPs after this separation and determination using ICP-MS were 50–65% whilst detection of Au deposition on the hollow fibre using LA-ICP-MS indicated a sample loss of about 8%. A method was developed by Holbrook *et al.* for the direct analysis of multi-elemental particles in sediment samples using LA-spICP-ToF-MS.[264] The technique was applied to AgAu core–shell particles and also to environmental samples obtained *via* cloud point extraction procedures of a road runoff water. Using the results obtained from the analysis of the AuAg NPs, statistics were then used to test the usability of the LA-spICP-ToF-MS approach on unextracted sediment. Three main groups of signals were identified: overly abundant signals which cannot be used for single-particle analysis at the chosen measurement parameters; highly abundant signals that when compared with two previously cited methods produced comparable results for elemental ratios and single-particle fingerprinting. Finally, low abundant; well-defined elements such as the platinum group elements (PGEs); were ideally suited for measurement from unextracted sediment.

4.9.6 Platinum. Two papers by the same research group in Spain reported their *investigations into the measurement of Pt NPs in clinical samples*. The first of these reports, by Fernandez-Trujillo *et al.*, was on the detection of Pt NPs in urine and serum samples.[265] As no Pt NPs were detected in the samples they were subsequently spiked with 50 and 70 nm Pt NPs at concentrations of around 100 μg L^{-1}. Two reagents, TMAH and/or Triton™ X-100, were also evaluated as a suitable extraction and stabilisation reagent, and all samples underwent ultrasound assisted extraction to disperse the added NPs which were then diluted to give Pt NP concentrations of around 300 ng L^{-1}. The optimal sample treatment was shown to be the addition of TMAH to a final concentration of 1% with no further sample preparation required. Particle sizes were, in all cases, in accordance with values determined using TEM or SEM. Particle concentration recoveries ranged between 92 and 101% whilst the precision obtained for particle number and mass concentrations was <1% RSD. The LOD values for size and concentration were 21.6 nm and 1.9×10^5 particles per L, respectively. The influence of matrix on the determination of Pt NP sizes and number- and mass-based concentrations was evaluated. Studies suggested that the Pt NPs were stable in male urine for 24 hours but this was not the case for the particle number concentrations of 50 nm Pt NPs in female urine samples. The second paper by Fernandez-Trujillo *et al.* reported on the speciation of Pt NPs in different cell culture media with analysis using HPLC-ICP-TQ-

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MS.[266] In this work 5 and 30 nm Pt NPs and ionic Pt species were added to different forms of Dulbecco's Modified Eagle Medium (DMEM), DMEM-high glucose, DMEM-F12, DMEM 31053-028, and Roswell Park Memorial Institute, RPMI-1640 (supplemented with 10% fetal bovine serum (FBS) and antibiotics) at several incubation times (24, 48, and 96 h at 37 °C). Separations were performed using a C18 column with a mobile phase of phosphate buffered saline, 2 mmol L^{-1} at pH 7.3, and 10 mmol L^{-1} SDS flowing at 0.5 mL min^{-1} for 8 minutes. The work showed that the NPs partially dissolved in all media, leading to the release of ionic species. An increase in the hydrodynamic volume of the Pt NPs was also observed, probably related to a protein corona forming on the NPs. The magnitude of both processes was dependent on the cell culture media type and incubation time duration. Dynamic light scattering and SEM also showed the formation of soft and hard protein coronas.

A continuous flow is the usual method for solution sample introduction for NP analysis with ICP-MS but there is a growing use of *microdroplet generation to introduce discrete volumes to the plasma* as it eliminates the need to determine sample transport efficiency. The combination of a microdroplet generator (MDG) and an ICP-TOF-MS instrument was used for the size determination of Pt NPs with on-line isotope dilution analysis.[267] For the microdroplet generation, the He carrier flow rate used was 0.5 L min^{-1} with a droplet generation frequency of 50 Hz. For IDMS the ^{194}Pt : ^{195}Pt isotope ratio was used with mass bias monitored *via* the ^{182}W : ^{183}W isotope ratio. The ID-MDG-sNP-ICP-TOF-MS approach was used for the size determination of three different sizes of Pt NPs (50 nm, 63 nm, 70 nm diameter) and the results compared with those obtained using sNP-ICP-TOF-MS and TEM. After optimisation of the system such that the measured ^{194}Pt : ^{195}Pt isotope ratio was approximately 6 the NP sizes measured with the two approaches were 42 nm ± 1 nm and 62 nm ± 1 nm for the nominally 50 and 70 nm NPs with the difference being ascribed to particle degradation during storage. Subsequently, a well characterised Pt NP of 63 nm diameter was analysed with the results obtained being in statistical agreement at 64 ± 1 nm. It was also found that a matrix of up to 100 mg L^{-1} sodium chloride did not affect the accuracy or precision of the particle size determinations.

The use of *laser ablation of solids in a liquid (LASIL)* has been applied to investigate the Pt NP decoration of $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF) thin films prepared on one-side of polished yttria stabilised zirconia single crystals.[268] The LASIL, in combination with ICP-MS detection, allowed a spatially resolved analysis of the sample composition. After optimisation of the LA parameters and the carrier solution, which is discussed in detail along with other aspects of the work presented in the paper, a depth resolution of 30 nm was achieved. This allowed a clear separation of the Pt signals from the surface decoration and the underlying current collector. The amount of platinum on the surface was determined using calibration with a matrix matched standard and validated using ICP-MS after an aqua regia-based extraction procedure. The imaging capabilities were then employed to assess the homogeneity of the Pt-decoration, and significant variations of this factor were observed within the investigated area.

4.9.7 Silver.
The most commonly studied NPs using ICP-MS are probably Ag due to their widespread use as an antibacterial agent and two papers *report their detection in biological systems*. The first of these, by Zanoni *et al.*, used porcine buccal mucosa, mounted on vertical Franz diffusion cells, as an *in vitro* model to investigate the penetration of Ag NPs (19 ± 5 nm Ø).[269] The permeability experiments were performed using a physiologically-relevant saline solution in the receiver chamber and known concentrations of Ag NPs or ions in the donor chamber, all under physiological pH conditions. The passage of Ag ions and NPs through the mucosa was evaluated using sNP-ICP-MS and a flux of 4.1 ± 1.7 ng cm^{-2} min^{-1} with a lag time of 159 ± 17 min was observed through mucosa exposed to silver NPs. The authors suggested that the NPs travel through the porcine mucosa and release Ag^+ in the receptor fluid, which agreed with the predictions of a computational model. The authors also suggested that, due to physiological similarity between human and pig membranes, it is reasonable to assume that a trans-oral mucosa penetration could occur in humans upon contact with silver NPs. The second study in this area, by Kohl *et al.*, investigated the translocation of Ag and Au NPs across the gastrointestinal barrier along with related biological effects using an *in vitro* 3D-triple co-culture cell model.[261] Analysis using sNP-ICP-MS of the samples resulting from incubations with Caco-2 in high glucose DMEM revealed a time-dependent increase of translocated NPs independent of their size, shape, surface charge and stability in cell culture medium. This quantitative data provided the experimental basis for the successful mathematical description of the NP transport kinetics using a non-linear mixed effects modelling approach. *In vitro* assays and quantitative PCR showed no significant influence of the applied NPs on both cell viability and generation of reactive oxygen species. The use of TEM indicated that the cell barrier remained intact during the translocation study.

Some form of *extraction and or preconcentration method is usually needed for the assessment of the NP concentration in natural waters*, which is generally low. This is due, in part, to the high volume of the receiving body but also due to particle agglomeration and removal processes through adsorption onto natural particles. Filtration, with the expectation that NPs will pass through 0.45 μm membranes is often used as a clean-up step. The effect of six different filter membrane materials (cellulose acetate, nylon, polyethersulfone (PES), polypropylene, PTFE and polyvinylidene difluoride) on the stability of Ag and CeO_2 NPs in spiked rain and river waters was evaluated by Jreije *et al.*[255] The filtrates were analysed using sNP-ICP-MS and the residues on the filter membranes using ICP-MS after a HNO_3 and H_2O_2 extraction. For Ag NPs, the highest recoveries were observed for polypropylene membranes, with 55% and 75% recoveries being found for rain and river waters, respectively. For CeO_2 NPs, recoveries for the polypropylene membrane were 60% in rainwater and 75% in river water. Membrane preconditioning with mono-, di- or tri-valent metal salts or a commercially available 21 element solution increased NP recoveries to over 80%. The authors concluded that NP retention on the filters was attributable to particle aggregation and

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that a mass balance approach should be adopted when quantifying NPs in natural water samples. An alternative approach to filtration is the use of magnetic solid phase extraction of Ag based NPs and this was reported by Urstoeger et al.[270] Ten different types of Ag based NPs were synthesised for this work, AgCl, Ag_2S and eight with an Ag core but with different organic coatings and these were spiked at concentrations of between 5 and 200 ng L^{-1} into high purity water adjusted to a pH of 6.2 with an acetic acid : sodium acetate buffer. Iron oxide magnetic particles were then added to give concentrations ranging from 1 to 500 mg L^{-1} and the mixture sonicated for 60 s, and shaken for 1 hour. The iron oxide magnetic particles were then attracted to a magnet external to the solution container, removed from solution and the collected NPs eluted with EDTA. Analysis was achieved using sNP-ICP-MS. River water and water with added natural organic matter were also spiked and extracted in the same manner. Extraction efficiencies ranged from 80 to 100% and environmentally relevant inorganic ions and TiO_2 particles exhibited no major effect on the extraction efficiency. This was not the case for samples with natural organic matter added to above 1 mg L^{-1} which reduced the extraction efficiency by 50%. This effect was overcome by adding Ca^{2+} (at 10 mmol L^{-1}) or increasing the iron oxide magnetic particle concentration to 500 mg L^{-1}. The organic matter also eliminated the co-extraction of Ag^+, which would reduce the baseline in the sNP-ICP-MS particleogram thus improving the LOD. Cloud point extraction (CPE) in conjunction with sNP-ICP-MS has been used by Wei et al. to detect Ag_2S NPs in water samples.[271] The CPE procedure involved pH adjustment to 3, the addition of bis(p-sulfonatophenyl)phenylphosphane dehydrate dipotassium salt, shaking, addition of $Na_2S_2O_3$ and Triton X-114, incubation at 60 °C, phase separation by centrifugation, collection of the organic phase which was diluted with glycerol and subjected to ultrasound assisted extraction prior to analysis. The extraction efficiency, based on particle number concentration, ranged between 76 to 106% in environmental waters. However, the particle size increased from 77 to 94–97 nm. Nanomaterials are being increasingly used in the oil and gas industry and two methods for extracting Ag NPs spiked into these materials, using a procedure similar to that used in the previous paper were compared by Gajec et al.[272] After optimisation, which was fully described in the paper the authors concluded that for water samples centrifugation at 2800 rpm for 12 minutes, gave the best recoveries in terms of particle size and particle concentration whilst for solid wastes the CPE procedure, which is similar to that used in ref. 271 was most appropriate for extracting AgNPs spiked into solid waste material. Particle detection was by sNP-ICP-MS.

A report on *the use of FFF-ICP-MS for the detection and quantification of Ag NPs* was published this year by Taboada-Lopez et al. who used asymmetric flow field-flow fractionation (AF4) coupled with UV-Vis and ICP-MS to quantify Ag NPs in bivalve molluscs.[273] The NPs were extracted from locally purchased clams, oysters and variegated scallops using an enzymatic (pancreatin and lipase) hydrolysis procedure The results obtained showed that the Ag NPs were detected at the same elution time as proteins (UV detection) and the amount of Ag

NPs detected ranged between 4% (oyster) and 56% (clam) of the total Ag content as determined by microwave assisted extraction followed by ICP-MS detection. The presence of Ag NPs in the enzymatic extracts was confirmed using SEM.

One study reported *the use of laser ablation for detecting the signals from Ag NPs*. Firstly, Spanu et al. used LA-ICP-MS for the quantitative determination of the spatial distribution of Ag NPs supported on planar substrates.[274] Calibration was carried out on a sacrificial sample. The LA-ICP-MS data from this sample were used to define three-dimensional functions describing the spatial distribution of NPs and the volume integrals were calibrated to obtain the mass distribution of Ag NPs, in conjunction with the total Ag mass determined using ICP-MS after an HNO_3 based extraction procedure. An aqueous Ag standard was used to monitor laser fluence and instrumental drift. The method was then applied to a model sample consisting of a low-density polyethylene disk decorated with Ag NPs, and a high spatial resolution over cm^2-sized samples was demonstrated.

4.9.8 Titanium. Due to use of *TiO_2 as an additive in foods and consumer products, and therefore possible implications on human health and the environmental impact*, there remains interest in the detection of TiO_2 NPs in various sample types. An assessment of the bioaccessibility of TiO_2 NPs and Ag NPs from molluscs has recently been undertaken by Taboada-Lopez et al.[275] Initially, the presence of NPs in the molluscs was assessed using sNP-ICP-MS, after an enzymatic extraction with pancreatin and lipase. Subsequently, the wet molluscs were homogenised and suspended in an HCl/pepsin mixture at pH 2, to represent the gastric phase, followed by adjustment of the solution pH to 7 and the addition of pancreatin, bile salts and sodium dihydrogen carbonate, to represent the intestinal phase, with each phase shaken at 37 °C for two hours. The bioaccessible fraction ranged from 3 to 89% for TiO_2 NPs and from 7 to 51% for Ag NPs when compared with the total Ti and Ag content, determined after a microwave assisted extraction with HNO_3 and H_2O_2 and ICP-MS. The mollusc samples were also incubated in the presence of Caco-2 cells, as a model for the human epithelium and NP transport into these cells ranged between 17 and 82% and from 2.1 to 22% for TiO_2 and Ag NPs, respectively. Triple-quadrupole and high-resolution ICP-MS, operated in sNP mode, have been used to characterise TiO_2 in chewing gum, chocolate, cake decorations and a spiked milk sample after extraction into water with ultrasound assisted extraction.[276] The obtained particle size distributions from both instrument types were similar in terms of particle shape and median (123 to 209 nm) and mean (146 to 223 nm) diameters. The results were also in agreement with those from two other techniques, SEM and AF4-MALS-ICP-MS. The use of a milk sample also showed that both ICP-MS instruments were similarly efficient in resolving Ca based interferences on Ti. For the TiO_2 powder and two food products, recoveries of TiO_2 were greater than 60%. The use of AF4-MALS-ICP-MS for the size characterisation of TiO_2 NPs in coffee creamer and instant drink powders was presented by Li et al.[277] The NPs were extracted from the samples using a procedure involving sodium dodecyl sulfate (SDS), hexane, ultrasound assisted extraction and shaking. The AF4 size calibration was achieved using

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polystyrene nanospheres and verified using 100 nm TiO$_2$ NPs. The TiO$_2$ particle sizes detected ranged from 24–544 nm for coffee creamer and 27.7–574.3 nm for instant drink powders, with detection recoveries of 75% and 92%, respectively. A study by Vidmar *et al.* reported the levels of TiO$_2$ NPs in waters and sediments at selected sampling sites along the Sava River, a tributary of the Danube, using sNP-TQ-ICP-MS.[278] Water samples were analysed after sonication and dilution with high purity water whilst NPs in the sediment samples were extracted with 0.1 molar NaCl, sonication and centrifugation followed by dilution. The highest particle mass and particle number concentrations of TiO$_2$ NPs in river waters were from sampling locations impacted by urban, agricultural, and/or industrial activities, suggesting that these NPs are likely of anthropogenic origin whilst the sediment samples all contained a broadly similar amount of the NPs. The Ti : Al elemental concentration ratios of NPs in water and sediments at these sites were higher than the natural background ratios, again suggesting an anthropogenic origin.

It is becoming more common to use both *single cell and single particle ICP-MS to track the evolution and fate of NPs* in biological systems. One example of this is the work of Cosmi *et al.* who investigated the bio-tribocorrosion of Ti metal and alloys used for dental implants in different biological media, including artificial saliva and in the presence of the mucosal bacterium *Streptococcus mutans*.[279] The results revealed lower aggregation when suspending standard TiO$_2$ nanoparticles at neutral pH in artificial saliva and no additional effect on the agglomeration or particle size due to the presence of bacteria in the media. Subsequently, different Ti-based dental implants made of an alloy of Ti, Al and V were incubated in the presence of artificial saliva for 48 hours to evaluate the *in vitro* release of metallic species. The presence of Ti-, Al- and V-containing nanoparticles was observed using sNP-ICP-MS with confirmation by TEM. The addition of mucosal bacteria to the media caused a significant decrease in the production of NPs due to the formation of a biofilm on the surface of the incubated implants. The incubation of the implants released nanoparticles with osteoblast cells (Saos-2 cell culture) and further analysis by single-cell-ICP-MS revealed a significant uptake of the nanostructures by the bone cells with as yet unknown effects.

The *detection of Ti by ICP-MS can be hampered by the presence of Ca and P based polyatomic interferences*. One approach to negate these interferences is to react the Ti ions produced in the plasma with NH$_3$ gas in a collision/reaction cell to produce Ti/NH$_3$ clusters, shifting the *m/z* of the detected ion away from that of the interfering ions. The development of this approach for detection of TiO$_2$ NPs was described in detail by Suarez-Oubina *et al.*[280] In this work the effects of parameters such as NH$_3$ flow rate and dwell time on the peak width, the NP transient signal in sNP-ICP-MS were comprehensively studied along with the influence of the NP size. After optimisation, which is discussed in full in the paper, the developed method realised an LOD$_{size}$ of 23 nm, and LOD$_{number\ concentration}$ of 4.5×10^5 particles per L measured in mass shift mode at *m/z* 131. The method was also applied to the detection of Cu and ZnO NPs, for which the

LOD$_{size}$ was 7 and 13 nm and the LOD$_{number\ concentration}$ was 3.5×10^4 and 8.4×10^4 particles per L, respectively when measured at *m/z* of 63 for Cu and 64 for Zn.

4.9.9 Other elements. The *quantitative bioimaging of the uptake of quantum dots (QDs) in single cells* by LA-ICP-MS was described by Pisonero *et al.*[281] This task requires a high sensitivity and high spatial resolution and method validation is hampered by the lack of matrix-matched reference materials. The paper reports that high spatially resolved quantitative bioimaging of CdSe/ZnS QDs uptake in single HT22 mouse hippocampal neuronal cells and in single HeLa human cervical carcinoma cells was investigated by combining: (a) ns-LA-ICP-SF-MS; and (b) the spatially resolved analysis of dried pL-droplets from a solution with a known concentration of the QDs to obtain a response factor that allows quantification of elemental bioimages. Single cells and dried pL-droplets were also morphologically characterised by Atomic Force Microscopy (AFM) to determine their volume and thickness distribution. After optimisation of the LA operating conditions (*e.g.* spot size and energy per laser pulse) the cells and pL droplets were completely ablated at high spatial resolution and constant operating conditions for the analysis of the single cells and calibration samples were used to reduce potential fractionation effects related to mass load effects in the ICP. After incubation in the presence of a QD suspension in a standard cell culture medium the uptake of CdSe/ZnS QDs by the HT22 or HeLa cells was estimated to be between of 3.5×10^4 and 48×10^4. Mono-elemental bioimaging at subcellular resolution appeared to show a higher number concentration of the CdSe/ZnS QDs in the cytosol around the cell nucleus.

The development of sNP-ICP-MS has led to other applications, such as single cell and *single virus ICP-MS*. This was undertaken for viral DNA, with sample treatment involving a digital loop-mediated isothermal amplification (LAMP) assay, [Ru(bpy)$_2$dppz]$^{2+}$ as a label and Eu labelled polystyrene spheres as an internal standard.[282] The sample and LAMP reagents were mixed and encapsulated in agarose droplets, generated by in-house fabricated centrifugal droplet generators, and only agarose particles, containing virus DNA were labelled with Ru compound. The copy number of virus DNA was estimated from the ^{101}Ru : ^{153}Eu ratio detected using SV-ICP-MS. The lowest quantification achieved was 25 copy per μL virus DNA in one analysis without the need for a calibration curve. The theoretical requirements needed to accomplish direct SV-ICP-MS, with C, N, P and S as the analyte elements has been comprehensively described by Degueldre.[283] A sector field instrument operating at a resolution of 4000 or above would be needed to allow the analyte ions to be resolved from the numerous polyatomic interferences present for these elements. Of these, this writer is not aware of any papers describing the measurement of N$^+$ ions by ICP-MS and thus the measurements may be practically unfeasible due to the high background levels of N that may be encountered. It is also suggested that MC-ICP-MS should be used, to allow simultaneous signal detection for each virus particle that enters the plasma. This would require a centre detector mass of 20 and a collector mass range of 60% of this value, which is not available on any current instrument. It

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would be possible to operate the instrument in detector switching mode, whereby C and N signals were measured followed by those of P and S, but it is doubtful that current instrumentation could achieve this at a rate rapid enough to allow the two sets of signals to be determined for one virus particle. It would be interesting to see a report on an attempt to turn the theoretical approach into a practical reality.

The multi-element capability of LA-sNP-ICP-TOF-MS was used by Holbrook *et al.* to analyse environmentally relevant road runoff samples.[284] Using the data realised different particle classes were proposed for multi-elemental particles and three major classes of particles were identified namely based on the literature, those containing rare earth elements, which include

potential anthropogenic and geogenic sources, brake and tyre wear particles, and platinum group elements from catalytic converters. All the samples analysed were compared based on these arbitrary classes, and discernible differences were observed for the different locations sampled. A machine learning model was used to automate the dataset labelling and classification, which allowed a rapid and efficient method for inter/intra sample comparison in terms of multielement particle elemental correlations.

Table 2 shows other applications of nanomaterial characterisation and/or detection presented in the literature during the time period covered by this review.

Table 2 Applications of nanomaterial characterisation and/or detection

Analyte	Technique	Comments	Reference
Ag and Au NPs	sNP-ICP-MS	Development of an alkaline extraction method (2% TMAH) for NPs from spiked chicken meat. Extraction efficiency was >94% for all spiked tissue samples	285
Ag NP modified SnO$_2$	XRD, XRF, Raman spectroscopy, FTIR, XPS, TGA	Characterisation of synthesised organometallic materials for use as a H$_2$S sensor	286
Ag NPs Ag$^+$	GFAAS	Chemometric approach (SIMCA and PLSR) applied to Ag ions and NPs in consumer products. For SIMCA, correct identification rate of the Ag forms was only in the range 25–60%, depending on the composition of the tested samples. This indicates limitations of this approach	85
Ag, Au, Cd, Mg TiO$_2$ NPs	sNP-ICP-MS	Analysis of wastewater and sludge samples for metallic or metal-containing NPs. Centrifugation used to separate NPs from wastewater sludge, with high recoveries (>84%) for Au and Ag NPs	287
Ag NPs	sNP-ICP-MS	Determination of Ag NPs in cosmetics. 0.1% (v/v) methanol solution was selected as the optimal extraction agent. Total Ag content in samples ranged from 0.45 to 20.0 μg g^{-1} and the estimated contribution of AgNP to the total Ag content ranged from 0.02 to 1.9%	84
Ag NPs	ICP-MS, SEM, EDX, TEM, FT-IR	Synthesis, characterization, and evaluation of antibacterial activity of the NPs	288
Ag NPs	sNP-ICP-MS	Determination of the NPs in aqueous dispersions. The reliable determination of the sizes of silver nanoparticles of 60 and 100 nm at the duration of an analysis of 60 and 180 s, respectively, was achieved at a concentration of 2–4 ng mL^{-1}	289
Ag, Au, Ti and Zn NPs	sNP-ICP-MS	Simple standardized protocol for separating and analysing metal-containing NPs in sediment samples was developed. A settling time of 6 h was recommended for the separation. The optimal sediment to water ratio, ultrasonication power, time, and temperature are 0.4 mg mL^{-1}, 285 W, 20 min, and 15–25 °C, respectively	290
Ag NPs	MC-ICP-MS	Size and isotopic ratio measurements of individual NPs by MC-ICP-MS. Signal intensities obtained from Ag NPs (40, 60, 80, 100, and 200 nm) exhibited a good linearity with the sizes of the Ag NPs. The variations of the measured $^{109}Ag/^{107}Ag$ ratio for the particles of each size in the isotopic ratio measurements were about: 12% for 40 nm, 4.9% for 60 nm, 1.9% for 80 nm, 1.2% for 100 nm, and 0.26% for 200 nm	291
Au NPs	SIMS	Use of Au-conjugated nanobodies for targeted imaging of proteins enabling the possibility of correlating the investigation of cellular isotopic turnover to the positions of specific proteins and organelles	292
Au–Mn–Zn NPs	XRD, XRF, UV-vis, TEM	Preparation and characterisation of functionalised NPs for use in magnetic resonance imaging	293

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Table 2 (Contd.)

Analyte	Technique	Comments	Reference
Au NPs	LIBS	Study of signal enhancement by NPs with proteins. Although the investigated NP-protein systems are simple cases in biological applications, this work demonstrated a different beyond elemental analysis and it opens the way for sensing the nanoparticle protein corona	294
Au NPs	GFAAS	Modelling of experimental results for NP sizing and quantification. Analyte concentration was predictable over the range 5–45 ppb of experimental datapoints. Limits are observed for very small particles (dP < 40 nm) due to the nano effect and for changing heating rates (100–750 K s^{-1}) due to model simplicity	295
Au NPs	SAXS, TEM	Characterisation of synthesised NPs. The SAXS curve shows the presence of a large number of small aggregates with a fractal structure stabilized by strong long-range repulsive interactions	296
AuCu$_2$O coreshell NPs	EDX, XPS, XRD, FT-IR, ICP-MS	Study of the optimization of a Cu$_2$O shell on a gold nanoparticle core for electrocatalytic nitrite detection. Nanostructures was investigated	297
Au NPs	XPS	Study of the surface chemistry of Au NPs produced by laser ablation in waters. The Au photoelectron spectra with a depth profiling investigation were used to evaluate the degree of nanoparticle surface oxidation	298
Au NPs	XRF	Study on the impact of internal standard heterogeneity on Au quantification by XRF. Close to 100% recovery was obtained, regardless of the elemental spatial distribution in the samples. This provides insights into the quantification potential for AuNPs inside tumours that are histologically processed into thin tissue slices	299
Au nanostars	UV-vis, TEM, EDX, FT-IR, XRD	The synthesis of Au nanostars with collagen by a one-step reduction method. The investigation results reveal that AuNS-collagen remains stable in NaCl 2.0% (w/v), from mildly acidic to neutral pH (4–7), below the temperature of 40 degrees C, and within 21 days post-synthesis	300
Au and Fe$_x$O$_y$ NPs	ICP-MS	The bioassay of a carcinoembryonic antigen. The Fe isotope in magnetic particles and Au isotope in report probes were simultaneously and sensitively detected by the elemental mass spectrometry. ^{197}Au/^{57}Fe isotopic ratios and CEA concentrations showed good linearity in the range of 0.6–300 ng mL^{-1}, with a detection limit of 0.09 ng mL^{-1}	301
Au NPs	sNP-ICP-MS	Investigation into improving the LOD$_{size}$. Two approaches were employed to improve the signal-to-noise ratio of ion signals from small nanoparticles. One was enhancement of the instrumental sensitivity using a desolvating system. The other was separation of the ion signals from background signals through a deconvolution method. A combination of these approaches enabled measurement of 5 nm gold nanoparticles. The calculated LOD$_{size}$ was 3.8 nm	302
CeO$_2$Ti$_3$O$_7$ NPs	XPS, FTIR, TEM	Characterisation of the NPs for use in F removal from waters. XPS data helped show that ion exchange between the surface hydroxyl groups and the fluoride ions in water played a vital role during the defluoridation	303
CeO$_2$ NPs	XANES	Investigation of the dissolution and retention of the NPs during soil aging processes. The XANES showed that most of Ce species were present as Ce(IV) (94.0–97.8%) in all soils after a long-term (30 days) aging process	304
Co and Ni ferrite NPs	XRD, XRF, XPS, TEM, FT-IR	Synthesis, characterization and in vitro cytotoxicity study of Co and Ni ferrite NPs. The average particle size was 25–35 nm and they were haemo-compatible	305
CoS, CuS, NiS NPs	sNP-ICP-MS	Study of the dissolution and aggregation of metal sulfide NPs. Dissolution and disaggregation of NiS was fastest under strongly oxidizing conditions (with H$_2$O$_2$) and were slower under near-neutral conditions (HEPES buffer/H$_2$O) or in the presence of dilute acid (1 mM nitric)	306

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Table 2 (*Contd.*)

Analyte	Technique	Comments	Reference
Co–Zn ferrite NPs	XRD, FTIR, SEM, XRF, ICP-OES, XPS	Assessment of the phase purity, composition, surface area, and oxidation states of the NPs. Materials analysed were $Co_xZn_{1-x}Fe_2O_4$ (where $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$)	307
Cu NPs	LIBS	Analysis of Cu nanoaerosols using a time-resolved LIBS programme. Linear intensity *versus* mass correlation and similar signal stability which is linked to the seeding effect caused by smaller particles yielding hotter, but shorter plasmas	308
CuO, ZnO NPs	XRF	Characterisation of the NPs for use with a plasticiser for X-ray detector applications. The mean sizes of nanoparticles were 10 ± 4 nm and 8 ± 3 nm, for CuO and ZnO, respectively	309
Fe NPs	ICP-MS, XRD, XAS, Mossbauer spectroscopy	Preparation and characterisation of sodium ferric gluconate as a nanodrug. The analysis revealed ferric-iron-oxide structures. Measurements focused on the carbohydrate shell comprised of the gluconate ligands	310
Fe_2O_3 NPs	ICP-MS	Study of serum protein-mediated transformations of magnetic nanoparticles. The aim was to monitor the formation of the protein corona and alterations in the concentrations of relevant metals due to binding of specific metalloproteins	311
Magnetite NPs	sNP-ICP-MS	Determination the mass distribution and number concentrations of environmental NPs and colloids. Homo-aggregation behaviour of synthetic microplastic and magnetite (abiogenic and biogenic) nanoparticles was measured. Sequential elemental analysis evaluated the mobility of a toxic arsenic metalloid and its inferred association with colloidal Fe(III) (oxyhydr)oxides	312
Eu-polymer NPs	sNP-ICP-MS	Study on the use of the NPs as nanoprobe for the determination of Cu^{II}. The fluorescence readout yielded a facile and rapid detection method but with a limited linear range of 2 μM to 50 μM. The LOD was 0.29 μM. The sp-ICPMS readout provided a far more sensitive analysis method with a linear range from 1 pM to 10 μM and a LOD of 0.42 pM	313
In_2O_3 NPs	XRD, XPS, SEM, TEM	Characterisation of the synthesised NPs	314
$LiNbO_3$Au coreshell NPs	XPS, ICP-OES	Study of the characteristics of the synthesised NPs. Here $LiNbO_3$ core nanoparticles of 45 nm were coated with various densities of gold nano-seeds (AuSeeds). Both bear negative surface charge, so a positively-charged polymer was first coated onto the $LiNbO_3$. The number of polymer chains per $LiNbO_3$ was evaluated using XPS. Then, the surface coverage percentage of AuSeeds onto $LiNbO_3$ was estimated to be a maximum of 30% using ICP-AES	315
$Mg_{1-x}Ni_xFe_2O_4$ nanocrystals	ICP-MS, TEM, XRD, Mossbauer spectroscopy	Study on the effects of Ni_2^+ doping on the lattice and magnetic properties of the nanocrystals. Highly crystalline nanoparticles with average size of 20–30 nm and stoichiometric chemical compositions are indicated by results from TEM and ICP-MS, respectively	316
Nd	sNP-ICP-MS	Investigation into Nd speciation in the presence of fulvic acid. With single particle ICP-MS analysis, we found 0.25–2.36% of Nd was in the form of colloids when the total Nd concentrations varied from 8.5×10^{-9} to 4.7×10^{-7} M, with the average particle sizes in the range of 26.5–39.2 nm. The presence of fulvic acids decreased the number of Nd colloids significantly but increased the average particle size	317
Pd, Pd–Sn NPs	ICP-OES, XPS, TEM/EDX	Preparation and investigation of the NPs on gamma-Al_2O_3. Composition determined using ICP-OES whereas XPS was used to determine the composition and electronic properties of Pd and Sn on the gamma-Al_2O_3 support	318
SiO_2 NPs	sNP-ICP-MS, TEM	Characterisation of spherical porous-hollow SiO_2 NPs. Single particle (ICP-MS) was applied to assess the mono-dispersity of the hollow particles prepared using different reaction parameters. Both TEM and spICP-MS measurements revealed that fused particles were also formed under suboptimal reaction parameters, causing the broadening of the size distribution, which can be preceded by using appropriate concentrations of the starting materials	319

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Table 2 (*Contd.*)

Analyte	Technique	Comments	Reference
Si_3N_4, SiO_2 NPs	Grazing incidence XRF	Characterisation of NPs using the X-ray standing wave field. Huge amounts of computing time were avoided by employing Machine learning to ensure timely results were obtained	320
SiO_2 NPs	ICP-OES, ICP-MS, SEM	Study of natural mineral nanoparticles as potential reference nanomaterials. Major (Al, Na, K, Ca, Fe), trace (Ti, Co, Cu, Zn, Tl, Pb, Bi, *etc.*) and REE were determined in the suspensions of kaolinite, montmorillonite and muscovite nanoparticles	321
SiO_2	ICP-MS	Detection of SiO_2 NPs for semiconductor applications. Triple quad instrument used with detection of Si being shifted from $^{28}Si^+$ to SiO^+ at *m/z* 44 through the addition of oxygen to reaction cell	322
SiO_2 coated MoO_2, Rh and Ru NPs	XRF	Study using optical and X-ray fluorescent NPs for bioimaging of cells. The metallic nanoparticles were given a silica (SiO_2) shell, using ethanolamine as the catalyst	323
TiO_2 NPs	Modified SIMS	Used to demonstrate the capabilities of an in-house modified SIMS instrument. The new instrument is based on focused ion beam microscopy technology using a gas field ion source as a key enabler and combining it with specifically developed secondary ion mass spectrometry and scanning transmission ion microscopy technology	324
TiO_2	TOF-SIMS	Study of the sorption of fulvic acids onto the NPs extracted from commercial sunscreens. Clustering analysis confirmed the ability of TOF-SIMS to detect the sorption of fulvic acids. A unique sorption pattern was recognized for each TiO_2 subset of sunscreen, which implied different fractionation of fulvic acids based on the initial specifications of nanoparticles, *e.g.*, size, coating, *etc.* Random forest was used to extract the most important fragments for predicting the presence of fulvic acids on the surface of TiO_2 subset of sunscreen	325
TiO_2 NPs	sNP-ICP-MS, TEM	Measurement of the NPs in sunscreens. Asymmetrical flow field-flow fractionation (AF4) coupled online with multiangle light-scattering (MALS) and dynamic light-scattering (DLS) detectors. And applied to the analysis of two commercial sunscreens, exhibiting promising separation and detection efficiency. Single particle ICP-MS yielded data on particle size distribution	326
Yb_2O_3 NPs	ICP-OES	Used to investigate the effects of plasma temperature on sNP-ICP-OES. Correlation plot of the intensities of individual Yb_2O_3 particles at observation positions of 8.5 and 19.5 mm above the load coil shows extensive scattering. Computer simulation shows that the amount of heat required to bring the Yb_2O_3 particles to boiling is substantial and the duration of the heat transfer process increases with particle mass. Therefore, large particles have a relatively small degree of vaporization at low observation positions where SP-ICP-OES intensity is not proportional to particle mass. The calibration curve is therefore concave at lower measurement positions, meaning it is more prone to error	327
ZnO NPs	XRD, UV-vis, SEM, TEM, LIBS	Study on the effect of reaction temperature on the properties of tunable ZnO NPs. The intensity of the characteristic Zn peak of LIBS spectrum decreased because of the increase of their particle size as the reaction temperature increased. The dielectric behaviour of the prepared samples was studied revealing the dependence on their particle size	328
ZnO nanorods	Nano-XRF microscopy	Study on the transformation of the nanorods after wastewater and sludge treatment processes. A complete transformation of isolated ZnO nanorods into ZnS occurs after only 1 h in influent water, but larger aggregates of the ZnO nanorods transform only partially, with small contributions of ZnS and Zn-phosphate ($Zn_3(PO_4)_2$) species, after 3 hours	329

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Table 2 (*Contd.*)

Analyte	Technique	Comments	Reference
$ZnFe_2O_4$, $CoFe_2O_4$, $Zn_{0.5}Co_{0.5}Fe_2O_4$ NPs	FT-IR, XRF, XRD, TEM	Synthesis, electronic and crystallographic characterisation, and evaluation of antibacterial activity of the NPs	330
ZnO NPs	sNP-ICP-MS	Study on the release of NPs from four commercial facemasks after washing in deionized water and 4% detergent for five washing cycles. Acid dissolution and ICP-MS analysis indicated total Zn concentration of 60–100 $\mu g\ g^{-1}$. The Zn released from mask samples was approximately 0.25–1.17% in the first washing cycle in deionized water, but around 1.97–3.12% in 4% detergent. Particles were 100–200 nm in diameter	331
ZnSe quantum dots (QDs)	SAXS, UV-vis, TEM, MP-OES	Study on the correlation of quantum dot absorption with particle size and concentration. A series of ZnSe QDs with diameters ranging from 2 to 6 nm were characterised using SAXS, TEM, UV-vis spectroscopy, and microwave plasma atomic emission spectroscopy. SAXS-based size analysis enabled the practical inclusion of small particles in the evaluation, and elemental analysis with MP-AES elucidated a nonstoichiometric Zn : Se ratio consistent with zinc-terminated spherical ZnSe QDs	332
ZnO NPs	SEM, ICP-MS, FT-IR, XRD, AFM	*In situ* synthesis of the NPs on cotton using a pomegranate peel extract. Four methods compared	333

5   Forensic analyses

It is important when analysing forensic samples that they remain as undamaged as possible and that they do not change their nature during analysis. Leaving them in exactly the same state as before the analysis will enable future, improved methods to be used retrospectively. This is obviously not possible if the sample has been destroyed. The use of non-destructive (X-ray based) or minimally destructive (laser-based, *e.g.* LIBS, LA-ICP-MS) techniques is therefore far more common than acid dissolution followed by nebulization into ICP-MS or OES instruments. The use of chemometric packages on the analytical data to aid classification of materials is a very popular area of research.

5.1   Glass analysis

The forensic analysis of glass has proved to be an extremely active area of research during this review period. As with all types of analysis, the use of certified reference materials and/or inter-laboratory studies to evaluate the accuracy is of prime importance. A paper reported by Lambert *et al.* described the results obtained from an *inter-laboratory study to evaluate the accuracy of analysis and interpretation of glass evidence*.[334] The study involved LA-ICP-MS analysis using the standard method ASTM E2927-16e1, where a new calibration material entitled CFGS2 was sent to 10 laboratories. The laboratories were given instructions to follow the ASTM E2927 protocol and to use the reference materials NIST 612, FGS2 or CFGS2 as calibrants. Also sent was the full set of CFGS standards (CFGS1–CFGS3), so that they could be used as test samples (FGS2 was the calibrant under those circumstances). All laboratories also used

a calibration verification standard, which was either NIST 1831 or NIST 612. The results of the comparison were treated in two ways: the match criterion specified in ASTM 2927 and the likelihood ratio calculation. Both methods were described in the paper. The likelihood ratio method relied on two databases of glass material composition. These were the Florida International University (FIU) vehicle glass database and the Bundes-kriminalamt (BKA) database. As expected, glass fragments originating from the same windowpane were indistinguishable, resulting in high likelihood ratio values, *i.e.* they had a strong association. Glasses originating from different vehicles could be distinguished, *i.e.* the likelihood ratio of them being the same was smaller. Glasses originating from different vehicles but from the same manufacturer, year and model were also found to be chemically similar. The agreement between the laboratories was very good, with an RSD value of better than 5% reported. The conclusion, therefore, was that if different laboratories follow the same protocol, they end up with the same results. Although this is hardly a novel revelation, it is obviously a prerequisite for forensic work.

Another paper, by some of the same authors, reported the development of something described as "a new R-based Shiny graphical user interface" to *calculate likelihood ratios for glass discrimination*.[335] The authors stated how the FIU database was developed, with contributions from LA-ICP-MS as well as solution-based ICP-MS data from the FBI and some input from BKA. The paper explained how the likelihood ratios were calculated using a two-level, multivariate kernel model and calibrated using a Pool Adjacent Violators algorithm. The logarithm of the likelihood ratio was then calculated and compared with the match criterion recommended by the ASTM

E2927-16e1 method. The R shiny app and the FIU database were provided in the ESI for researchers to access. A related paper, by Ramos *et al.*, described the probabilistic two-level modelling of the within-source and between-source variability that is required for the calculation of likelihood ratios.[336] The probabilistic machine learning algorithms used comprised both a variational autoencoder and a warped Gaussian mixture. It was stressed that the model developed had significant advantages over previous models used to calculate likelihood ratios. The main advantage was the significantly improved calibration of the model. The authors did acknowledge that there was also a loss in the discriminating power. A paper by Malmborg and Nordgaard validated a feature-based likelihood ratio method for the SAILR open-source software.[337] The validation of the model was achieved using the performance characteristics of accuracy, discrimination and calibration. The paper described the process in full. Although all of the papers described in this paragraph are not advances in atomic spectrometry, they are advances in the way the data from atomic spectrometry may be used. Consequently, it was thought that they merit inclusion.

A paper by Kaspi *et al.* discussed the use of the combination of *PIXE to obtain analytical data followed by a machine learning algorithm* to support the workflow for glass fragment classification.[338] The algorithm was written in Python and included Box plots, PCA, KNN, cluster analysis and random forest. As with many algorithms of this kind, once built, the model had to be trained by inserting data of known origin. It is then evaluated with samples of known origin to determine whether or not it classifies them correctly before being used to classify unknown samples. The authors used glass fragments donated by the Israeli police's forensic department and comprised glasses from various vehicles, including different manufacturers and years of production. The methodology provided a model that had an accuracy of >80% in classifying glass fragment origins. Although this is clearly not perfect, the authors thought it a good start and theorised that it may be useful for other forensic applications including gun shot residue, flammable liquids and illegal substances.

Particle induced gamma-ray emission (PIGE) and instrumental neutron activation analysis (INAA) was used by Sharma *et al.* to obtain analytical data from 25 car windshield glass samples from six manufacturers.[339] The external (in air) PIGE was used to determine the concentrations of the major analytes Al, Mg, Na and Si whereas the INAA determined 19 analytes including the REE. Both techniques used matrix matched CRMs as validation. Once the analytical data had been obtained, they were input to the statistical packages ternary plots (to obtain preliminary groupings) and then K-mean, PCA and cluster analysis. The statistical tests were very successful, with PCA classifying the samples into six clear groups representing the six different manufacturers.

Discrimination of automotive glass was also undertaken by Merk *et al.* who used *a combination of LIBS and Raman spectroscopy using the same instrument* followed by data analysis using the multivariate technique of PCA.[340] The LIBS part of the instrument utilised a Nd:YAG laser operating at 1064 nm whereas the Raman employed two lasers; one operating at 532 nm and the other at 785 nm. All lasers were focussed onto the same spot so both measurements could be made at the same place simultaneously. A total of 20 positions were used for the analysis with a raster of 5 × 4 using a separation of 300 μm. Once obtained, the data were input to PCA using the singular value decomposition algorithm. The Mahalanobis distance between the sample point groups in space of the principal components was used as the criterion of discrimination. The joint instrument managed excellent discrimination, with 99% of samples being classified correctly. Comparison was made when LIBS and Raman measurements were taken individually, *i.e.* not simultaneously. The discrimination power was similar to the conjoint instrument. However, the Mahalanobis distances observed for the conjoint instrument were larger which, theoretically, should enable greater discrimination power. Comparison was also made with existing methods for glass discrimination, *e.g.* μ-XRF and SEM-EDS. These also managed to discriminate successfully, largely because of the trace elements Ba, Fe, Sr and Ti. The overall conclusion was that this joint instrument offers a convenient, rapid and successful method of glass discrimination.

Another paper, by Palasti *et al.*, employed *LIBS analysis, this time in conjunction with refractive index measurements, to discriminate between four types of glass* (borosilicate, flint, soda-lime and fused silica).[341] In total, 127 samples of glass, of which 95 were soda-lime were analysed. Most of the samples were <1 mm in size. The samples originated from bottles, car side windows, jars, headlights, crystal glasses *etc.* and were an assortment of different colours. Numerous multivariate techniques were used to interrogate the analytical data. These included: linear discriminant analysis (LDA), quadratic discriminant analysis (QDA), PCA, classification tree and random forest. Using only the LIBS data, most of the chemometric tests had some success in discriminating between glasses. However, when the refractive index was also used, the success rate improved by on average 15%, with some cases improving by 40%. Classification tree and random forest were found to be the most consistent and successful of the discrimination methods, with a success rate of between 92 and 99% for the different types of soda-lime glass (float, security, container and patterned). The study is one of the first to concentrate on samples of <1 mm using LIBS and managed to discriminate between even closely related glasses.

Counterfeiting is a steadily increasing problem in modern society. An interesting application by von Wuthenau *et al.* used *LA-ICP-MS to identify counterfeit perfumes by analysing the glass bottles in which they were contained*.[342] Bottles obtained from Germany, India, Poland and Peru were analysed using LA-ICP-MS with NIST 612 being used for calibration and daily tuning. The LA was performed over a linear area to ensure that different depths of sampling did not cause element fractionation. One sample was smashed so that both the inner and outer surface of the glass could be analysed. No difference was found. At first, a suite of 63 analytes were determined. When the data from these were input to the statistical tests of *t*-test, ANOVA and PCA, it was realised that this number could be reduced to 15 (Al, Ba, Ce, Co, Er, La, Li, Mo, Na, Pb, Pr, Rb, Sr, Ti and V) without

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significant loss of discriminating power. Six different production sites over the four countries were identified with a prediction accuracy of 100%. The capability of identifying counterfeit perfumes by analysing the outside of the bottle without the necessity of opening it and leaving no visible evidence of the testing is a nice example of how analytical chemistry can help consumers.

5.2 Polymer analysis

The analysis of skid marks is an almost abandoned branch of forensic science because anti-lock brakes often ensure that there are no skid marks to analyse. However, Lucchi *et al.* have *used LIBS to analyse tyres followed by chemometric analysis of the data (PCA combined with linear discriminant analysis)* to classify tyres.[122] A total of 34 tyre samples (32 individual tyres, one of which was sampled in triplicate) were used for the study. Samples were analysed using the LIBS system operating at a power of 17 mJ and producing a 100 μm crater per spot. A raster of 10 3.75 mm lines, 0.15 mm apart was used for the analysis. The data were normalised to the C signal at 193.1 nm to minimize fluctuations. The samples were split into a 4 : 1 ratio of the "training set" and the "testing set". Prior to proceeding with PCA, the data were standardized by subtracting the sample means and then dividing by standard deviations. This placed them on the same scale of measurement. This was necessary to ensure that PCA was not impacted by differing magnitude scales of spectra. Once the data had been treated using PCA, it was reduced to 15 principal components, which were input to LDA. This then achieved a correct classification rate of 98.52% (it made oner error out of 68). Although not perfect, it was a good start and, with further refinement, the method could potentially be used for helping to solve criminal cases.

Takahara *et al.* used *TXRF followed by PCA to classify individual polyester fibres* of the type that typically constitute car boot mats or clothing.[123] Polyester fibres (52) from 15 manufacturers in six countries were obtained for the study. Individual fibres were then analysed using a benchtop TXRF instrument where a suite of 10 analytes was determined. Most samples contained Ti, but relatively few contained Cu and Ge. Synchrotron radiation μ-XRF was also performed on the same samples and showed broadly similar trends to the TXRF. The data for the10 analytes were input to PCA which produced six principal components, accounting for almost 90% of the data. Classification with different manufacturers was partially successful. The incomplete success was attributed to individual fibres having different shapes which can affect the TXRF measurements adversely. Similarly, the position of the fibre on the carrier with respect to the detector can also affect the signals. Work is on-going to try and iron out these teething problems so that better classification results.

5.3 Organic materials

The *forensic dating of documents can be a challenge*. An overview of some of the methodologies used was presented by Kapoor *et al.*[343] The review cited 86 papers and covered a host of static,

dynamic and supplementary methods of analysis. The review is split into numerous sections. For instance, in the "static" section numerous subsections covering the analysis of inks, toners, paper *etc.* Further subsections then present examples of analytical methods for elemental analysis. The paper is an interesting read. However, it is good for background information and for the papers it cites. There is very little chemistry detailed in the review itself.

Another review presented a *chronological overview of analytical techniques for the forensic identification of toners*.[344] This review, by Tomar *et al.*, contained 55 references and covered many aspects of analysis, including physical examination to identify defects. The majority of the review focussed on the analytical chemistry involved and the techniques used. These include chromatographic methods, spectroscopic methods and microscopic methods. In the spectroscopic section, subsections included: IR, Raman and laser-based techniques (LA-ICP-MS and LIBS). Although they do not have subsections of their own, XRF and TOF-SIMS applications were also reviewed. Included in the review were the assorted chemometric tools used to help discriminate between different materials. It was noted that the emerging techniques are minimally damaging to the samples, require no (or very little) sample preparation and when used in conjunction with the chemometric packages, are very powerful tools.

A *comparison of optical techniques and MeV SIMS* for the determination of the deposition order between inks which are optically distinguishable (*e.g.* a fountain pen and a ballpoint pen or two ballpoint pens of different colour) and indistinguishable inks (*e.g.* two ballpoint pens of the same colour) from different writing tools was made by Barac *et al.*[345] Model examples were prepared by writing on A4 paper, waiting an hour and then writing again using a different pen. The intersections of inks from several writing tools were studied using the standard non-destructive methods such as optical microscopy, Raman spectroscopy and under IR light. The SIMS instrument employed an 8 MeV Si^{4+} primary beam to produce the secondary ions. A mass spectrum of ink from each writing tool was measured by scanning smaller areas (100×100 μm^2) of the sample away from the intersection region. Then the intersection region of up to 1400×1400 μm^2 was scanned and 2D molecular map created. The SIMS data were then treated using PCA to highlight the differences in chemical composition between each data point. Since SIMS is effectively a surface analysis technique there should be a distinct change in chemical signature for the ink applied first at the point of intersection of the two inks; whereas this difference would not be present for the ink applied second. If two writing tools of the same colour and from the same manufacturer were used, then distinction could not be made. The SIMS analysis therefore had some advantages over the optical methods because they were far less successful in discriminating the inks. However, the one big drawback of the SIMS is that it is semi-destructive of the sample (small portions of a document must be cut to insert it into the vacuum chamber). It is still possible to use it as a last resort in an attempt to prove forgery though.

A paper was presented by Chen *et al.* who *identified writing marks from pencil lead through machine learning based on LIBS*.[346] In this study, writing marks from different pencils (*i.e.*, 6B, 4B, 2H and 4H) were taken as the examples. They used LIBS to obtain analytical data for Al, C, Ca, Fe, Mg and Si. The chemical composition was similar for all four sample types and so it was difficult to distinguish them directly from the spectrum. Therefore, data mining and analysis were conducted and assisted by machine learning. The data were interrogated using PCA to build a model to represent the sample in the principal component space. Then BP neural network and k-Nearest Neighbour (KNN) based on the PCA results were employed to build writing marks identification models. A total of 600 samples were collected from each type of pencil lead, and 100 of them with high SNR were randomly taken for classification using BP neural network. For this, 70% of the data were used as a training set and 30% as test set. The success rate of identifying the pencil mark was 97.9%. The PCA alone was capable of differentiating the four types of pencil, although the separation of the groups was not extremely clear. When combined with KNN a correct identification rate of 98.33% was achieved. Both chemometric methods were therefore extremely good for discrimination purposes and, when combined with a rapid and non-destructive method of analysis such as LIBS, offer an excellent method for forensic scientists.

A similar paper was presented by Li *et al.* who used *XRF followed by a support vector machine (SVM) algorithm to successfully classify ash from 90 different papers*.[347] Both the paper type and the brand source could be identified. The paper is in Chinese, so details are scarce. It has been included to show the reader another example of what can be achieved.

An interesting application by Szynkowska-Jozwik *et al.* used *TOF-SIMS to visualize amphetamine residues in fingerprints*.[348] An amphetamine-contaminated fingerprint was deposited directly on a glass slide surface. The fingerprint was treated with black latent fingerprint powder and lifted by tape in order to mimic the process usually followed at a crime scene. Since TOF-SIMS is essentially a surface analysis technique capable of extremely good depth resolution, the fingerprint could be analysed without interference from the tape. The black fingerprint powder was also found not to interfere. The TOF-SIMS instrument was capable of detecting inorganic ions as well as molecular fragments in the same mass spectrum. Therefore, using positive mode, NH_4^+, $C_6H_5^+$, $C_7H_7^+$ and $C_9H_{14}^+$ were chosen as representatives of the amphetamine and K^+, Na^+ and NH_4^+ as being representative of sweat. The TOF-SIMS imaging obtained from the studied fingerprints made it possible to gather information about the distribution of chemicals of detected components on fingerprints. This, combined with the spectral analysis enabled correlation between specific ions and their possible source. It was concluded that TOF-SIMS offers huge potential as a detection method of drugs in fingerprints.

Analysis of single fibres can be an important forensic application. Komatsu *et al.* discriminated between *single red fibres from eight commercially available red silk scarves*.[349] The authors pointed out that a single fibre may only be a few μm wide. Therefore, techniques such as LIBS and ICP-MS that leave craters, typically with μm diameter in a sample, cannot be regarded as being non-destructive. They therefore employed a benchtop TXRF instrument and synchrotron radiation XRF for the analysis. The TXRF instrument was calibrated using wool dyed with a standard chromium mordant. The Cr content had been determined using an acid digestion followed by ICP-MS analysis. The fibres were placed on a glass wafer and then analysed using TXRF employing the Mo-Kα line (17.446 keV) with measurements made at 50 kV and 12 mA. The incident X-rays were formed into 10 mm wide and 5 mm long using slits and irradiated at an angle of 0.05° to the Si wafer surface. Using such a low angle meant that the X-rays penetrated only 3 nm into the wafer, leading to decreased background irradiation from the support. Nitrogen was flowed in front of the detector to decrease signal noise. For the synchrotron radiation XRF, calibration and lower limit of detection calculation was achieved using ERM-EC681k (a low density polyethylene material). Each sample had three fibres analysed and each of these was analysed three times. A total of nine measurements per sample was therefore made. Each measurement took 200 s. Some elements enter the silks through the environment in which the silkworm is living (*e.g.* Ca, Co, Fe and Zn). Other elements *e.g.* Cr enter through dying processes. Synchrotron radiation XRF was more sensitive than TXRF. The TXRF had a discrimination success rate of 85.7%. Although very good, it cannot be relied on to provide conclusive evidence. The conclusion therefore was that it was unsuccessful. The synchrotron radiation XRF was more successful (100%), but suffers from the obvious drawbacks of not being portable, requiring specialized facilities and requiring these facilities to be booked ahead of time.

5.4 Inorganic materials

There has been a large increase in the number of inorganic forensic applications during this review period, especially for gunshot residue analysis.

Analysis of solders from improvised explosive devices found at crime scenes can be analysed and compared with solder found at a suspect's house or workplace, thus facilitating identification of the guilty party. Such an application has been undertaken by MacConnachie *et al.* who used electrothermal vaporization (ETV)-ICP-OES for determining Ag, As, Bi, Cu and Sb as well as the matrix elements Pb and Sn.[38] The method was calibrated by using the material NIST 1131 solder, *i.e.* it was a matrix matched calibration. To overcome problems associated with plasma loading changing the relative sensitivity of the analytes, the authors used the intensity at the Ar 763.511 nm line as an internal standard. Several other aspects were tested. Included in these was the analysis with and without the organic resin at the core of the solder (placed there to help the melting process). The authors also tested the effect of melting of the solder on the trace metal concentration levels – an obvious but extremely important experiment to undertake since it is vital to know if the concentrations change after use. Once calibrated, the method was validated through the analysis of NIST C2416 bullet lead. Further validation of the method was obtained through a dissolution procedure followed by ICP-MS analysis. It

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was concluded that the method developed was rapid, accurate, could discriminate between different solders whether it had been melted or not and had the advantage of using only 1.5 mg of sample. It should be noted though, that the precision associated with the analysis was very poor. This is exemplified by the results of the CRM NIST C2416, where the certified value for Sb is 0.79 ± 0.01% and the experimental value obtained was 0.67 ± 0.12%. This could potentially be because of the problems associated with weighing such small samples.

5.4.1 Gunshot residue. A potentially very important paper by Menking-Hoggatt *et al.* discussed the production of a *series of reference materials that may be used for inter-laboratory studies, method development or method validation*.[350] Various leaded and lead-free primers (10 in total) were discharged under controlled conditions and prepared in triplicate. The bullet was first removed, the gun fired into a clean 2 L Erlenmeyer flask, the neck immediately covered with parafilm and allowed to settle for a minute. The particles collected were then rinsed with 100 mL of acetone and transferred to a 100 mL capacity polypropylene bottle. The result was 30 stock microparticle suspensions. The authors took care to clean the gun between different primers to avoid cross-contamination. Analysis was then undertaken using ICP-MS, LIBS and SEM-EDS. For the ICP-MS analysis, the solutions were first vortex mixed, an aliquot of 100 μL removed and placed in a 50 mL capacity digestion tube, allowed to evaporate for an hour, 100 μL of a mixture of Sc, Y and In added as internal standards followed by 5 mL of 10% nitric acid. The solutions were then refluxed at 80 °C for and hour, cooled, an aliquot of 2.5 mL was diluted to 10 mL and then analysed, with 34 analytes being determined. For the LIBS analysis, 100 μL of the vortexed suspensions were placed on a carbon stub and allowed to evaporate. Two commercial instruments were used (identical, but one with an intensified CCD to enhance sensitivity in the UV region) to determine multiple wavelengths covering atom and ion lines for 11 analytes. The results obtained using the three different techniques were compared and were in good agreement. A 12 week long-term stability test undertaken using ICP-MS indicated that the materials stayed chemically stable. and maintained morphological integrity. The diameter of the collected microparticles ranged from 0.5 μm to 10 μm and contained spheroid particles. Work is on-going to test the effects of different storage containers, testing other methods of analysis, inter-laboratory studies *etc.* The materials and the methodology used to produce them could be of significant assistance for forensic analysis in the future.

Another paper by the same research group described *the analysis of primer gunshot residue particles using LA-ICP-MS and LIBS*.[351] The methods used 159 samples, 40 of which were used as standards to characterise the elemental composition of leaded, unleaded and mixed primers. In addition, 119 skin samples of which 60 were not from shooters were analysed to determine thresholds and error rates. Overall, the success rate for identifying the different primers was 94.9% and 88.2% for LA-ICP-MS and LIBS, respectively. The success rate dropped when the unleaded primers were analysed. Although the drop for LA-ICP-MS was only marginal (85.2%), the drop in LIBS success rates was significant (down to 44.4%). The laser-based methods provided rapid chemical profiling and micro-spatial information of gunshot residue particles, with minimal destruction of the sample and high accuracy. The analysis of 25 micro-regions per sample was possible in 2–10 minutes using the two techniques, offering quick and efficient screening.

A *method for gunshot residue using TXRF* was reported by Gong *et al.*[352] Six types of ammunition were tested by firing guns and collecting the particulate discharged on a white cotton trill backed by cardboard placed exactly 15 cm from the muzzle of the gun. Two guns of the same class but of slightly different calibre were used and were expected to produce a similar residue type. The guns were again cleaned between firing of different ammunition types. A 10 cm radius circle was then cut from the target and digested in 200 mL of nitric acid for 24 h. After dilution so that the diluted form contains 5% dissolved material plus an aliquot of Y internal standard (1 mg L^{-1}). The sample was then spotted (in triplicate) on clean and polished quartz disks and dried in an oven at 60 °C. Each sample was subjected to 4000 scans at one second per scan, and using 50 kV and 600 μA under optimized fit profile Bayes deconvolution for quantitative analysis. The method identified six analytes that may be used to differentiate between different ammunition types: Ba, Cu, Fe, Pb, Sb and Zn. Although the method is extremely lengthy, the TXRF technique can simultaneously identify the individual elements in the residue and provide absolute elemental quantification. This is in contrast to SEM-EDS scans which report the relative elemental compositions of localized GSR samples rather than giving absolute quantitation.

Elemental profiling of primers in ammunition available in Turkey was undertaken by Yuksel *et al.* who used *SEM-EDS, ICP-MS and XPS* for the analysis followed by chemometric interrogation of the data.[353] The samples were collected in the same way as Menking-Hoggatt described (see previously) but preparation for the ICP-MS analysis used a microwave assisted digestion. Aliquots (100 μL) were transferred into Teflon® microwave vessels and left to evaporate for 20 min. Then, 9.5 mL of nitric acid 4% (v/v) and 0.5 mL of hydrogen peroxide were added and the contents microwave digested at 800 W and 210 °C for 15 minutes. The resulting solutions were then analysed for a suite of analytes. Data obtained were then input to PCA and Pearson's correlation coefficient. Three sets of groupings were observed: Ba–Sb–Pb–Cu–Gd, Ti–Sr–Zn and Al–Ca–Ga, The XPS analysis revealed the mean surface composition of multiple gunshot residue particles and associated particles of varied diameters in the region beneath the irradiating X-ray spot.

In a related topic, a paper by Saide *et al.* reported a comparison of rifle bullets using wavelength dispersive X-ray fluorescence spectroscopy and chemometric analysis.[354] Fifty four lead core fragments from 7.62 mm rifle bullets from five different manufacturers were obtained. The bullet casing was removed, the brass alloy was removed and then the lead core fragment was removed from the bullets with the aid of a goldsmith's saw. This yielded samples of approximately 5 mm in diameter weighing 0.4 g. The samples were then compressed using

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a bench vice to 1 cm in diameter in order to fit the WDXRF sample holder. A filter paper was used to ensure that no metal on metal contact was made during the compression stage. Data obtained from the WDXRF instrument were treated using several chemometric tools, including principal component analysis (PCA) and hierarchical cluster analysis (HCA) for exploratory analysis of the data. The subsequent classification used the parametric method of soft independent modelling of class analogy (SIMCA) and the nonparametric method of the k-nearest neighbour (KNN). Both PCA and HCA identified five groups of ammunition corresponding to the five manufacturers. The classification methods were then used to try to determine if "unknown" fragments could have their manufacturer identified. These methods employed 74% of the samples in the training set and 26% of the samples in the test set. Both methods scored 100% success in predicting the manufacturer of the fragments.

5.4.2 Explosives and propellants. A paper by Zhao *et al.* discussed the *forensic analysis of explosives/energetic materials*.[355] The paper was entitled "Laser induced breakdown spectroscopy for the determination of explosives based on the ReliefF algorithm and support vector machines". Three explosives (RDX, HMX and CL-20) and three non-explosives (flour, talcum powder and PTFE) were used in the study. The materials were spread over some double-sided tape attached to a glass plate. Excess material was shaken off and the LIBS instrument was used ensuring that a fresh area of sample was analysed for each laser shot. The full spectra over the range 200–1000 nm was obtained during the LIBS analysis and the data input to a SVM algorithm, the classification was fairly successful, with 83.3% of CL-20 being classified correctly (the errors being 10% HMX and 6.67% RDX), 96.67% classified correctly as HMX (with 3.33% mis-classified as CL-20) and 86.67% RDX classified correctly with mis-classification rates of 3.33% CL-20 and 10% HMX. For the non-explosives talcum powder was completely classified correctly, but the flour was successfully classified at 96.67% (with 3.33% mis-classified as HMX) and the PTFE at 96.67% correct (with 3.33% mis-classified as CL-20) were not infallible. When the full data were narrowed down to 13 wavelengths of interest by the ReliefF algorithm (two for CN, two for Ca, two for Na, three for N, two for K, one for O and one for H), the classification success rate improved significantly. All three non-explosives were correctly classified with 100% success, as were CL-20 and HMX. The only slight error was for RDX that was classified correctly 96.67% of the time with 3.33% being mis-classified as CL-20. Another model was then constructed using six regions of the spectrum (for instance the Fe region between 357.55 nm and 358.13 nm). Other regions for H, Na, CN and two for K were also constructed. When these data were inserted into the SVM, classification reached 100% for all materials. Once the method had been developed, it was quick to use and accurate; which is the ideal scenario for real time explosive detectors.

Another example was presented by De Tata *et al.* who attempted to determine the source of homemade ammonium nitrate using ATR-FTIR spectroscopy, trace elemental analysis using ICP-MS and chemometrics.[356] Ammonium nitrate is widely used in industry but is also used by terrorists to form bombs. It can be made from combining numerous materials that, on their own pose no threat. A total of nine ammonium nitrate products were obtained, three of which were classed as "pure forms". Five of the other six were prepared in-house from various readily available materials purchased from hardware shops (*e.g.* calcium nitrate and various brands of ammonium sulfate). The last one was prepared from laboratory grade chemicals. For the ICP-MS analysis, ammonium nitrate (200 mg) was dissolved in nitric acid (3 mL) in a 20 mlL capacity polypropylene tube. This was then placed in an oven at 90 °C for 2 hours. Pure water was then added to give a volume of 10 mL before diluting a further 10 or 100-fold. Initially, 57 analytes were determined. However, to aid the statistical analysis, those present as contaminants or present at concentrations below the calibration range of 0.2–50 μg L^{-1} were removed from the dataset. This left 10 analytes (B, Ba, Cu, Mn, Ni, Rb, Se, Sr, Ti and U) whose data were mean-centred and then input to PCA. Linear discriminant analysis was then undertaken on the first four principal components. Discriminant models were then generated using a randomised leave-one-out approach. This combined approach was very successful, with repeated LDA identifying the source of every ammonium nitrate sample tested correctly. The ability to use a simple chemical analysis and then using chemometrics to identify whether the source of the explosive is home-made, prepared from pure chemicals or is already available commercially is potentially important for forensic evidence.

6 Cultural heritage

As always, there has been a great deal of research into the analysis of cultural heritage samples. In common with the forensic analysis of samples, the focus has been on causing minimal sample damage and the use of chemometrics data analysis to glean as much information as possible from the analytical data. Unfortunately, many of the papers in the area of cultural heritage analysis are very routine and so will not be included. Similarly, those papers that focus almost entirely on the archaeology and give very little experimental detail, will also not be reviewed.

Several papers have *reviewed different aspects of the analytical chemistry* associated with cultural heritage samples. These will be reviewed in this sub-section of the review. A very brief overview of the use of handheld (portable) XRF for the analysis of archaeological artefacts highlighting the challenges, advantages and limitations was presented by Gherardi.[357] The review contained only seven references and was therefore more of a technical note or a perspective than an authoritative review/overview. However, its fast, on-site and non-destructive nature were highlighted and a few interesting applications noted. Another overview was presented by Zhou *et al.* who discussed the progress of the application of X-ray spectrometry (both XRF and X-ray absorption fine structure, XAFS) in the non-destructive analysis of relics.[358] This paper (with 13 references and unfortunately written in Chinese), discussed how obtaining

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elemental composition and structural information may help conservation and provenance determination.

An *evaluation of pattern recognition techniques for the attribution of cultural heritage objects based on portable XRF data* was presented by Andric *et al.*[359] A study campaign conducted jointly by scientists, art historians and curators used portable XRF instruments to examine well-preserved and reliably dated icons from four different centuries. A large number of spectra of each were obtained and the data were then treated using an assortment and sometimes a combination of pattern recognition techniques including PCA, Hierarchical Cluster Analysis (HCA) and Scattering Matrix-Based Dimension Reduction (SMBDR). These methods managed to reduce the number of dimensions of the datasets. The efficiency of the process was evaluated using the calculated Index of Informativeness and Bhattacharya's distance. The overall result was that a method was devised that enabled artwork origin to be determined based on PCA data reduction followed by linear classification.

The *construction of a low cost, home-made portable EDXRF instrument* for use especially for the analysis of cultural heritage samples was described by Ruschioni *et al.*[360] The geometry was optimized so that sample types that contain large concentrations of low mass analytes, *e.g.* glasses and ceramics, as well as those that contain large quantities of medium to high mass analytes, *e.g.* metals and alloys could be analysed with good sensitivity and accuracy. The instrument was tested for both qualitative (pigment layers) and quantitative (gold-based certified alloys) analysis. For the pigment layer analysis, the results were comparable to those obtained using a commercial XRF spectrometer, a result the authors were rightly pleased with.

A procedure for the *determination of Pb isotope ratios in archaeological materials using a coupling of liquid chromatography with a multi-collector (MC)-ICP-MS instrument* was presented by Penanes *et al.*[361] The determination of Pb isotopes can be useful because they may give pointers as to the geographical origin of the material. After dissolution, the Pb was separated from concomitant ions using EDTA chelates on an anion exchange column and a mobile phase of ammonium nitrate. A flow injection system was used to introduce a spike of NIST 981, a Pb isotopic standard, before and after the Pb peak from the sample for "bracketing" purposes. Thallium was introduced for mass bias correction. The method was validated in two ways. The first was by injecting NIST 981 as the sample and passing it through the chromatographic system. The other was to compare the results obtained for real samples with those obtained using a conventional off-line separation procedure using the commercial Pb-Spec resin. Once optimized, the procedure was applied to the analysis of archaeological samples with varying Pb concentrations. No preconcentration procedure was attempted and so the method was limited to those samples with a Pb content in excess of 500 $\mu g\ g^{-1}$.

The *LIBS characterization of a range of materials (metal artefacts, bones, potsherds and coloured glazed pottery) found at a military settlement* in the Argentinian Pampas was reported by Pace *et al.*[362] The samples were damaged slightly by using the LIBS laser to drill though corrosion layers and superficial weathering to expose the underlying bulk composition of the material. This was done to assist in the identification of the pigments in the paints and to analyse the glazing process. Discrimination between analytes in the pigments, the binder medium and from the paste matrix was achieved. The outermost varnish layer was removed to ensure contamination from the earth it had been buried in did not contribute any elemental signatures. The primer layer was white lead $Pb(OH)_2 \cdot 2PbCO_3$ A pink painted layer was found to contain Pb and Sn. The authors hypothesised that this was a mixture of red lead ($Pb_3O_4(2-PbO \cdot PbO_4)$) with lead–tin yellow ($Pb_2SnO_2$). The results of the analyses provided useful information on the characteristics, raw materials, manufacturing processes, use and provenance of the objects. For instance, it was concluded that the lead bullets and the iron-rich alloys were probably prepared locally, from locally sourced materials, whereas the porcelains were probably of European origin.

Two papers have discussed the *LIBS analysis of archaeological mortars and/or construction materials*.[363,364] The paper by Richiero *et al.* discussed the analysis of lime mortars, a class of mortars used from the Roman empire through to the industrial revolution. The recipes used varied between geographical area, the historical period, the craftsmen making it and its use. Three lime mortars from different geographical areas (Angers, France; Dardilly, France and Pompeii) and having different uses (a cathedral, an aqueduct and a house, respectively) were studied using a µ-LIBS instrument. This enabled the compilation of an elemental image for each of the mortars. The LIBS instrument consisted of a Nd:YAG laser operating at 1064 nm, a pulse duration of 8 ns, a pulse energy of 700 µJ and a repetition rate of 100 Hz. The result was a crater in the sample of ∼8 µm in diameter. The emitted light was detected using fibre optics attached to three different spectrometers covering three spectral ranges and with CCD as detectors. It was possible to determine the chemical signature of each of the mortars because using the three spectrometers over 25 analytes could be determined. The nature of the aggregates were determined in terms of elucidating the granulometry (the size and shape of the particles) and circularity (a parameter measuring how closely the shape of an object approaches that of a perfect circle). The circularity provides information on whether the material is alluvial or colluvial. The use of masks helped simplify the image processing. The methodology for the masks was given in the paper and ESI. The advantage of using LIBS was that it could detect the light elements with good sensitivity – something that many XRF spectrometers cannot achieve. Its speed of analysis and ability to map large areas were also identified as advantages. The other paper to use LIBS for the analysis of archaeological construction materials was presented by Zivkovic *et al.* who applied it to form elemental maps of materials from the foundations of the Smederevo Fortress in Serbia.[363] The LIBS instrument employed a double pulse Nd:YAG laser operating at 1064 nm and a spectrometer equipped with a CCD. Coupling this instrument with a commercial microscope enabled the elemental mapping with resolution at the micro-scale which, given the inhomogeneous nature of the sample, was more than sufficient. The combined use of the calibration-free analysis and the inputting of data to an unsupervised clustering

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algorithm enabled a good discrimination between different materials to be obtained. Both papers commented on the potential of LIBS in the future for this type of work.

Shen and Shen reported the use of a *portable combined XRD-XRF instrument* capable of being taken into the field.[365] The instrument was used to identify cinnabar (alpha-mercury sulfide) in assorted material types including raw materials, polished gemstones and Chinese ink sticks. The novelty in this paper is obviously the portable nature of the instrument because XRD is normally very much a laboratory-based technique. A comparison of the results obtained using the portable instrument with those obtained using a conventional laboratory-based XRD instrument and a μ-Raman spectroscopy method was made. The XRD results were in reasonable agreement. Meanwhile, the XRF component of the instrument was used to qualitatively identify the elements present so that the range of possible phases could be defined. The XRF detector was reportedly sufficiently sensitive to discriminate between the cinnabar and another red pigment (Pb_3O_4) without causing damage to the sample. The conclusion was that the portable instrument when used in conjunction with the Raman system presents researchers with a convenient and rapid method of identifying minerals and that its use could cover research fields including mineralogy, cultural heritage, materials science, *etc.*

Numerous other applications more specific to sample types were also reported. These will be discussed in the individual sections below, often with the assistance of tables for easy reference for the reader.

6.1 Metallic artefacts

Steenstra *et al.* have described the analysis of *the cultural heritage alloy reference materials (CHARM) set of Cu-alloys* using excimer ns LA-ICP-MS and assessed the matrix effects and its applicability to artefact provenancing.[366] The extent of the matrix effects was very variable between different alloys. This was attributed to the variation in the Zn/Cu ratio, with those samples rich in Zn significantly affecting the melting and boiling points (and hence, laser ablation properties). This makes those samples with higher concentrations of Zn more prone to matrix effects. Using 32XLB14F, a Pb-rich CHARM reference material and internal standardization enabled results of good accuracy (better than 20% error) to be achieved for virtually all the brass and bronze materials studied. This represented a significant improvement compared with using silicate glasses as an external reference material. This highlights, once again, that the certified materials to use for calibration should be as closely matched as possible to the sample types. Clearly, an alloy is closer in matrix composition than glass to alloys and serves its purpose better.

The viability of obtaining *quantitative analytical data using XRF on (a) a corroded surface, (b) a stripped patina area and (c) polished cross sections of 25 archaeological copper alloys* from Iran was assessed by Holakooei *et al.*[367] The LOD, LOQ, precision and accuracy of the analytical data were assessed using 12 CRMs. In addition, the same samples were also analysed using ICP-OES and the data from the two techniques compared statistically.

The corroded surfaces were depleted in Ni and Zn and enriched in As, Pb and Sn. This means that the XRF could potentially give mis-leading results if conclusions for the bulk of the sample are assumed from the surface analysis. However, it was thought that the areas with the lowest Sn concentration were probably the best representation of the composition of As, Cu, Pb and Zn in ancient copper alloys. The quantitative data obtained from the stripped patina and from the polished cross-sections for the two analytical techniques were comparable, leading the authors to conclude that the μ-XRF technique could be used with confidence to obtaining accurate results.

An interesting paper that tackled the problem of *obtaining sufficient material for accurate Pb isotope ratio measurements* was presented by Merkel *et al.*[368] A portable LA system was utilised that employed a pulsed diode pumped solid state laser operating at 532 nm and with a pulse duration of <1 ns. Repetition rate could be varied between 1 and 10 000 Hz, but a value of 100 was used. The laser beam was focussed using lenses to a fibre optic and the resulting beam was 100 μm in diameter. Ablated sample (obtained after ~9000 pulses) was retained on a pre-cleaned Teflon filter *via* a vacuum pump. The material on the filter was then dissolved using 7 M nitric acid (1.5 mL) assisted by sonication. After matrix removal and Pb enrichment, the samples were ready for analysis using MC-ICP-MS with a standard sample bracketing method. The material NIST 981 was used for quality control purposes. Approximately 1 μg of Pb was collected per filter which was significantly higher than the blank values (20 pg). The methodology was applied to the analysis of silver objects and to nine reference materials: one commercial (MBH 133X-AGA3, batch A), six produced in-house and the final two being archaeological materials used for inter-laboratory studies. The precision of the method was approximately five times better than ns LA-MC-ICP-MS used *in situ*. The method obviously does not require the transport of precious artefacts away from the museum and could open up the possibility of enabling a large number of unanalysed samples to be studied.

The *determination of gilding thickness using EDXRF* has been studied previously and usually requires the use of different energies of the X-rays and measurement of the fluorescence K_α or K_β, L_α or L_β ratios using any of three models. These three models are: the self-attenuation method in which Au-Lα/Au-Lβ, varies with gold thickness, the ratio of X-ray intensity method in which Kα/a-Kβ (or a-Lα/a-Lβ), which varies with gold thickness and only depends on the different attenuation by gold of the two and finally, the Au-Lα/a-Kα (or Au-Lα/a-Lα), which also varies according to the gold thickness. A paper by Cesareo *et al.* tested these models to determine their limits, *i.e.* how thin or thick the layers can be before problems arise.[369] Three scenarios were studied using various artefacts. One scenario was gilded lead, the second was gilded copper and the third was gilded silver. For the first scenario, a painting by Raphael and the state coach of Dom Pedro II were studied. For the second scenario, three crowns and a pendant from the tomb of the Lady of Cao (dated 350 AD) were studied and for the third scenario, a vase from the Chavin civilization from North Peru (dated several hundred years BCE) was studied. For the gold self-attenuation model, the useful layer thickness was 2–8 μm. For the attenuation by gold

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of the X-rays of an internal element the useful thickness was ~1 μm and for the gold to internal element X-ray ratio, the useful thickness layers ranged from 0.05 to 10 μm approximately, depending on the internal element. Therefore, for layers with thin gilding (as in these samples that have layers of <1 μm), the first two models are of no use and the third model is the only one capable of providing reliable data.

Other applications of the analysis of metallic artefacts are described in Table 3, below.

6.2 Organic origin

Three reviews directly applicable to this sub-section were produced. This included one by Burgio entitled "Pigments, dyes and inks: their analysis on manuscripts, scrolls and papyri".[377] This review contained 159 references and discussed the potential methods that could be used, with the methods being grouped according to their invasiveness/destructiveness. The review was aimed at scientists, curators, students, conservators and practitioners. It was a well-written review and would be of great interest to people in the subject area. The second review was by Cappa and Sterflinger and overviewed the non-invasive physico-chemical and biological analysis of parchment manuscripts.[378] This overview had 49 references and concentrated on XRF elemental analysis and compound specific techniques such as FTIR and Raman. Also discussed were the DNA analysis techniques to identify the biological origin of the materials. The latter could also help identify any viruses, micro-organisms and insects that may be present. The third review, by Bouvier *et al.* contained 134 references and focussed on the TOF-SIMS analysis of old paintings.[379] The method is capable of determining the organic composition by detecting the molecular ions and fragments of binders as well as the mineral contents of most of the pigments. The technique is almost non-destructive and has

Table 3 Applications of the analysis of metallic cultural heritage materials

Analyte	Matrix	Technique	Comments	Reference
Various	Silver	pXRF	Silver items from the San Gennaro Treasure in Naples analysed. The XRF data were input to a multivariate statistical analysis program (PCA). The classification criterion of Ag/Cu ratio could be used to classify the materials into four main groups	370
Pb isotopes	45 pieces of Hacksilver from five hoards	MC-ICP-MS	A minimally destructive method was employed to extract Pb from the materials and then to isolate it using anion exchange chromatography. The Pb isotope ratios were determined using MC-ICP-MS. Data were input to a new clustering method algorithm that minimized variance between isotopic clusters and maximised variance between isotopic clusters. The isotopic record indicated that during the iron age although the Aegean region dominated silver supply, exchange between east and west Mediterranean continued	371
Pb isotopes and various	13 Zhou dynasty bronze vessels and two slags	LA-MC-ICP-MS, EDXRF	Results of Pb isotope analysis showed there were two types of Pb material in the bronzes. Class one was thought to originate in the Wannan region and were used during the Western Zhou period. Class two bronzes possibly originated from the local mines in Zongyang county and were present mainly during the Warring States period. Results from determination of other analytes confirm the two classes. The reference material GBW02137 was used for quality control	372
Pb isotopes and various	Bronze dagger axes	pXRF, MC-ICP-MS	18 dagger axes excavated from the cemetery at Shuangyuan Village were analysed to try and elucidate the source of their raw materials and to identify imitations. Two different styles identified. Most were of the Ba-Shu system but others were of the Central Plains style. The pXRF data indicated that the average Sn content was in excess of 15%. The Pb concentrations ranged from <1% to >2%. The Pb isotope analysis indicated that the sources of Pb materials underwent a diachronic change that seemed to originate further south rather than locally. Long range sharing of resources was indicated but the items themselves were not imported. Reference material NIST 981 used for validation of Pb isotopes	373
Various, Pb isotopes	182 metal items from a tomb at Xijuan cemetery, China	MC-ICP-MS; pXRF	Analysis using pXRF indicated that two thirds of samples were made of a Sn/Pb alloy. The MC-ICP-MS determined Pb isotope ratios and found that the Pb in bronzes came from a different source than the Sn/Pb alloy with the latter at variance to the majority of samples from the early-middle Warring States period from Nanyang. However, they were similar to artefacts from the Chu State and from some Zeng state artefacts. It was	374

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Table 3 *(Contd.)*

Analyte	Matrix	Technique	Comments	Reference
			concluded that these prestigious artefacts were made from materials from South China and were possibly distributed as gifts by the Chu court	
Various	30 archaeological metallic objects	Portable LIBS	Fast, *in situ* analysis of artefacts from the Museum of Malaga. Statistical analysis of data using Euclidian distance analysis and binary diagrams indicated that differentiating between different archaeological sites is feasible. A new mathematical algorithm called "coordinate obtaining method" was evaluated. It is based on a linear algebra model to obtain the relation between the sample and a library of spectra. Full details were provided in the paper. It was claimed to have advantages over linear correlation	375
Various	23 pieces of pre-Roman bronze armour	pXRF	Analysis of materials undertaken using single point assays and cluster analysis (the five points sampled in a cross configuration over a 1 cm area). It was noted that XRF can mis-represent the composition of bulk materials by measuring the surface patina. This study took care to avoid such errors and gave recommendations for best practise. The data indicated that ancient smiths tailored the bronze composition for different functions. Also evident was a decrease in Fe and Sn content over time. This may be because of recycling and purification of materials	376

a lateral resolution of less than 1 μm. The review was conveniently split into sections discussing primary beams, the mass analysers, imaging, matrix effects and a series of applications.

As discussed previously, the analysis of any cultural heritage samples should cause minimal damage. A paper by Muller *et al.* identified *invisible modifications under the surface of painted parchments induced by proton beam irradiation from techniques such as PIGE, PIXE and RBS*.[380] These techniques are generally regarded as being non-destructive and so studies finding that they induce changes are important. Various modifications were observed in the cross-section of the parchment after irradiation. These included: discoloration (yellowing), the formation of cavities and the denaturation of collagen fibres. Damage was noted to a depth of 100 μm for a beam fluence of 4 μC cm^{-2} and higher. Interestingly, the presence of the blue paint ultramarine on the parchment surface appeared to exacerbate the problem. Based on experimental data, the authors recommended a maximum fluence of 0.5 μC cm^{-2} for 2.3 MeV PIXE analysis.

Another paper to discuss damage inflicted on paintings during analysis was presented by Zhang *et al.*[381] In this example the *damage inflicted by synchrotron radiation on ancient paintings* was examined using ED-XAS and IR. The effects of synchrotron radiation on pure rabbit skin glue, and a mixed sample of rabbit skin glue and zinc white were investigated. The effects of low energy X-rays (7775 eV) were more severe on the rabbit skin glue whereas for the mixed sample the effects of the radiation were exacerbated by the presence of the inorganic pigment. This was attributed to the pigment absorbing more of the radiation. The damage was worst when energy close to the Zn K-edge was used. The damage manifested itself in the secondary structure of proteins. The damage caused started rapidly and then slowed and therefore did not increase in proportion to the irradiation

time. The authors recommended that synchrotron radiation induced damage can be minimized if the X-ray energy used is far away from the X-ray absorption edge of all of the main elements in the pigments. This would affect techniques such as XRF and XRD. As an alternative, time-resolved techniques such as QXAFS or ED-XAS during XAFS experiments would also reduce the effects.

Macro-XRF has become a frequently used tool for the analysis of paintings because it is non-invasive, rapid, can cover relatively large areas quickly and can provide useful information on the chemical makeup of paints and can reveal images underneath the painting. A paper by Yan *et al.* described *an automatic algorithm that was capable of extracting and identifying elements and their distribution from macro-XRF datasets*.[382] The algorithm was described in full in the paper, but it was essentially comprised of three parts: pre-processing steps, pulse detection and model order selection based on Finite Ratio of Innovation theory and finally chemical element estimation based on Cramer–Rao bounding techniques. The performance of the algorithm was assessed through the processing of macro-XRF datasets obtained from the analysis of paintings from the National Gallery, London. The algorithm proved very successful, having the ability to identify weak signals from noisy XRF spectra, separate overlapping chemical signals and, in the case of a Leonardo da Vinci painting, observing a hidden underdrawing below a masterpiece.

An instrument of quite poor resolution (18% at full width at half maximum at 5.9 keV) was used by Lach *et al.* to provide *XRF spectra of historical paintings that were subsequently processed using factorisation methods*.[383] The design of the full field imaging instrument was described in full in the paper. It employed a position-sensitive and energy dispersive gas electron multiplier

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detector. The gas electron multiplier detector has several advantages. These include having a large area that can be manufactured easily at low cost. They do not require cooling and can be operated at room temperature. Since they have such a large area, they are ideal for performing macro-XRF, which has a primary use for the analysis of flat areas, *e.g.* paintings. Three factorisation methods of the data were evaluated: region of interest, non-negative matrix factorisation and PCA. The paper explained how each method worked and applied them to the datasets obtained from two paintings. Both PCA and non-negative matrix factorisation enhanced the selectivity of the elements determined using the poor resolution spectrometer. This demonstrates the power of the chemometric tools.

A paper attempting to *elucidate the cause and mechanism of the darkening of "fake-gilded" decorations in a painting* was presented by Monico *et al.* who used several synchrotron X-ray-based techniques for the task.[384] The painting unusually consisted of a mixture of the pigment orpiment (As_2S_3) and metallic silver and so these materials were the main focus during this study. The paper described a multi-material and multi-method approach based on the combination of synchrotron radiation X-ray-based techniques such as XRD, XRF and XANES and vibrational micro-spectroscopy methods. The high specificity, sensitivity and lateral resolution of the techniques provided evidence of the presence of black acanthite (alpha-Ag_2S), mimetite ($Pb_5(AsO_4)_3Cl$) and syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$) as degradation products. It was also proved that the metallic Ag and moisture were the key factors in transforming As_2S_3 into alpha-Ag_2S and arsenic oxides and that sulfide ions arising from the degradation of As_2S_3 were responsible for the formation of alpha-Ag_2S.It was also demonstrated that exposure to light exacerbated the processes. The evidence provided by atomic spectrometry therefore allowed the authors to construct a degradation mechanism. Although the analysis was applied to only one painting, the approach could be used for others and potentially, other sample types.

Several other applications were published in the field of organic cultural heritage and the noteworthy ones are summarized in Table 4, below.

6.3 Ceramic materials

Quality control of data is the mainstay of analytical chemistry and so it is good to report the production of open-source calibration materials for quantitative portable XRF analysis.[392] The Bricks and Rocks for Instrumentation Ceramic Calibration (BRICC) sets are 10 sets of materials each of which contain 20 specimens mounted in epoxy disks. These comprise: 12 bricks and 8 geological specimens for the calibration of the instrument, a certified reference material (a shale analysed by 85

Table 4 Applications of the analysis of cultural heritage artefacts of organic origin

Analyte	Matrix	Technique	Comments	Reference
Fe and S	Waterlogged archaeological wood	ICP-OES; FTIR; Raman	Iron and S species are harmless to waterlogged wood when a sample is buried but are very damaging when exposed to air and must be removed. A new two-stage biological extraction scheme involving *Thiobacillus* denitrificans and siderophores was compared with the usual chemical treatment. The efficiency of removal was evaluated using ICP-OES, Raman and FTIR. The new biological scheme removed the Fe and S better than the chemical treatment that left residues of S. However, alteration to the sample was observed with pine showing signs of oxidation. Using PCA and ANOVA, the method was optimized to cause less damage	385
Various	Paint layers in stained glass	Macro-XRF; SEM-EDS	Vitreous paints used in stained glass were analysed using macro-XRF, highlighting the advantages of the technique. Seven samples from the Dominican monastery near Krakow, the Diocesan Museum in Kielce and the National Museum in Poznan were analysed. The macro-XRF enabled the legibility of damaged fragments to be improved as well as distinguishing the elemental composition between vitreous paints of different colour. The drawback was that it was not very sensitive for the determination of light elements. For these, SEM-EDS was used	386
Various	Painting materials	Macro-XRF	The painting "the Entombment of Christ" by the artist Roger Van der Weyden was studied. The scanning macro-XRF instrument developed was lightweight and easily transportable to work *in situ*. The authors acknowledged that macro-XRF on its own could not answer all the questions asked, but it did make a valuable contribution and provided an initial overview of the painting materials and techniques used	387

Table 4 (*Contd.*)

Analyte	Matrix	Technique	Comments	Reference
Various	Pigments of the murals at Magao grottoes	LIBS	A depth-profiling analysis was undertaken to provide information for suitable restoration and conservation techniques. The different shades and tones of the green layers were studied in this work using LIBS to cause minimal damage. The effect of the pigment particle size on the LIBS measurement was evaluated because the different shades of green originate from different particle size. Simulated green layers composed of five particle sizes were prepared and studied. The average ablation rate increased as the particle size decreased. The relationship was hoped to be used to study layer thickness	388
Various	Paper mulberry and paper	ICP-OES; ICP-MS	Analysis of papers found in Korea and raw materials were analysed and data input to Partial Least Squares-Discriminant Analysis to form a prediction model for their origin. Both the ICP-OES and ICP-MS data yielded traits that could be used for discrimination. For instance, the Chinese Bast fibres contained high levels of B, Ca and especially Zn. Bast fibres from Japan, China and Thailand all had high levels of Al, Ca and Na. The overall prediction for domestic and imported products was 86.4% and 72.7% for ICP-OES and ICP-MS data, respectively, which was deemed acceptable	389
Various	Layers of paint on icons	XRF; FTIR; digital radiography	Icons originally painted at the beginning of 18th century were overpainted in 1911. The original paint layers comprised lead white, red lead, red ochre, yellow ochre and orpiment. The re-painted layer contained zinc white, Prussian blue and some Cr-based pigments. The study enabled information to be gleaned on the painting techniques and materials used	390
Various	A pellet of unsuccessfully produced Egyptian blue pigment	μ-XANES; SEM-EDS; μ-Raman, high resolution, SR-μ-XRF	The paper examined the production technology of the ancient pigment Egyptian blue. 171 μXANES spectra of samples and of a series of Cu-based compounds were obtained and data input to PCA. Large variation in some of the XANES spectra were observed and this was attributed to different speciation and to orientation effects. The manufacture of this pellet failed not because they used an inadequate firing temperature, but because the starting materials had unexpectedly high Fe levels	391

laboratories) to assess the accuracy of data produced and a high purity silica blank. A set of materials may be used at Yale Peabody Museum or may be borrowed and used elsewhere. The function of the materials is to meet requirements for accuracy, reproducibility and transparency.

Other examples of ceramic-based cultural heritage sample analysis are given in Table 5, below.

6.4 Glass materials

This area has seen an increase in activity during this review period. Again, the focus was *on non- or minimally destructive analysis*. This was highlighted in two papers by Oujja *et al.* who used a variety of techniques including LIBS, LIF, non-linear optical microscopy and multi-photon excitation fluorescence to analyse historical glass Grisailles[406] and medieval-like glass alteration layers.[407] Both papers managed to analyse layers and the depth of these layers causing no damage in most cases and minimal damage in the case of LIBS. In the latter case, the thickness of the layers determined using multi-phase excitation fluorescence microscopy were compared and were in agreement with thickness determined using SEM-EDS and optical microscopy.

A *comparison of minimally invasive ICP-MS approaches to $^{87}Sr/^{86}Sr$ isotope analysis of medieval stained glass known to have elevated Rb and REE levels* was conducted by van Ham-Meert *et al.*[408] The techniques used were: an acid dissolution followed by chromatographic analyte isolation and pneumatic nebulization into a MC-ICP-MS instrument; LA-MC-ICP-MS and LA-ICP-MS/MS using CHF_3/He as the reaction gas. The LA-MC-ICP-MS method was unsuccessful in that the high Rb/Sr and the presence of REE at elevated concentration led to a large bias which could not be corrected for using a higher resolution setting or by using mathematical correction algorithms. The LA-ICP-MS/MS method was more successful, with the Sr signal monitored at *m/z* 86, 87 and 88 as well as the F adducts at 105, 106 and 107. This successfully overcame interferences arising from the Rb and the doubly charged REE. Unsurprisingly, the precision obtained (0.3% RSD) was worse using this sequential quadrupole-based instrument than using a MC-based one (0.03% RSD). However, the results were still in reasonable agreement with those obtained using the digestion, chromatographic separation and pneumatic nebulization MC-ICP-MS method. The latter method took significantly longer and was more damaging than the LA-based method. It would therefore

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Table 5 Applications of the analysis of ceramic cultural heritage artefacts

Analyte	Matrix	Technique	Comments	Reference
Various	Terracotta wall panel	Macro-XRF; XRD; SEM-EDS; Raman	The wall panel was part of the Getty collection and had been thought to be associated with a Caeretan wall panel. The results from the analysis of the Getty panel along with PCA suggest that the clay support is similar in composition to those of panels from Cerveteri. A manganese black pigment was also identified which, although not commonly employed elsewhere, was a marker for the Cerveteri workshop. Macro-XRF also identified some invisible ruling lines on the Getty panel. The study enabled a better understanding of the Cerveteri workshop practice	393
Various	Wall paintings	XRF; Raman	The semi-quantitative XRF data were input to PCA. The pigments used were identified as hematite, lapis lazuli, cinnabar and possibly carbon. The XRF and PCA combination identified areas of past intervention with Ba, Pb and Zn found. The preparation layers were studied by undertaking a cross-sectional analysis of two microsamples. Several layers of lime plaster were found. The characteristics of the pictorial layer and the presence of calcium oxalate indicated the use of a Secco-technique	394
Various	Archaeological pottery from Chavdar, Bulgaria	pXRF; LIBS; optical microscopy; FTIR	A fragment of neolithic red slip pottery decorated on both sides with white paint was analysed using multiple techniques. The LIBS was used for smaller area analysis and for depth-profiling. The LIBS and pXRF data were in agreement. The white paint had high levels of Ca and the ceramic body high levels of Fe. Estimates of the firing temperature were made from the FTIR analysis (not exceeding 650 °C)	395
Various	Bronze age ceramics from Hungary	pXRF; LA-ICP-MS, XPS; FTIR; XRD; SEM-EDS	pXRF used for most measurements of encrustation samples and data for 21 analytes corrected against 13 NIST and USGS standard materials. Soil samples were analysed as loose powders, ceramics as pressed pellets. The interior paste composition was analysed using LA-ICP-MS. Encrustations composed mainly of calcite. Evidence was found of leaching of mobile analytes into ceramic pastes	396
Various	Pottery from Mexico	LIBS; ICP-OES	Analytical data input to PCA. Most fragments identified as local, but a few with high levels of Ca, K, Mn, Na, Rb and Sc found to be foreign. Depth-profiling using LIBS on red paints identified a diversity thanks to differing hematite concentrations. Analysis of interior pastes using a microwave assisted digestion followed by ICP-OES yielded similar data to LIBS. Reference material NIST 2710 used for method validation of acid dissolution	397
Various	Early medieval pottery from Tuscany	pXRF	A large repository of ceramic samples analysed using LIBS and data input to statistical program (PCA) to identify geographical clusters. Sets of ceramics were then compared with reference ceramic samples from the same region. Results indicated that there was a well-defined organization of pottery manufacturing present	398
Various	Ru-type ware from Henan province, China	EDXRF	A study of the colouring, glaze formulation and microstructure was made. The EDXRF data were input to multivariate statistical analysis. It was concluded that the samples belonged to the Celadon class of glazing. The formulas of different glazes were also similar, but not identical. Different glaze colours arose through different amounts of Fe_2O_3 and TiO_2	399
Various	Porcelain from Dehua, China	pXRF; LA-ICP-MS	Ware from 19 kiln sites from five villages were analysed. Results from the two techniques indicated that the samples were of two groups. Kilns from the same village were more likely to be grouped together than kilns from separate villages. The study showed that LIBS data, although less accurate than LA-ICP-MS, was still capable of identifying compositional patterning	400

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Table 5 (*Contd.*)

Analyte	Matrix	Technique	Comments	Reference
Various	46 potsherds of Torre Alemanna type pottery	XRF; XRD; SEM-EDS	Chemical data from the ceramic bodies were input to PCA. A strong compositional homogeneity was noted. The XRD data indicated a maximum firing temperature of between 750 and 1000 °C had been used. Analysis of the glaze using SEM-EDS indicated a firing of between 780 and 950 °C. Given the overlap in firing temperatures, the authors hypothesised that only one firing occurred	401
Various	Ceramic from Iberia from 8th to 3rd century BCE	XRF; XRD	XRF data plus statistical analysis of 107 sherds enabled groups to be determined. From these groups, the economic relationship between two sites could be inferred. The XRD identified three different groups of firing temperatures	402
Various	Dxi beads	XRF; XRD; XANES	Mystery surrounds the origin of these beads with an "eye pattern". No previous analysis had been undertaken. Beads were found to be agate (silicon dioxide) with etched parts containing regular hotspots of Cu. A study was then undertaken to determine if the beads were natural or man-made. Results indicated that they were a natural earth-formed agate but with the pattern crafted	403
Various and Fe valence state	Tianqing Porcelain	EDXRF; SEM; XAFS	The chemical composition and Fe valence of the glazes of the porcelains were determined. Results indicated that the composition converted calcium glaze to calcium alkali glaze. In addition, the crystallization of anorthite was encouraged by increasing the Ca and K content and reducing the Si/Al ratio. The Fe valence was complex, with about one third being Fe^{2+}. Between one and two thirds of the Fe was four coordinated with low symmetry with the nearest neighbour. The Fe atoms were therefore in a disordered local environment	404
Co and Fe	Manufactured models of Chinese blue and white porcelain	Variable pressure SEM; XANES	The underglaze colouring was examined to determine Co and Fe valence as a function of firing temperature and atmosphere (*i.e.* if a reducing atmosphere was used). Data were compared with those obtained using historical samples. The atomic spectroscopy enabled the firing conditions to be determined	405

seem that the protracted dissolution method followed by MC-ICP-MS that causes more damage to the sample is still the best way of obtaining precise isotope ratio data although the rapid LA-ICP-MS/MS method is a viable alternative.

Back reflection-enhanced LIBS analysis was conducted on archaeological glasses by Abdel-Harith *et al.*[409] A highly polished metal reflector (copper or silver) in direct contact with the underside of the sample reflects the laser beam back through the sample and the plasma it had created from the sample. As it passes through, it reheats the plasma increasing the intensity of the light emitted from it, the result is that the signal to noise ratio of the analytes improves significantly compared with analysis without the reflector. In a way, it is similar to double pulse LIBS, but with the advantage of using only one pulse, not requiring instrumentation for gate delays or a second laser, *etc.* The only drawback is that the sample type must be transparent. Therefore glasses, in this case archaeological glasses from Egyptian Synagogue windows, were the ideal sample type. Signal enhancements were between three and four-fold and this was dependent on the colour of the glass and its thickness. Comparison of data with those obtained using energy dispersive X-ray spectroscopy found they were in excellent agreement. The authors hoped that their methodology could also be used

for other transparent sample types, *e.g.* gemstones and polymers.

It is well known that LA-ICP-MS is a rapid way of obtaining data causing minimal damage to the sample. However, it suffers the drawback of requiring a large number of data processing steps for the results to be coherent. These steps include: data segmentation, background correction, calibration and normalisation. Faltusova *et al.* developed a *standalone processing software that allows easy and straightforward processing of data for bulk analysis and imaging.*[410] The software, written in Python and named Ilaps, was built around the free and open-source Python package called imgMS. This simplified the customization of the used functions. The combination of imgMS and a stand-alone graphical software made it possible for researchers with no programming knowledge to use it. The software package Ilaps required no data preparation and can process bulk analysis data or convert data into an image in minutes. The software can automatically select the signals that are representative of the sample, but is sufficiently flexible also to allow manual removal of data, *e.g.* to exclude contaminants. The software was applied successfully to the bulk analysis of archaeological glasses and to the imaging of a mouse brain.

Other applications of the analysis of glasses of cultural heritage origin are given in Table 6, below.

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Table 6 Applications of the analysis of glass cultural heritage samples

Analyte	Matrix	Technique	Comments	Reference
Various	Glass from North American Great Lakes region	INAA; LA-ICP-MS	A comparison of INAA and LA-ICP-MS for the analysis. Samples analysed by two different laboratories using different LA-ICP-MS protocols. Results between the two laboratories and between the two techniques were in good agreement. The good comparability hopefully enables newly obtained and legacy data to be combined to explore inter-regional archaeological questions	411
Various	Sixty 3rd and 2nd century BCE glasses from Western and Central Europe	LA-ICP-MS	Composition was found to be in accordance with Celtic and Hellenistic glass artefacts. Five compositional groups of natron glasses were identified using major, minor and trace analytes: two corresponding to Egyptian glass and the other three to Levantine glass. The similarity of compositions recorded in Western and Central Europe indicate a wide network of glass exchange (through trade or gifts)	412
Pb isotopes	Glass of the Mesolitic period from Nubia (Sudan)	LA-MC-ICP-MS	The Pb isotopes of 13 samples spanning high to low Pb concentrations were analysed. Results indicated an Eastern Mediterranean source of the Pb ore – possibly Greece or Turkey. NIST 610 and Corning C glasses used for calibration for low and high Pb, respectively	413
Various	Monochrome glass beads unearthed from sites in China	LA-ICP-MS	Twenty seven soda-alimina glasses and 87 potash glass beads from different sites in China were analysed. Data analysis using Multi-Kernel Density Estimation and Maximum Mean Discrepancy indicated the silica source of all of the soda-alumina and most of the potash glasses unearthed from Guangxi were identical. These were thought to originate in North-eastern India or South-eastern Asia. The soda-alumina glasses from Hanan and the rest of the potash glasses are very similar (but not identical). These were thought to originate from Southern India or Sri Lanka	414
Various	Chinese lead-barium glass	LA-ICP-MS	Samples (49) excavated from five provinces were analysed and analytical data analysed using the statistical tools of multivariate kernel density estimation using four variables in a tetrahedron plot and then maximum mean discrepancy and hypothesis testing to identify clusters of sample types. It was discovered that the materials were made by mixing Chinese lead and barium ores with natron glass possibly imported from coastal area of Syria/Israel/Palestine	415
Various (56)	Monochromatic beads from Nanyang, Central China	LA-ICP-MS; Raman; IR	Glass type, colour-presenting mechanism, and origin were studied. All beads were potash glass. Their composition suggested that they originated from South Asia, Southeast Asia or South China. They are the earliest beads found in central China so far. The land silk road was in chaos during this period and so the authors concluded that the Maritime silk road and river-ocean combined transportation had been used. NIST 610 and 612 as well as Corning C and D glasses used for calibration and quality control	416
Various and Sr–Nd isotopic ratios	Glass collection from San Lorenzo	LA-ICP-MS; SEM-EDS; TIMS	Major and minor elements (SEM-EDS) and trace elements (LA-ICP-MS) as well as Sr and Nd isotope ratios (TIMS) were determined in 23 samples of tableware and lightingware. Two goblets were natron-based glass, one of Egyptian provenance, one likely to have been recycled. The other 21 samples were made of plant ash-based glass. Of the 21 samples, 17 were split using analytical data and Binary plots into three groups: Mediterranean or Adriatic origin; Mediterranean or Mesopotamian and Slovenian or North Adriatic. NIST 610 and ^{29}Si used as external and internal standards	417
Various	Glass ingots (200) and five Mycenaean glass relief beads from bronze age shipwreck	LA-ICP-MS; TIMS	In addition to the full chemical composition analyses, 49 Sr isotope ratios were also determined. NIST 610 and Corning B, C and D glasses used for calibration and validation. The glass ingots originated from as few as 28 production batches, the largest of which represented 16 ingots (40 kg). Cluster analysis, PCA and comparison of Ti/Cr and Li/Zr indicated	418

Table 6 (*Contd.*)

Analyte	Matrix	Technique	Comments	Reference
Various	Thirteenth century stained glass windows	PIXE; PIGE; UV-Vis; near IR	that all ingots were of Egyptian origin. The Mycenaean beads were also made of Egyptian glass PIXE data obtained for most analytes and Na data obtained using PIGE. The geochemical diorite DR-N sample and Brill glasses were used as reference materials to calibrate the PIGE data and control PIXE results. Hierarchical cluster analysis using Ward's method and Euclidean distances used to analyse the data. The colours were made from six materials with typical medieval recipes. Insights into medieval glazing work practices were made	419

7 Abbreviations

2D	Two dimensional
3D	Three dimensional
AAS	Atomic absorption spectrometry
ABS	Acrylonitrile butadiene
AES	Auger electron spectrometry
AFFF	Asymmetric field flow fractionation
AF4	Asymmetric flow-field flow fractionation
AFS	Atomic fluorescence spectrometry
AFM	Atomic force microscopy
AMS	Accelerator mass spectrometry
ANOVA	Analysis of variants
ARECV	Average relative error of cross-validation
ASTM	American Society for Testing of Materials
ATR	Attenuated total reflection
BCR	Community Bureau of Reference
CCD	Charge coupled device
CE	Capillary electrophoresis
CFFF	Centrifugal field flow fractionation
CIGS	Copper indium gallium selenide
CRM	Certified reference material
CS	Continuum source
CT	Computerised tomography
CV	Cold vapour
DA	Discriminant analysis
DLS	Dynamic light scattering
DLTV	Diode laser thermal vaporisation
DMEM	Dulbecco's modified Eagle medium
DMSO	Dimethylsulfoxide
DP-RLIBS	Double pulse resonance laser induced breakdown spectrometry
DRC	Dynamic reaction cell
EAST	Experimental advanced super conducting tokamak
EDIXS	Energy dispersive inelastic X-ray scattering
EDS	Energy dispersive spectrometry
EDXRD	Energy dispersive X-ray diffraction
EDXRF	Energy dispersive X-ray fluorescence
ELM	Extreme learning machine
EPMA	Electron probe microanalysis
ESI-MS	Electrospray ionisation mass spectrometry
ETAAS	Electrothermal atomic absorption spectrometry
ETV	Electrothermal vaporisation

EXAFS	Extended X-ray absorption fine structure
FAAS	Flame atomic absorption spectrometry
FESEM	Field emission scanning electron microscopy
FFFF	Flow field flow fractionation
FI	Flow injection
FIB	Focused ion beam
FI-CVG	Flow injection chemical vapour generation
FTIR	Fourier transform infrared
FWHM	Full width at half maximum
GC	Gas chromatography
GD-MS	Glow discharge mass spectrometry
GD-OES	Glow discharge optical emission spectrometry
GF-AAS	Graphite furnace atomic absorption spectrometry
GI-SAXS	Grazing incidence small angle X-ray scattering
GIXRD	Grazing incidence X-ray diffraction
GIXRF	Grazing incidence X-ray fluorescence
HAXPES	Hard X-ray photoelectron spectroscopy
HDC	Hydrodynamic chromatography
HG	Hydride generation
HPLC	High performance liquid chromatography
HR-CSAAS	High resolution continuum source atomic absorption spectrometry
IAEA	International Atomic Energy Agency
IBA	Ion beam analysis
ICA	Independent component analysis
ICP	Inductively coupled plasma
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICP-QMS	Inductively coupled plasma quadrupole mass spectrometry
ICP-TOFMS	Inductively coupled plasma time-of-flight mass spectrometry
ID	Isotope dilution
IL-DLLME	Ionic liquid-dispersive liquid–liquid microextraction
IP	Institute of Petroleum
IRMS	Isotope ratio mass spectrometry
ISO	International Organisation for Standardisation
ITER	International thermonuclear experimental reactor
JET	Joint European Torus
K-SVM-RFE	k-Fold support vector machine recursive feature elimination

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LA	Laser ablation
LASIL	Laser ablation of sample in liquid
LC	Liquid chromatography
LDA	Linear discriminant analysis
LIAS	Laser induced ablation spectrometry
LIBS	Laser induced breakdown spectrometry
LIBS-LAMS	Laser induced breakdown spectrometry-laser ablation mass spectrometry
LIF	Laser induced fluorescence
LIPS	Laser induced plasma spectroscopy
LOD	Limit of detection
LOQ	Limit of quantification
MALDI-TOF	Matrix-assisted laser desorption ionisation time-of-flight
MALS	Multi-angle light scattering
MAS	Magic angle spinning
MC	Multicollector
MEIS	Medium energy ion scattering spectroscopy
MIBK	Methylisobutylketone
MIP	Microwave induced plasma
MIP-AES	Microwave plasma atomic emission spectrometry
MS	Mass spectrometry
MSFA	Mono-segmented flow analysis
MWCNT	Multi-wall carbon nanotubes
NAA	Neutron activation analysis
NAAR	Neutron activation autoradiography
ND	Neutron diffraction
NDI-MS	Near-field desorption ionization mass spectrometry
Nd:YAG	Neodymium doped-yttrium aluminium garnet
NEXAFS	Near edge X-ray fine structure
NIST	National Institute of Standards and Technology
NMR	Nuclear magnetic resonance
NRA	Nuclear reaction analysis
OES	Optical emission spectrometry
PARAFAC	Parallel factor analysis
PBS	Phosphate buffered saline
PCA	Principal component analysis
PCR	Principal component regression
PET	Polyethylene terephthalate
PFC	Plasma facing components
PGAA	Prompt gamma neutron activation analysis
PGM	Platinum group metals
PIGE	Particle induced gamma ray emission
PIXE	Particle-induced X-ray emission
PLAL	Pulsed laser ablation in liquids
PLS	Partial least squares
PLS-DA	Partial least squares discriminant analysis
PLSR	Partial least squares regression
ppb	Parts per billion
ppm	Parts per million
QD	Quantum dot
RAFM	Reduced activation ferritic/martensitic
RBS	Rutherford backscattering spectrometry
RDA	Regularised discriminant analysis
REE	Rare earth elements
rf	Radiofrequency
RIMS	Resonance ionisation mass spectrometry
RMSECV	Root mean square error of cross validation
RMSEP	Root mean squared error of prediction
RoHS	Restriction of hazardous substances
RSD	Relative standard deviation
RSF	Relative sensitivity factor
SDS–PAGE	Sodium dodecyl sulfate–polyacrylamide gel electrophoresis
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
SEM-EDS	Scanning electron microscopy-energy dispersive spectrometry
SF	Sector field
SIA	Sequential injection analysis
SIBS	Spark induced breakdown spectrometry
SIMCA	Soft independent modelling of class analogy
SIMS	Secondary ion mass spectrometry
SNR	Signal to noise ratio
SP	Single particle
SPION	Superparamagnetic iron oxide nanoparticles
SR	Synchrotron radiation
SRM	Standard reference material
SXRF	Synchrotron X-ray fluorescence
SV-ICP-MS	Single virus ICP-MS
SVM	Support vector machine
SVR	Support vector regression
STXM	Scanning transmission X-ray microscopy
TEM	Transmission electron microscopy
TDS	Thermal desorption mass spectrometry
TGA	Thermogravimetric analysis
TIMS	Thermal ionisation mass spectrometry
TOF	Time of flight
T-PGAA	Time-resolved prompt gamma activation analysis
TPR	Temperature programmed reduction
TXRF	Total reflection X-ray fluorescence
UAE	Ultra-sound assisted extraction
UV-Vis	Ultra-violet -visible
WDXRF	Wavelength dispersive X-ray fluorescence
WEEE	Waste electrical and electronic equipment
XAFS	X-ray absorption fine structure spectrometry
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
XRPD	X-ray powder diffraction
XRR	X-ray reflectometry

Conflicts of interest

There are no conflicts to declare.

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