

2019

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

Carter, S

<http://hdl.handle.net/10026.1/15628>

10.1039/c9ja90058f

Journal of Analytical Atomic Spectrometry

Royal Society of Chemistry (RSC)

All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.

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

Simon Carter,^a Robert Clough,^b Andy Fisher,^{*b} Bridget Gibson,^c Ben Russell^d and Julia Waack^c

* Corresponding authors

^a Hull Research & Technology Centre, BP, Saltend, East Yorkshire, UK

^b School of Geography, Earth and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth PL4 8AA, UK

* E-mail: afisher@plymouth.ac.uk

^c Intertek Sunbury Technology Centre, Shears Way, Sunbury, Middlesex, UK

^d National Physical Laboratory, Nuclear Metrology Group, Teddington, Middlesex, UK

1 Metals

1.1 Ferrous metals

1.2 Non-ferrous metals

1.3 Cultural heritage: metals

2 Organic chemicals and materials

2.1 Organic chemicals

2.2 Fuels and lubricants

2.2.1 Petroleum products - gasoline, diesel, gasohol and exhaust particulates

2.2.2 Coal, peat and other solid fuels

2.2.3 Oils – crude oil and lubricants

2.2.4 Alternative fuels

2.3 Pharmaceuticals and personal care products

2.4 Cultural heritage: organic materials

2.4.1 Polymers and composites

3 Inorganic chemicals and materials

3.1 Inorganic chemicals

3.2 Building materials

3.3 Catalysts

3.4 Forensic applications

3.5 Ceramics and refractories

3.5.1 Industrial ceramics

3.5.2 Cultural heritage: ceramics

3.6 Glasses

- 3.6.1 Industrial glasses
- 3.6.2 Cultural heritage: glasses
- 3.7 Nuclear materials and chemicals
 - 3.7.1 Nuclear forensics
 - 3.7.2 Nuclear de-commissioning and waste monitoring
 - 3.7.3 Nuclear accident response
 - 3.7.4 Reactor materials
 - 3.7.5 Fusion
- 3.8 Electronic materials
 - 3.8.1 Wafers, thin films and multilayer materials
 - 3.8.2 Solar cell materials
 - 3.8.3 Electronic equipment and devices
- 3.9 Nanostructures

Abstract

There has been a large increase in the number of papers published that are relevant to this review over this review period. The growth in popularity of LIBS is rapid, with applications being published for most sample types. This is undoubtedly because of its capability to analyse *in-situ* on a production line (hence saving time and money) and its minimally destructive nature meaning that both forensic and cultural heritage samples may be analysed. It also has a standoff analysis capability meaning that hazardous materials, e.g. explosives or nuclear materials, may be analysed from a safe distance. The use of mathematical algorithms in conjunction with LIBS to enable improved accuracy has proved a popular area of research. This is especially true for ferrous and non-ferrous samples. Similarly, chemometric techniques have been used with LIBS to aid in the sorting of polymers and other materials. An increase in the number of papers in the subject area of alternative fuels was noted. This was at the expense of papers describing methods for the analysis of crude oils. For nanomaterials, previous years have seen a huge number of single particle and field flow fractionation characterisations. Although several such papers are still being published, the focus seems to be switching to applications of the nanoparticles and the mechanistic aspects of how they retain or bind with other analytes.

Foreword: This is the latest review covering the topic of advances in the analysis of metals, chemicals and materials. It follows on from last year's review¹ and is part of the Atomic Spectrometry Updates series¹⁻⁶

1 Metals

The largest single topic researched in the area of the atomic spectrometric analysis of metals in this review period has been that of *laser induced breakdown spectrometry (LIBS)*. This is especially true for

the ferrous metals where LIBS can be used at the production line, providing real-time analysis and hence cutting costs.

There have been three review papers that have discussed the application of LIBS. One by Fu *et al.*⁷ discussed, with 168 references, the accuracy improvement that has happened to calibration free LIBS in recent years (mainly since 2010). Calibration-free LIBS was first proposed in 1999, but its use has been limited because it does not provide the same accuracy as other LIBS techniques or of more traditional methods of analysis. The review discussed methods for the accurate measurement of spectral intensity, the spatial and temporal window of local thermal equilibrium and the accurate calculation of temperature and the electron number density. Also discussed was the use of standard samples in combination with the calibration free LIBS algorithm. The authors acknowledge that this loses some of the advantages, i.e. it is no longer truly calibration-free, but since it is a new direction of research, it was included. The review's final section offered conclusions and their perspectives for future research. A review by Noll *et al.*⁸ was entitled 'LIBS analyses for industrial applications – an overview of developments from 2014 to 2018'. It contained 39 references and focussed on the combined use of in-line measured three-dimensional geometry information and LIBS for high speed sorting tasks, e.g. of refractories. Also included were identification of steel blooms in a rolling mill and the recovery of valuable materials from the end of life electronic goods. The authors emphasised that LIBS instrumentation can be used in exceptionally harsh environments with measuring distances often between a few cm and a few metres from the sample. In general, the closer to the material the smaller the spectrometer need be. A discussion of the commercial hand-held spectrometers, several of which have been produced recently, was also presented. The third review was of a more general type and covered LIBS mapping in the biomedical, geological and industrial fields⁹. This review presented (with 151 references) descriptions of the recent instrumental configurations, data processing methodologies and applications relating to LIBS-based imaging. The instrumental configurations discussed including the scanning configuration, the focussing systems, laser properties and spectral detection tools.

1.1 Ferrous metals

In addition to the review by Noll, discussed previously, numerous applications of LIBS have also been reported. A large number of these have used a chemometric tool to aid in regression or to aid classification of steel type. The first topic to be discussed in detail will be those papers that have described the *chemometric tools used to aid regression*. Kim *et al.*¹⁰ developed a LIBS device and tested it for the determination of alloying elements, e.g. Cr, Mn, Ni and Ti in low-alloy steel samples. The low spectral resolution of the spectrometer (0.9 nm) ensured that it was impossible to resolve these

elements spectrally from other species. Partial least squares regression (PLSR) was therefore employed to extract the unresolved spectral features enabling calibration and quantification. This still proved to be very difficult for the congested part of the spectrum in which the Cr and Ti were being measured. It was, therefore, decided to use the first derivatives of the LIBS spectra. This enhanced the performance of the spectrometer further. Singh and Sarkar¹¹ also used PLSR and compared its performance in terms of accuracy and precision with Principal Component Regression (PCR). Identical LIBS spectra from stainless steel samples were used for the comparison. A detailed study was undertaken of the role of the two algorithms so that an understanding of how they form the regression could be obtained. It was concluded that there were situations where both algorithms are equally appropriate and other situations where the use of one would be more suitable than the other. These situations were identified and some guidelines for other users presented.

Many papers have used *machine learning or similar algorithms* to “train” models to aid analysis. They usually use a series of samples to train a model and then test the model on ‘unknown’ samples. Analysis at elevated temperature is regarded as being less accurate than when undertaken at room temperature. Yang *et al.*¹² attempted to overcome this problem to reduce costs and enhance the potential of on-line analysis. They collected LIBS data at room temperature and then applied ‘transfer learning’ to the spectra obtained at higher temperature. Fifteen standard samples were used to train the model at room temperature and four at elevated temperature. A further three “test” samples were then analysed at elevated temperature. The model was tested for determining Cr in certified alloy steel samples. The proposed method reduced the average absolute and relative errors by 1.8% and 20.6%, respectively. Mei *et al.*¹³ attempted to overcome the self-absorbance interferences and matrix effects that can be so prevalent in LIBS analyses. A multivariate calibration approach called genetic algorithm – kernel extreme learning machine (GA-KELM) was used to enable the quantification of Cr, Cu, Mn, Mo, Ni, Si, Ti and V in 47 certified steel and iron samples. A full description of the complex process was given. The performance of the model in terms of R-squared factor and root mean square errors of calibration were favourable compared with those obtained using traditional partial least squares. The conclusion was that the method could reduce matrix and self-absorption effects during LIBS analyses. Li *et al.*¹⁴ also attempted to overcome interference effects during LIBS analyses. They developed a semi-supervised quantitative analysis procedure that was based on a co-training regression model using a selection of effective unlabelled samples. Again, a large number of samples of known composition were used to train the model (11 CRMs) and five samples were used as labelled concentrations. The model was tested on seven other CRM samples for the determination of Cr in high alloy steel samples. A full description of the construction of the model was given. Results were impressive, with the root mean square error decreasing from 1.80% to 0.84% and the relative

prediction error decreasing from 9.15% to 4.04%. The other paper of this type that deserves mention was presented by Guo *et al.*¹⁵. This paper also reported improved accuracy of LIBS analyses, this time using a hybrid sparse partial least squares and a least squares support vector machine model. The models were used to determine total Fe and the oxides Al₂O₃, CaO, MgO and SiO₂ in iron ore samples. Again, 24 samples were used to train the model and only 12 used for prediction. The two models were used for different things: the sparse partial least squares was used to select variables and establish the multi-linear regression model between spectral data and concentrations and the least squares – support vector machine was used to compensate for non-linear effects. The hybrid model outperformed either of the two individual models with root mean square error of prediction values of 0.0456, 0.0962, 0.642, 0.2157 and 0.359, for total Fe, Al₂O₃, CaO, MgO, and SiO₂ respectively.

Many of the mathematical models used for aiding regression have also been used for *classification processes*. A paper by Guo *et al.*¹⁶ compared the use of partial least squares – discriminant analysis with a support vector machine approach to classify different steel types. Forty steels with similar composition were analysed using LIBS. The spectra were then treated using the two algorithms with the partial least squares providing discrimination between 96.25% of the samples and the support vector machine 95%. The paper then described how a hybrid of the two algorithms was made, called least squares support vector machine, which yielded 100% discrimination efficiency. Shin *et al.*¹⁷ used LIBS followed by PCA to distinguish between different stainless steels, cast steels, aluminium alloys and copper alloys. A PCA of the full LIBS spectra provided good discrimination power but at the expense of computing time. This is a potential problem when used for sorting in the scrap metal industry as many hundreds of samples per day may require analysis. Consequently, the authors decreased the number of variables input to the PCA model. This was achieved by first obtaining full LIBS spectra and then using PCA to identify the input variables of greater significance for each element to be determined. The PCA was then repeated only on these more significant variables for future analyses. Although discrimination was marginally less good than PCA on the full spectra, the computational time required was decreased by a factor of at least 20. Xie *et al.*¹⁸ developed a novel method to achieve precise compositional prediction of steel samples based on wavelet packet transform and relevance vector machine (a machine learning technique that uses Bayesian inferences to obtain solutions for regression and probabilistic classification) analysis of LIBS data. The authors discussed the algorithms and how the spectral features extracted using the wavelet packet transform differed from those extracted using the traditional method. Using the absolute error of prediction and the mean relative error as measurement criteria, the wavelet packet transform outperformed the traditional method for extracting relevant spectral features to be introduced to the relevance vector machine. A better performance of the relevance vector machine was achieved through a modified Laplacian kernel

function. The mean values of the root mean square error prediction of the modified relevance vector machine, the calibration curve, the unmodified relevance vector machine and the support vector machine were 0.159, 0.210, 0.303 and 0.179, respectively. It was concluded that the use of the wavelet packet transform of LIBS data followed by the modified relevance vector machine possessed superior efficiency generalization ability and robustness for accurate and reliable compositional prediction.

Three papers discussed the analysis of *steels used in the nuclear industry*. In one paper, a LIBS spectrometer was developed that utilised a fibre-optic to deliver the laser energy¹⁹. The spectrometer design was presented and the authors optimised the distance between the end of the fibre-optic and the sample. A clear optimum, based on the maximal spectral intensity and minimal spectral fluctuations, was observed. When the distance was too short, self-absorption was observed and too long a distance led to plasma density and temperature dissipating after as little as 1 μ s. The spectrometer developed was then used under optimal conditions to determine Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni and Si in Z3CN20-09 steel samples, which are normally used for structural materials in the pipelines of nuclear power plants. The same research group also used this instrument for the analysis of both Z3CN20-09 and 16MND5 steels, the second of which is used for the nuclear reactor pressure vessels²⁰. Under the same incidence laser power, the plasma from the Z3CN20-09 produced significantly lower emission intensity compared with the 16MND5 steel. This was attributed to it containing Cr at much higher concentration. This led to problems for calibration between different sample types. The authors reported the use of internal standardisation, support vector machine and random forest regression calibrations being established. Under optimal conditions, the Cr present at a concentration of 19.3% in the Z3CN20-09 was determined with a relative error of 3.5%, whereas when it was present at trace amounts (e.g. 0.11% in the 16MND5) the best root mean square error of prediction was 0.032% by weight. The Mn content which was present at between 1.19 and 1.51% by weight in both steels, was determined with a relative error of approximately 10%. The third paper used LIBS to analyse type 316 stainless steel weld parts that had been corroded by exposure to liquid lithium for 30 days at 450 °C²¹. Repeated analysis of the same spot enabled depth-profile analysis with sub-micron depth resolution to be obtained. The extent of penetration of Li in the steel matrix was a measure of the level of corrosion.

The *measurement of the corrosion of steels* is another topic of interest. As well as the paper by Ke *et al.* above²¹, several others have been published during this review period. Many of these have come from one group who also specialised in using LIBS²²⁻²⁴. In the first, they used LIBS to obtain temporally and spatially resolved analysis of T91 steel which is used extensively for building industrial pressure-bearing heat exchange surfaces. The surfaces of several samples of the steel that had been aged to different extents were analysed and atom to ion line ratios and matrix element to alloying

element ratios measured. The spectrometer and analytical procedure were described in full. For lesser aged steel, the maximum line intensity was located at greater height above the sample at a delay time of between 300 and 700 ns. Conversely, the steels aged to a greater extent gave maximum intensity just above their surface for the same time delay range. The line intensity ratios were dependent on the delay time and on the age of the steel. In addition, it was also noted that the depth and volume of the craters left from the LIBS analysis depended on sample age, with older samples providing deeper craters with greater volume. The second and third of the papers^{23, 24} both used chemometric packages to assist in the estimation of the steel aging process. Lu *et al.*²³ analysed eight T91 and seven 12CrMoV steels and then used ANOVA and logistic regression filter to reduce the number of LIBS variables into a smaller, more manageable number for introduction to the classification models logistic regression and support vector machine. Three different feature selection methods were tested and their effects on the models discussed. The performance of the models could be improved to some degree by implementation of all of the feature selection methods. However, one called layered interval wrapper performed the best. For T91 steel the prediction accuracy improved to 0.92 for logistic regression and 0.94 for the support vector machine when the layered interval wrapper was used to streamline the data. Without its use, prediction was less impressive (0.76 and 0.81). Results were less impressive for the 12MoCrV steels, but prediction accuracy still improved from 0.69 for both models to 0.87 for logistic regression and 0.90 for support vector machine. Unsurprisingly, it was concluded that the layered interval wrapper is a very effective feature selection method. The final paper by this research group²⁴ also analysed T91 steels with different degrees of micro-structure ageing and then used a range of multivariate analysis methods to correlate the surface hardness (measured using emission line intensity) with age. These methods included PCA, canonical correlation analysis (both used to identify the important variables from the entire spectrum), and then two regression algorithms to form calibrations using the selected variables: partial least squares regression and support vector regression. Results demonstrated that coupling canonical correlation analysis with support vector regression enabled a hardness estimation to be made from spectral line intensity. Maximum values for mean relative error, RSD and root mean square error of prediction were 2.47%, 2.94% and 6.14, respectively. The other papers in this research area used methods other than LIBS. Barlow *et al.*²⁵ used X-ray absorption near edge spectroscopy (XANES) as well as XRF to characterise erosion at a buried polymer – steel interface. The samples were exposed to high pH potash brine to induce corrosion. The XRF was used to determine Cl, Fe, K and Mn and then construct maps so that areas of anodic pits could be identified. The XANES was used to determine the phase of the Fe corrosion products present. The second paper²⁶ was very similar. The XRF maps were produced using an excitation energy just above the metallic Fe K-edge threshold. The maps produce a sharp contrast between areas with and without corrosion. The μ -XANES was again used for confirmation.

Calibration free LIBS is a technique that is rapid, low-cost and is highly adaptable. However, it suffers badly from problems associated with self-absorption from major elements, it has few usable spectral lines from trace elements and requires correction of the relative efficiency of the experimental system. This means that accuracy and long term stability of calibration free LIBS can be compromised very easily. Several papers have described methodologies to overcome these deficiencies. As discussed previously, a recent development has been to combine calibration-free LIBS algorithms with standards. Although some advantages are lost, the overall effect is an improvement in accuracy. Hao *et al.*²⁷ used an instrument made in-house and a two point standardisation method to measure the trace elements Al, Cr, Cu, Mn, Mo, Ni, Si, Ti and V in low alloy steel samples. The method was described in detail in the paper and was used prior to quantitative analysis of real samples. Six test samples were analysed every 24 hours for three days. Instrumental drift was effectively overcome using the two point calibration method. In addition, the average relative errors of repeated measurements decreased by 11, 3, 15, 45, 54, 16, 32, 91 and 11% for Al, Cr, Cu, Mn, Mo, Ni, Si, Ti and V, respectively when compared with data obtained without the standardisation. A method using a standard reference line combined with one point calibration was described by Fu *et al.*²⁸ who determined six analytes in three stainless steels and five heat-resistant steels. The Stark broadening and Saha-Boltzmann plot for Fe was used to calculate the electron number density and plasma temperature, respectively. The standard reference line method alone was compared with the standard reference line method combined with one point calibration in an attempt to overcome the aforementioned problems with calibration-free LIBS. The combined use of the two methods improved the accuracy of the quantitative analysis. In addition, careful examination of the intercept along with the one-point calibration also improved the LOD. One point calibration was also employed by Hao *et al.*²⁹ who also used multi-line calibration to determine Cr, Mn, Ni and Ti in low alloy steel samples. A combination of the methods led to improvements in the average relative errors by 22, 9, 21 and 36% for Cr, Mn, Ni and Ti, respectively. The advantages of the system are that it does not require a large number of standard samples, has no complicated calculations and it provides a flexible, low cost quantitative LIBS analysis method.

As described previously, there is huge potential for *LIBS to be employed at the production line* of steel plants. This saves time, money and modifications to formulations can be made rapidly. Two papers have discussed such an application. Zeng *et al.*³⁰ combined a near IR instrument with a LIBS system to measure the temperature and the composition of molten carbon steel simultaneously. This was because the combined system utilised the same optical system and the same light collection fibre optic. The full schematic of the system was presented in the paper. Method validation for the thermometry was achieved by comparison with data from a commercial pyrometer. The relative root mean square error between the two was only 0.95%. The relative standard errors of Cr and Mn

detection were lower than 10%. The other paper, by Cabalin *et al.*³¹, described the installation and use of a stand-off, on-line LIBS system at a steel production plant in Bilbao. The LIBS system had been reported in a previous publication. The present paper discussed its installation 3.6 m from the hot billet in the continuous casting line and then its optimisation. Its positioning just before the oxy-cutting unit was ideal because it is at this point that billets of different steels need to be identified. Minor constituents such as Pb (from 0 to 0.17%) or V (0 to 0.1%) were useful in aiding discrimination between different steel types. The results from the system were compared with those obtained using an off-line LIBS system in a laboratory and with those from optical emission spectrometry. The results from all three were in good agreement. They were also in agreement with a mathematical model designed to predict the temporal evolution of the elemental content in the intermix region.

There is a large number of more simple applications of the analysis of iron and steels. One of the more novel of these was reported by Hegetschweiler *et al.*³² who described the use of *single particle ICP-MS for the determination of titanium and niobium carbonitride precipitates* in acid digests of micro-alloyed steels. The composition and particle size distribution of these particles are of importance for the mechanical properties of the steel. The single particle ICP-MS methodology is normally used for the analysis of nanoparticles, so this was a real application useful to industry. The results obtained from the ICP-MS were compared with those from electron microscopy. The single particle ICP-MS analysed over 2000 particles in one minute whereas the electron microscopy method could analyse far fewer. Both techniques identified two distinct particle populations: smaller particles contained only Nb and larger particles that contained both Nb and Ti. Electron microscopy also yielded information on the morphology of the particles. The larger ones were complex and 'overgrown' structures. The combination of the two techniques enabled a better understanding of the precipitation process that forms the particles during steel production at different stages of the thermo-mechanical – rolling process. This, in turn, would help improve the rolling process and help production.

Two applications have used *ICP-MS to determine analytes in ferrous materials*. In one by Steenstra³³ laser ablation–ICP-MS (LA-ICP-MS) was used to determine analytes in iron-rich alloys. The premise of the work was to assess the matrix effects that occur when calibration is against glass standards rather than matrix matched standards. This was achieved using a 193 nm excimer laser system operating at ns firing times to ablate the materials and then compare the data obtained with those from electron probe microanalysis (EPMA). Measurements from LA-ICP-MS consistently overestimated the concentration of volatile elements and under-estimated the concentrations of non-volatile elements compared with EPMA data. An attempt to quantify the matrix interferences was made resulting in the fractionation index being presented. This index was independent of the concentration and on the type of iron-rich alloy under analysis. Values for the fractionation index

ranged from 0.14 for the most volatile analyte to 1.8 for the most refractory element. The authors then used their findings to interrogate previously published data and to calculate metal-silicate partition coefficients. Comparison was made between corrected and uncorrected LA-ICP-MS data, where the corrected data were obtained by multiplying the uncorrected data by the appropriate fractionation index. Results demonstrated that erroneous data would be used if correction were not undertaken. The conclusion was that such a correction should be made for all samples of this type when analysed using LA-ICP-MS with this type of laser. A study by Wada *et al.*³⁴ determined ultra-trace S in high purity metals including zinc and iron using isotope dilution-sector field-ICP-MS (ID-SF-ICP-MS). After dissolution of the metal, a chromatographic separation of the S from the metal matrix was undertaken using an alumina column. This served two functions: to prevent polyatomic interferences arising from the metal matrix and to prevent signal suppression arising from space-charge effects. The sector field instrument used was also capable of removing polyatomic interferences through use of medium resolution mode. Operating parameters such as detector dead time (that affects precision) and the washout conditions (to remove the possibility of memory effects) were optimised. The method was validated through analysis of the iron CRM JSS-001-4. The result obtained ($1.86 \pm 0.12 \text{ mg kg}^{-1}$) was in good agreement with the certified value ($1.90 \pm 0.40 \text{ mg kg}^{-1}$).

Three papers also reported *applications for steel analysis using LIBS*. Amongst this number is one by Zeng *et al.*³⁵ who described the use of a portable fibre-optic LIBS system for the determination of the minor elements Cr, Mn, Ti and V in steel and pig iron. The R^2 values for the calibration curves for the four analytes were all better than 0.99 and their root mean square errors of cross-validation were 0.0501, 0.0054, 0.0205 and 0.0245 weight percent for Mn, Ti, V and Cr, respectively. Six test samples were used with average relative errors being 5.6, 2.5, 11.7 and 13.0% for Cr, Mn, Ti and V, respectively. The data were comparable to those obtained using a normal LIBS setup. A paper by Cui *et al.*³⁶ described the use of a collinear long-short double pulse LIBS system for the determination of Mn in steel washer samples. The long pulse (60 μs) was generated using a Nd:YAG laser operated in free running mode. The performance of the long-short double pulse LIBS was compared with that of the single pulse version. When operated under the same conditions, the double pulse LIBS had far superior linearity of calibration (R^2 of 0.988) compared with the single pulse LIBS ($R^2 = 0.810$) and had greater sensitivity. The second of these was attributed to the pre-irradiation effect. In addition, precision was also improved (10.5% RSD compared with 29.3% for single pulse LIBS). The biggest effect of the double pulse LIBS was on the average relative error of prediction which was 4.9% compared with the huge value of 94.9% obtained using only single pulse. The last paper of interest in this section was presented by Li *et al.*³⁷ who used μ -LIBS assisted by laser induced fluorescence (LIF) to determine Si in low alloy steels. The presence of Si in steels has an important role in hardness and strength improvement.

Unfortunately, it also leads to increased problems with corrosion and is harmful to ductility and therefore its concentration requires monitoring. The paper described the analytical setup and the mechanism by which the LIF assists the μ -LIBS. A comparison of analytical figures of merit for both the μ -LIBS-LIF and for μ -LIBS alone under their individual optimal working conditions indicated that the combination was far superior. The μ -LIBS-LIF yielded a calibration with R^2 of 0.9998, a LOD of 2.8 mg kg⁻¹ and a root mean square error of cross validation (RMSECV) of 63 mg kg⁻¹. To the authors' knowledge, this was the first time a LOD of less than 10 mg kg⁻¹ had been reported using LIBS.

1.2 Non-ferrous metals

The readers' attention should be drawn to the review papers discussed in section 1, since these are equally applicable to the analysis of non-ferrous materials. As with the ferrous metals, LIBS continues to increase in popularity. In common with the applications for ferrous metals, one of the most popular areas of study has been the use of *algorithms to improve the accuracy of measurement, to overcome interferences or to improve the long term stability*. An example was presented by Pan *et al.*³⁸ who described an efficient procedure for the construction and selection of calibration models for LIBS analysis. The procedure included the data pre-processing, construction of the calibration model and then the calculation of analyte concentrations in the samples. All of these steps could be pre-programmed with no further manual intervention. Using the developed procedure, the concentrations of 10 analytes were determined in nickel-based alloys. Most analytes had an average relative standard error of less than 10%. Zhan *et al.*³⁹ used the machine learning algorithm called Random Forest for pattern recognition of LIBS spectra to aid in the classification of different aluminium alloys. As with the majority of such papers, a training set of samples is required for the model to function correctly. Once trained, the model can be used for test or unknown samples. The best classification accuracy obtained was 98.59%. The accuracy was dependent on the number of trees in the random forest and on the size of the training set of samples. It was concluded that LIBS with Random Forest provides a rapid, accurate and precise way of classifying aluminium alloys. Owolabi and Gondal⁴⁰ also used algorithms to improve the performance of LIBS. They used a hybridisation of Extreme Learning Machine (ELM – a non-linear method that can approximate any non-linear relation) and Support Vector Regression (SVR – a non-linear tool based on learning theory). The former can, on occasion, suffer from over-fitting which can effect its accuracy. The SVR overcomes the problem of over-fitting if its parameters are properly optimised. The hybrid algorithm was used with LIBS analysis of seven standards bronze samples. A comparison of ELM-SVR, SVR-ELM, SVR and ELM was made, with best data in terms of root mean square error, being obtained for ELM-SVR. Each of the models had their hyper-parameters optimised

using a gravitational search algorithm prior to the comparison. Three different normalization techniques were compared by Sattar *et al.*⁴¹ for the minimization of matrix effects during the LIBS analysis of silver – zinc binary compounds. These methods were: normalization with background, internal normalization and three point smoothing. The LIBS spectra of five composites were determined using various laser irradiances, with calibration for the Ag being at 338.28 nm and the Zn at 481.053 nm. The slopes of the calibration graphs provided an evaluation of the matrix effects. After optimising the parameter settings, the best analytical results were obtained using the three point smoothing normalisation method which yielded calibration curves with R^2 values of between 0.995 and 0.998. Two papers were published by the same research group who explored ways of improving accuracy for different LIBS systems^{42, 43}. In one⁴³, Fe, Mg and Zn were determined in aluminium alloys using fibre optic-LIBS. Use of spatially resolved fibre optic-LIBS enabled the workers to collect spectra at different positions along a direction parallel to the surface of the sample rather than from the centre of the plasma. By selecting different acquisition positions along the X-axis, it was possible to overcome problems associated with self-absorption. Root mean square errors of cross validation were improved from 0.388 to 0.172, 0.348 to 0.224 and from 0.097 to 0.024 weight% for Fe, Mg and Zn, respectively. In the other application⁴² a method of calibration entitled ‘Single Sample Calibration’ was developed and tested for the determination of several major elements (Cr, Cu, Fe, Mo, Nb, Ni and Zn) in three sets of matrix matched certified samples. A full description of the method was given. Compared with multi-point calibration, the results were much improved. Using Cu as an example, the R^2 value, the root mean square error of cross validation and the average relative error improved from 0.40 to 0.97, 3.55 to 0.76 weight% and from 5.19 to 1.05%, respectively. The average RSD also decreased from 16.22 to 1.15%. The average relative error was dependent on the concentration range of the analyte, but was less than 5% for all ranges except 0-10 weight%, where it was 5.16%. For much higher concentration ranges, e.g. 90-100% the average relative error was 0.44%. Another paper to discuss the use of a chemometrics package in conjunction with LIBS was by Shin *et al.*¹⁷. This paper was discussed in detail in section 1.1.

Partial least squares regression was used by Takahashi *et al.*⁴⁴ for the *underwater LIBS analysis of brass samples*. The concentrations of Cu and Zn were determined using several different signal processing steps. These included normalisation, smoothing and background subtraction. Eleven certified brass samples were analysed to ascertain accuracy. Of the processing steps used, the normalisation provided the best results because it reduced the effects of both peak and background fluctuations. Database segmentation by excitation temperature further improved the partial least squares calculations. The method was applicable to real-time analysis and could potentially be used for fast, accurate and automated analysis at oceanic pressure.

One paper described the use of *LIBS in-situ* to provide *multi-elemental analysis and detect failures in an additive manufacturing process*⁴⁵. A compact LIBS instrument was designed and installed on an industrial robot for real time analysis of the formation of a highly resistant coating of nickel alloy reinforced with tungsten carbide particles. The positioning of the probe within the production line had to be chosen carefully because of the inhomogeneity of the tungsten carbide particles in the upper surface layer. Scanning electron microscopy was used to check that the LIBS sampling had no deleterious effect on the cladding process. The LIBS analysis of the main elements (Ni and W) yielded data in good agreement with those obtained using offline XRF measurements. The conclusion was that LIBS was a very good prospect for the on-line measurement of the cladding process. A similar paper was also presented by Lednev *et al.*⁴⁶ who used LIBS to quantify loose metal powders by first attaching them to double-sided tape. The technique reportedly worked even for materials of very different particle density, e.g. tungsten carbide and nickel alloy powder. Again, the methodology was validated by offline XRF analysis. A third similar paper by the same group was also reported⁴⁷.

Two papers discussed calibration free LIBS analysis of non-ferrous samples. In one by Mal *et al.*⁴⁸ a thorough explanation of what is required for calibration-free LIBS, and why, was given. Accuracy is known to depend enormously on obtaining optically thin conditions (since self-absorption occurs at optically thick conditions) and local thermal equilibrium. Evaluation of the temporal evolution of the plasma enabled the authors to identify the optimal temporal window where both of these fundamental criteria were met. This was achieved by studying the plasma temperature through the emissions of atomic Cu *via* a Boltzmann plot and estimating electron number density through the Stark broadening of the profile of the Cu ion wavelength at 510.5 nm. These estimates were then inserted to a one-line calibration-free LIBS algorithm to determine the percentage composition of three copper alloys. Results were in good agreement with those obtained using EDX. The other paper, by Li *et al.*⁴⁹ corrected for self-absorption effects during calibration-free-LIBS using a new method which they entitled 'black body radiation referenced self-absorption correction'. An algorithm was devised that calculated plasma temperatures and collection efficiency of the optical collection setup by comparing the measured spectrum with the corresponding theoretical black body radiation for self-absorption correction. The proposed method had several advantages over existing methods including simpler programming, higher computational efficiency and independence from line-broadening coefficients that, even if available, may not be very accurate. Titanium alloy samples were used as the testing materials. Correction of self-absorption effects was demonstrated by improved linearity of the Boltzmann plots and accuracy of the analysis was also improved when compared with data obtained when the algorithm was not used.

Three papers have discussed the use of *laser ablation – spark induced breakdown spectroscopy* (LA-SIBS) for the analysis of copper alloys⁵⁰, aluminium alloys⁵¹ and both brass and aluminium alloys⁵². This technique uses a spark to re-excite a plasma produced by a laser ablation unit and then the light emitted is characterised and quantified. A Nd:YAG laser operating at 1064 nm and at a repetition rate of 1 kHz was used to ablate the samples in the first instance and then the spark was used to prolong the plasma and promote the breakdown of the ablated sample further. In one example⁵¹, the detection limits for Cr, Cu, Mg and Mn were 9, 7.8, 11.1 and 20.1 mg kg⁻¹ which represented improvements of 4 – 10 fold compared with ordinary LIBS. Precision was excellent, with RSD values of 3 – 4% being obtained. Another of the papers⁵⁰ described the compact multi-channel fibre-based spectrometer used. Detection limits for Al and Pb using the system in a non-gated operation mode were 1.9 and 15.5 mg kg⁻¹; again representing an improvement of between 6 and 11 fold compared with those obtained using LIBS alone under the same laser-ablation conditions. The third of the papers⁵² used a gated pulsed high voltage power supply as power source for the spark discharge and then studied the delay between the high voltage pulse and the laser pulse. The orientation of the electrodes was also studied. By changing electrode orientation and by increasing the time delay, it was possible to change the discharge from a V-shape to a parallel arrangement. Both configurations had advantages. The v-shaped discharge could ablate more sample and increase the diameters and depths of the craters, whereas the parallel arrangement was more discrete in that it did not ablate new sample area other than that already ablated by the laser. In the parallel configuration, emission intensity decreased with increasing time delay but increased with discharge voltage. Under optimal conditions, improvements in sensitivity were again reportedly 4 – 10 fold better than standard LIBS.

Two papers have reported the *analysis of solder*. In one by Huang *et al.*⁵³ a forensic analysis of lead-tin solders was undertaken using ICP-MS. The authors pointed out that lead-tin solder is an integral part of many improvised explosive devices and therefore a forensic analysis of them could help in evidence gathering. Samples of solder (approx. 10 mg) were acid digested using 2 mL of nitric and 0.5 mL of hydrochloric acids and then heating to 150 °C. After further addition of nitric (8 mL) and hydrochloric (2 mL) acids, the digest was diluted to 50 mL. Samples were then diluted a further 100-fold prior to analysis. The analytes Bi, Cu, Ni and Sb as well as Pb and Sn were then determined. External calibration was achieved through acid digestion and appropriate dilution of the standard solder sample NIST SRM 1131. Eight different solder samples were analysed and distinguishable differences between the analytes were observed enabling a discrimination to be made. The authors then extended the study to see the effects of a heating gun on two different solder types. An increase in Cu concentration was observed for the sample with a rosin core. This contamination could, according to the authors, be used to provide information on the type of soldering gun used if the solder used contained a rosin

core. The other paper described the use of LA-ICP-MS to analyse lead-free solder chips⁵⁴. The analytes Ag, Cu, Pb and Sn were determined. Calibration was achieved using a standard solution matrix matched to the Sn content of the sample. This solution had to be prepared in nitric acid to prevent precipitation of Ag. This helped maintain linearity of the Ag calibration curve. Analysis of NMIJ CRM 8203-a provided data in good agreement with certified values as long as the fluence of the LA system was maintained at over 12 J cm⁻². At fluences below that, elemental fractionation occurred. It was noticeable that uncertainty values were very high. This was attributed to potential inhomogeneity of the sample at the micro-scale.

A host of other disparate applications have been published. These included a *room temperature chelate vapour generation* prior to atomic fluorescence detection for Ni determination in a variety of samples including aluminium alloy⁵⁵. The alloy (0.1 g) was dissolved in 30 mL of 6 M HCl. The presence of methanol or ethanol at a concentration of 2% v/v enhanced vapour generation by a factor of 2.6. Under optimal conditions, a vapour formation efficiency of 50% was achieved. The LOD was 1.12 ng mL⁻¹ and precision at 40 ng mL⁻¹ (n=10) was 2.9%. The mechanism of formation of the Ni-diethyldithiocarbamate chelate vapour was not fully understood and will be examined in future work. Alkali and alkaline earth elements caused no interference, but transition elements, e.g. Fe, Mn and Zn did – even at quite low concentration. These interfering ions had to be removed using a solvent-impregnated resin with a tertiary amine extractant prior to the vapour generation step. The method was validated through the analysis of a certified water sample (GSB07-3186-2014) and digests of a certified aluminium alloy (LD2). Results were in good agreement with certified values.

The *analysis of high purity metals* has been the subject of three papers. One by Medvedev *et al.*⁵⁶ described the analysis of high purity cadmium. The solid sample was weighed into an electrothermal vaporisation (ETV) device prior to detection using ICP-OES. The temperature program of the ETV device was optimised and an ash / char temperature of 900 °C was sufficiently high to remove the cadmium matrix. The analytes (Al, Au, Be, Bi, Co, Cr, Fe, Ga, In, Mn, Ni, Re, Sn and V) were then vaporised at 2400 °C and transferred to the ICP-OES instrument for detection. Detection limits were improved by a factor of between 3 and 670 when compared with ICP-OES using a 2% cadmium solution and conventional nebulisation. No suitable CRM was available and so method validation was through an independent technique (ICP-MS) and through spike / recovery experiments. It is noticeable that Cu, Pb and Zn are not among the analytes. This is presumably because they will also be at least partially lost at a char temperature of 900 °C. A paper by Fu *et al.*⁵⁷ described the analysis of high purity (5 N, i.e. better than 99.999% pure) cobalt powder using a triple quadrupole ICP-MS instrument. The sample was first dissolved using a mixture of nitric and hydrochloric acids with microwave assistance. The dissolved samples then underwent analysis using the instrument with a range of reaction gases being

tested to overcome interferences. Addition of oxygen enabled the analytes As, P, S, Se and V to be determined at their respective oxide mass, e.g. AsO^+ at m/z 91, etc. Addition of hydrogen to the reaction cell helped shift interferences on Ca and Si enabling the two analytes to be determined at their own isotopic mass. A mixture of ammonia and helium introduced to the cell helped form cluster ions and enabled interference-free determination of Cr, Cu, Fe, Mn, Ni, Ti and Zn. The same reaction gas mixture also enabled Al, Mg and Na to be determined because polyatomic interferences on these analyte isotopes formed cluster ions and were, hence, shifted away from the measurement regions. In all cases, matrix effects were overcome by the on-line addition of internal standard elements. Detection limits were in the range 0.02 – 97.5 ng L⁻¹ and calibration curves demonstrated good linearity. Analyte spikes gave recoveries in the range 91.6 – 109%, which was deemed acceptable. The third paper⁵⁸ determined S in copper metal and copper alloys using isotope dilution (ID)-LA-ICP-MS. The aim of the study was to combine the benefits of ID and LA-ICP-MS to avoid the time-consuming and laborious sample preparation procedures (matrix separation) that are usually required for conventional ID-MS for the determination of S. The samples were spiked with the isotopically enriched solution, dissolved and then the resulting digests absorbed onto polyethylene frits. The frits were then analysed using LA-ICP-MS. The advantages of the method included the very low S signal in the blank samples and that spiking with known amounts of S showed that the frits absorbed more than 99.5% of the S. Calibration curves demonstrated good linearity up to 40 µg of S. The methodology was validated through the use of the reference materials BAM-376a, BAM-228 and BAM-227 which delivered 2, 5 and 11 µg of S to the frits, respectively. Pre-analysis of the samples using external calibration LA-ICP-MS had indicated values of 0.9, 5.1 and 8.5 µg g of S (measured at m/z 32). Results for the ID-LA-ICP-MS were compared with those using conventional ID-ICP-MS with Pearson's coefficient correlating the two sets of data giving a value of 0.999. The relative expanded measurement uncertainty of the ID-LA-ICP-MS data ranged between 10 and 26%. The procedure was, according to the authors, traceable metrologically to the SI because of an unbroken chain of comparisons, each with their own uncertainty budget. The overall methodology was deemed to be reliable and acceptable.

The determination of Hg during the analysis of *dental amalgams* using LIBS was described by Castellon *et al.*⁵⁹. Several samples with matrices composed of differing proportions of silver, copper and tin were analysed. Delay times between the laser pulse and the measurement of the spectra were tested over the range 1 to 5 µs. Calibration curves were prepared and steps were taken to compensate for the matrix effects and changes in electron number density and plasma temperature that arise from them. The paper discussed this in detail as well as the effect of the delay time on the accuracy of analysis.

Two papers were presented that discussed *the analysis of parts of nuclear reactors*. A paper by Galmed *et al.*⁶⁰ discussed the measurement of surface hardness of titanium samples that had been bombarded by carbon ions. The titanium samples comprise the inner reactor walls of a *nuclear plant* and their exposure to energetic ions is known to change their physical properties. The authors used LIBS for the analysis. The surface hardness was assessed by measuring variation in the plasma excitation temperature. The results were in good agreement with those obtained using conventional means. A similarly nuclear themed application was presented by Warchilova *et al.*⁶¹. These authors described the use of LA-ICP-MS for monitoring the corrosion of nickel-based samples used as structural materials for nuclear reactors that had been exposed to molten fluoride salts.

1.3 Cultural heritage: metals

With cultural heritage samples, it is usual to try and inflict as little damage as possible. This is true whether they be metal objects, ceramics, glasses or any other material. The premise, of course, is that there is little point in analysing priceless materials if they are to be destroyed or disfigured during the analysis. The use of analytical techniques that are either non-destructive (e.g. XRF) or minimally destructive (e.g. LA-ICP-MS/OES, LIBS) are therefore more common than other techniques. A review of LIBS analyses in cultural heritage samples was presented (with 212 references) by Botto *et al.*⁶². The review covered several material types including pottery, metals, pigments, glass etc. It also covered the use of different types of LIBS analysis and LIBS used in conjunction with other techniques, including Raman, XRF and MS. Specific applications, e.g. those analyses made under water and those used in support of restoration were also discussed. New trends for LIBS in the area were also discussed. These include μ -LIBS, 3D elemental imaging and nanoparticle enhanced LIBS.

A paper by Lazic *et al.*⁶³ compared the techniques of LIBS, XRF and PIXE for the analysis of egg tempera pigments on gypsum, oil paints on gypsum, glazed ceramics and Roman coins. The LIBS analyses were undertaken for all sample types, an XRF instrument was used for the coins and a portable XRF instrument used for the pigments and ceramics and the PIXE was used to analyse pigments and ceramics. Both major and minor analytes were determined. The results were compared as were the possibilities for lateral and depth-resolved data. The PIXE was capable of best lateral resolution (1 μm) compared with the LIBS (10 – 50 μm) and the μ -XRF (50 – 100 μm). In all cases, the sensitivity decreased with the spot size. For depth resolution, the LIBS had by far the best resolution (1 μm compared with tens of μm for the other techniques).

The reliability of the data produced using a portable XRF instrument when *analysing corroded copper-tin alloys* was discussed in a paper by Robotti *et al.*⁶⁴. Samples of copper – tin alloy (88:12), similar in composition to ancient Egyptian alloys, were corroded in three different solutions containing

aggressive anions. Solution 1 was ammonium chloride and ammonium carbonate, solution 2 was potassium chloride, copper sulfate pentahydrate and sodium sulfate decahydrate adjusted to pH 3 using sulfuric acid and solution 3 was copper nitrate and sodium chloride. After the corrosion period of up to three months, the samples were removed, and analysed using portable XRF. Cross-sections of the samples were also analysed using SEM-EDS. A chloride-based solution led to a de-cuprification and made the XRF data less accurate. This was attributed to a build up of tin compounds. Another problem was the onset of bronze disease, i.e. the formation of atacamite and paratacamite. Using the “patina” and “metals” algorithms of the instrumental software enabled accurate information to be obtained from samples immersed in solutions 1 and 3. However, without their use, it was impossible to obtain accurate data.

Many of the applications for cultural heritage samples give good detail of the archaeology aspect, but are often somewhat light on analytical detail. Those that give no detail will therefore not be discussed further. Those that give an indication of method validation / quality control or those that use the data in a novel fashion, e.g. elucidating trade routes, provenance studies etc. are shown in Table 1.

Table 1 Cultural heritage applications of metals

Analyte	Matrix	Technique	Comments	Reference
Ag and Cu	A tetradrachm from the period of the emperor Claudius	XPS TOF-SIMS SEM-EDX	Surface analysis techniques as well as some depth profiling using TOF-SIMS used to identify composition and distribution of analytes. Minimal damage caused.	⁶⁵
Ag, Au, Cu	Necklace of Carambolo hoard	μ-XRF	Portable μ-XRF instrument developed that had a spot beam with radius of a few μm. The technical details of the instrument were given. Ternary diagrams plotted to distinguish between two different alloys used to manufacture some of the pins of the necklace.	⁶⁶

Cu, Pb, Sn	Soldering found on handle attachments of Roman situlae	μ-EDXRF SEM-EDS Optical microscopy	μ-EDXRF instrument used that had a spot size of approximately 70 μm in diameter. Quantitative analysis using fundamental parameters method. Two reference materials used: phosphor bronze 551 and leaded bronze C50.01. Solders contained 30 – 60% Sn.	67
Organic coatings	Ancient silver artefacts	XRF	Thickness of protective organic coatings on silver artefacts determined. Three mylar sheets with certified thicknesses were placed on a silver substrate and measured for validation. Three different quantification protocols tested: empirical and theoretical calibrations and a Fundamental Parameters approach. Data compared with the eddy current technique. The empirical approach provided the most accurate data.	68
Various (16)	Ancient gold products from the Black Sea region	LA-ICP-MS	Micro-geochemical features of micro-inclusions in the artefacts examined using LA-ICP-MS. Platinum group elements and other metals determined. Ternary plots of Ir, Os and Ru used to distinguish samples from different sites.	69

			Two sources of gold identified and cupellation suggested as being the most common method of refinement.	
Various (18 +REE)	Slag materials from early iron production in Croatia	XRF ICP-MS ICP-OES SEM-EDS	Microwave assisted digestion employed for ICP-OES and -MS detection. Pellets prepared for XRF analysis. Two CRM used for validation: NIST 1155a steel and TRM-2 rare earth ore. Analytical data underwent auto-scaling and logarithmic transformation prior to being input to hierarchical cluster analysis and PCA. Three types of slag identified: iron rich tap slag, bloom slag and ceramic-rich slag.	⁷⁰
Various (16)	Prehistoric bronze artefacts from Naples and Salerno in Italy	μ -XRF ICP-MS X-ray powder diffraction SEM-EDS	Provenance study of artefacts made using Pb isotope ratios. Samples (5 mg) were dissolved in HNO ₃ , passed through a column of Sr-Spec resin and the matrix components washed off using 1 mL of 1 M HNO ₃ . Lead eluted with 3 mL of 0.01 M HNO ₃ and isotope ratios determined on a multicollector ICP-MS instrument. Mass bias was corrected for using Tl and NIST 981 was used for monitoring external reproducibility.	⁷¹

Various (Ag, As, Bi, Cu, Ni, Sb and Sn) + Pb isotopes	Late Roman Republican lead artefacts from Portugal	ICP-MS	Twenty two samples acid digested and analysed using quadrupole ICP-MS. NIST 981 common Pb isotope standard and BCR 288 used for quality control purposes. Factor analysis and cluster analysis using Ward's method used for data analysis. Binary plots used for Pb isotope ratios. Galena was the most probable Pb source although some samples with high Cu may have been produced from litharge. Lead isotope ratios indicate a probable Iberian provenance.	⁷²
---	--	--------	---	---------------

2 Organic chemicals and materials

2.1 Organic Chemicals

Overcoming matrix effects remains a challenge within the analytical community; especially in secondary ion mass spectrometry (SIMS). This can impact the results. In order to establish the extent of matrix effects three binary organic mixtures were sputtered with argon and analysed utilising 25 keV Bi_3^+ and depth profiles obtained using SIMS⁷³. It was observed that matrix effects approximately scale with mass to charge ratios as smaller effects were noted for low mass ions. In addition, the presence of hydrogen was crucial as the likelihood of charge transfer decreases after a loss of H^+ and therefore becomes less favourable. The authors discussed the theory of the observed phenomenon in great detail and could conclude that ion velocity, fragment chemistry and the point of secondary ion point of origin are all contributing factors to the observed matrix effects.

Routine *determination of Br* has been a challenge in AAS because of its resonance line lying in the UV region at 148.86 nm. Turhan *et al.*⁷⁴ therefore developed a method to determine Br *via* the molecular absorption of BaBr (520.819 nm). Following method optimisation, pyrolysis and volatilisation temperatures were set at 700 and 2,200 °C, respectively. Neither Pd modifier nor a Zr coating was utilised in the developed method. The formation of molecular BaBr was achieved by using

10 µL of 25 mg L⁻¹ Ba. Spike recovery studies on commercial drug samples showed no significant non-spectral interferences. The characteristic mass was 4.0 ng with a method LOD of 1.7 ng. However, it was noticed that spike studies were only performed for two of the four drug samples present. It would have further supported the accuracy of the developed method had all four samples been investigated for their spike recovery. In addition, excellent linearity of R² = 0.999 was reported. However, this had only been investigated for a range of up to 1 µg Br, which seems rather narrow. Nonetheless, it was a promising approach to enable Br detection using AAS.

2.2 Fuels and Lubricants

This year the numbers of papers in this section has increased, particularly in the fields of crude oils and alternative fuels. There seems to have been a shift from conventional oil and crude oil analysis to more environmentally friendly alternatives, some somewhat unconventional such as Amazonian Sailfin Catfish. There also seems to be interest in using fly ash and other by-products as possible feed stocks for other industries such as REE extraction, possibly reflecting the global demand for these elements in the modern world and the subsequent increase in their price.

The analysis of coal has seen a decrease in papers this year, including in the number using LIBS. However, ETV seems to have had a renaissance as it is perceived to be more environmentally friendly than conventional sample dissolutions with solvents and acids. The technique of ETV was used by several authors as a sample introduction step linked to other instrumentation.

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

Three papers were of interest in this section, the first by Souza *et al.*⁷⁵ investigated the use of *GF AAS for the determination of volatile and non-volatile Ni and V in gasohol after extraction by emulsion breaking*. The determination by difference of the total, non-volatile and volatile fractions containing Ni and V was carried out by assessing the differences in the thermal behaviour of the species during the pyrolysis step. The detection limits for Ni were 3.5 µg L⁻¹ for total content and 1.7 µg L⁻¹ for the non-volatile fraction and for V 1.1 µg L⁻¹ for total content and 0.42 µg L⁻¹ for the non-volatile fraction. This is an interesting approach and yields more information on the forms of the Ni and V present and their possible origin than the total Ni and V concentrations alone.

The next paper of interest, by Wu *et al.*⁷⁶, described a method for the *determination of As, Cd, Hg, Pb and S in fuels using ETV-ICP-MS*. The aim of this method was to simplify sample preparation from acid digestion or ashing to a simple emulsion step and to minimise interferences. The sample was introduced in the form of an emulsion and Pd used as a modifier. Oxygen was used in the dynamic reaction cell of the instrument and As was measured as AsO at m/z 91 and S as SO at m/z 48. The

detection limits estimated from standard addition curves were 0.07, 0.1, 0.07, 0.07 and 39 ng g⁻¹ for As, Cd, Hg, Pb and S, respectively. A number of samples were analysed and good correlation between the ETV-ICP-MS method and conventional sample digestion was obtained.

Lu *et al.*⁷⁷ described a method for the determination of S in petroleum fuels using sector field ICP-MS. Legislation by the EU requires that gasoline and diesel contain less than 10 µg g⁻¹ of S and they are looking to lower this limit. Therefore, more sensitive methods for this analysis are currently required. For this method the samples were diluted 1000 fold with IPA or an IPA-toluene mix and Co added as an internal standard. The dilution factor could be decreased if lower detection limits were needed. The isotopes ³²S and ³⁴S were used for the analysis with the resolution of the sector field ICP-MS instrument adjusted to 4000 to resolve the polyatomic interferences. Detection limits for this method were between 0.09 and 0.17 ng g⁻¹.

2.2.2 Coal, peat and other solid fuels.

The first contribution in this section is from Henn *et al.*⁷⁸ who assessed the *feasibility of As, Sb, Se and Te determination in coal using ETV-ICP-MS*. In order to overcome the limitations of sample preparation methods, ETV was proposed for the introduction of solid coal samples to the ICP-MS instrument. A permanent modifier was made on the graphite platform by adding a solution of 1000 mg L⁻¹ Ir to it and then drying using an IR lamp. Samples were weighed on to the graphite platform, which was then inserted into the furnace connected to the ICP-MS instrument. The analysis was acquired in peak hopping mode and the peak area integrated. The Ar dimer signal was monitored to compensate for plasma oscillations during the vaporisation step. Samples and the CRMs NIST1632b, NIST1632c and NIST1635 were also digested using a conventional method to compare with the new ETV method. Results from both methods showed good agreement with the certified values. The LOQs from the ETV method were 0.03 µg g⁻¹ for As, 0.01 µg g⁻¹ for Sb, 0.03 µg g⁻¹ for Se and 0.006 µg g⁻¹ for Te. These compared favourably with the LOQs obtained using the digestion method which were 0.02 µg g⁻¹ for As, 0.04 µg g⁻¹ for Sb, 0.07 µg g⁻¹ for Se and 0.007 µg g⁻¹ for Te.

A paper by Iqbal *et al.*⁷⁹ was the first of two LIBS papers and investigated the *compositional analysis of Coal using calibration-free LIBS*. A high-power Q-switched Nd:YAG Laser, (532nm, 5ns pulse width and 10 Hz repetition rate) was used and the optical emission spectra were obtained using a HR 4000 spectrometer covering the wavelength region from 200 nm to 1100 nm. The emission spectrum contained the lines for Ca, Si, Fe, Ti, Mg, Na, K, Li, Al and C along with traces of Ba, Sr and Mn. The intensities of the observed spectral lines were corrected for self-absorption using the internal reference line. The excitation temperature was calculated using the Boltzmann plot method and the Stark broadened H-alpha line profile was used to determine the electron number density. A

calibration-free technique with a fixed slope was used for the quantification of C and other elements and a laser-ablation time of flight LA-TOF-MS instrument was used to obtain mass spectra of the same samples. All the elements identified in the optical emission spectrum were also observed in the LA-TOF-MS mass spectrum. A CRM coal sample SARM 20 and a sample of the Pakistani Thar Coal were analysed. The values obtained for the CRM were in good agreement with the certified values. The second paper in this section to use LIBS was submitted by Yao *et al.*⁸⁰ who investigated the *LIBS spectral properties of coal with different volatile contents*. Five coal samples with different amounts of volatile components were analysed and were compared with the same coal samples after heating at 900 °C for 7 minutes to produce char samples. The intensities of nearly all the emission lines were lower for the raw samples than those of the char samples. This indicated that a large amount of energy from the laser pulse is used in the pyrolysis process causing variation in the elemental results. This was improved by using the char samples which showed less variation.

Zhu *et al.*⁸¹ described an interesting new instrument for *laser ablation single particle aerosol mass spectrometry for the direct analysis of raw coal samples*. Particles were ablated from the surface of the solid material and these particles then entered the single particle aerosol mass spectrometry instrument for on-line simultaneous size and chemical composition analysis. The results were then processed by software to characterise the coal sample. The main components observed in the mass spectra of the samples included metallic and non-metallic elements, elemental carbon, organic carbon, and other compounds. The particles ablated from the five coal samples were divided into nine classes according to their primary chemical composition and were used as particle markers to characterise the coal samples. This approach avoided time-consuming chemical digestion procedures usually used for coal characterisation. Although the method has merit, further work on optimisation of the data analysis methodology is required to achieve the levels of accuracy required for its routine use.

Another interesting paper, by Husakova *et al.*⁸² described the *determination of 11 elements in fly ash by orthogonal acceleration ICP-TOF-MS*. This analysis is commonplace on conventional ICP-MS instruments, however the orthogonal acceleration ICP-TOF-MS instrument has some advantages over conventional quadrupole instruments. This includes its higher resolution which can be an advantage for resolving interferences observed in conventional ICP-MS instruments. The CRMs CTA-FFA-1 and NIST 1633b were used for validation of the method and were prepared using microwave extraction with NH₄F. Eleven elements were determined: As, Be, Cs, Li, Ni, Rb, Sb, Se, Tl, U and W. All recoveries were within $\pm 10\%$ of the certified values. The LOD values obtained were 150, 98, 2.1, 37, 314, 209, 31, 476, 1.6, 0.09 and 17 $\mu\text{g kg}^{-1}$, respectively.

The final paper in this section is by Souza *et al.*⁸³ who investigated *petroleum coke sample preparation strategies for Ce and La determination using ICP-OES employing a desolvating nebuliser*. Various digestion strategies were tested, however microwave induced combustion using 400 mg of coke, an oxygen pressure of 20 bar and the addition of 50 μL of 6 mol L⁻¹ NH₄NO₃ with the final solution containing 2.5 mol L⁻¹ HNO₃ gave the best recoveries. The concentrations of Ce and La obtained in the final solutions were 0.65 ± 0.07 and $3.32 \pm 0.08 \mu\text{g g}^{-1}$, respectively. These compared well with data obtained using NAA with agreement between the two being greater than 94%.

2.2.3 Oils – crude oil and lubricants

One review article containing 73 references from Sama *et al.*⁸⁴ was of note in this section. It covered *recent trends in elemental speciation of crude oils and heavy petroleum fractions*. This article covers most techniques including GC-ICP-MS and -OES, LC-ICP-MS and -OES, TLC ICP-MS and GPC-ICP-MS and gives a reasonable overview of the current state of play of these techniques with regard to crude oils and their fractions. Another paper in this section was by Sanchez *et al.*⁸⁵ who looked at the *analysis of crude oil and heavy fractions using a high temperature torch integrated sample introduction system*. The elemental analysis of heavy cuts is problematic because of their high viscosity and because they require large dilution factors to avoid nebuliser blocking and matrix effects that are commonly seen with conventional solvent dilution work. The authors described a method using a low inner volume spray chamber with a wall temperature set at 400 °C. This increased the analyte transport efficiency to virtually 100% regardless of sample matrix allowing universal calibration for all matrix types. The resulting sensitivity was an order of magnitude higher than that seen using a conventional spray chamber and quantitation limits were reduced by a factor of between 2 and 20 depending on the sample and element considered. The high transport efficiency, lower sample dilution and narrower peaks also allowed increases in sample throughput by a factor of 2.

A contribution by Vieira *et al.*⁸⁶ described a method for the determination of *Ca, Mg, Na and Sr using a nano-emulsion and ICP-OES analysis*. The emulsion was prepared from 0.2 g of crude oil, 1.0 mL of HNO₃, 0.6 mL of o-xylene and 0.80 g of Triton X-100 made up to 20 mL. This emulsion proved to be stable for 8 days. The accuracy of the procedure was evaluated through the analysis of standard reference materials NIST 1085b and NIST 1634c and by addition/recovery tests. The values obtained with this procedure were in accordance with the certified values for Ca, Mg and Na for both standard reference materials. Spike recoveries in crude oil were between 92.8 ± 3.8 and $102 \pm 7.2\%$ for all elements.

A novel paper by Ruhland *et al.*⁸⁷ investigated the *analysis of metal containing nanoparticles in gas condensates using asymmetric field flow fractionation coupled with ICP-MS/MS*. Fractograms

obtained indicated the presence of nanoparticles containing a number of elements including Al, As, Co, Fe, Hg, Mn, P, S, Ti and Zn. This work is very much in the development stage and identified the need for new field flow fractionation membranes that are more suitable for organic matrices. This is however a promising field for future work.

A paper by Fetter *et al.*⁸⁸ described a sample preparation protocol for the *accurate determination of radiogenic Pb and stable Zn isotopic compositions of crude oil*. This protocol which can be used on sample sizes as low as 5 mL used liquid-liquid extraction into an aqueous phase followed by standard anion-exchange column chromatography to separate the elements of interest. The sample was split into two aliquots with 95% being used for multicollector-ICP-MS isotopic determinations while the other 5% was used for conventional ICP-MS quantitative measurements. Reproducibility was on a par with routine state-of-the-art Pb and Zn isotopic measurements for other types of geological materials and procedural blanks were negligible relative to the amounts of Pb and Zn typically separated from the crude oils.

Silva *et al.*⁸⁹ undertook a study to show the feasibility of REE determinations in crude oils using ETV-ICP-MS. A citric acid modifier was used to produce calibrations using aqueous solutions and pyrolysis and vaporization temperatures were 700 and 2200 °C, respectively. Since the REE have the affinity to form refractory compounds inside the electrothermal vaporiser, the use of a modifier gas (Freon R-12) at a flow of 3.0 mL min⁻¹ was necessary for this analysis. The influence of sample quantity was evaluated, and accurate results were obtained even using a relatively high mass of crude oil (up to 18 mg). Accuracy was evaluated by comparison of these results with those obtained using ICP-MS with an ultrasonic nebulizer after a high pressure microwave assisted wet digestion and a microwave induced combustion procedure. No statistical difference was observed between the results. The limits of quantification for REE by ETV-ICP-MS were 0.02-0.8 ng g⁻¹, which were lower than those obtained using the ultrasonic nebulizer ICP-MS technique (0.6-5.1 ng g⁻¹). Negligible blank values and precision of better than 12% RSD show the feasibility of the proposed ETV-ICP-MS method for routine determination of REE in crude oils.

An interesting paper from Michel *et al.*⁹⁰ described a *portable XRF technique for the rapid identification of Deepwater Horizon oil residues*. Oil residues are found on Gulf of Mexico beaches because of the Deepwater Horizon incident alongside oil residues from natural seepage and other anthropogenic sources. To identify the origin of oil residues found on the beaches it is critical to have techniques that can be used in the field and can provide rapid identification. In this technique no extraction steps were performed on the samples prior to analysis. A total of 595 sub-samples from 119 unique samples were used to train interpretable machine learning models to infer the presence or

absence of Deepwater Horizon oil from the XRF data. Twenty five elements were used for the model which was able to determine with 95% accuracy if the sample was of Deepwater Horizon origin. This approach could be widely applied to different oil spills worldwide to aid oil spill identification.

2.2.4 Alternative fuels.

The first contribution in this section is from Lourenco *et al.*⁹¹ who described a method based on *reverse-phase dispersive liquid-liquid micro-extraction for the extraction and preconcentration of Ca, K, Mg and Na in biodiesel samples*. Flame spectrometry was used for analysis in the emission mode for K and Na and in absorption mode for Ca and Mg. The extraction/preconcentration step of the analysis was performed using a mixture of isopropanol and HNO₃. The aqueous phase containing the analytes was separated by centrifugation. Parameters such as sample mass, volume of dispersant and extractant solutions, use of ultrasound, centrifugation time and temperature were evaluated. Analysis was performed using external calibration with aqueous reference solutions. The LOQ for Ca, K, Mg and Na was 0.05, 0.02, 0.08 and 0.04 µg kg⁻¹, respectively. The accuracy was evaluated by recovery tests, which ranged from 93.9 to 108.1%, with a precision of better than 3% RSD for all analytes. The proposed method was then applied to five biodiesel samples produced from different raw materials. Compared with conventional sample preparation techniques this method was simple, low cost with low reagent consumption and provides LOQ values significantly below the limits required for these elements in biodiesel. A similar extraction method was proposed by da Silva *et al.*⁹². This method was developed for the determination of Ca, K, Mg and Na in biodiesel using AAS and was based on the extraction of the analytes into a 'micro drop' of an acid/alcohol extraction solution at the bottom of a conical tube. The best results were obtained with a sample mass of 3.0 g and 780 µL of 5.0% (v/v) HNO₃/isopropyl alcohol at a ratio of 3:1. The efficiency of the sample preparation procedure was evaluated using a recovery test, with recoveries within 90.2–94.7% for all elements being obtained at a precision of better than 2%. The LOD were 32.3, 5.8, 4.3 and 3.0 µg kg⁻¹ for Ca, K, Mg and Na, respectively.

A similar approach was also used by Vinhal *et al.*⁹³ for *the GFAAS determination of Cu, Ni, Pb and V in gasolines containing ethanol*. This was an emulsion-breaking extraction method, again using HNO₃ and a short chain alcohol. After breaking the bottom phase containing water, the dispersing agent and ethanol were analysed using GFAAS. Recovery tests were performed and produced analyte recoveries of between 87 and 116%. The LODs for this method were 0.7, 0.1, 0.8 and 1.6 µg L⁻¹ for Cu, Ni, Pb and V, respectively.

An interesting method was proposed by Meira *et al.*⁹⁴ who described the *determination of Cd, Cr, Cu, Mn, Pb and V in ethanol fuels using XRF after magnetic solid phase extraction using CoFe₂O₄ nanoparticles impregnated with 1-(2-pyridylazo)-naphthol*. The extraction and preconcentration step

was followed by direct determination of the analytes in the solid phase using EDXRF. The proposed method produced detection limits of: 0.013, 0.012, 0.012, 0.011, 0.016 and 0.009 mg L⁻¹ for Cd, Cr, Cu, Mn, Pb and V, respectively. This method was then successfully applied to the extraction and determination of these analytes in ethanol fuel samples.

Barela *et al.*⁹⁵ developed a method for *microwave assisted ultraviolet light digestion of biodiesel and subsequent analysis by sector field ICP-MS*. In this method a microwave with high pressure quartz vessels was used with ultraviolet radiation generated by a cadmium electrodeless discharge lamp working at 288 nm inside each quartz vessel. For the digestions, a sample size of 950 mg with 10mL of 7 mol L⁻¹ HNO₃ was optimum resulting in 4740 mg L⁻¹ of C in the final solutions. The reduction of the C content in the solutions to below 5000 mg L⁻¹ was important to reduce possible polyatomic interferences. This method was suitable for the simultaneous determination of Ca, Co, Cr, Cu, Mn, Ni, Pb, Sr and V. Low resolution was used for all elements except Cr which required medium resolution to resolve the ArC interference seen at m/z 52. Detection limits for this method were below 1 ng g⁻¹ for all elements except Cu, Mn and Ni which were 6.9, 4.8 and 2.8 ng g⁻¹, respectively. This is an interesting method but somewhat expensive and time-consuming for commercial routine industrial analysis where simpler, quicker methods are available for these elements at these detection limits.

A paper utilizing sector field multi-collector ICP-MS was presented by Barela *et al.*⁹⁵. This described a method for the *direct lead isotopic analysis of bioethanol using multi-collector ICP-MS with a total consumption sample introduction system*. In biodiesel samples, the determination of the total content of Pb is the normal analytical measurement made. However, isotopic analysis can give information on geographical provenance and type of raw material used for production. In this study isotopic reference materials for Pb (NIST SRM 981) and, to correct for mass bias, Tl (NIST SRM 997) were used. A high temperature torch integrated sample introduction system was also used, operating at 125°C to minimise mass bias. The results showed a lighter Pb isotopic composition for the bioethanol samples than the NIST Pb standard but they are similar to those reported for wine and other alcoholic beverages coming from fermentation and distillation processes.

Two papers describing methods for the analysis of biomass were of note. The first, by Liu *et al.*⁹⁶, described combining *polarizing filtered planar laser induced fluorescence with simultaneous laser absorption, quantitative LIBS and two colour pyrometry to analyse a burning biomass pellet*. The K release during the combustion of biomass fuel pellets was investigated. The temporal release profiles of volatile atomic K and its compounds from a corn straw pellet showed a single peak, whereas woody biomass pellets produced a dual-maxima distribution. For both biomass types the highest concentrations of K occurred in the devolatilization stage. The mass ratios between volatile atomic K

and its compounds in corn straw and poplar were 0.77% and 0.79%, respectively. These values agree well with chemical equilibrium predictions that 0.68% of total K will be in atomic form. A two-step kinetic model of K release was developed which gave better predictions during the devolatilization stage than the existing single-step model. Finally, a map of K transformation processes during combustion was developed.

The second biomass paper by Viljanen *et al.*⁹⁷ described *the real time release of Ca, K and Na during thermal conversion of biomass using quantitative microwave assisted LIBS*. A new burner which allowed linear calibration of LIBS measurement for release studies during thermal conversion was developed. Many of these fuels contain high concentrations of alkali metals and chlorine which are harmful for boiler structures and may cause operational problems. Therefore, detailed quantitative information on release behaviour is required. The analytical performance of conventional LIBS measurement was significantly improved by introducing microwave radiation to the laser-induced plasma. An enhancement of linearity and a 60-fold improvement of LOD were observed with microwave-assisted LIBS compared with conventional LIBS. The LOD of Ca, K and Na were 16 ppb, 19 ppb and 10 ppb, respectively. In-flame microwave radiation-LIBS measurement was then applied to record time-traces of K, Na and Ca during thermal conversion of a poplar pellet.

2.3 Pharmaceuticals and Personal Care Products

Spectrochemical elemental analysis has become *a requirement for pharmaceuticals and the raw materials used for their production*. This is to comply with regulations issued by the International Council for Harmonization of Technical Requirements for Registration of Pharmaceuticals for Human Use (ICH Q3D). There is a requirement to determine impurities to ever lower levels. A review containing 54 references of the research and development articles and scientific papers published since 2000⁹⁸ focused on ICP-OES and ICP-MS analysis of pharmaceutical products. The review included aspects of sample preparation, potential interferences, different calibration approaches as well as their analytical performance and validation parameters. The coupled technique of LC-ICP-MS has become an extremely useful tool for elemental speciation. A review focusing on the analytical performance in organic matrices and the effect interfaces have on factors such as efficiency, resolution, sensitivity and extra-column solute dispersion was published recently⁹⁹. For this purpose, 55 published studies were evaluated. Interfaces in the form of the sample introduction systems (nebuliser and spray chamber) and a flow-splitter to reduce the organic solvent load are most common. However, their effect on peak broadening during the initial separation has often not been addressed. An excellent graphical representation was given, highlighting that extra-column variance introduced by the interface can significantly affect the separation by reducing the available number of plates and therefore the

method's performance in terms of resolution and sensitivity. A second review highlighted that ICP-MS has become a valuable detection method when coupled to separation techniques such as (U)HPLC¹⁰⁰. Coupling methods and quantifying approaches for the detection of, for example, Br, Cl, I, P, S and Se in non-metal drugs were reviewed (149 references). In addition, the authors stressed the need for derivatisation when an ICP-MS detectable hetero-element is missing. This can be achieved by derivatising -OH, -COOH, -SH or -NH₂ functional groups.

Sample preparation remains a vital aspect of any analytical approach and recent publications have focused on its optimisation. An ultrasonic assisted micro-extraction of Cd and Pb in lipsticks and eye shadow utilising deep eutectic solvent was developed¹⁰¹. This approach is more favourable compared with the use of other ionic liquid solvents as they are biodegradable, biocompatible as well as non-toxic. An extensive multivariate approach (Plackett-Burman design) enabled the authors to show that the main factors affecting the extraction were time, volume of deep eutectic solvent and pH. Both Cd and Pb were complexed with ammonium pyrrolidine dithiocarbamate. Compared with other studies, the designed approach performed well, but LODs were amongst the higher ones reported. Results of multi-level spike studies further demonstrated excellent performance of this method with reported recoveries of 96.6 - 98.4% for Cd and 97.0 - 98.7% for Pb. Similarly, Koosha *et al.*¹⁰² developed a Cd extraction and preconcentration procedure following an extensive multivariate approach. Factors such as pH, concentration of complexing agent, volume of solvent, number of injections and time were assessed using a Plackett-Burman design. The optimisation of these factors was achieved following a Box-Behnken design and resulted in the following optimal parameters: complexing agent was 0.00155 mol L⁻¹ 1-nitroso-2-naphthol, extraction solvent was 130 µL of octanol, an ionic strength of 2 mol L⁻¹ NaCl and a pH of 6.5. A linear range of 2.5-650 µg L⁻¹ (R² 0.997) was achieved as well as a limit of detection of 0.68 µg L⁻¹. Excellent intra-day and inter-day precision of <2% were demonstrated. Applying the developed procedure to water, pharmaceutical materials and a certified reference sample showed spike (n=3) recoveries of 96.8 - 102.7%, highlighting the excellent accuracy and precision of the extraction. In addition, it was a highly specific approach as no interferences were observed for the 18 ions investigated.

Generally, sample preparation for traditional ICP-OES approaches is very labour intensive and can involve the use of strong acids such as HF, which is a serious safety concern and is often avoided by laboratories completely. Speranca *et al.*¹⁰³ reported a method of sample preparation that involved *using polyvinyl alcohol to convert sunscreen sample into a solid*. The obtained thin sample disc was analysed using LIBS to determine the Ti concentration. The LIBS spectra obtained were normalised and standardised utilising instrumental software. Results obtained using a digestion followed by ICP-OES detection were in agreement with LIBS results when applying a multi linear regression multivariate

calibration. However, no actual spike studies were performed. This would be beneficial in future studies to assess the method's accuracy. Currently, a labour-intensive and time-consuming ICP-OES preparation is used as a reference method. However, the recovery of the digestion has not been investigated and is likely to be affected by the multistep process. This work reported a promising alternative with simplified sample preparation helping to avoid the use of strong acids.

A different sample preparation approach utilised a sequential co-precipitation scheme. This was based on $\text{Mg}(\text{OH})_2$ and CaF_2 precipitation for detection of Cd in multivitamin/mineral supplements utilising an isotope dilution (ID)- ICP-MS method¹⁰⁴. The authors aimed to remove matrix interference (Mo and spiked Sn) from the supplements. Best results were achieved following a three-step co-precipitation approach. Interfering Ca was first precipitated in the form of CaF_2 after the addition of hydrofluoric acid, which also resulted in significant Mo and Sn co-precipitating. Addition of triethylamine to the supernatant further reduced Mo and Sn levels. After further addition of triethylamine 99.7% of Mo and 96.5% of Sn were successfully removed from the sample solution. In addition, this approach also removed salts (Ca, Cu, Fe, K, Mg, Mn, P and Zn) commonly found in the supplement matrix. This is beneficial as it helps to avoid matrix suppression effects as well as preventing salt build up in the ICP-MS components. Applying the developed procedure to CRMs showed excellent recoveries (ranging from 95.6 to 98.5%) for all three Cd isotopes assessed. In addition, it was demonstrated that 99.6 and 97.7% of Mo and Sn, respectively were removed from the supplement CRM. One drawback of this method is the safety concern arising from the use of HF. However, for experienced, well trained analysts this should not present any difficulties.

Ansar *et al.*¹⁰⁵ developed a capillary electrophoresis (CE)-ICP-MS/MS method for the detection of S (external and intra-liposomal) in doxorubicin HCL liposomal formulations, which are used in the treatment of leukaemia and various cancers. These liposomes encapsulate doxorubicin and promote targeted drug delivery as well as reducing negative side effects. The CE was utilised to separate external and intra-liposomal S which was achieved within 8 min. Traditional detection methods, such as UV/VIS spectrometry and conductivity measurements rely on the disintegration of the liposomes in order to measure intracellular S. This step becomes obsolete with the developed ICP method as the plasma itself disintegrates the liposomes. Utilising a triple quadrupole ICP-MS instrument, the interfering oxygen dimer at m/z 32 can be avoided as the mass transition of $^{32}\text{S}^+$ to $^{32}\text{S}^{16}\text{O}^+$ was achieved utilising O_2 as the reaction gas. Other figures of merit include a calibration range of 3 – 600 $\mu\text{g mL}^{-1}$, spike recovery of 95 – 102%, a LOD of 0.8 $\mu\text{g mL}^{-1}$, LOQ of 2.6 $\mu\text{g mL}^{-1}$ and inter- and intra-day precision at 3.2 – 4.4% and 1.9 – 5.8%, respectively.

Mercury remains an important contaminant monitored within pharmaceutical formulations.

The determination of thimerosal and inorganic Hg in vaccines utilising Fe³⁺- induced degradation with cold vapour atomic fluorescence spectrometry (CV-AFS) detection was reported by Xu *et al.*¹⁰⁶. Ferric iron has an induction effect on the vapourisation of organic Hg and was introduced into both sample and carrier stream. Inorganic Hg was determined in the presence of potassium borohydride and the concentration of thimerosal was calculated by subtraction of inorganic Hg concentration from the total detected amount of Hg. The presence of Fe³⁺ increased the fluorescence signal of thimerosal at concentrations of up to 10 mg L⁻¹, while not affecting the fluorescence signal of inorganic Hg. The developed method was applied to the analysis of rabies and hepatitis-B vaccines that had been spiked (n=3) with total Hg and thimerosal at three different levels, each. Excellent spike recoveries of 96.0 - 103% and 97.5 - 103% were obtained for inorganic Hg and thimerosal, respectively.

In recent years, the use of e-cigarettes has increased considerably. Hence, there is a need to ensure they are safe to use and meet regulatory requirements. Utilising gallium as an internal standard, Kamilari *et al.*¹⁰⁷ analysed e-cigarette liquids and their individual components for the presence of heavy metals (As, Cd, Cr, Cu, Ni and Pb). In contrast to a more traditional ICP based approach, the authors utilised total reflection XRF for the analysis. Results showed some individual components exceeding the regulatory limits for Cd and Cr. However, considering the dilution of these within the final product, the levels were judged to be acceptable. It was noted that no method validation data were available, which would be beneficial to illustrate the analytical performance of this method. In addition, it would have supported the method's performance claims to compare results with those obtained using other analytical methods.

In common with last year's review, *the manipulation and processing of large amounts of data* has been the focus of a number of studies. Some spectroscopy techniques, e.g. LIBS, are favourable because of their quasi-non-destructive nature and the speed of analysis. However, due to the large amount of data created, the interpretation requires time and expertise. A curve fitting regression model used in combination with WDXRF was utilised for the detection of Cd, Ni and Pb in seven pharmaceutical powders¹⁰⁸. The authors compared this methodology with results obtained by applying ordinary least square regression and partial least square approaches. Performance in terms of correlation (R²) and root mean square error (RMSE), which represents the average distribution scatter, was assessed. In 86% of data sets, curve fitting regression produced statistically smaller RMSE compared with the other two methodologies when calculated on a validation data set. The overall absolute error achieved was 3-5 ppm, which does not meet the needs of pharmaceutical applications. Nonetheless, it is a promising WDXRF quantification method for less demanding applications. In addition, it could further enhance the performance of more efficient XRF systems such as total

reflection XRF. It has been shown that analytical performance could be enhanced when using a multiple spectral line correction approach for the determination of Bi in different medicines utilising microwave induced plasma optical emission spectrometry (MIP-OES)¹⁰⁹. By summing the intensities of multiple Bi lines (223.061 and 306.772 nm) for both calibration standards and samples, it was possible to improve the analytical performance. The LODs reported were ~10 times lower compared with a more traditional direct analysis approach. In addition, the results were compared with a hydride generation method as well as a standard addition approach. Performance was comparable to that of hydride generation, without the need for time-consuming sample preparation. This is a promising technique for faster analysis with enhanced performance. However, it needs to be assessed for specific cases if lower specificity can be accepted for faster and more cost-effective analysis.

The suitability of Machine learning has been evaluated in analytical chemistry. In an effort to decrease sample preparation time, Parhizakar *et al.*¹¹⁰ assessed the suitability of attenuated total reflectance infrared (ATR-IR) spectroscopy in combination with partial least square – least square support vector machine modelling for the determination of Fe in ferrous syrups and drops. The spectra were baseline corrected (standard normal variate method). For this purpose, 158 samples were used to calibrate the model to then allow the analysis of 40 test specimens. In addition, Fe concentrations were obtained utilising AAS. This resulted in a multivariate model of spectral data obtained with both methods, allowing the prediction of Fe content utilising the developed model. The authors addressed the potential of over-training, which can be an issue for machine learning methods. Excellent correlation was observed for both calibration and cross-validation samples with R^2 values of 0.99 and 0.98, respectively. Since pharmaceutical preparations need to abide by strict regulations, it remains questionable if machine learning methods can fulfil the required precision and accuracy of more traditional methods. Nevertheless, it could prove to be useful, for example, to identify potential counterfeit preparations.

This approach to *counterfeit identification* has been investigated, for example, utilising EDXRF in combination with principal component analysis (PCA) and Soft Independent Modelling of Class Analogies (SIMCA)¹¹¹. The XRF spectra (scanning Na to U) were obtained for Plavix tablets, an anti-platelet medication. Reference samples were available from registered manufacturers or purchased in pharmacies. In order to account for normal variation two of the reference samples were generic samples containing the same active ingredient, but a different salt. Utilising the data obtained using EDXRF scans, PCA was able to visualise the similarities and differences between these reference samples and 10 suspected counterfeit samples. Both PCA on its own and when utilised with SIMCA enabled the authors to distinguish counterfeit samples from authentic samples allowing for fast screening of suspect samples. In addition, other analytical methods (HPLC) were applied to confirm

the authenticity of one of the suspect samples. However, it was noted that the validated SIMCA model was no more capable of distinguishing samples than the simpler PCA. In fact, PCA was able to show clearer discrimination between the counterfeit samples compared with SIMCA.

2.4 Organic materials: Cultural heritage applications

*A recent review assessing the work published over 20 years and citing 125 references, focused on the use of portable and laboratory-based instruments for the analysis of mediaeval wall paintings*¹¹². The authors pointed out that the work published in more recent years has focused on identifying degradation processes in an effort to aid preservation and restoration. Multi-technique approaches have been proven to yield the most information. Techniques that have been utilised were, for example, XRF, UV/VIS, FT-IR and Raman spectroscopy as well as SEM-EDS, MS and GC-MS. When sample preservation was not crucial, LIBS has proven useful for elemental characterisation. It should be noted though that the damage inflicted using LIBS can be minimal. A second review (84 references)¹¹³ highlighted the increasing use of synchrotron X-ray nano-probes in cultural heritage studies. Utilising nano-X-ray fluorescence, nano-X-ray diffraction and nano-X-ray absorption spectroscopy, it is possible to obtain insights into elemental composition, crystalline structure and speciation, respectively. The challenges that remain are the focusing of the beam, the sample preparation as well as data acquisition, analysis and interpretation.

The potential of *X-ray luminescence for cultural heritage applications* has been investigated by analysing samples of various shapes and dimension¹¹⁴. Initial tests with laboratory-based equipment showed results comparable to those obtained utilising cathodoluminescence and ion-beam-induced luminescence. This justified further optimisation with the aim of establishing a portable set up. For this purpose, a lead collimator, which narrows the X-rays from a tungsten anode to a spot, was utilised. The generated light was passed through a collecting lens and further transported to the spectrometer (250-630 nm) *via* an optical fibre. To avoid scatter X-rays, lead shielding was employed. In addition, a camera was utilised to evaluate the area under study. The collection lens was vital to obtain maximised signal and enable luminescence signals for a portable device which was based on a typical XRF set up. The developed device recorded luminescence spectra with an integration time of three minutes. This allowed the discrimination of lapis lazuli samples and aided provenance studies.

A hybrid system was developed for the analysis of heritage stones and model wall paintings that utilised pulsed laser excitation Raman, laser-induced fluorescence (LIF) and laser-induced breakdown spectroscopy signals¹¹⁵. For this purpose a nanosecond Q-switched Nd:YAG laser and a spectrograph were utilised. The spectrograph was coupled with a time-gated intensified charge coupled device which enabled detection with temporal resolution. Raman and LIF spectra were

obtained simultaneously, whereas after a changeover of approximately 2 minutes LIBS could be used. It took about 10 minutes to change to different excitation wavelength utilised in this work (532, 355, and 266nm). The Raman results enabled the differentiation of sulfate-based stones from those made of carbonate, whereas LIF provided information with regards to the nature of the organic residues. Moreover, the time-resolved LIF signals provided information of fluorescence origin, which can help to identify organic and inorganic emitters in both matrices studied. The combined results obtained for the model wall painting analysed by the hybrid system allowed identification of the pigment as red vermilion (HgS).

In common with other fields, *data manipulation and interpretation* remains a most vital step in the analysis of cultural heritage samples. Cheung¹¹⁶ reported a three-step pre-processing scheme for plume laser induced fluorescence, a minimally destructive multi-element analysis technique the data from which may be used for chemometric sorting. It was possible to reduce the single-shot uncertainty from 54% down to only 6.5% by rejecting dim featureless parts of the spectra as outliers (dimpest 5-10% of captured spectra), as well as subtracting the baseline. Finally, taking advantage of the linearity of fluorescence, the spectral areas were normalised. The developed scheme was applied to pre-process red seal inks and Chinese black inks which were consequently sorted using PCA. Applying this methodology, clean sorting was achieved even when using single-shot spectra.

The development of a *reliable and fast classification of LIBS spectra based on various computational intelligence models* was reported¹¹⁷. The aim was to simplify the current labour-intense process of LIBS data interpretation. Fifty ink samples were applied to 50 paper samples. Then LIBS spectra (185-904 nm) were collected utilising a Q-switched Quantel Ultra Nd:YAG laser working at a wavelength of 1064 nm and a 6 channel spectrometer equipped with a charge coupled device detector. Initial visual inspections after PCA allowed differentiation of the various papers used. However, the identification of inks proved to be more challenging. Hence, seven different computational intelligence algorithms, as well as pre-processing of the obtained spectra, were assessed for their ability to separate paper-ink samples. Best results were achieved utilising the Random Forest method achieving an accuracy, sensitivity, and specificity of 99.1, 86.3 and 99.5%, respectively. The methodology could provide useful information for both cultural heritage and forensic applications from an identification point of view.

Table 2 Applications of atomic spectroscopy of organic materials

Analyte	Matrix	Technique	Comments	Reference
As, Ba, Cd, Cr, Pb	Commercial fertilisers	MIP-OES	Microwave assisted digestion	118

			<p>of samples. "Multi-energy calibration" used for elemental determination. Digested sample split in two. One aliquot mixed 1:1 with a standard and the other mixed 1:1 with a blank. Multiple wavelengths used for determination. Full description was given. Agreement with certified values for the CRM NIST 695 was between 96 and 101%. Spikes yielded recoveries of 92 – 105%. Comparison with external calibration and standard additions made, with developed method being far superior for some elements.</p>	
Dinitrotoluene (DNT) isomers	Condensed phase	LIMS followed by LIBS	<p>Direct analysis of ground and pelletised powder samples of three DNT isomers. Samples were irradiated at 266 nm and the optical emission (300-900nm) passed to a CCD containing spectrograph <i>via</i> optical fibre. Initial laser shot (energy below ablation threshold) allowed collection of mass spectra. Second laser shot of higher energy at the same location enabled</p>	119

			associated LIBS spectra. Combined approach allowed differentiation of three DNT isomers following processing by discriminant function analysis.	
Various (12)	Drugs	HR-CS AAS	Time and wavelength-resolved screening test following acid digestion enabled pass/fail approach for elements detected at levels above LOD. The LODs reported were lower than permitted concentration as per guideline for elemental impurities in drugs. If any of the elements were detected they could be quantified separately. Method validation was performed. In drugs analysed Cr, Cu and Ni resulted in fails. However, once quantified levels were below permitted concentration.	120
Various	<i>Painting Exit from the Theater</i>	Synchrotron macro XRF	High energy synchrotron scans were performed at 12.9 keV and 38.5 keV. This enabled visualisation of new As, Cd, Cu, Sb, and Sb details in an underlying landscape.	121

Various	Wall paintings	External reflection FTIR, sequentially shifted Raman spectroscopy and XRF	Analysis performed directly on wall paintings; multi-analytical non-invasive approach allowing both mineralogical and chemical analysis of pigments. Main pigments identified were calcite, cinnabar, red and yellow ochre, green earths, Egyptian blue and carbon black.	122
Al, Ba, Ca, Co, Cu, Cr, Fe, K, P, Rb, S, Si, Sr, Ti, Zn	Painting model samples	LIBS, XRF	Depth resolved analysis of created model paintings. Unusual for cultural heritage field to use LIBS because of its partially destructive nature. However, LIBS (Nd:YAG laser 266nm) used to distinguish layers of different composition and to estimate their thickness as well as chemical composition. Results obtained by XRF analysis were comparable to those obtained utilising LIBS.	123
Multiple (scan 350-850nm)	Paper	Laser-induced fluorescence spectroscopy	Direct analysis of paper samples which enabled determination of the paper's age based on changes of the first derivative of the spectral peak at	124

			443nm (exponential curve $R^2=0.99$). Classification of paper samples was achieved through principal component analysis and <i>k</i> -means clustering algorithm.	
Multiple	Pigments on gypsum ground, glazed ceramic, Roman coin	LIBS, XRF and PIXE	Comparative analysis of different matrices to establish best suited technique. Once difference in sample area and thickness was taken into account results obtained for various techniques agreed well. LIBS showed superior sensitivity, but its destructive nature needs to be considered.	63
Relative intensity Al/O	Aluminized 2,4,6-trinitrotoluene	LIBS (in air and argon atmosphere)	For the LIBS analysis a Nd:YAG laser at 1064nm and with a 7 ns pulse duration was employed. Plasma emissions were recorded and principal component analysis was applied to differentiate samples. A calibration curve utilising relative intensities of Al/O enabled determination of detonation velocity and pressure as well as	125

			Al content in aluminised TNT.	
--	--	--	-------------------------------	--

2.5 Polymers and composites

There is no doubt that the most extensively researched analytical topic for polymers is *LIBS classification*. As well as numerous applications, a review article by Liu *et al.*¹²⁶ has also been presented. The review, containing 82 references, covered the instruments that have been used for plastic analysis, methods of discrimination between different plastic types, the qualitative and quantitative analysis of plastics and other applications. Also discussed were the calibration protocols used (including calibration-free LIBS) and the chemometric algorithms used to help classification of different plastic types. The last section discussed the use of LIBS for the analysis of plastic toys, food containers and E-waste. The authors finished off by proposing potential future applications and areas of research.

In addition to the review discussed above, numerous *applications of the LIBS analysis of plastics* for sorting or classification purposes have also been described. Many of them have the same format, i.e. the LIBS spectra of assorted plastics are used to train an algorithm and then the algorithm is used to identify the plastic type of 'unknown' samples. Included in this type of paper is one by Liu *et al.*¹²⁷ that described differentiation between 11 plastic types. There were 20 samples of each plastic type and each sample was analysed at 10 different places to minimise any effects of laser pulse energy on the spectra produced. The spectra produced were interrogated using several algorithms including Random Forest, Random Forest with Variable Importance, Partial Least Squares Discrimination Analysis (PLSDA) and Partial Least Squares Discrimination Analysis with Variable Importance (PLSDAVI). A brief description of each was given to aid a new worker in the field. This included a helpful schematic diagram for the PLSDAVI. Of the 2200 spectra collected (11x20x10), 1980 were used for training the models and 220 were treated as unknowns. All of the algorithms had a high success rate of correct classification, with the Variable Importance versions being even more successful than those not using it. The most successful algorithm was VI followed by PLSDA which had a success rate of 99.55%. An added bonus was that it also had the shortest classification time (0.096 ms). Other good examples of this type of paper are two by the same research group^{128, 129}. These papers used the C-N line at 388.3 nm and the atom lines of C (247.86 nm), H (656.3 nm) and O (777.3 nm) and the unsupervised learning algorithm K-means and cluster analysis to differentiate 20 industrial polymers. In the paper by Tang *et al.*¹²⁹, self-organising maps (a type of artificial neural network) was also used. When self-organising maps alone was used, only 18 of the 20 plastics could be differentiated; with polycarbonate and polystyrene being problematic. When K-means was used as well, the success rate was 99.2%. It was also in excess of 99% in the paper by Guo *et al.*¹²⁸. Jull *et al.*¹³⁰ used LIBS followed by k-nearest

neighbour and Soft Independent Modelling by Class Analogy (SIMCA) to analyse several types of recyclable materials. These included brown, green and clear glass, aluminium, tin and the polymers polyethylene terephthalate (PET), high density polyethylene and the bioplastics Novatein and polylactic acid. Although the glass types could not be distinguished, the biopolymers could easily be separated from the other polymers. The k-nearest neighbour algorithm provided better classification than SIMCA. Similar results were obtained when the range of the LIBS spectra was decreased from 182.26 – 908.07 nm to 313.20 – 495.12 nm. Another example was by Roh *et al.*¹³¹ who used LIBS along with PCA and Independent Component Analysis, Fuzzy C-means, Fuzzy C-means clustering algorithm and Radial Basis Function Neural Networks Classifier to classify black plastics. Black plastics can be extra-problematic to classify because the usual technique of IR cannot be used. Again, a brief description was given of how each of the algorithms works. The black plastics polypropylene, polystyrene and acrylonitrile butadiene styrene were classified according to their resin type with a maximum success rate of 95.83%. A further paper, by Kim and Choi¹³² used the C/H line intensity ratio, the presence of the C-C delocalised bonds, and any signal from a heteroatom to distinguish between the black plastics polypropylene, acrylonitrile butadiene styrene, PET and polystyrene. The PET was easily identifiable because of the strong O peak at 777.2 nm, but the other plastics could also be identified through the other measurands. The final paper in this sub-section was presented by Dastjerdi *et al.*¹³³ who used LIBS combined with the Support Vector Machine model to separate polyvinyl chloride (PVC) from other polymers. Again, the basic principles of the algorithm were given along with schematic diagrams of the LIBS setup and the automated sorting system. Although not infallible, the method did manage a successful differentiation 90.5% of the time. The authors concluded that the combination of LIBS and Support Vector Machine had great potential for such a differentiation.

Techniques other than LIBS have also been used to distinguish between different polymer types. Two papers by Madiona *et al.* used TOF-SIMS followed by multivariate analysis techniques to distinguish between similar polyamide materials¹³⁴ and between PET, PTFE polymethyl methacrylate and low density polyethylene¹³⁵. In recent years TOF-SIMS has advanced significantly with the most recent instruments having far greater capability and resolution compared with previous versions. The higher resolution leads to a larger dataset and therefore algorithms have been used to reduce these to a more manageable level. In the first example¹³⁴, self-organising maps and PCA were used to differentiate between seven polyamide samples (types of nylon). The PCA separated a few sample types, but failed to differentiate between all of them. However, following 'up-binning' (where more data is inserted through higher spectral resolution) both supervised and unsupervised training of the self-organising maps led to successful differentiation (98% and 99%, respectively). The successful

differentiation was true for both positive and negative ion modes during the TOF-SIMS analysis when spectra covering the mass range 1-500 m/z. The other application¹³⁵ was very similar, but with data within the spectral range 1 - 300 m/z used at an interval of 0.01 m/z, i.e. 30,000 equal segments. This 'up-binning' enabled decreased user intervention, removal of bias and provided a larger dataset so that all features within a mass range can be taken into account. The authors concluded that their approach held a great deal of potential in the field of materials and biomaterials analysis.

Several other applications of the analysis of polymers have been produced during this review period. This has included a *LA-ICP-MS and LA-ICP-OES method utilising a novel calibration approach*¹³⁶. The paper, by Villasenor *et al.*, reported the determination of Al, As, Ca, Cr, Hg, Mg, Si, Ti and Zn in the polymers polyethylene and polypropylene. The calibration method was entitled 'dried droplet calibration approach' and involved a small volume (at the μL range) of an aqueous standard being placed on the polymer surface and then dried prior to LA sample introduction. The concentrations of the analytes in the samples were obtained by extrapolation of the calibration curves. The method reportedly overcame matrix effects that are a known problem for LA sample introduction because the sample and the added standard were ablated simultaneously and hence the generated aerosols reached the plasma at the same time. Accuracy of the method was demonstrated through the analysis of three CRMs. In general, good agreement between experimental results and the certified values was obtained. The exceptions were for elements that are very volatile, e.g. As and Hg or those that are present at very low concentration, e.g. Ti. These analytes showed significant deviation from the certified values.

Three papers have described the determination of *silicone materials*¹³⁷⁻¹³⁹. In the first example, Vogel *et al.* coupled size exclusion chromatography (SEC) with ICP-OES to obtain speciation information of polydimethylsiloxanes in volatile and non-volatile solvents. The SEC enabled separation of silicones over the mass range 311 – 186,000 Da and the ICP-OES gave good sensitivity detection with LOD being below mg L^{-1} . The average precision was 5.5% RSD. The second paper was presented by Ledesma *et al.*¹³⁸ who reported the determination of silicone material contaminants on epoxy composites. The surface analysis techniques of XPS and LIBS were used with data from the two being compared with respect to their reliability. The advantages of LIBS over XPS in terms of speed, lack of necessity for sample preparation, real-time results and ease of use were all highlighted. The Si concentrations determined showed an excellent correlation between the two techniques. The paper by Chen *et al.*¹³⁹ used LIBS to evaluate the tracking and erosion test performance of materials. The normal test, termed the inclined plane is very time-consuming and the LIBS test was significantly faster. Twenty seven materials were tested with either the aluminium hydroxide or the silica in the fillers being the target analytes. Thermogravimetry was also undertaken on the materials. Full experimental details of all

three tests were given including a schematic diagram of the LIBS system. The LIBS spectra were complex and, although some Al lines, e.g. 308.2 nm, could clearly be identified, further assistance was required to obtain more information. The authors therefore used PCA and a neural network algorithm. The PCA could distinguish between several of the sample types but not all. The neural Networks algorithm used after the PCA enabled distinction between the rest.

Laser ablation along with other techniques has been used for polymer analysis. Bezemer *et al.*¹⁴⁰ used LA-ICP-MS, XRF and IRMS to obtain analytical data from the plastic caps of flash bangers and then used PCA on the data to classify them. A total of 202 samples were tested by LA-ICP-MS and 53 elements screened for. For blue caps, only 13 analytes were present in all samples and a further 26 analytes were present in at least one sample. The white caps had fewer elements and those that were present were at lower concentration. Only 89 samples were analysed using XRF. Since it has far lower sensitivity, it was less useful. However, it did analyse the whole of the cap rather than a small spot and therefore did not suffer potential inhomogeneity problems experienced by LA-ICP-MS. For those analytes that could be detected using both techniques (Ca, Cr, Cu, Mg, S and Si) correlation between the two was very good. The XRF analysis of post-explosion caps was not straightforward because the samples were no longer flat and were also contaminated by residues of the explosive powder. The PCA analysis of the LA-ICP-MS data identified seven classes of blue cap and three classes of white cap. Isotope ratio measurements of C and H gave further discrimination. It was concluded that the protocol could easily be applied to forensic samples. Another example of LA-ICP-MS this time in tandem with LIBS was presented by Bonta and Limbeck¹⁴¹. Under normal circumstances, both techniques suffer matrix effects and often require matrix matched standards for calibration. The techniques used in tandem, i.e. data obtained using both instruments from one laser shot, actually overcomes these problems. A full description of the system was supplied including the sample preparation procedure which involved the samples being spin coated as a layer on a high purity silicon wafer. The LIBS was capable of determining alkali and alkaline earth elements and LA-ICP-MS was used to determine other elements at the $\mu\text{g g}^{-1}$ range. Analytical data from the combined techniques were input to PCA. The protocol was applied to three plastic types (polymethyl methacrylate, polyimide and polyvinylpyrrolidone) totalling 23 samples. The PCA could easily differentiate between the three polymer types. Future work would involve the analysis of more polymer types and to investigate the possibility of depth-profile measurements.

Two papers have claimed *novel instrumentation* for the analysis of polymers^{142, 143}. The paper by Pardede *et al.*¹⁴³ utilised a novel double pulse LIBS system to determine Cl, F and H in PTFE and PVC. Normally, halogens show very poor sensitivity during LIBS analysis. However, using two lasers firing at an aluminium target in a helium atmosphere produced a helium plasma that was capable of exciting

the analytes in the samples. One of the lasers was a nanosecond Nd:YAG operating at 54 mJ and the other a picosecond Nd:YAG laser operating at 2 mJ. Both lasers operated at their fundamental wavelength. Full details of the setup were provided. The system was also applied to the determination of H and D in a zircaloy sample. The authors proposed a mechanism by which the excitation occurred. The other proof of principle paper¹⁴² described the use of a compact near edge X-ray fine structure (NEXAFS) microscope to form an elemental map on a 30 x 30 μm^2 piece of PET. The paper described in detail the source, the system, the spectral measurements and the results, with a useful schematic diagram of the instrument also being provided. Briefly, in the proposed system spatially localised spectra are taken using a broad band soft X-ray source and the overall image is obtained by raster scanning. Using conventional synchrotron sources, the image is obtained from a series of full field images taken at different energies.

Several more *straightforward applications* have been published. This includes one by Devouge-Boyer *et al.*¹⁴⁴ who described the determination of Cu, K and I in polyamide samples. The analysis is necessary because excess I can lead to corrosion of the electronic components in the automotive industry. Sample (0.200 g) was cut into small pieces and placed in a microwave bomb. Nitric acid (5 mL) was added and the bomb heated using microwave irradiation to 150 °C and maintained at that temperature for 30 min. After cooling, the digests were transferred to polypropylene flasks and diluted to 50 mL using ultrapure water. The acid digest could then be analysed using ICP-OES for the Cu and K content. The I was determined using ICP-MS following dilution of 1 mL of the acid digest with 24 mL of 0.5% ammonia solution (to decrease memory effects). Unfortunately, no CRM was used to validate the method. However, a spike of 50 mg kg⁻¹ I yielded a recovery of 100 ± 0.8%. The LOD was calculated to be 150 ng L⁻¹ for ICP-MS correlating to 0.9 mg kg⁻¹ in the solid material. A microwave assisted alkaline extraction using ammonia or TMAH yielded results approximately 10% lower than the acid extraction. Analysis of the plastics yielded I concentrations from below LOD to 1000 mg kg⁻¹ with a precision of between 2.2 and 4.5% RSD. A total of 18 analytes were determined in high purity polyimide materials using either ICP-OES or ICP-MS detection¹⁴⁵. Santos *et al.* used a microwave induced combustion on a sample size of 600 mg to bring the analytes into a more readily analysed form. A range of absorbing solutions was tested with a mixture of 4 mol L⁻¹ HCl and 3 mol L⁻¹ nitric acid providing full recovery for all analytes except Cr, whereas water yielded no better than 65% recovery and nitric acid improving recovery of only some of the analytes. The sample powder had to be mixed with ammonium chloride volatilisation aid for complete recovery of Cr. Method validation was achieved through the analysis of the CRM EC 680K – low density polyethylene. Analytical data obtained were in good agreement with certified values (better than 94% and with a t-test indicating that there was no significant difference). Detection limits were at the ng g⁻¹ range. A paper by Lazic *et al.* described the LIBS and portable XRF

determination of Sb in some widely used plastic objects¹⁴⁶. The portable XRF instrument operating in the low-density plastics mode was used to give reference Sb values for the LIBS determinations and to provide an indication of the concentrations of some other, potentially interfering elements. Initially, the LIBS was tested on high purity antimony in order to identify the most prominent wavelengths. Unfortunately, the most prominent lines occurred in the UV region and were interfered with by Fe, Si and Ti. Weaker ionic lines occurred in the visible region. Despite there being a weak Fe interference, the Sb wavelength at 276.99 nm was used for all measurements. The authors provided details of how the Fe signal was subtracted from the total signal yielding a reliable Sb measurement. Samples including luggage tags, light bulb fittings, christmas decorations and numerous others were analysed giving Sb concentrations between the LOD (approximately 1400 mg kg⁻¹) up to over 65,000 mg kg⁻¹. A full experimental description was provided along with schematic diagrams of the LIBS setup.

3 Inorganic chemicals and materials

In a continuation of the previous year's review, papers detailing the development, or interesting application, of atomic spectrometry have been grouped into the following topic areas; inorganic chemicals, building materials, catalysts and forensic analysis. A lack of papers covering the analysis of fertilizers sees this topic removed from this year's review.

3.1 Inorganic chemicals

This review period has seen an eclectic assortment of matrix types from aluminium smelt cells to inorganic supplements, examples of which are included in Table 3. Dos Santos et al.¹⁴⁷ reported the use of ICP-OES for the determination of phosphine gas released from aluminium phosphide fumigants. The proposed procedure comprised the passing of moist air over the sample and collecting the released gas in a bubbler containing acidified potassium permanganate to convert phosphine to soluble phosphate. The resulting solutions were diluted and the P determined using ICP-OES at the P 213.618 nm analytical line. Ten commercial samples of fumigants were analysed with good agreement with the more laborious molybdenum complexation spectrophotometry method.

Confirmation of the quality of high purity solvents is critical for both analytical and industrial applications such as semiconductor production. To that end, an electrolyte cathode discharge atomic emission spectrometry method was reported for the direct determination of metallic impurities in high purity NH₄OH, H₂O₂ and H₂SO₄¹⁴⁸. The system consisted of a tungsten anode wire, glass capillary tube for flowing the cathode solution and an atomic emission spectrometer with a Czerny-Turner Grating monochromator. The optimised operating parameters included a 2 mm inter-electrode gap with a 770 V, 56 mA discharge. The system was capable of determining Ag, Ca, Cd, Cu, Fe, Mg, Mn, Pb and Zn with

detection limits ranging between 2 and 52 ng mL⁻¹. Results for all materials were comparable to those obtained using GFAAS and ICP-MS methods. A detailed description of the optimisation of ICP-MS/MS for the determination of non-metallic impurities in ultrapure TMAH was produced by Fu *et al.*¹⁴⁹. The report details the selection, advantages and optimisation of mass shift reaction with O₂ and H₂ for interference removal on each analyte, As, B, Cl, P, S, Se and Si. The use of MS/MS significantly reduced the detection limits for each analyte when compared with standard He collision mode ICP-MS. For example, the LOD for Cl reduced from 41.8 µg L⁻¹ to 3.1 µg L⁻¹ when employing a hydrogen mass shift and setting Q₁=35/ Q₂=37. Accuracy was examined using spike / recovery experiments and comparing with results obtained using SF-ICP-MS.

Table 3 Applications of atomic spectrometry to the analysis of inorganic materials

Analytes	Matrix	Technique	Comments	Reference
Al, Ca, F, Mg, Na	Aluminium smelt cells	WD XRF	A high accuracy XRF method as an alternative to XRD for calculation of cryolite ratio in smelt bath samples. Samples were ground and pressed to pellets with cellulose prior to analysis.	¹⁵⁰
As, Cd	Multi-vitamin / mineral supplements	ICP-MS	A three step sequential coprecipitation of As and Cd using TEA and HF-NH ₄ OH for the removal of high salt interferences such as Ca, K, Mg,	¹⁵¹

			Na together with other interferences from Mo, Mn and Sn	
F, K, O, P	F doped potassium titanyl phosphate crystals	GD-TOF-MS	Combined instrumental and mathematical corrections for the interferences of $^{38}\text{Ar}^{2+}$ and $^1\text{H}_3^{16}\text{O}^+$ on $^{19}\text{F}^+$	¹⁵²
K	Biochar fertilizer	LIBS	Addition of Li_2CO_3 to increase the electron density of the plasma and increase the emission intensity of analyte	¹⁵³

3.2 Building Materials

The determination of Cl is still one of the main tasks for the evaluation of reinforced concrete structures as chloride penetration to the rebar is the dominant damage process affecting structural lifetime. The analytical technique of LIBS can be a fast and reliable method to quantify Cl in cement-bound materials and its use has been reviewed and validated by Millar *et al.*¹⁵⁴. The group described the production of a series of reference materials of varying Cl salts and additives and their use for calibration. A calibration model with a precision of $s(x_0) = 0.023 \text{ wt\%}$ was obtained and mean error of the validation test set was $0.595 \pm 0.063 \text{ wt\%}$, which was comparable to standardised methods such as potentiometric titration or photometry. A second paper by the same group discussed a similar application of the determination of total Cl content in cement pastes¹⁵⁵. The use of Cl molecular lines as a means of avoiding purged spectrometers for Cl determination was reported¹⁵⁶. Calcium monochloride radicals, formed in the plasma, have observable band emissions at 593.4nm and 621.2nm. Determining Cl using these molecules avoids any purge requirements. Furthermore, the

shot-to-shot reproducibility was increased by calculation of the intensity ratio of Cl related and unrelated molecular bands e.g. CaCl:CaOH ratios. The LOD was 0.075wt% Cl related to the cement mass. This is below the critical threshold of 0.2wt% of chlorides related to the cement in reinforced concrete. Micro-XRF was used by Bran-Anleu *et al.*¹⁵⁷ for mapping Cl in hardened cement. The paper discussed, in detail, the preparation of relevant standards and appropriate sample preparation. The method LOQ was 0.011wt%, but more importantly, it offered accurate spatially resolved analysis with minimal sample destruction.

ElFaham *et al.*¹⁵⁸ showed a linear relationship between the compressive strength of concrete and the ratio of calcium atomic and ionic emission line intensities observed using LIBS. The report highlighted the importance of correction for self-absorbance of the calcium lines, doing so by comparison of electron densities with those computed from the hydrogen H α -line at 656.27 nm which was in the same spectra under the same state. The technique was considered a useful semi-non-destructive concrete strength test. A second paper by ElFaham, discussed the use of online LIBS for the fast processing of cement waste material for prospective co-processing¹⁵⁹. However, LIBS alone was not sufficient as it could not identify low level of hazardous heavy metals, therefore a combined approach with ICP-OES was necessary. Guo *et al.*¹⁶⁰ demonstrated that LIBS was successful for the on-line component analysis of powder cement. Calibration models based on PLS and support vector regression (SVR) methods were used to quantify Al, Ca, Fe, Mg and Si in cement with comparable accuracy to the specimens analysed off line as pressed powders.

The development of portable devices is helping researchers to resolve problems in the field in a fast and easy way. The use of handheld EDXRF instruments to aid the understanding of degradation processes that take place in bricks exposed to marine environments was discussed by Morillas *et al.*¹⁶¹. The team performed the bulk of the analysis *in-situ*, choosing to verify select results in the laboratory. Handheld XRF was also used by Ramacciotti *et al.*¹⁶² for the analysis of archaeological mortar specimens located in Sagunto, Spain. Again, the team chose to verify samples in the laboratory highlighting that whilst portable instruments are useful, laboratory analysis is still required for ultimate confidence in the trueness of results.

Garcia-Florentino *et al.*¹⁶³ demonstrated the usefulness of a combined macro- and micro-EDXRF instrument for the *analysis of historical mortars*. The report highlighted the importance of sample homogeneity at the chosen resolution for true quantification, as well as the necessity of suitably matrix-matched reference standards. With the exception of the lightest elements (Na and Mg) there was good agreement with result obtained using WDXRF methods employing pressed pellet and fused bead preparations, as well ICP-MS analysis following an alkaline fusion preparation. A TXRF-

based quantitative methodology for the determination of Ca, Fe, K, Mn, Pb, Rb, Sn, Sr and Ti in water and acid extracts of mortars from culturally important buildings was reported¹⁶⁴. Samples were prepared by mixing a 1 mL portion of sample with 50 μL of 100mg L^{-1} Rh solution. A 10 μL aliquot was then transferred to a reflector disk, prepared with silicon, and dried under an IR lamp. Calibration was based on Fundamental Parameters with internal standardisation using the known Rh concentration. The LODs ranged from 0.01-12 mg L^{-1} , depending on the analyte. The method proved to be a quick and simple alternative to the more classic quantitative techniques such as ICP-MS. Acid leaching of concrete and the determination of the acid soluble elements by ICP-MS was shown to be a useful tool to establish common origin of fragments for forensic investigations¹⁶⁵. As only part of the sample was dissolved during leaching, the concentration ratios of nine elements: Ba, Ce, Cu, Nd, Pb, Rb, Sr, Zn and Zr, normalised to the concentration of La were used as a means of determining whether two specimens were of the same material. This approach negated the need to calculate moisture content and the extracted weight of the sample to be determined.

Yakubenko *et al.*¹⁶⁶ provided a detailed description of the optimisation of a microwave digestion methodology prior to ICP-OES analysis. The optimised method allowed for complete digestion of 0.1 g of sample with 11 mL of a mixture of HF, HCl, HNO_3 and H_3PO_4 acids (6:3:1:1) following a five-step heating profile and a mid-run addition of 2 g of H_3BO_3 . Whilst the method proved to be accurate by recovery of reference values of a standard sample, it is the writer's opinion that a simpler, and potentially safer, approach would be to use XRF following fused bead preparations.

3.3 Catalysts

A review of the current state and problems of analytical control of spent automobile catalysts was produced by Alekseeva *et al.* (65 references)¹⁶⁷. The review focusses on the chemical preparation of samples using autoclave and microwave procedures, assay procedures and spectroscopic developments. Kim *et al.*¹⁶⁸ discussed the increased ICP-OES matrix complexity from interfering elements present when determining PGMs obtained from low-grade ores and recycled automotive catalytic converters. Low-grade grade ores are often rich in other metals such as Al, Ca, Cu, Cr, Fe, Mg, Mn, Pb and Si, all of which were found to cause either spectral, ionisation or chemical interferences with the common PGM analytical lines. The team used statistical analysis of the measured interferences to determine a set of guidelines for selecting the appropriate analytical lines depending on the matrix complexity. A rapid LIBS method as an alternative to chemical digestion followed by ICP-OES procedures for the determination of PGMs in supported catalysts was reported by Jaine and Mucalo¹⁶⁹. A series of bespoke reference materials was produced by evaporation of known volumes of liquid stock solutions in a Pyrex beaker, followed by reconstitution in neat ethanol containing 50 mg

of poly(vinyl pyrrolidone) and 2.97g of silica or alumina support material. The solutions were evaporated again to produce supported metal nanoparticles. The production was confirmed using TEM. Reference concentrations were determined using NAA and they were then used to produce a PLS model for calibration of the LIBS system following pelletisation of the powdered materials. The entire work flow for sample analysis required less than 10 mins and concentrations were predicted with as little as 0.1 wt% error. A LIBS system with a motorised XYZ sample stage was used for mapping the diffusion of Ni and V containing asphaltenes into mesoporous alumina supports¹⁷⁰. The benefits of such a system include having good sensitivity and spacial resolution without the need to subject materials to vacuum as with SEM.

Electrochemical flow cells coupled with ICP-MS continue to be used for the determination of anodic and cathodic dissolution of fuel cells. The configuration enables potential- and time-resolved dissolution monitoring of individual metal counterparts with extremely high sensitivity and has been effectively employed to monitor electrochemical dissolution of Pt-SnO₂/C electrocatalysts in ethanol cells¹⁷¹, Pt/C electrocatalysts¹⁷² and commercial PtCo alloys under cyclic potentials¹⁷³.

The ability to study the *behaviour of catalysts under operational conditions* is important when trying to understand activation and deactivation mechanisms. It was therefore no surprise that multiple example of Operando and *in-situ* characterisation featured during the review period. *In-situ* XAS with millisecond time resolution was utilised by Gonzalez-Flores *et al.* to understand the synergistic effects of Ni-Fe water oxygen evolution reaction catalysts under cyclic potentials¹⁷⁴. Analysis was performed at the beamline KMC-3 (bending magnet) of the Berlin synchrotron radiation source (BESSY). All X-ray absorption signals were collected in fluorescence mode, with detection at right angle to the exciting X-ray beam. K-edge absorption spectra of the sample were recorded immediately before and after each time-resolved experiment, to normalize the time-resolved data and to assess film dissolution. The team discovered that the Fe sites do not undergo a distinctive redox transition but are enslaved by the oxidation state changes of the Ni ions. Another sub-second time resolved XAS application was reported by a team at the Diamond Light Source, UK¹⁷⁵. Although not capable of electrochemical cycling experiments, the setup is capable of reproducible cycling between different states triggered by gas atmosphere, light, temperature, etc. and opens up new perspectives for mechanistic studies on materials such as automotive catalysts, selective oxidation catalysts and photocatalysts.

In-situ XAS was utilised to follow the formation of precursor-dependant supported Pd nanoparticles during calcination¹⁷⁶. Gamma-Al₂O₃ and activated carbon supports were loaded with various metal precursors, e.g. Pd(NO₃)₂, PdCl₂ and Pd(OAc)₂. The results indicated that the thermal

stability of the metal precursor plays an important role in the size and speciation of the formed Pd nanoparticles after the activation process. Beale *et al.* investigated the effect of oxidation state and geometry of Fe species present on prepared Fe-containing zeolites on the selective reduction of NO with NH₃ using high energy resolution fluorescence detected X-ray absorption near-edge spectroscopy (HERFD-XANES) and K β XES at the I2O beamline at Diamond Light Source, UK¹⁷⁷. Samples were measured under flowing gas using a borosilicate capillary tube heated to 300 °C. The study revealed that highest activity was achieved when octahedral Fe³⁺ species were formed when preparing the catalyst. The technique was also used for the characterisation of Cu species on Cu-CHA zeolites used for the same reaction¹⁷⁸. Chemometric methods were employed to pinpoint the composition impact on the material reducibility and highlight Cu-speciation-productivity relationships. Operando HERFD-XANES and XES was also used by Zhou *et al.*¹⁷⁹ to gain mechanistic insight into the photothermal catalytic oxidation of CO over Pt/TiO₂. The technique was sensitive enough to uncover changes in electronic structure of the Pt sites under light illumination that led to increased oxidation. This resulted in a 20-fold rate increase in CO oxidation at 45°C compared with non-illuminated material.

Methods of surface specific analysis of catalytic materials unsurprisingly continues to be a growing area of research. Mino *et al.*¹⁸⁰ provided a comparative review of the key X-Ray micro- and nanoprobe available for space-resolved characterisation of solid materials. The paper, containing 660 references, covers the general concepts, characterisation strategies and recent significant applications, whilst highlighting their views on possible future development areas.

Physico-chemical insights into the *surface structure of alumina- and silica-supported catalytically active iron oxide nanostructures* were obtained using TOF-SIMS with a Bi₃⁺ primary ion source¹⁸¹. Powdered samples were pelletized and attached to a Si wafer for analysis using a 30 keV primary ion acceleration voltage with an analysis area of 500 μm x 500 μm . Interrogation of the spectra revealed secondary cluster ions Fe-O-Al showing a strong chemical interaction between the catalytic species and support. However, this was less pronounced for the respective Si species on the silica supported catalyst which was also found to have lower catalytic performance.

Müller *et al.*¹⁸² reported the application of extreme ultraviolet LA-TOF-MS for the nanoscale depth profiling of *CoNCN-coated electrodes*. The self-developed laser, operating at 46.9 nm, represents a factor of 4 reduction in wavelength with respect to the previously reported state-of-the-art 193 nm excimer laser. A reduction of the wavelength was used as an alternative to a shorter pulse duration in order to enhance the ablation characteristics and obtain smaller quasi-non-destructive ablation pits. The reported instrumental setup provided lateral resolution of 80 nm, depth resolution of 20 nm and a detection limit of approximately 50 ppm depending on the analyte of interest.

3.4 Forensics applications

As found in previous review periods, the *analysis of gunshot residues (GSR)* dominates the forensic application of atomic spectrometry techniques. Dona-Fernandez *et al.*¹⁸³ evaluated the performance of a portable LIBS system for the optimisation of GSR evidence collection. The portable instrument was able to determine the characteristic GSR elements Ba, Pb and Sb at the crime scene, allowing target collection of evidence for verification by the established SEM methods. A laboratory-based 2D scanning LIBS system was used to produce elemental maps of GSR around bullet holes¹⁸⁴. Forty-five pieces of fabric were shot at known distances to create training set for PCA and a further 28 materials were analysed as test specimens. The LIBS analysis resulted in 100% correct identification of the shooting distance compared with a 78.6% correct classification using the conventional chemical colour test. Furthermore, the LIBS analysis produced a permanent digital image that could be further interrogated if required. A comparison of different swabs for the sampling of GSR from gunshot wounds prior to analysis using ICP-MS was reported¹⁸⁵. Four different swab types: tapes in graphite, Leukosilk (R) white tape, 3M (R) transparent tape and a cotton swab wet with 10% HNO₃ were compared for their ability to collect the highest amounts of GSR from skin samples with the lowest contribution to the blank. The cotton swab with nitric acid was the best performer. McKenzie-Coe *et al.* described the detection of discharge residue from skin swabs using TIMS-MS¹⁸⁶. The method was based on the simultaneous extraction of inorganic and organic species using 15-crown-5 ether. The analytical performance was illustrated as a proof of concept for the case of the simultaneous detection of Ba²⁺, Cu⁺, , K⁺, NO₃⁻, Pb²⁺, diphenylamine, ethyl centralite and 2,4 dinitrotoluene in positive and negative MS modes.

*A single particle ICP-MS technique was investigated as a screening technique for GSR nanoparticles recovered from a shooter's hand*¹⁸⁷. Unlike many single particle ICP-MS applications where a single mass is monitored, the authors reported the monitoring of analyte pairs by 'hopping' between the two masses. The paper described the optimised quadrupole and detector parameters to ensure high ion velocity and minimum quadrupole settling and detector deadtime. This allowed single events to be detected for each element. Material was washed from the shooters hand with ultrapure water and analysed without further treatment allowing simple sample collection and rapid analysis. Comanescu *et al.*¹⁸⁸ utilised the low detection limits achievable using GFAAS to study the background levels of Ba, Pb and Sb on vehicle surfaces. Samples were collected on wet cotton swabs, which were then extracted with nitric acid for analysis. Instrumental limits of detection were 0.052, 0.06 and 0.013 µg per swab for Ba, Pb and Sb, respectively. Transfer of the GSR was dependent on both the shooting conditions and the exposure time. Multiple random vehicle swabs and the low detection limits allowed very low cut-off lower limits, below which it is impossible to determine whether a sample is GSR

positive or not. The values obtained were 0.04 µg for Sb, and values of at least 0.10 µg of Ba and Pb. These were a significant improvement when compared with 0.3 - 0.5 µg achieved using NAA.

3.5 Ceramics and refractories

3.5.1 Industrial ceramics

Ceramics are, by nature, difficult to dissolve and are very resistant to heat. Their analysis can therefore be problematic. Most methods therefore rely on the direct analysis of the solid materials. Consequently, analytical techniques such as LA-ICP-MS, LIBS, XRF or glow discharge methods are commonly reported.

The *LIBS analysis of aluminium oxide powder materials* has been reported in two papers. A paper by Myhre *et al.*¹⁸⁹ deliberately mixed alumina powder with metal oxide powders of Eu or Sm and then pressed them at 15 tons into pellets with dimensions of 1 cm diameter and 2 mm thickness. Two approaches to building a univariate simple linear regression curve were taken. One correlated the known concentration of an analyte in a standard to the normalised value of an integrated emission line to give a response signal. The integrated area of a nearby background region was used to normalise the data. The second approach used the intensity at one of two Al wavelengths to normalise the data. Both methods were described in the paper. Linearity extended from 0.086 to 12.4 weight%. The LOD for the analytes depended on which wavelengths were used, but ranged from 0.001 to 0.108% for Eu and from 0.001 to 0.183% for Sm, respectively. The second paper, by Pandey *et al.*¹⁹⁰, described the determination of Ni impurities in alumina powders of different particle size. Three materials were used for the analysis, the first had a particle size of 190 ± 64 nm, the second of 500 ± 160 nm, but was prone to agglomeration forming particles with an average hydrodynamic size of 1.7 µm (although this varied between tens of nm to hundreds of µm). The third material had an average particle size of 35 ± 13 µm. Samples were doped with a Ni solution to varying concentrations, dried and then pressed into pellets of known density. Sensitivity of the LIBS analyses increased as the grain size increased for a given density. It was concluded that both the particle size and the density of the pellet should be specified when preparing calibration curves.

A study undertaken by Takahara *et al.*¹⁹¹ developed a method for *ceramic powder analysis* that minimised both matrix effects and position effects of spin coated samples. Different certified silicon nitride powders (10 mg) were suspended in a solution of polymethyl methacrylate (0.1% in 990 µL of toluene and 10 µL of 100 mg L⁻¹ Ga added as an internal standard). The materials were then spin coated on quartz disks and the samples analysed for Cr, Fe and Mn using TXRF. A poor correlation was observed between fluorescence intensity and standard concentration which was not improved

through the use of an internal standard. This was attributed to the internal standard being in a different part of the spin coating rather than in the ceramic powder. It therefore did not correct for matrix effects. However, the background intensity ratio did improve the correlation coefficient of the empirical calibrations, effectively overcoming grain size, position differences, sample particle shape irregularities and matrix effects.

The technique of LA-ICP-MS was reported for the determination of Pb isotope ratios in lead-glazed ceramics¹⁹² and for the examination of the mass transfer of additive elements in barium titanate ceramics during the sintering process¹⁹³. The first example used a multi-collector instrument to collect the isotope ratios and used TI to correct for mass bias effects. The ratios of $^{206}\text{Pb}:^{204}\text{Pb}$, $^{207}\text{Pb}:^{204}\text{Pb}$, $^{208}\text{Pb}:^{204}\text{Pb}$, $^{207}\text{Pb}:^{206}\text{Pb}$ and $^{208}\text{Pb}:^{206}\text{Pb}$ obtained using LA-ICP-MS were within 0.027% of those obtained using conventional nebulisation. The proposed method provided accurate and precise lead isotopic compositions using non-matrix-matched standards for calibration, was minimally damaging to the sample, could obtain data within 10 minutes per sample and was highly spatially resolved. The paper by Sakate *et al.*¹⁹³ analysed multi-layered ceramic capacitors. Two barium titanate pellets containing different concentrations of Ho and Mn with the sintering agent Si were prepared and then sintered. Once prepared, the samples were analysed in a helium atmosphere which was then ad-mixed with argon before entry to the plasma. The operating parameters and method were discussed in the paper. The mass transfer of Mn was significantly higher than that of Ho during the sintering process. It was concluded that LA-ICP-MS could be used to improve the manufacture of the ceramic capacitors.

Tang *et al.*¹⁹⁴ determined K in ceramic raw materials using LIBS. The LIBS setup and operating parameters were described at length in the paper. Materials were pressed into pellets at a pressure of 20 MPa to increase the density prior to analysis. Initially, self-absorption effects were severe, limiting the accuracy obtained. A method of profile fitting using a Lorentz function was developed to overcome these problems. The rationale behind the selection of the analysis wavelengths and the theory of the Lorentz function were given in the paper. The methodology was validated through the use of seven certified materials with a K_2O content ranging from 0.049 – 8.6%. These materials were also ceramic raw materials and included feldspar, clay and kaolin. When using the Lorentz function, the regression improved from 0.993 to 0.998, the root mean square error of cross validation improved from 0.458 to 0.145 and the average relative error decreased from 13.7% to 5.1%.

Gold-coated ceramics were analysed using glow discharge (GD)-TOF-MS by Bouza *et al.*¹⁹⁵. Insulating samples are not easy to analyse using GD because the voltage drop across the sample leads to low power deposition and non-efficient sputtering. The ceramic samples were 6 mm thick and were coated with gold with a thickness determined to be in the range 20 – 120 nm. The operating conditions

were carefully optimised to obtain good sputtering. The optimal conditions were: 30 W of RF power, 95 Pa pressure in the discharge chamber, and a pulse width of 500 ms with a period of 1.49 ms. In addition to analysing the ceramics, it was also possible to analyse the gold coating. This was found to contain impurities of Bi, Ir, Pd, Pt and Rh.

3.5.2 Cultural heritage: ceramics

As usual, this has been a very popular area of research with non- or minimally damaging analysis techniques being the most common. *Reviews or overviews* are often the most useful articles for workers new to an area and this year has provided an example for cultural heritage ceramics. A critical review, by Botto *et al.*⁶², discussed the applications of LIBS to archaeology and cultural heritage. Sample types included metalliferous samples, glass, pigments, bones and teeth and pottery. The review, containing 212 references, was conveniently split into the relevant sections and included the more recent research topics of nanoparticle enhanced and underwater LIBS. Also included were micro-LIBS and 3D elemental imaging. Another overview, by Nord and Billstrom¹⁹⁶ containing 148 references, discussed the use of isotopes in cultural heritage. As well as the well-known isotopes of Pb and Sr that are used for provenance elucidation, a series of other analytes were also discussed. The review was split into numerous sections that discussed methods of analysis, the different isotopes determined and what the isotopic information could be used for. Included among the isotopes were ¹⁴C, tritium, ³⁶Cl, ²³⁰Th, ²³²Th and ²¹⁰Pb for dating purposes, and a host of less common stable isotopes for provenance studies. Analytical techniques discussed, albeit briefly, included isotope ratio mass spectrometry, SIMS, TIMS, MC-ICP-MS and fission track methods. The authors also provided insights into potential future applications. A final review, by Panchuk *et al.*¹⁹⁷, was a tutorial on the application of chemometric methods to XRF data. The review, containing 146 references, discussed the different subject areas, e.g. forensic, cultural heritage, agriculture, etc. and gave a useful pie diagram clearly demonstrating that the most common methods used are PCA, hierarchical cluster analysis and partial least squares. Numerous other chemometric methods including artificial neural networks, linear discriminant analysis, soft independent modelling of class analogy, etc., were also discussed. A description of how many of the methods work was given, with the main three given in detail.

A paper by Lazic *et al.*⁶³ compared the techniques of LIBS, XRF and PIXE for the analysis of egg tempera pigments on gypsum, oil paints on gypsum, glazed ceramics and Roman coins. This paper was discussed in more detail in section 1.3 and will therefore not be discussed further here.

Other papers in this research area have been summarised in tabular form (Table 4). The papers summarised have some novelty, either in term of the analysis itself or in the chemometric analysis of

the analytical data. Numerous other papers do exist, but from an atomic spectrometric perspective, they offer little in terms of novelty.

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

Analytes	Matrix	Technique	Comments	Reference
Al, Ca, Fe, Mg and Si	Archaeological ceramics from China	LIBS	Data from the LIBS analysis of 35 ceramics from different Chinese dynasties were treated using five different pre-processing techniques. These were: normalised by maximum integrated intensity, by extremum integrated intensity, mean centering, first order derivatives and second order derivatives. The data were then treated using variable importance threshold values. The treated data were then interrogated using the Random Forest chemometrics technique. Under optimal conditions, the sensitivity, specificity and accuracy were described as being 0.8528, 0.9710 and 0.9433, respectively. The procedure was sufficiently efficient to distinguish samples from different dynasties.	¹⁹⁸

Al, Fe, K, Mg, Si and Ti	Archaeological pottery from India	LIBS	Analysis of pot sherds using LIBS and SEM-EDS with results from the two being in good agreement. The LIBS analysis required no sample preparation, was quick and could be used <i>in-situ</i> . The types of clay used were identified and the firing temperature was determined to be less than 800 °C.	199
Nd and Sr	Raw materials, ceramic replicas and ancient pottery	TIMS	The samples were acid digested and the analytes separated from the matrix by ion exchange techniques. The $^{87}\text{Sr}:$ ^{86}Sr and $^{143}\text{Nd}:$ ^{144}Nd ratios were obtained using TIMS were used as a tool for provenance determination. The method was validated using NIST SRM 987 for Sr and the La Jolla Nd reference standard. The isotopic characterisation was an effective fingerprint for pottery.	200
Various (16)	Pre-colonial pottery from Brazil	EDXRF PIXE	A total of 63 fragments of pottery from three sites analysed using computed radiography (for internal structure), EDXRF and PIXE. Analytical data were	201

			<p>analysed using multivariate statistics such as hierarchical cluster analysis and PCA to separate and correlate the samples. Samples were split into two clusters: one from two of the sites and the other from the third. This indicated that samples from two of the sites were made from the same clay.</p>	
Various (> 20)	Late bronze age Cypriot ceramics	WDXRF ICP-MS	<p>For XRF analysis, potsherd were ground to a powder and fused to form a glass. Powders were acid digested prior to ICP-MS analysis. It is unusual for a cultural heritage paper to destroy / significantly damage the sample nowadays. Binary plots of the data enabled a trading system to be elucidated.</p>	²⁰²
Various (16)	Late Byzantine period pottery from Serbia	WDXRF ICP-OES FTIR μ -Raman XRD	<p>Pottery samples (63) from different periods covering 13th – 15th century from the same monastery were analysed using multiple techniques. Microwave assisted acid digestion was undertaken prior to ICP analysis. Multivariate statistics (PCA) performed</p>	²⁰³

			on FTIR and powder XRD data. Combining the data from all the techniques demonstrated that there was no significant difference between any of the samples mineralogical or chemical composition, indicating continuous pottery preparation. Firing temperatures were also estimated.	
Various (22)	Prehistoric pottery from Japan	XRF	Pottery sherds from a Japanese island from two time periods analysed using XRF. Samples mixed 1:10 with flux and fused into a glass bead. Calibration was against synthetic standards. Analytical data input to PCA cluster analysis and scatter diagrams. Results from the three classification techniques were in good agreement, with five provenance groupings identified. Most had been imported from Honshu.	204
Various (20)	Late antique pottery from the Balearic Islands	XRF XRD Optical microscopy	Sherds from 78 ceramics were pulverised into a powder, mixed 1:20 with a flux and fused into a glass bead prior to XRF analysis. Dendrograms and PCA used	205

			on analytical data to garner provenance information. Results indicated that the area was participating in trade with other regions.	
Various	Chinese blue and white Kraak porcelain from Ming Dynasty	μ -XRF XANES	Two different groups of samples were analysed using XRF with a fundamental parameters standard-free quantification method. Main body, two glaze layers and pigment were all analysed. Data were input to PCA. Results demonstrated that the two groups of samples came from the same source. The XANES was used to analyse the cobalt pigment.	²⁰⁶
Various (46)	Ceramics from France	LA-ICP-MS	Inclusions in the pottery were analysed using LA-ICP-MS. Four standard reference materials analysed to monitor accuracy. Data input to PCA, hierarchical cluster analysis and ternary diagrams. Methodology enabled discrimination between imported and local pottery and also managed to link the pottery with the source rock.	²⁰⁷

Various (13)	Qingbai porcelains from a Java sea shipwreck	Portable XRF	The provenance of porcelains found in a shipwreck dating from 12 th - 13 th century was undertaken. Portable XRF used to determine analytes. Data input to hierarchical cluster analysis, binary plots and PCA. Glazes and pastes both analysed. Different manufacturing sites clearly identified.	208
Various (17)	Potsherds from the Yaeyama Islands, Japan	XRF microscopy	Two analysis methods used: elemental mapping and multi-point spectral measurement, enabling an elemental distribution on the surface as well as a detailed multi-point elemental composition to be obtained. The data were introduced to PCA and non- metric multi-dimensional scaling analysis.	209

3.6 Glasses

3.6.1 Industrial Glasses

One of the more common themes of analysis in this review period has been the *elucidation of corrosion mechanisms*. Two papers by Rodrigues *et al.* discussed the use of SIMS²¹⁰ and TOF-SIMS²¹¹ to examine surface alteration of glasses under museum-like environments. Other techniques, e.g. μ -Raman and FTIR were also used in both studies. In the first paper²¹⁰, the effect of room temperature and relative humidity on degradation of replicas of three soda-rich glass types were studied. The thickness of the altered layer was proportional to the exposure time and to the relative humidity of the atmosphere.

Data indicated that Na was leached from lower level in the glass leading to deficient areas whereas the surface became enriched. In the second paper, the secondary ions determined included Al, As, Ca, Fe, H, K, Mg, Mn, Na, Pb, Si and some molecular species. Results demonstrated that Ca and Pb played dominant roles in the hydration and hydrolysis of the glass surfaces. Again, different conditions likely to be found in a museum environment were tested. A third paper to discuss corrosion of glass was presented by Zhang *et al.*²¹². These authors used TOF-SIMS to monitor the H / Na interface on a corroded International Simple Glass. The H / Na interface could be imaged directly using positive ion imaging without any auxiliary sputtering beam under high vacuum (2×10^{-8} mbar). The H background was approximately 5% in the pristine glass, rising to 15% in the alteration layer.

The *forensic analysis of glass* has also been a topic of interest. In common with the analysis of other forensic sample types, minimally destructive analytical approaches are adopted. Seyfang *et al.*²¹³ discussed the TOF-SIMS, sensitive high resolution ion microprobe (SHRIMP) and SEM-EDS analysis of glass frictionators in 0.22 calibre rimfire ammunition. Such materials have replaced the antimony sulfide frictionator in a lot of ammunition. The composition of the glass particles does not change after use. In this study, 37 samples from 25 different manufacturers in 11 countries were analysed along with five standard reference glasses. For the TOF-SIMS analysis, the signals from 52 analyte ions were ratioed against the $^{28}\text{Si}^+$ signal and the resulting data input to PCA. The SHRIMP analysis determined $^6\text{Li}^+$, $^7\text{Li}^+$, $^{204}\text{Pb}^+$, $^{206}\text{Pb}^+$, $^{207}\text{Pb}^+$, $^{208}\text{Pb}^+$, $^{232}\text{Th}^+$ and $^{238}\text{U}^+$. The major isotopes of Be, Li, Mg, O and Si were also detected. Using TOF-SIMS data alone, 94.1% of the sample brands could be discriminated using a pairwise comparison. The SEM-EDS was capable of discriminating only 79.4% of the samples. When SHRIMP analysis was combined with the other techniques, successful discrimination was achieved for 95.6% of brands.

Several other applications of the analysis of glass were presented. Two of them discussed *the use of LIBS*. Skruibis *et al.*²¹⁴ used multiple pulses from a femtosecond Yb:potassium gadolinium tungstate laser (Yb:KGW) to improve the analytical performance of LIBS. The laser operated at an average power of 5 W and at 60 kHz, producing a wavelength of 1030 nm and a pulse width of 280 fs. The effect of a water film of thickness 0.8 mm on the LIBS analysis of glass was determined. The single pulse LIBS signal diminished significantly in the presence of water. This was attributed to quenching. The signal from multiple pulse LIBS was less affected, being both stronger and having longer duration. It has recently been found that the presence of nanoparticles enhances the LIBS sensitivity. Sanchez-Ake *et al.*²¹⁵ used gold nanoparticles deposited on the sample and produced from a gold thin film coated on the sample to enhance the sensitivity of the LIBS analysis of glass. The thickness of the film, the laser fluence and the number of laser pulses were all studied. The nanoparticles produced from the thin film gave a lower signal to noise ratio than the pre-formed nanoparticles. The mechanism of

enhanced sensitivity was hypothesised as being improved heat transfer from the particles to the glass surface. This enabled lower laser fluence to be used.

The final paper of interest to industrial glass analysts was presented by Zhang *et al.*²¹⁶ who devised a solution-based calibration method for LA-ICP-MS analysis. The system employed a desolvating nebuliser system that was connected to the instrument via a Y piece between the LA cell and the spectrometer. The desolvating nebuliser system employed a semi-permeable membrane drier tube with a counter flow of argon to sweep the moisture away. Internal standards corrected for the differences in aerosol transport efficiencies between the nebuliser and the LA system. The method was validated through the analysis of several glass CRMs (NIST 610 – NIST 616) and Acrylonitrile Butadiene Styrene reference materials (GBW 08407 – 08411). Results were in good agreement with certified values. Detection limits for REE and other elements such as Cd, Co, Cr, Mn, Ni, Pb and Zn were at the ng g⁻¹ range. The results obtained from the analysis of biological materials were compared with those obtained using solution-based nebulisation and were also in good agreement.

3.6.2 Cultural heritage: Glasses

In accordance with other cultural heritage sample types, non- or minimally destructive methods of analysis, e.g. LA, LIBS, varying forms of XRF etc. are used extensively for glass samples. The large majority of papers describing the analysis of cultural heritage glasses are summarised in Table 5 because although interesting they are often not a significant advance in atomic spectroscopy. Instead, the ones discussed in the Table describe a sample introduction system or chemometric analysis of the data to try to elucidate provenance, trade routes, etc.

A review of LIBS for cultural heritage and archaeological samples was presented by Botto *et al.*⁶². The review, containing 212 references, had sections for the analysis of metals, pigments, pottery and ceramic objects, bones, teeth and other organic materials and glasses. Other sections concentrated on the combination of LIBS with other techniques, e.g. Raman, XRF and MS. A further section discussed underwater applications of LIBS. The final sections concentrated on the most recent applications, e.g. those that use nanoparticles to enhance the LIBS signal and those that perform 3D mapping.

Table 5 Applications of the analysis of cultural heritage glasses

Analytes	Matrix	Technique	Comments	Reference
----------	--------	-----------	----------	-----------

Various (20)	Antique glass from Cyprus	LA-ICP-MS	Rare earth elements and others determined and data analysed using PCA to elucidate extent of re-cycling. Once elements common in re-cycling (Co, Cu, Pb, Sb and Zn) had been removed from data sets, provenance could be elucidated. Analytical accuracy verified using NIST 612.	217
Various (>40)	Late antique Apulian glass samples	LA-ICP-MS EPMA SEM-EDS	Trace elemental data and isotope ratios of $^{87}\text{Sr} / ^{86}\text{Sr}$ and $^{143}\text{Nd} / ^{144}\text{Nd}$ determined. Analytical data investigated using ternary diagrams enabling provenance determination. Analytical validation was achieved using USGS BCR-2, with accuracy being within 20% for analytes at the sub ppm level. Re-cycling of glass also studied. Different parts of one glass sample were identified as coming from different batches.	218
Various (~30)	Late antique and early Christian glasses from Bulgaria	ETV-ICP-OES	Finely ground glass (0.2 – 1 mg) analysed directly using CF_4 as an evaporation aid.	219

			Calibration achieved using dried aqueous standards or with certified materials (coal BCR-038, stream sediment GBW 07312 and soda lime glass BAM-S005. The content of some major and minor elements used to determine the type of glass and potential origin.	
Various (55)	Archaeological glasses from Prague castle	LA-ICP-MS EPMA	Major, minor and trace analytes determined with analytical accuracy validated using NIST 612. Analytical data interrogated using binary and ternary diagrams as well as PCA. Three sets of glass identified: wood ash glass, potash glass and potassium crystal-clear glass. Some glasses found in Lisbon found to have the same chemical signature, indicating a possible trade.	220
Various (>40)	Bronze age glass beads from Poland	LA-ICP-MS	NIST 610 and glasses from the Corning glass museum were used for method validation with the latter comparing results with literature	221

			values. Two groups were distinguished depending on the MgO to K ₂ O ratio. High Mg glasses were thought to originate in Mesopotamia whereas high K glasses came from Italy.	
Various	Mycenaean glass from Greece	XRF SEM-EDS PGAA	Ternary diagrams and PCA used to distinguish between samples manufactured in Greece and those imported from Egypt. NIST 620 and NIST 621 used for method validation. Data obtained from the different techniques were compared and were, in general, in good agreement.	²²²
Various	Early Islamic glass from Egypt	LA-ICP-MS	Method validation using NIST 610, NIST 612 and Corning glasses B, C and D. Analytical data from Al, Ca, Mg, Na, Ti and Zr were analysed using PCA which identified four main composition types. Other analytes associated with colouring or opacification, e.g. Cu, Pb, Sb, Sn and Zn were also determined.	²²³

Various (>50)	Glass beads from early medieval Illyricum	LA-ICP-MS	An ArF laser operating at 193 nm was used for ablation of the samples (48 glass beads and four vessel fragments). Method validated using NIST 610 and 612 and Corning B, C and D. Chronological and geographic differences of some beads could be distinguished through the source of the Co colorant. Other analytes also used to elucidate trade and recycling.	224
Various (20)	Plant ash glass from United Arab Emirates	LA-ICP-MS XRF ICP-OES	Nd isotope information obtained using pneumatic nebulisation – multi-collector ICP-MS following acid digestion of the sample and successive ion exchange analyte isolation procedures. The LA-ICP-MS employed a ns ArF excimer laser to determine Sr isotope ratios. Other analytes determined using ICP-OES following a fusion sample preparation procedure or μ -XRF for volatile analytes such as	225

			S. The elemental composition indicated a unique source.	
Various (>30)	9 th – 15 th century glasses from South East Asia	LA-ICP-MS	Single point analysis of glass samples. Method validation using NIST 610 and 612 as well as Corning glasses B and D. Analytical data analysed using PCA. Three compositional groups were identified. One of middle eastern origin, another from Southeast Asia and the third from China. The extent of regional exchange / trade was elucidated.	226
Various (19)	Early Byzantine glass in Serbia	PIGE PIXE	Rapid, non-destructive analysis of glass. NIST 620 and 621 glasses used for method validation. Power transformation performed on analytical data prior to insertion into PCA. Hierarchical cluster analysis did not make clear distinction between types of glass, but PCA identified three distinct groups of windowpane glass.	227

3.7 Nuclear Materials

Accurate measurement of isotopic ratios in materials for nuclear safeguards and forensics is a popular subject area, most commonly through the measurement of actinide elements using ICP-MS or TIMS. The absence of reference materials or limited application of those reference materials that are available is also mentioned or addressed in several studies. The measurement of nuclear materials to improve understanding of fallout from the Fukushima Nuclear Power Plant accident is addressed in several studies. Similarly, the monitoring of material properties in operating reactors to minimise the risk of accidents occurring also features in numerous studies. As the sensitivity and interference removal capability of multiple techniques continue to improve, decommissioning radionuclides that are more challenging to measure (such as ^{93}Zr and ^{129}I) are now considered to be routinely measurable, with ICP-MS and accelerator mass spectrometry (AMS) commonly used, as well as TIMS, SIMS, XRF and LIBS. For the testing of material properties for nuclear fusion, LIBS remains the dominant measurement technique. Across all nuclear material applications, a common theme is minimising the procedural time, either through direct, non-destructive analysis, or rapid online radiochemical separation prior to measurement.

3.7.1 Nuclear Forensics

Accurate measurement of *isotopic ratios in nuclear materials* is a key area for identifying the source of contamination following a radiological incident and for locating the source of illegally acquired nuclear material. The capabilities developed can also be applied to numerous other fields including geological dating and historical climate change studies. The measurement of actinide isotope ratios is the most common, in particular U and Pu using ICP-MS or TIMS.

Quemet *et al.* compared two approaches for minor U isotope ratio measurements using TIMS, which was conducted within a framework developed by the International Atomic Energy Agency for nuclear material round robin exercises²²⁸. The total evaporation method was compared with the classical method with multi-dynamic sequences with respect to accuracy, analysable quantity, analysis time and versatility. Applying a mathematical correction of the abundance sensitivity and the detector calibration reduced the uncertainty and bias of the classical method compared with the total evaporation method. The same author used the total evaporation TIMS method for measurement of Am isotopic ratios as part of a round-robin exercise organised by the Analytical Methods Committee of the French Atomic Energy Commission²²⁹. For the $^{241}\text{Am}:$ ^{243}Am isotopic ratio and Am concentration, biases below 0.0001 % and 0.02 %, and estimated expanded uncertainties of 0.1 % and 0.8 % were calculated, respectively.

Improving the sample loading procedure for TIMS was the focus of some studies. Baruzzini *et al.* used Pt and Re porous ion emitter sources to investigate isotopic fractionation in U and Pu reference standards²³⁰. A comparison of the correction of fractionation using the Linear, the Power and the Russell's laws was a further focus of the study. The porous ion emitter sources were successful, with Pu and U isotopic ratio values agreeing with those on the certificate. For both elements, the Power law was the most suitable for the experimental setup used, although all laws produced results that were statistically identical to the certificates. In a separate study, Mannion *et al.*²³¹ used a polymer thin film for ultra-trace measurements of Pu. The aim was to simplify the single filament sample preparation method and to eliminate sample losses associated with the resin bead loading method whilst maintaining sensitivity and accuracy. Rhenium filaments were coated with a toroidal, hydrophilic anion-exchange polymer spot surrounded by a hydrophobic base polymer, which were loaded with 10 pg of New Brunswick Laboratory Certified Reference Material 128. The use of dimpled filaments improved sample loading of drop deposits, and the polymer coating improved the shelf-life of the filaments, enabling bulk production. The ²³⁹Pu:²⁴²Pu values measured were in good agreement with the certified values and no sample losses were recorded over 65 analyses.

Actinide isotope ratio detection using MC-ICP-MS remains a popular topic. Ronzani *et al.* measured multiple U isotopes in various particles using MC-ICP-MS coupled with laser ablation²³². The laser aerosol and water vapour were simultaneously injected using a desolvating nebuliser and mass bias, gain factors, polyatomic and tailing interferences were all corrected. Particles of a few hundred nm were successfully measured, with detection limits in the attogram range achievable. The relative standard uncertainties ranged from 3.3% to 32.8% for ²³⁴U:²³⁸U, and from 0.4% to 4.0% for ²³⁵U:²³⁸U. Krachler *et al.* also employed LA-ICP-MS for U-bearing materials, focusing on evaluation of homogeneity using line-scan analysis²³³. The procedure was validated using two low-enriched CRMs (~1 wt % and ~4 wt % ²³⁵U), with the experimental values agreeing well with the certified value. Following this, two UO₂ pellets prepared from identical source materials were measured, with the ²³⁵U isotopic abundance ranging from 0.75-1.6 % in the first sample and 0.45-3.0 % in the second sample. This unexpected variation provided information not previously known on the production process of the materials, and showed the technique developed would be valuable for forensic investigation of unknown nuclear material. Varga *et al.* used LA-MC-ICP-MS for measurement of U isotope ratios in six CRMs²³⁴. The powdered materials were pressed into pellets prior to analysis, with good agreement between experimental and certified values being obtained. Subsequent SEM measurement of ablated material revealed that only 5 ng of material was used per measurement. Therefore, LA-ICP-MS can be considered a quasi-non-destructive technique, and the material can be further analysed by other techniques. In a separate study, Wang *et al.* dissolved U particles prior to MC-ICP-MS measurement of

isotopic ratios²³⁵. The relative expanded uncertainty in the reference materials measured ranged from 3.5 % (k=2) for ²³⁴U:²³⁵U to 15 % for ²³⁰Th:²³⁴U.

Several *other analytical techniques were also applied to measurement of actinide isotope ratios* for forensic applications. Chamizo *et al.* demonstrated the capabilities of AMS upgraded with He stripping for U transmission and assessment of background sources that affect ²³⁶U:²³⁸U measurement²³⁶. Scattered ²³⁸U³⁺ molecular fragments were detected that were not identified previously using Ar gas, with a maximum U³⁺ stripping efficiency of ~50 % when operating at an energy of 650 keV. However, the overall background using He (0.8-1.3×10⁻¹⁰) was at least a factor of three higher compared with Ar gas. A study by Hotchkis *et al.* also tested He gas stripping, with an efficiency of >40 % for +3 charge states at an energy of 1 MeV²³⁷. In the case of Pu, sub-attogram detection limits were achieved for several isotopes, with an ionisation efficiency and overall detection efficiency of 3 % and >1 %, respectively. Song *et al.* used LIBS to analyse U isotopes in a series of fused glassy disks²³⁸. The ²³⁵U content ranged from natural abundance to ~94 atom %, and the LIBS spectra were analysed using a database of 12 U-lines in the region of 423.3-424.5 nm. Multi-pair spectral fitting produced an analytical bias of ±1 % for absolute ratios (²³⁵U:(²³⁵U+²³⁸U)), compared with ±4 % for single-line pair fitting (424.412 nm for ²³⁵U and 424.437 nm for ²³⁸U). The inclusion of hyperfine structure and Stark broadening into the algorithm as fitting parameters was investigated, but was found to cause overfitting, negatively impacting the analytical accuracies. Wang *et al.* employed laser ionisation mass spectrometry (LIMS) in combination with SEM for rapid determination of U isotope ratios in bulk samples and single particles of ~50 µm diameter²³⁹. The deviation from certified values was <1 %, with a measurement uncertainty of <5 %.

Whilst studies using TIMS and LA-ICP-MS highlighted the benefits of direct measurement of solid samples, others focused on *reducing the procedural time for destructive analysis techniques* using online chemical separation prior to detection. Studies by Fenske *et al.* and Roach *et al.* described the development of rapid analysis of post-irradiation debris (RAPID)^{240, 241}. This is an automated online separation and direct analysis method for measurement of >40 elements at pg levels. The study focused on measurement of highly enriched U and measurement of anthropogenic isotopes in a bulk uranium matrix. The isotopic ratios measured were within 1-2 % of the expected values based on results from isotopic depletion and decay modelling software. Martelat *et al.* coupled capillary electrophoresis with MC-ICP-MS for online isotope ratio measurements²⁴². A method using acetic acid as the electrolyte and complexing agent was applied to the separation of U, Pu and the minor actinides Am and Cm. Reproducibility of several parts per thousand for U and Pu isotope ratios was obtained, which was considered comparable to TIMS. Compared with ion exchange separation, the analysis time

was shorter and the analyte mass and liquid waste were reduced to ng and μL levels, respectively. A description of the interface between the CE and ICP-MS instruments was also presented.

The ICP-MS instruments equipped with a reaction cell have been proven to offer online interference separation for multiple radionuclides, including actinide elements. Childs *et al.* used CO_2 reaction gas for separation of U and Pu isotopes based on the differential formation of single and doubly charged oxide reaction cell products²⁴³. Uranium was determined as UO_2^+ , with isotope ratios measured within 12% of expected values for several reference materials in nitric acid and digested cellulose filter paper solutions. The stability of the Pu signal at higher CO_2 flow rates and ^{238}U tailing and ^{238}U interference removal needed to be improved further before the same samples could be measured for Pu isotopic composition. A study by Xing *et al.* achieved U/Pu separation using NH_3 as a reaction gas, with U forming UNH and UNH_2 , whilst Pu did not react²⁴⁴. Limits of detection of 0.55 fg mL^{-1} and 0.09 fg mL^{-1} were achieved for ^{239}Pu and ^{240}Pu , respectively, and the method was successfully applied to measurement of $^{239}\text{Pu}:^{240}\text{Pu}$ in sediment reference materials.

The ongoing need for suitable reference materials to validate mass spectrometric procedures for isotopic ratio measurements was identified and addressed in several studies. Penkin *et al.* measured the isotopic composition of ten U chemicals and standards from various suppliers using TIMS²⁴⁵. In most cases, materials were depleted in ^{234}U and ^{235}U and enriched in ^{236}U compared with what was expected in natural U. This is significant in the case of materials that are measured by end-users expecting natural uranium composition. The technique of TIMS was also applied to the certification of the isotopic composition of the IRMM 2019-2029 series of uranium nitrate solutions²⁴⁶. Uranium hexafluoride materials were converted into uranyl nitrate solutions, with the $^{235}\text{U}:^{238}\text{U}$ ratio measured using a $^{233}\text{U}:^{236}\text{U}$ double spike for materials with low ^{236}U abundance. Dittmann *et al.* used AMS to characterise a new mixed Pu standard (^{239}Pu , ^{240}Pu , ^{242}Pu , ^{244}Pu) for isotopic ratio measurements²⁴⁷. The standard was prepared by gravimetric mixing of single isotope standards from the Institute of Reference Materials and Measurements and measured by five AMS instruments and one MC-ICP-MS in an inter-comparison exercise. Mathew *et al.* undertook an evaluation of $^{240}\text{Pu}:^{239}\text{Pu}$ values in a CRM that was produced, characterised and certified between 1966 and 1971²⁴⁸. The motivations were improved isotope ratio measurement capability since 1971 (specifically TIMS in this study), and the systematic bias previously measured in multiple U isotopes in several standards. In CRM138, a $^{240}\text{Pu}:^{239}\text{Pu}$ bias of 0.07-0.08 % was measured, which was higher than any bias reported for any U CRM from the same series of standards. A study by Parsons-Davis *et al.* also focused on the lack of up-to-date measurements, focusing on the nuclear decay data for ^{238}U by measuring the decay constant using isotope dilution mass spectrometry, based on the ingrowth of ^{234}Th in high purity ^{238}U

solutions²⁴⁹. The current decay constant is based on a single value from 1971, and the preliminary result calculated was in good agreement with that determined by alpha counting within the elevated uncertainty (0.462% (k = 2)).

3.7.2 Nuclear decommissioning and waste monitoring

Nuclear decommissioning requires measurement of a range of sample matrices containing various radionuclides and activity levels. As measurement techniques have improved, the number of radionuclides measurable has increased, contributing to the global need for safe and cost-effective decommissioning. A number of papers have demonstrated the high throughput and increased number of radionuclides measurable using mass spectrometric techniques, often combined with rapid online sample preparation techniques. Other studies have recognised that, equally important to accurate waste characterisation, is the long-term monitoring of radionuclides in waste storage and disposal facilities and the environment surrounding them.

Accelerator mass spectrometry was successfully used for measuring multiple radionuclides. Enachescu *et al.* used AMS for measurement of ¹⁴C in a facility that could handle activities that could not be tolerated in laboratories dedicated to ¹⁴C dating²⁵⁰. The bulk and depth profile concentrations of ¹⁴C were measured in thermal column disks of a decommissioned reactor, with activities of 75 kBq g⁻¹ close to the reactor core, compared with 0.7 Bq g⁻¹ close to the end of the column, which is significant for waste categorisation. The presence of ¹⁴C in irradiated steel was assessed using compound specific radiocarbon analysis (CSRA) AMS by Cvetkovic *et al.*²⁵¹ to better understand the release of ¹⁴C during anoxic steel corrosion in the cementitious near field of a low/intermediate level repository. Carbon-14 bearing formate, acetate and lactate were the main corrosion products identified, but further work was required on the source of stable C and temporal evolution of the species detected. The same authors combined ion chromatography with AMS for measurement of ¹⁴C in the femtomolar to picomolar range in a leaching solution from neutron-activated steel²⁵². Hosoya *et al.* demonstrated improvements in ³⁶Cl measurement by AMS by reducing the isobaric interference from ³⁶S²⁵³. Sample preparation using AgBr under acidic conditions was combined with detection of ³⁶Cl at a charge state of +8 to optimise ³⁶S interference removal. A ³⁶Cl:Cl background of 3×10⁻¹⁵ was achieved. A further radionuclide relevant to decommissioning is ⁴¹Ca, which can be measured using AMS, provided isobaric ⁴¹K can be removed. Fu *et al.* outlined the potential need for ⁴¹K interference correction using ³⁹K at ⁴¹Ca:⁴⁰Ca ratios of 10⁻¹¹ – 10⁻¹² in previous studies²⁵⁴, before demonstrating that AMS is capable of ⁴¹Ca:⁴⁰Ca background levels of close to 10⁻¹³ without interference correction. The method was tested on ⁴¹Ca tracer samples.

The technique of AMS was also applied to the assessment of migratory behaviour of radionuclides in decommissioning wastes and storage and disposal facilities. Quinto *et al.* applied AMS to low-level detection of ^{99}Tc that may be present following nuclear energy production, and in groundwater after diffusion through bentonite which is used as a barrier in some storage facilities²⁵⁵. A gas-filled analysing magnet in AMS was proven to effectively remove the isobaric ^{99}Ru interference in samples including seawater, a peat bog lake and groundwater, with measurement at the fg g^{-1} level achieved. This would be applicable to routine environmental monitoring. Zhang *et al.* addressed the challenges of low-level ^{129}I detection of airborne radioactivity using AMS²⁵⁶. Samples were collected on a glass fibre filter, followed by pyrolysis and AgI-AgCl co-precipitation prior to measurement. A chemical yield of $81.5 \pm 5.8\%$ was achieved, with a detection limit of 1.3×10^4 atoms per m^3 . The method was used to analyse samples in an inland Chinese city, with iodine concentrations and $^{129}\text{I}:^{127}\text{I}$ ratios comparable to those collected in Japan before the Fukushima accident. The procedure developed can help to improve understanding of the transport and dispersion of radioactive iodine contamination away from nuclear sites, as well as for rapid measurement for emergency preparedness.

The measurement of the long-lived fission and activation product ^{93}Zr was the focus of several studies, given its contribution to the total nuclear waste inventory over long timescales. The most significant interference that must be removed is isobaric, monoisotopic ^{93}Nb . Pavetich *et al.* investigated the properties of AMS for removal of ^{93}Nb , including different molecular ion species and the ^{93}Nb background in different sample holder materials²⁵⁷. A ^{93}Zr background of $\sim 10^{-12}$ was achieved, with a ^{93}Nb suppression factor of 13,000-90,000 in the detector. The removal of isobaric ^{93}Nb was investigated by Hain *et al.* using a passive absorber and a gas filled magnet in combination with a time-of-flight path to identify neighbouring ^{92}Zr and ^{94}Zr , and final measurement by AMS²⁵⁸. A range of ion beam energies was investigated to determine the stopping powers of both ^{93}Zr and ^{93}Nb as a function of energy. The ^{93}Zr detection limits using the passive absorber and gas-filled magnet were 1×10^{-10} and 5×10^{-11} , respectively. Asai *et al.* measured ^{93}Zr using ICP-MS following separation employing a microvolume (0.08 cm bed volume) anion exchange cartridge (TEDA)²⁵⁹. The separation was complete in just over one minute, with accurate detection of ^{93}Zr and all stable Zr isotopes in a spent nuclear fuel pellet using isotope dilution mass spectrometry. The isotopic composition was consistent with the values predicted in a burnup calculation code (an algorithm that models the events during nuclear reactions).

Automated and rapid separation techniques were developed for multiple radionuclides for decommissioning and environmental monitoring applications. Goldstein *et al.* combined sequential

chemical separation with multiple ion counting ICP-MS for detection of Am, Np and Pu in a single aliquot in environmental samples²⁶⁰. The sequential chemical separations included co-precipitations and extractions using resins such as TEVA and 50wX8. Measurement of a single aliquot reduces the procedural time, and the method was validated using environmental reference materials, achieving good agreement with certified values on samples with $>3 \times 10^6$ atoms ²⁴¹Am. Kolacinska *et al.* compared different chromatographic methods for separation of ⁹⁹Tc using a sequential injection analysis lab on valve system coupled with ICP-MS²⁶¹. Factors including sorption capacity and selectivity were assessed, with the extraction chromatography resin TEVA proving to be the optimal approach. A minimum detectable limit of 6 mBq L⁻¹ was achieved in 50 minutes. The procedure was validated using reactor coolant and sewage, river water surrounding the reactor and an inter-laboratory exercise. Furukawa *et al.* focused on the sample introduction system of an ICP-MS instrument coupled with solid phase extraction to improve ⁹⁰Sr sensitivity²⁶². Compared with using Ar gas alone, an Ar-N₂ mixture introduced into the nebuliser improved the sensitivity by a factor of 3.7, removing the need for relatively time-consuming custom tuning of the instrument to improve sensitivity. A detection limit of 0.3 Bq L⁻¹ was achieved within 30 minutes, and results for environmental water from the Fukushima Nuclear Power Plant agreed with values from radiometry.

3.7.3 Nuclear accident response

Although it has been eight years since the accident at the Fukushima Nuclear Power Plant, there are still multiple papers published on the subject, with a common area being long-term monitoring of the surrounding environment, and characterisation of materials at the site. The ability of different analytical techniques to be deployed in the immediate aftermath of a radiological incident also remains a popular area of research.

Radioactive caesium isotopes (¹³⁵Cs:¹³⁷Cs) have been identified as a useful long-term tracer in the environment surrounding Fukushima. Bu *et al.* applied a two-stage chemical separation procedure to achieve separation factors of >100 from multiple interfering elements prior to TIMS measurement, including Rb that can act as an ionisation suppressor ²⁶³. The method achieved an isotope ratio precision that was generally better than 10 % for samples containing as little as 10 fg ¹³⁷Cs. The method was validated on contaminated marine sediment from the North Pacific. A separate study by Sakamoto *et al.* aimed to develop a technique that could achieve micro-imaging capability and selective elemental detection that would be applicable to fine particles in a mixture of other constituents²⁶⁴. A TOF-SIMS instrument and wavelength tuneable Ti/sapphire lasers were developed for interference-free resonance ionisation of target elements. Using two lasers at different wavelengths for a two-step

resonance ionisation of Cs led to the successful measurement of a contaminated radioactive particle with no interference from isobaric Ba isotopes. This represents a significant reduction in procedural time compared with offline chemical separation.

Mishra *et al.* measured total U by ICP-MS and ^{235}U : ^{238}U using TIMS in Fukushima-contaminated soil and water samples to investigate the mobilisation of radionuclides in soil into aquatic systems²⁶⁵. Soils were chemically characterised, and whilst there was no evidence of ^{235}U enrichment from isotopic ratio measurements, the U distribution coefficients ranged from 30-36,000 L kg⁻¹. This shows the importance of soil characteristics on U mobility, in particular Fe, Mn and CaCO₃ concentration, soil pH and organic content. In a separate study, Stan-Sion *et al.* set up a new AMS study for low-level measurement of ^{129}I in North Pacific seawater in response to ongoing public concern following the accident²⁶⁶. The ^{129}I concentrations ranged from 0.9-1.6×10⁸ atoms L⁻¹, with concentrations up to 6.4×10⁸ atoms L⁻¹ in a river close to the damaged reactor. The authors concluded that Fukushima and its vicinities were an isolated area of contamination.

Total reflection XRF (TXRF) was also applied to analysis of materials and the environment affected by the Fukushima accident. Matsuyama *et al.* developed a method that could measure U in 15 minutes using TXRF at a minimum detectable activity below the effluent standard value in drainage water of 20 mBq cm⁻³²⁶⁷, suggesting it could be deployed as a routine analytical technique. Solutions were prepared by mixing a multi-element standard with a liquid containing the components of demolition debris, with Gaussian fitting performed to overcome the Rb K-alpha peak overlapping with the U L-alpha and Th L-alpha peaks. The same technique was applied by Yoshii *et al.*, with 10 μL of sample solutions dropped onto a quartz optical flat directory both with and without extraction chromatography separation²⁶⁸. Following chemical separation, there was no overlap in the TXRF spectrum from the Rb K alpha peak, and the measurement time needed to reach the detection limit described was 5 minutes. This compared favourably to 15 minutes in unseparated samples.

As well as Fukushima, *the release of radionuclides and materials in the immediate aftermath of a nuclear accident* was also considered in some papers. Obada *et al.* used surface analysis techniques (XPS and TOF-SIMS), Raman spectroscopy and SEM to understand the behaviour of radioactive Cs and I released from degraded fuel and into the reactor coolant system following an accident in pressurised water reactors²⁶⁹. Caesium-iodide aerosols were deposited on oxidised surfaces representative of a reactor coolant system following an accident, and the materials were analysed following reheating at up to 750°C in air or steam. The composition of the carrier gas during reheating had a significant impact on Cs release. Song *et al.* used a range of techniques including ICP-AES, XRD, SEM and EPMA to

investigate the potential chemical and physical properties of post-accident fuel debris²⁷⁰. A series of melting and solidification experiments was performed with different U:Zr atom ratios and Zr oxidation indexes from 36-100 %. The composition of particles was found to vary between different particles and within particles, highlighting the complexity of material produced following a nuclear accident, and the importance of complete characterisation.

3.7.4 Reactor materials

The long-term monitoring of materials used during reactor operation and reprocessing is key to ensuring safe and efficient operation, in particular the presence, behaviour and subsequent removal of impurities. Rapid and non-destructive techniques are frequently tested for routine analysis of reactor materials that reduced the time, handling, exposure and secondary waste associated with destructive analysis. A range of analytical techniques are used, in contrast to some other applications where one or two techniques are dominant.

Several studies investigated the *applications of LIBS for reactor material components*. Qiu *et al.* used fibre-optic LIBS instrument for multi-elemental analysis of a steel sample used for main pipelines in nuclear power plants (Z3 CN20-09 M)¹⁹. A key focus of the paper was the distance between the fibre output end face and the lens, which was studied using plasma diagnostic methods. Self-absorption was observed if the distance was shorter than optimal, and the plasma temperature and density became lower if the distance was longer than optimal. Fibre-optic LIBS was also used for measurement of steel by Wu *et al.*, with the Cr content of the steel noted as having an impact on the emission intensity of the laser produced plasma from the steel²⁰. Fobar *et al.* used double pulse LIBS on a robotic system for remote detection of Cl contamination on a stainless-steel surface canister, overcoming the issue of having no direct line of site for the canister²⁷¹. The field deployable configuration is useful for harsh environments and constrained space, with detection of Cl concentrations down to 10 mg m⁻². A hand-held LIBS instrument was evaluated by Manard *et al.* to determine rare earth elements in a uranium oxide matrix, as a rapid and on-site approach that reduces handling, transport and exposure to radioactive materials²⁷². Europium, Nd and Yb were spiked into a uranium oxide powder and measured with preliminary detection limits were of the order of hundreds of mg kg⁻¹. The rare earth elements tested could be distinguished when tested on National Institute for Standards and Technology glass and uranium SRMs.

X-ray – based techniques were also recognised for impurity measurements. Sanyal *et al.* used TXRF to measure multiple elements at ng-µg mL⁻¹ levels in plutonium samples²⁷³. A small volume (2 µL)

of solution previously separated from the plutonium matrix was deposited on TXRF supports. The ng levels of Pu deposited meant that samples could be analysed without having to operate in a cumbersome glovebox, as well as limiting worker exposure and radioactive waste. The average relative standard deviation for spiked plutonium solutions was 4.5 % (k=1), increasing to 10.6 % for two real plutonium samples with elemental concentrations of 0.2-61 $\mu\text{g mL}^{-1}$. Measurement employing TXRF of 100-160 ng of Pu was reported by Dhara *et al.*²⁷⁴, with 10% collodion solution in amyl acetate added to the deposited sample to fix Pu on the TXRF supports. An average precision of 3 % (k=1) was calculated, with a standard deviation of 6 % from expected values based on a sample size of 100-160 ng of Pu. Pandey *et al.* used WDXRF to characterise mixed oxide nuclear fuels²⁷⁵. With U content ranging from 2.9-4.2 weight %, the RSD for U and Th was 0.4 % and 0.25 %, respectively, with good agreement with results obtained following chemical analysis.

Trace and ultra-trace analysis of materials was carried out using destructive techniques, most commonly ICP-MS. Nagar *et al.* measured metallic impurities in U-Zr alloy fuel after solvent extraction to separate U and Zr matrix elements to $<10 \mu\text{g mL}^{-1}$ ²⁷⁶. Recoveries of 36 elements were determined using a standard addition method, with a relative standard deviation of $<10 \%$ for more than 90 % of elements tested, and detection limits of between 0.01 and 1.1 $\mu\text{g L}^{-1}$. Reilly *et al.* also used ICP-MS to trace Ca, Mg and Th contaminants during the production of U metal produced using bomb reduction of suitable U precursors²⁷⁷. Samples were first doped with Th from 0-1000 $\mu\text{g g}^{-1}$, and then, following a digestion of the reduced metal, analysed. Results showed that Th fractionation was most significant at concentrations of $<100 \mu\text{g g}^{-1}$, whilst a significant portion of U and Ca migrated into the digestion crucible walls.

The accurate assessment of *graphite impurities* is important given its role as a neutron moderator during reactor operation. Plukiene *et al.* measured samples from a RBMK-1500 reactor using a range of techniques (including neutron activation analysis, gamma activation analysis and ICP-MS)²⁷⁸. The aim was to obtain the missing information on impurity distributions in nuclear graphite constructions, and then compare the data with historical inter-comparison measurements. The results provided new limits of the maximum impurity concentrations that could be present. Wu *et al.* assessed the impact of molten fluoride salt (2LiF-BeF₂ (FLiBe) exposure on the ability of graphite (IG-110) to absorb tritium²⁷⁹. After exposing the graphite to the molten salt for 12 hours at 700°C, samples were measured using techniques including XPS, GDMS, XRD and Raman spectroscopy. Graphite fluorination and changes in microstructure were confirmed, with the possible introduction of new active sites that form once existing ones are consumed. This is potentially an advantage for chemisorption of tritium.

3.7.5 Fusion

The characterisation of materials designed for fusion reactors remains a popular topic, with a focus on material damage and retention of contaminants during operation. The dominant technique is still LIBS, although a range of other spectrometric and bespoke analytical techniques have also been applied.

Maddaluno *et al.* reported the *retention and surface composition of deuterium* (measured as a proxy for ^3H) using LIBS in the Mo (titanium zirconium molybdenum) toroidal limiter tiles from the Frascati Tokamak Upgrade during short breaks in operation or during maintenance²⁸⁰. A single pulse technique was used under high vacuum, nitrogen or argon atmosphere, with differences in detection ability and resolution of D-alpha and H-alpha recorded between the three. The aim was to perform extended LIBS analysis of retained deuterium using a robotic arm. Zhao *et al.* developed a remote *in-situ* LIBS method for diagnosing the composition of plasma facing components, allowing measurement at a specific discharge operation or under specific plasma conditions²⁸¹. Depth and lateral resolutions of ~ 100 nm and ~ 3 mm were achieved, respectively, and elements and impurities including deuterium were successfully detected. The aim is to deploy the system in upcoming facilities such as ITER.

Paris *et al.* compared LIBS with two Nd/YAG lasers with 0.15 and 8 ns pulse durations for the quantitative assessment of fuel retention in first walls, with special focus on deuterium-doped W/Al coatings of ~ 3 μm thickness²⁸². In the case of ps laser, deuterium was detected at considerably lower fluence values and with an acceptable degree of accuracy. Li *et al.* applied LIBS in combination with XRD and SEM/EDX for assessing Er_2O_3 as a coating to prevent liquid lithium corrosion in a tokamak device²⁸³. The LIBS measured the depth distribution of Li and other elements in the corroded layer, with depth profiles obtained as a function of laser pulse number. The results were consistent with EDX line-scanning of the target specimen cross-section, indicating that the liquid Li penetration depth can implicate the corrosion resistance of the oxide layer.

The *characteristics of LIBS in various pressure environments on the quantitative determination of Mo in the multi-component alloy first wall material* in the Experimental Advanced Superconducting Tokamak (EAST) was the focus of a study by Liu *et al.*²⁸⁴. Normalisation methods and the partial least squares methods were combined, with different normalisation methods compared for their impact on spectral accuracy and uncertainty. Partial least square methods based on inter-element interference were better than the other methods for Mo elemental determination. A second study by the same author focused on the use of LIBS for diagnosing Li-wall conditioning and Li-H/deuterium co-deposition on the first wall of the EAST²⁸⁵. The deuterium fuel and co-deposition of multiple impurities was

observed, whilst the degree of re-deposition of Li coating on the first wall could be assessed. The conditioning technique applied reduced the H/H+deuterium ratio due to strong Li adsorption, enhancing long-pulse H-mode plasma operation. The possibility of *in-situ* measurement of deposition, co-deposition and dynamic retention on the EAST first wall using laser induced ablation spectroscopy (LIAS) was published by Hu *et al.*²⁸⁶. The study draws attention to the commissioning of a system with high temporal resolution during long pulse discharges.

A range of techniques other than LIBS were also applied to measurement of fusion-related materials. Laser induced ablation quadrupole mass spectrometry (LIA-QMS) of graphite limiter tiles for quantitative H determination was investigated by Oelmann *et al.* to improve understanding of plasma wall interactions and lifetime of plasma facing components²⁸⁷. A series of locations were analysed, with H implantation observed in erosion zones, where a low fuel content is present due to the high temperature during plasma operation. Results compared favourably to thermal desorption spectrometry and simultaneously performed LIBS. Energy resolving mass spectrometry was used by Dinca *et al.* for investigating co-sputtering of W-Al materials in a dual-High Power Impulse Magnetron Sputtering discharge, operating with different Ar-deuterium gas mixtures²⁸⁸. The sputtering gas composition had a significant impact on the total ion flux and composition, with a difference in deuterium abundance in single and dual- High Power Impulse Magnetron Sputtering operation. Multiple techniques including XRD and GD-OES were also used, with the results showing high deuterium retention (up to 21 atomic %) in the mixed W-Al layers that was more dependent on the W-in depth concentration than the Al.

Tungsten was the focus of two studies by Zhang *et al.* In the first, a newly developed space-resolved spectrometer at 30-520 angstrom was developed to measure a radial profile of *W line emission in the EAST tokamak*²⁸⁹. Accurate profiles were achieved for impurities including Ar, Fe, O and W. The second study investigated W degradation in plasma-facing materials due to H permeation and trapping²⁹⁰. Several techniques (ToF-SIMS, SIMS and focussed ion beam combined with SEM and TEM) were used to characterise two polycrystalline W plates implanted with H. The results revealed detailed information on H behaviour, including the timescale of release at room temperature following ion implantation and blister formation of the as-implanted W that remained following thermal annealing.

Fazinic *et al.* identified the *composition of metal dust in fusion reactors* as a key topic with regards to safe operation, and focused on determining the composition of dust in the JET tokamak²⁹¹. Simultaneous Nuclear Reaction Analysis and Particle Induced X-ray Emission (PIXE) with a focused four MeV He-3 microbeam was used, focusing on Be-rich particles from the deposition zone of the inner

divertor tile. The main components of the dust were: deuterium from the fuel, Be and W from the plasma-facing components and Cr and Ni from the antennae grills for auxiliary plasma heating. The analysis identified large Be-rich particles (>90 atom %), and small Al and or Si-rich particles containing other elements such as Fe, Cu or Ti.

3.8 Electronic materials

There have been *three reviews published* that are pertinent to this section. The first, by Noll *et al.*⁸ was an overview of LIBS for industrial applications which covered the developments from 2014 to 2018. This was reviewed in more detail in other sections, including section 1, metals. It will not, therefore, be discussed further here. The other review, by Costa *et al.*²⁹², reviewed (with 84 references) the use of LIBS for the chemical analysis of waste electrical and electronic equipment (WEEE). The review was split into convenient sections starting with an introduction containing bar charts demonstrating the rapid increase in use of LIBS over the last 20 years. This was followed by sections on data handling, approaches for qualitative and quantitative analysis, the identification of polymers in WEEE and the analysis of printed circuit boards. It finished off with some potential areas of future research. Many of the applications discussed were also presented in easy to access tables. The third review was presented by Gamez and Finch²⁹³ who gave an overview of recent advances in surface elemental mapping using the glow discharge techniques GD-OES and GD-MS. The review, which contained 49 references, discussed instrumental advances, applications and 3D elemental surface mapping. The advantages of glow discharge, e.g. the speed at which it can map a surface compared with other techniques, were also discussed. Among the instrumental advances described are changes to the discharge chamber design so that larger samples can be analysed and the use of different spectrometers, e.g. monochromators, acousto-optic tunable filters and push-broom hyperspectral imagers.

3.8.1 Wafers, thin films and multi-layer samples

Measuring the thickness of thin films or layered samples is very important. However, results can be variable. A paper by Sakurai and Kurokawa²⁹⁴ reported the results of a round robin study for layer thickness determination using reference-free XRF. Two samples were obtained both containing layers of gold, nickel and copper. A total of 11 companies participated in the study producing 15 datasets. A variety of instrumentation (WDXRF and EDXRF) utilising assorted X-ray tubes (Ag, Mo, Pd, Rh and W) was used in the study and the participants were allowed to use whatever operating condition they wanted. Data were collected and a couple of outliers identified using Grubb's test. A comparison of XRF data with those obtained using ICP-OES, ICP-MS or ID-ICP-MS following dissolution of the individual layers was made. Results were in good agreement. The overall precision of the XRF data were 4.3 – 6.6%.

A paper by Van der Heide²⁹⁵ emphasised the critical need for *SIMS depth-profiling during the fabrication of complementary metal oxide semiconductors* (CMOS). The high sensitivity, low LOD and acceptably rapid throughput make it the technique of choice for this application. The paper has no research *per se*, but it provides a good overview of the capabilities of SIMS and discusses the future applications, e.g. analysis of three dimensional structures. Topics covered include the existing SIMS depth-profiling approaches for 2D and 3D structures, in-fabrication SIMS deployment, data analysis tools for the in-fabrication SIMS derived depth profiles that use pattern recognition and hybrid characterization approaches. The authors suggested that a hybrid of XRD and SIMS could potentially be viable.

The need for *reference materials* is as relevant to these sample types as any other, but thus far, there is a distinct paucity. Honicke *et al.*²⁹⁶ have reported the development of thin layer reference materials that have a total mass deposition at the ng level for analytes such as Ca, Cu, Fe, La, Mo, Ni, Pb and Pd. Two samples were prepared by physical vapour deposition on silicon nitride membranes. One sample had 10-times lower deposition than the other. Other materials were prepared that had single element films and others were prepared on silicon wafers. Samples were characterised using a multitude of techniques including three different synchrotron radiation beamlines at the BESSY II electron storage ring employing a reference-free XRF approach. Homogeneity of the samples was tested at the PO4 beamline at DESY. Good precision was obtained during the measurements, indicating good precision during manufacture.

The *analysis of wafers or silicon substrates* has been the focus of several papers because contamination of the wafers can have a huge effect on the quality and quantity of the end product. Mejstrik *et al.*²⁹⁷ discussed the re-installation of a TXRF instrument for silicon wafer surface analysis. A thorough description of the spectrometer as well as the robotic wafer manipulator was given. The authors prepared and validated a reference wafer with a known concentration of Ni contaminant. This was to be analysed after a set amount of time or after a set number of measurements. The wafer was then used as a reference for the analysis of some certified wafers. However, agreement with certified values was poor. The authors then used NIST 1640 spiked on to blank wafers as a second external check. Results for the Ni as well as Co, Cr, K and Mn were in good agreement with certified values, although the Cu, Fe and Zn data were in less good agreement. The authors concluded that the original certified wafers must have been contaminated during storage. A comparison of data obtained using the techniques of TXRF, TOF-SIMS, Deep Level Transient Spectroscopy and techniques used for the measurement of carrier lifetime was presented by Polignano *et al.*²⁹⁸. Various experiments were undertaken aiming to mimic assorted processes, including wet processes, ion implantation, surface contamination etc. Correlation between TXRF and TOF-SIMS data was pretty good with the TOF-SIMS

being better at determining the light elements than the TXRF. The relative advantages and disadvantages of each of the techniques were discussed. It was concluded that no one technique was capable of measuring the surface contaminants and the diffusivity. Two papers have discussed the determination of O in silicon. One reported the use of SIMS²⁹⁹ and the other the use of LIBS³⁰⁰. In the paper by Jakiela²⁹⁹, several modifications to the instrument were required. A very high primary flux of Cs⁺ (14.5 keV at an intensity of ~300 nA) was used, the turbomolecular vacuum pump was replaced with an ion pump, a titanium sublimation pump was also used to improve vacuum further (to 2×10^{-10} Torr when the ion beam was on) and the cryo-shield surrounding the sample chamber was cooled using liquid nitrogen. Once everything had been optimised, the LOD for O was 10^{15} atoms cm⁻³. This was, according to the authors, at least 10 times lower than that reported in any other application. Further studies elucidated oxygen indiffusion and outdiffusion during annealing in Ar and in vacuum. It was noted that the results are qualitatively and quantitatively different for float zone silicon compared with Czochralski-grown silicon. The paper by Davari³⁰⁰ described the LIBS analysis and experimental setup in detail. Two LIBS protocols were compared. One simply used the intensity at the O wavelength at 777.19 nm. This, however, yielded both poor calibration ($R^2 = 0.44$) and sensitivity. The other method used both the 777.12 nm O line and a Si line at 781 nm. This internal standardisation procedure improved linearity of calibration significantly ($R^2 = 0.95$) and led to less error. By using the Si internal standardisation, fluctuations in plasma excitation temperatures could also be accounted for. Under optimal conditions, the LOD was 8 ppm O, which was lower than that obtainable using a Standard FTIR method.

Grazing incidence XRF (GIXRF) has been reported for the analysis of thin films by three groups of workers. In one, Maderitsch *et al.*³⁰¹ used it to analyse organic light emitting diodes. Samples were prepared such that a buffer layer was deposited on a substrate and then a hole transport layer followed by a host layer were deposited on that. Samples were analysed using a combination of the two non-destructive techniques of GIXRF and X-ray reflectometry (XRR), with the diffraction instrument having an additional fluorescence detector added. An added advantage of the two techniques is that they require virtually no sample preparation. The angle curves produced from the two techniques were processed using the software package called JGIXA. The S distribution in the layers was dependent on the sample preparation method of the host layer. In addition to determining the distribution of S, the combined GIXRF/XRR approach provided information such as layer thickness as well as surface and interface roughness. A second paper to combine GIXRF and XRR analysis was presented by Pessoa *et al.*³⁰² who used the techniques to analyse telluride-based films that are often used for data storage devices and photovoltaic cells. The performance of both lab-based and synchrotron-based instrumentation was assessed for the characterisation of ultra-thin (< 10 nm) titanium-tellurium films

that had been prepared by physical vapour deposition and then capped with a 5 nm Ta passivation layer. Both setups were sufficiently sensitive to provide accurate chemical depth profiles, with data compared with those obtained using TOF-SIMS, XPS and plasma profiling TOF-MS. Inter-diffusion between the tellurium and tantalum cap was observed by all techniques. The third paper was presented by Yamada *et al.*³⁰³ who studied the alloying of gold-copper layers using an assortment of techniques including GIXRF, XRR, XRD and conventional XRF. The GIXRF was undertaken using a benchtop total reflection WDXRF instrument. The samples were prepared and then some were heat treated at 300°C for one hour. The angle-dependent GIXRF profiles were very different between heated and non-heated samples. Theoretical calculations indicated that alloying was occurring, even though the temperature was so low. The other non-destructive techniques confirmed the data found using GIXRF.

Hermann *et al.*³⁰⁴ used *calibration-free LIBS to analyse nickel – chromium - molybdenum thin films* with thickness of 150 nm that had been prepared using pulsed laser deposition. The experimental setup was described in detail and the operating conditions used assumed to produce a plasma in local thermal equilibrium. These conditions were an atmospheric pressure of argon with an ultraviolet laser pulse of ns duration. Optimisation of the delay time between laser pulse and the detector gate identified times of 1 or 2 μs to be optimal. The data produced by the system were input to a simple algorithm enabling concentrations to be calculated. The data obtained were supported by data obtained using Rutherford backscattering spectrometry and energy dispersive X-ray spectroscopy. The analytical performance of the LIBS technique was superior to either of the other techniques used.

Depth-profile analysis of chromium – nickel metal thin films with a *sub-100 nm depth resolution was achieved using near UV fs-LA-ICP-TOF-MS* by Kaser *et al.*³⁰⁵. The laser beam was guided through a homogenisation scheme which was based on aperture-assisted diffraction and re-assembly of the beam by an optical lens. The setup was described in full with a helpful schematic being provided. The setup produced craters that were cylindrical in shape. Fluences between 0.6 and 1 J cm^{-2} were applied resulting in an ablation rate of 27 nm per pulse. It was possible to depth-profile nine alternating layers of nickel and chromium each of which had a depth of approximately 60 nm.

3.8.2 Solar cell materials

The analysis of solar cells or *the copper indium gallium selenide (CIGS) thin films in solar cells* is still receiving attention from some researchers. Two papers have used LIBS for such an analysis^{306, 307}. In the first example, Choi *et al.*³⁰⁶ determined the effects of varying the laser spot size between 35 and

150 μm on the LIBS data produced. If the spectral lines are chosen correctly, then the signal intensity ratio rather than intensity alone should be used because it is nearly independent of laser spot size. Using the concentration ratio method the CIGS layer composition could be determined accurately, differing only 5% from data obtained using ICP-OES. The other paper to use LIBS for CIGS analysis was presented by Xiu *et al.*³⁰⁷ who optimised the operating parameters of the LIBS analysis and then provided both qualitative and quantitative data rapidly.

A *LA-ICP-MS method of analysing silicon solar cells* for contaminants such as Ag, Cu and Ni arising from plated metal contacts was reported by Colwell *et al.*³⁰⁸. Once prepared, the cells were heat-treated to 200 °C for up to 1000 hours prior to the analysis. The surface contamination was removed through a wet etching process involving mixtures of nitric and hydrochloric / hydrofluoric acids before LA-ICP-MS identified the analytes that had penetrated the silicon wafer. No suitable silicon reference material was available, so NIST 614 glass was used as a non-matrix-matched standard for calibration. A study of the laser operating conditions was undertaken which demonstrated that high energy laser pulses doubled crater depth and led to a build up of re-solidified Si around the crater. This, in turn, decreased analysis speed and led to a decrease in transport efficiency to the plasma. Another problem observed was a very high uncertainty ($\sim 50\%$). This was hypothesised to arise through non-uniformity in cell preparation as well as the line-scanning method used for LA-ICP-MS analysis.

Jang *et al.*³⁰⁹ reported the *quantitative analysis and band gap determination of CIGS absorber layers* using a variety of instrumental techniques (XRF, LA-ICP-MS and ICP-OES). The bulk composition of the samples was determined using XRF and, after an acid digestion, ICP-OES. A fundamental parameters calibration approach was used to obtain the concentration ratios for XRF. Data obtained using femtosecond LA-ICP-MS were compared with those obtained using XRF. Elemental depth profiles were also obtained using SIMS and XPS. The band gap energy was calculated using a simple ratio method, i.e. $\text{Ga}/(\text{In}+\text{Ga})$.

The setup, operation and application of a *laser induced ablation quadrupole mass spectrometer for the depth resolved-analysis* of thin film solar cells and of hydrogenated / deuterated thin films deposited on glass was reported by Oelmann *et al.*³¹⁰. After the introduction the authors described the setup in detail, giving schematic diagrams of the instrument. The idea of the instrument is that a picosecond laser operating at 355 nm ablates the sample and then the volatile gaseous products are analysed using the mass spectrometer. As with most laser-based depth-profile analyses, the same spot has to be sampled on numerous occasions. The spot was examined using surface profilometry and a confocal microscope to gauge depth per laser shot. The linear relation between the signal and the gas pressure within the ablation chamber simplified its calibration and reduced the

uncertainties compared with other techniques. Very high vacuum was required to obtain sensitivity below the percent level. However, no sample preparation was required and the method is flexible with respect to the ablation rate. The picosecond laser pulse ensures that the thermal penetration depth is similar to the ablation rate, enabling a depth resolution of approximately 100 nm to be achieved. Data were compared with those obtained using LIBS, with good agreement being achieved.

3.8.3 Electronic equipment and devices

Numerous papers have been published that describe the analysis of *lithium ion batteries or their components*. The large majority use atomic spectrometry only as a peripheral or supportive tool and therefore do not bring any novelty to the field of atomic spectrometry. These papers will therefore not be discussed in this review. Several papers have discussed the use of LIBS for 3D mapping of the electrodes within the batteries. These have included two papers by Imashuku *et al.* who analysed the anode³¹¹ and the cathode materials³¹². Both papers monitored the Li signal at 610.4 nm under a reduced argon atmosphere of 1000 Pa. In the first example, the graphite anode of a battery was analysed until a depth of 150 μm had been reached, i.e. the LIBS laser sampled from the same spot effectively drilling through the sample. Areas of both homogeneous and inhomogeneous Li content were observed after the charge and discharge processes. The areas of inhomogeneous Li distribution after the charge process were attributed to a preferentially reacted area in the anode. The inhomogeneous areas found after the charge - discharge process were thought to be attributable to the low desolvation reaction rate of the Li ions at the solid electrolyte interphase. The inhomogeneous Li distributions were consistent with the charge – discharge curves and the Li ion transfer mechanism. The second paper studied the Li distribution in the LiCoO_2 cathode material³¹². A calibration curve was constructed comprising varying amounts of lithium carbonate in cobalt oxide (Co_3O_4) giving ratios of Li to Co of 0, 0.01, 0.1, 0.3, 0.51, 0.62, 0.80 and 0.99. The distribution of Li in the cycled material as determined using LIBS was in close agreement with the data obtained using XAS, but the precision was less good. The conclusion of both papers was that LIBS was capable of semi-quantitative determination of Li distribution in the electrodes, but was far simpler to apply than XAS. A third paper describing the analysis of electrodes using LIBS was presented by Smyrek *et al.*³¹³. This paper was focussed more on the manufacture of structured nickel manganese cobalt electrodes through embossing or laser structuring or the unstructured electrode. However, the LIBS analysis and the instrumentation were described in full. The fully quantitative LIBS data were used to study chemical degradation mechanisms and the impact of the electrode architecture on the Li distribution.

The elemental mapping of lithium ion battery components was described in two papers by the same research group. The first used LA-ICP-MS³¹⁴ and the second TXRF³¹⁵. In the paper by Evertz *et*

*al.*³¹⁵, post mortem analysis of the electrolytes within the cells was undertaken using a novel calibration strategy. A specialist device capable of dispensing nanoliter volumes was employed to inject small volumes of electrolyte or standard onto quartz glass prior to the analysis. Three configurations were prepared: alternating pattern (30 electrolyte droplets, 30 standard droplets), centered pattern (28 electrolyte droplets, 13 standard droplets) and octagonal (24 electrolyte droplets and nine Standard droplets). Validation was achieved through an acid digestion followed by ICP-OES analysis. Recovery rates for the TXRF analyses were between 98 and 105%, which compared favourably to the 85 – 90% achieved using a conventional application procedure. The centered pattern gave the best results in terms of recovery and precision. However, there were some problems noted with the technique. This included the Co being below the LOD and the Ni concentration detected being three times that of Mn – even though they were known to be in the electrolyte at the same concentration. The paper by Harte *et al.*³¹⁴ described the optimisation of a LA-ICP-MS method in terms of speed and frequencies and determined the effect on the spatial resolution of the mapping experiments. Higher scan speeds led to a decrease of 60% in time and gas consumption.

Two papers have discussed the *analysis of mobile phone components*. A paper by Bookhagen *et al.*³¹⁶ discussed how 34 mobile phones from different manufacturers were disassembled and then the components acid digested using a microwave digestion system. Analysis using ICP-OES and ICP-MS was then undertaken on the digests. Method validation was achieved through the analysis of the CRM ERM (R)–EZ505 electronic scrap. Results for the eight certified elements were in reasonable agreement with certified values (Be, Ni and Pd were $100 \pm 1\%$, Au, Cu and In were $100 \pm 11\%$ and Pt was $100 \pm 20\%$). The problematic analyte was Ag that had poor recovery and precision ($75 \pm 35\%$). This was attributed to the presence of hydrochloric acid in the digestion mixture. In addition to the eight certified elements, a further 49 were also determined. Analysis of the printed circuit boards demonstrated that the most abundant elements in decreasing order were Cu, Fe, Si, Ni, Sn, Zn, Ba, Al, Cr and Ti. These 10 analytes accounted for approximately 80% of the weight of the board. The other paper described the use of LIBS to determine In in liquid crystal displays of mobile phones³¹⁷. Two calibration strategies were compared: conventional univariate calibration and multi-energy calibration. After phone disassembly the indium tin oxide films were mixed with a resin and pressed into a pellet. For the multi-energy calibration model, two pellets were pressed. One with sample, a standard and cellulose binder and the other with sample plus a blank (silica). The full procedure and the strategy behind each calibration model was given in the text. Results were compared with the standard method of microwave assisted acid digestion (Method EPA 3052) followed by ICP-OES detection. All of the LIBS data showed greatest accuracy where the analyte signal was normalised against the signal at the C wavelength at 193.09 nm. This had to be performed before the data were

input to either calibration model. The LOD and LOQ for the univariate calibration were 0.3 and 1 mg kg⁻¹, respectively, compared with the multi-energy calibration values of 2.1 and 7 mg kg⁻¹. The In content ranged from 35 to 47 mg kg⁻¹. The conclusion was that both strategies could usefully be used for recycling and e-waste management.

The analysis of *computer hard disk or Random Access Memory components* has been reported by Castro and Pereira³¹⁸ and by Nolot *et al.*³¹⁹. In the first example, over 50 hard disks from assorted manufacturers were collected and then disassembled so that both of the magnets (actuator and spindle) were isolated. These were then heated to remove the magnetism and ground using a knife mill before being sieved. Several acid digestion approaches (microwave assisted and hot block) using different acid concentrations were compared. No suitable CRM was available and so spike / recovery tests were undertaken. Overall, the treatment providing best results was using 100 mg of sample and a hot block using 7 mol L⁻¹ nitric acid. The elements present at highest concentration were Fe, Nd and Pr. The analytical data were input to PCA and Hyperspectral Image to help classify the disks. The paper by Nolot³¹⁹ described the use of TOF-SIMS, GIXRF and XRR to investigate the influence of variations in the deposition process of tantalum oxide on the tantalum oxide / metal structure of tantalum-based random access memory devices. Titanium nitride and nickel were tested as the bottom electrode material since they are both candidates to replace noble materials. All three techniques demonstrated significant inter-mixing between the titanium nitride and tantalum in the tantalum oxide titanium nitride stacks, even when optimised tantalum oxide deposition conditions were used. However, TOF-SIMS also demonstrated that if a H^{*} plasma step was used during the atomic layer deposition process of the tantalum oxide, the oxidation of the Ni and the inter-mixing of tantalum oxide and Ni were both minimised. The X-ray-based techniques also indicated the influence of the H^{*} plasma on the nickel – based samples when used with the model-based multi-layer combined analysis. It was concluded that GIXRF and XRR may be used as non-destructive and sensitive depth-profiling techniques.

The final sub-section of this part of the review is a *mixture of other sample types* that do not fit into any of the other sub-sections easily. Some of these are precursor materials, e.g. tetraethylorthoillate, were analysed for impurities using SF-ICP-MS by Lu *et al.*³²⁰. It was pointed out that such materials have to be of very high purity and therefore the contaminant levels must be very low. However, once dilution of the material has occurred so that it could be introduced to the ICP-MS instrument the concentration of the potential contaminants are likely to be at the pg L⁻¹ level, which is too low to be measured reliably. A simple liquid – liquid extraction using isopropanol and water was used to isolate the analytes of interest from the matrix and actually provide a preconcentration factor of approximately 19. Although some interfering species were also extracted, these could be overcome by use of an appropriate resolution factor on the SF-ICP-MS instrument. Spike – recovery tests yielded

acceptable data (94 – 113%) and precision was better than 9.46%. An interesting application was reported by Wang *et al.*³²¹ who used LIBS to analyse high voltage transmission line insulators. Under normal circumstances, these can only be analysed during a power cut, when samples are removed, taken back to a laboratory and tested for sugars, bird droppings and heavy metal particulates. The rapid LIBS test that may be undertaken *in-situ*, with minimal sample damage is therefore a clear advance in methodology. The study optimised the LIBS conditions (laser energy, delay time, etc.) and then the analytical data produced were analysed using PCA, k-means and partial least squares regression. These multivariate techniques gave a significant improvement in trace metal contamination analysis compared with normal calibration. Another LIBS application was described by Wang *et al.*³²² who used it to determine the halide concentrations in the quantum dots CsPb(X)₃ where X can be Br or Cl. These are materials that can be used to prepare nanometer scale semiconductors. Again, LIBS operating conditions were optimised and several samples with different Br/Cl ratio were analysed. Calibration curves correlating weight to LIBS emission intensity were obtained using mixtures of CuBr₂ and CaCl₂. The LIBS method showed better sensitivity than electron dispersive spectroscopy without the need for sample preparation.

3.9 Nanostructures

Atomic Spectrometry, through techniques such as XRD, XPS, XRF, single nano particle (sNP) ICP-MS and ICP-OES has a key role in the characterisation and detection of NPs with over 150 papers published in the period covered by this ASU. However, most of the articles only mention the technique(s) used without any further analytical detail and as such are not discussed here.

In any growing analytical field *method validation protocols and metrology* tend to develop at a slower rate than the methodologies used, although this should not be the case and a metrological approach should be the starting point for method development. It is timely then that the current status of NP detection, with a focus on analytical metrology, has been reviewed by Lopez-Sanz *et al.*³²³ The review (with 139 cited references) proposes some metrological definitions for NPs and covers the analytical methods used for both their characterisation and detection. The latter was split into two areas; methods in which NPs are used to extract and / or pre-concentrate other target analytes and methods where the NP is the analyte. After a brief section on microscopy-based techniques the main focus is on the use of separation by CE, FFF and LC coupled with a variety of detectors including dynamic light scattering (DLS), multiangle light scattering (MALS), ICP-MS and UV. The use of these techniques reported over the past five years was summarised in a table (60 references) with many also being discussed in the text. The authors pointed out that maintaining sample integrity during both analyte characterisation studies and detection methodologies is, as for any analysis, still the key to

providing analytical validity. However, this can prove more challenging because of the tendency of NPs to aggregate and the wide range of complex matrices, e.g. from consumer products to biota, which may contain them. It was also pointed out that whilst NPs are available as standards, often containing a stabilising agent, with a given mass concentration, particle concentration, size or size distribution these parameters may change upon dilution (or other use) into a different matrix. A further problem highlighted is the lack of available CRMs for method validation and that, from a strict metrological point of view, recovery studies are only admissible when the other alternatives are not available. Bustos *et al.* at NIST reported on the validation of sNP ICP-MS for routine measurements of nanoparticle size and number size distribution³²⁴. The validation comprised three stages: (i) calibration based on the certified particle size of NIST SRM 8013 (Au NPs); (ii) comparison with HR-SEM data as a reference method (which is traceable to the SI) and (iii) evaluation of the uncertainty associated with the measurement of the found mean particle size to enable comparison of the sNP ICP-MS and HR-SEM methods. After method optimisation the particle size results obtained for NIST SRMs 8012 and 8013 by sNP ICP-MS were 27.2 ± 0.1 and 54.1 ± 0.1 nm, respectively. These data were in good agreement with those obtained using HR-SEM of 27.0 ± 0.1 and 54.7 ± 0.4 nm, respectively and also with the certified values of 26.8 ± 0.1 and 54.7 ± 0.4 nm, respectively. The particle size distributions obtained by both methods for the two SRMs were also in good agreement with the sNP ICP-MS data showing a broader tail in both sides of the distribution than the HR-SEM data. Both analytical approaches were also used to characterise commercial AuNP suspensions of three different sizes (30, 60, and 100 nm). The measurements revealed the existence of two distinct sub-populations of particles in the number size distributions for four of the 60 nm commercial suspensions. The paper also gave a detailed account of the uncertainty estimations and concluded that additional work is still needed to establish the metrological traceability of sNP ICP-MS for NP size determination. This is because of the assumption that all particles are spherical and that the TEM data supplied by commercial producers of NPs may be inadequate.

In *single NP (sNP) ICP-MS analysis* it is usual, due to instrumental limitations on the need for rapid data collection and processing, for only one isotope to be monitored during an analytical run. Two research groups however have explored the acquisition of multiple isotope data using sNP ICP-MS. The first of these papers, by Naasz *et al.* explored the capabilities of two quadrupole ICP-MS and two TOF-ICP-MS instruments for determining the composition, size distribution, and concentration of BiVO_4 , $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$, steel (IRMM-383 CRM) and Au-core/Ag-shell NPs³²⁵. Both instrument types used could estimate the size of Au-core/Ag-shell NPs with uncertainties ranging from 25 to 50% relative. Measurements by the two quadrupole ICP-MS instruments generally had the lower uncertainty estimate. For the other multi-element nanoparticles, the particle sizes found were not in agreement

with those obtained from analysis using SEM. The data presented for the particle number concentration appears acceptable for the Au/Ag NPs but again differences were reported with the SEM data for the other types of NP analysed. The particle mass concentration presented again shows poor agreement with the expected values. These differences between the expected and found data were attributed to aggregation and/or agglomeration of the NPs in solution prior to analysis. Thus, these results emphasise the need for maintaining sample integrity prior to analysis as highlighted in the previous paragraph. With regard to identifying multi-element NPs, the TOF instruments could determine the four different elements in the steel NP ion cloud simultaneously without a reduction in sensitivity. This was not the case for the two quadrupole ICP-MS instruments. This is, in part, because of the much greater number of data points that can be acquired during a single particle event which were calculated to be up to 15 for TOF-ICP-MS and 1 to 2 for quadrupole ICP-MS. The paper by Hirata *et al.* (in Japanese) on multi-isotope sNP ICP-MS used a MC-ICP-MS instrument, equipped with a high-time resolution data integration system, to measure the elemental composition, the $^{195}\text{Pt}:^{194}\text{Pt}$ ratio and particle size distribution of Pt and Au/Pt NPs³²⁶. Sample introduction was by the laser ablation in a liquid technique, the Pt signals were measured using Daly counters whilst the Au signal was monitored on the electron multiplier of the instrument. The results obtained showed that the repeatability of the isotope ratio measurements was mainly controlled by the counting statistics of the signal. This suggested that effective data acquisition could be achieved under transient signals produced from the NPs. Both the measured NP size and the Au:Pt ratio of the NPs varied significantly with changes in the laser ablation conditions and possible mechanisms for these observed variations were discussed in the paper.

With all analytical techniques there is *a continual quest to improve the methodologies* and NP analysis is no exception. The use of an online micro-droplet calibration approach, with the aim of achieving matrix independent nanoparticle sizing, was reported by Hendriks *et al.* this year³²⁷. To achieve this, a micro-droplet generator, which included a desolvation device, was inserted between the spray chamber outlet and the torch of the ICP- TOF-MS instrument. A calibrated video camera was used to determine the size of the micro-droplets introduced. Thus, conventionally aspirated NPs and the calibrants in the micro-droplets were introduced simultaneously to the instrument. After optimisation, which included sampling depth, nebuliser gas flow, acid related matrix effects and accounting for space charge effects, the method was applied to the determination of Au NPs in phosphate buffered saline (PBS). The PBS attenuated the Au signal, with a decrease in attenuation observed with decreasing PBS concentration, such that the measured mean particle size decreased, and the size distribution broadened with increasing PBS concentration. The authors pointed out that 'real' samples could be diluted prior to analysis to reduce matrix effects but that this is not always

possible if the number of NPs in the original sample is low. In addition, it was also noted that matrix matching of the calibrants and samples could also be undertaken. It would have been of great interest to see the latter approach undertaken here and the results obtained with the micro-droplet calibration approach compared with calibrants prepared in PBS. For sNP analysis it is necessary to know the sample transport efficiency of the analyte to the plasma and this is usually measured by either analysing a NP standard or gravimetrically. It can also be advantageous to have a high transport efficiency value if the sample size is limited or if it has low analyte concentrations. The transport efficiencies of three different sample transport systems were assessed by Lin *et al.*³²⁸. These were: a high-performance concentric nebulizer with a heated cyclonic spray chamber and a three-stage Peltier-cooled desolvation system (HPCN), a conventional sample introduction system and a total consumption system. In each case the sample flow rate was estimated gravimetrically and for the HPCN and total consumption systems the sample was introduced *via* a sample loop of 60 and 100 μL , (with flow rates of 10 and 100 $\mu\text{L min}^{-1}$), respectively. Commercially available Pt nanoparticles with a size of 70 nm were diluted to a concentration range of 60 to 1.2×10^5 particles per mL for the study. The transport efficiencies of the conventional sample introduction system, the total consumption system, and the HPCN were 10.6, 99.4, and 103.6%, respectively with the lower value for conventional nebulisation attributed to the smaller Sauter mean diameter obtained from this device. The size detection limits obtained were 11.6, 11.6, and 7.2 nm for the conventional sample introduction system, total consumption system and HPCN-APEX, respectively whilst the particle number LOD values were 126, 154 and 14, respectively. Interestingly the sensitivity, on a signal intensity per Pt mass basis was similar for all three systems.

The linear dynamic range of sNP can be limited by momentary signal pulse pile-ups at the electron multiplier detector. These can be mitigated by signal broadening from the use of a collision gas in ICP-MS³²⁹. In this study by Rush *et al.* the simultaneous secondary electron multiplier was operated in both dual (pulse counting switching to analog) and pulse counting only modes. With no collision gas and the electron multiplier in dual mode, the linear response for Au NPs was from 20 to 150 nm whilst with He as a collision gas the linear range extended to 250 nm. In pulse counting mode, both with and without the He collision gas, the linear response was reduced to 20 to 60 nm. This is presumably due to detector overload from the increased signal from particles larger than 60 nm in diameter. It is now possible to acquire sNP data with a dwell time as short as 10 μs . The effect of using the short dwell times of 10, 20, 50, and 100 μs was investigated by Kana *et al.*³³⁰. It was found that zero signal values occurred inside the transient signal corresponding to an individual NP with the probability of this increasing with decreasing dwell time and NP size. This leads to the false detection of a larger number of smaller peaks with a consequent effect on the calculated particle size

distribution. Therefore, a new approach to identifying the 'true' particle signal was developed which consisted of searching for an uninterrupted zero signal point sequence with a total length of 50 μs or 100 μs . Only the 100 μs delay between adjacent peaks resulted in values of the number of detected peaks, the most frequent peak areas and the width of peak area distribution that were virtually independent of the dwell time. The same research group then applied the method to the detection of Ag NPs in water samples collected from river Vltava in the Czechia³³¹. The Ag NP content ranged from 0.1 to 3.2 ng mL^{-1} with a particle size range of 32 to 1114 nm and a number concentration range of 340 to 1670 particles mL^{-1} with uncertainties in the latter two values in the range of 40 and 15%, respectively.

A number of reports on the use of *separation techniques coupled with ICP-MS for the detection of NPs* have been published in the period covered by this review. Bouzas-Ramos *et al.* developed a procedure, based on the measurement of a metal:sulfur ratio, for an assessment of the bioconjugation between CdSe/ZnS quantum dots and a monoclonal antibody with a known amino acid sequence³³². The CdSe/ZnS QDs were conjugated to rat antibody (Ab) *via* the amine groups of the Ab and asymmetric flow field flow fractionation (AF4)-ICP-MS was used as the separation and detection system. Oxygen was used as a reaction gas for S and Se measurements, as $^{48}\text{S}^{16}\text{O}^+$ and $^{80}\text{Se}^{16}\text{O}^+$ respectively, whilst ^{106}Cd was measured directly. As the Cd and S content of the quantum dots and the S content of the antibody was known the measured signal from the AF4 peaks in the fractogram could be used to calculate the quantum dot to Ab ratio, with full details of these calculations given in the paper. The authors concluded that the proposed approach is general and could be applied to any type of NP containing S in the core, shell or on surface attached ligands and conjugated to any S containing biomolecules. Iron-carbohydrate NPs are used to treat iron-deficiency anaemia but regulatory acceptance of generic forms of this drug is hampered by lack of a direct method to monitor the fate of Fe NPs in clinical samples. An HPLC-ICP-MS based method has thus been developed by Neu *et al.* to address this³³³. The separation of the NPs from serum samples was undertaken using two SEC columns (3 μm , 300 \AA , 4.6 mm \times 300 mm and 3 μm , 300 \AA , 4.6 mm \times 50 mm) in series with a mobile phase of 10 mmol L^{-1} Tris (pH 7.4) flowing at 0.4 mL min^{-1} in 20 min. This allowed the separation of the Fe drug from other iron binding species, e.g. transferrin, albumin, ferritin and citrate. The ICP-MS was operated in collision cell mode with He as the collision gas with a solution of transferrin, introduced by a post-column switching valve used to monitor signal drift at the beginning and end of each HPLC separation. Peak identification of the compounds eluted was by fraction collection and either matrix-assisted laser desorption ionisation (MALDI)-MS or ES-MS. The HPLC-ICP-MS LOD value for the Fe drug was 0.3 mg L^{-1} . The transformations of Au NPs in a cell culture medium, Dulbecco's Modified Eagle Medium, which contained 10% fetal bovine serum and antibiotics, were studied by Lopez-Sanz *et al.* using AF4-ICP-MS

with the AF4 carrier solution being 0.01 % sodium dodecyl sulfate³³⁴. The AF4-ICP-MS fractograms showed that the culture medium induced oxidation of the Au NPs to ionic Au which was subsequently conjugated with proteins or other matrix components. An increase in Au NP size was also observed which the authors suggested could be due to the formation of a protein corona or to an aggregation/agglomeration process. Most reports on NP detection cover aqueous environmental or biological samples but this year sees a report by Ruhland *et al.* of the FFFF-ICP-MS detection of natural NPs present in a gas condensate sample using tetrahydrofuran as the carrier liquid⁸⁷. The results obtained confirmed the presence of various NPs and colloids, some containing aromatic compounds as well as various metals, including Hg in the gas condensate. Offline sNP ICP-MS was used to confirm the presence of the Hg-containing NPs which were identified as HgS by STEM-EDX. Other particulate matter containing Al, As, Cd, Co, Cu, Fe, Mn, Pb, P, S, Se, Ti, V and Zn was also identified which could make the upstream use of the gas condensate problematic if, for example, catalysis is involved. Tan *et al.* coupled a differential mobility analyser with an ICP-MS instrument operated in sNP mode to determine the geometry of Au nanorods³³⁵. The differential mobility analyser step size was 2 nm with a step dwell time of 31 s and samples were introduced *via* electrospray. Coupling of the differential mobility analyser to the ICP-MS instrument was *via* a gas exchange device, utilised to solve the incompatibility of air in the plasma, connected by conductive silicone tubing achieving a gas exchange efficiency of about 90%. Using this setup Au nanorods in the size range 12 x 50 (d x L) nm to 38 x 135 nm were successfully identified with each analysis taking 150 s. A full explanation of the theory and calculations required is given in the text.

Silver NPs are widely used due to their anti-microbial properties. A method was developed by Rujido-Santos *et al.*, with an emphasis on sample integrity during Ag NP extraction, to quantify them in moisturising creams³³⁶. The Ag NPs were separated from the samples using ultrasonic assisted extraction. One hundred mg of sample was suspended in 20 mL of methanol and the sample tube placed in an ice bath, the power level set to 60% (total power not given), and subjected to 15 x 59 s sonication cycles with a delay of 59 s between each cycle. For all but one sample sonication resulted in a clear extract while the remaining sample was centrifuged prior to analysis of the supernatant. Samples were diluted 40 fold in 1% v/v glycerol and further sonicated for 5 minutes before analysis using sNP ICP-MS. The RSD of the procedure (given by the analysis of 11 extracts from one sample) was 5%. The spike recovery for Ag NPs of 20, 40 and 60 nm ranged between 90 and 109%. The LOQ for the Ag NP concentration was 8.25×10^5 Ag NPs g⁻¹ the size LOD in size was within the 5-13 nm range depending on the calculation method used. Finally, moisturising creams prescribed for atopic dermatitis and on general sale were analysed for total Ag and for Ag NPs. Each of the three creams

analysed was found to contain NPs with mean sizes of 35, 52 and 91 nm and the Ag NP content was found to be between 0.2 and 1.1% of the total Ag content which ranged from 0.001 to 2.3 $\mu\text{g g}^{-1}$.

Table 6 shows other applications of nanomaterial characterisation presented in the literature during the time period covered by this ASU.

Table 6 Applications of nanomaterial characterisation

Analyte	Matrix	Technique	Comments	Reference
Ag ⁺ , Ag NPs	Odour remover spray and anti-bacterial spray	ICP-OES	Analytes adsorbed onto a silica gel functionalised with 3-aminopropyltriethoxysilane. The Ag ⁺ was eluted with thiourea whereas the Ag NPs were oxidised to Ag ⁺ then eluted with thiourea.	³³⁷
Ag	Phosphate buffered saline leachates from silver NP coated alloys comprising titanium, aluminium and vanadium	XRD, FT-IR, SEM, AFM, ICP-MS	Dispersion of AgNPs on the surface of Ti ₆ Al ₄ V and Ti ₆ Al ₄ V modified with a titania nanotube layer using a chemical vapour deposition method employing {Ag ₅ (O ₂ CC ₂ F ₅) ₍₅₎ (H ₂ O) ₍₃₎ }. After 14 days of immersion of the nanocomposite material in a phosphate buffered saline the Ag content in the saline was 2.5 mg L ⁻¹ .	³³⁸
Ag ⁺ and Ag NPs	Cell culture medium, acetone, sodium chloride solutions and alcohol	ICP-OES, XRD, TEM, UV-Vis	Synthesis of <10 nm \varnothing Ag NPs from AgNO ₃ by bioreduction with <i>Chlamydomonas reinhardtii</i> . The Ag NPs were stable over time in the cell culture media, acetone, NaCl (9 and 27 g L ⁻¹) and 70% reagent alcohol solutions for > 300 days at 4 °C.	³³⁹

Ag	Catechin, Catechin-borax or polycatechin NPs containing silver	UV-Vis, DLS, XRD, TEM, ICP-MS	AgNPs synthesised from AgNO ₃ and catechin borax or polycatechin. The mean NP sizes were Polycatechin 8.5 nm, catrchin-borax 18.4 nm and catechin 42.3 nm. Anti-microbial efficacy assessed against both Gram +ve and -ve bacteria, increased with decreasing NP size. A solution of 1.25 µg Ag mL ⁻¹ of polycat@AgNPs reduced biofilm viability and mass by 99.9% and 99.1%, respectively.	340
Ag	Silver nanoparticles	LA-ICP-MS	Japanese language paper. Size distribution determined using an ArF laser with nanosecond pulses. Results obtained compared favourably with solution nebulisation data for NP sizes ranging between 10 and 100 nm Ø. The developed LA-ICP-MS technique would be suitable for Ag NP mapping in tissue samples.	341
Ag and Au	Silver and gold NPs	UV-vis, dynamic light scattering (DLS), FT-IR, XRD, TEM EDX, ICP-MS	Synthesis of colloidal AuNPs and bimetallic Ag/Au alloy nanoparticles using starch as a reducing and capping agent. Mean particle sizes of 28.5 and 9.7 nm for AuNPs and Ag/AuNPs, respectively. Dose-dependent anti-microbial action of NPs with antibiotic-resistant bacterial strains. NPs showed cytocompatibility	342

			towards human dermal fibroblast. Dose-dependent anti-cancer effect found for human melanoma cells.	
Au	Certified gold nanoparticles	sNP ICP-MS	Chinese language paper. Discussion on the effects of dwell time and settling time on the analysis of nanoparticles using sNP ICP-MS. Au NPs from NIST and NCNST (30, 40 and 60 nm) analysed. Shorter dwell and settling times improved signal to noise ratio and “determination efficiency”. The optimal conditions were a dwell time of 0.05 ms and a settling time of 0. Experimentally found and certified sizes agreed. The LOD of size and number concentration of Au NPs were 8 nm and 1.1×10^5 particles L^{-1} , respectively.	³⁴³
Au	Gold nanoparticles	FFFF-ICP-MS	Separation and detection of Au NPs with different coatings, tannic acid and citrate and stabilising agents (polyethylene glycol, polyvinylpyrrolidone and branched polyethylene imine.	³⁴⁴
Co, Cu, Mg, Ni, Zn	CuO NPs and CuO NPs doped with varying amount of Co, Mg, Ni and Zn	ICP-OES, FT-IR, XRD, XPS, TEM, SEM, BET	Doping of CuO NPs to modify magnetic properties. Characterisation using a range of techniques. Concentration and number of dopants shown to have a crucial role in structural,	³⁴⁵

			morphological and magnetic properties of CuO nanostructures.	
Fe	Magnetic arginine-functionalised polypyrrole nanocomposite	FTIR, XRD, EDX, TEM, BET, XPS and IC-ICP-MS	Nanocomposite fabricated by <i>in-situ</i> polymerisation of pyrrole monomer in the presence of arginine and Fe ₃ O ₄ NPs for use as Cr ^{VI} sorbent from mine leachates. Maximum absorption capacity of 320 mg g ⁻¹ was obtained at 25 °C and pH 2.	346
Fe	Fe NPs embedded in <i>Citrus limetta</i> peel	ICP-MS, XRD, XPS, TEM	NP size 4-70 nm. Used for reduction of Cr ^{VI} to Cr ^{III} with Fe NPs oxidised to Fe ^{II} and Fe ^{III} . One g of material reduced 33 mg of Cr ^{VI} .	347
Fe	Iron NPs functionalised with 3-mercaptopropionic acid	ICP-OES	Fe ₃ O ₄ NPs prepared from FeCl ₂ , FeCl ₃ and NH ₄ OH in solution deoxygenised with N ₂ gas and at 70 °C. Then functionalised with 3-mercaptopropionic acid in toluene. Adsorption of Ag ⁺ , Hg ²⁺ and Pb ²⁺ from aqueous solution at a pH > 4.	348
Fe and Pt	FePt nanocrystals	XRD, Small Angle X-ray Scattering (SAXS), TEM, ICP-OES, ICP-MS	Non-aqueous sol-gel synthesis of FePt nanoparticles in the absence of <i>in-situ</i> stabilizers achieved by using Pt ^{II} acetylacetonate, Fe ^{III} acetylacetonate, benzyl ether, benzylamine, hexamethylenediamine, 1,2-hexadecanediol, oleic acid, oleylamine and triethylene glycol.	349
PEGylated I NPs	Mouse serum	HPLC-TQ-ICP-	PEGylated I NPs synthesised from NaI, polyethylene glycol-b-	350

		MS, DLS, Micro-CT NMR	polystyrene and polyvinyl phenol in dimethylsulfoxide. The NPs were spiked into mouse serum and then quantified using HPLC-ICP-MS. A polymeric RP column (150 × 0.3 mm ID, 8 μm), mobile phase of 10 mmol L ⁻¹ ammonium acetate: methanol (98:2) at 5 μL min ⁻¹ was employed for the separation. A LOD of 2 μg mL ⁻¹ was obtained with the high value attributed to endogenous I complexed with serum proteins.	
Se NPs	Selenium nanoparticles in an organic preparation matrix	MIP-OES	Synthesis of Se NPs using Se ^{IV} and either glucose, ascorbic acid or yeast. Reactions monitored online using photochemical vapour generation with 15% acetic acid. A LOD of 0.52 mg L ⁻¹ was achieved although matrix effects from the reaction mixture were observed.	³⁵¹
Sn	Tin on SiO ₂ NPs	FFFF, ICP-MS	Collected fractions from FFFF analysed for Sn content using ICP-MS. A 10 kDa polyethersulfone membrane with 0.25 mmol L ⁻¹ ammonium carbonate as carrier solution provided a good separation with minimal particle-membrane interaction. Tin adsorption onto silica NPs increased with decreasing NP size, 98.5%, 44.9%, and 6.5% for 60 nm, 100 nm and 200 nm NPs, respectively, when 40 μL of SnCl ₂	³⁵²

			(100 mg L ⁻¹) was added to 200 µL silica NPs (10 mg mL ⁻¹).	
Zn	ZnO nanorod and nanowire arrays	GIXRD, SEM, EDX, ICP-OES	Nanorods and nanowires synthesised using a two-step sol-gel/hydrothermal process from zinc acetate dihydrate and methanolic NaOH at 60 °C. Apoptotic assay of PC12 cells showed greater cell adhesion to nanowires than to nanorods.	353
Various (7)	CdSe/ZnS, InP/ZnS, and CuInS/ZnS quantum dots	UV-Vis, TEM, ICP-MS, Zeta Sizer and FTIR	Organic-to-water phase transfer behaviour CdSe/ZnS, InP/ZnS, and CuInS/ZnS quantum dots, coated with three different ligands: Oleic Acid, Oleylamine and Octadecylamine were compared under different environmental conditions including humic acid content, pH and ionic strength. The transfer rate increased as pH lowered and in the presence humic acids.	354

Glossary of terms

2D	Two dimensional
3D	Three dimensional
AAS	Atomic absorption spectrometry
AES	Auger electron spectrometry
AFFF	Asymmetric field flow fractionation
AF4	Asymmetric flow-field flow fractionation
AFS	Atomic fluorescence spectrometry

AFM	Atomic force microscopy
AMS	Accelerator mass spectrometry
ANOVA	Analysis of variants
APM	Atom probe microscopy
APT	Atom probe tomography
ASTM	American society for testing of materials
ATR	Attenuated total reflection
BCR	Community Bureau of reference
CCD	Charge coupled device
CE	Capillary electrophoresis
CIGS	Copper indium gallium selenide
CRM	Certified reference material
CPFAAS	Collinear photofragmentation atomic absorption spectrometry
CS	Continuum source
CT	Computerised tomography
CV	Cold vapour
CXRF	Coincidence X-ray fluorescence
DA	Discriminant analysis
DLS	Dynamic light scattering
DLTV	Diode laser thermal vaporisation
DRC	Dynamic reaction cell
DSC	Differential scanning calorimetry
EBS	Elastic back scattering spectroscopy
EDAX	Energy dispersive X-ray analysis
EDS	Energy dispersive spectrometry
EDTA	Ethylenediamine tetraacetic acid
EDXRD	Energy dispersive X-ray diffraction
EDXRF	Energy dispersive X-ray fluorescence
ELM	Extreme learning machine
EPMA	Electron probe microanalysis
ERDA	Elastic recoil detection analysis
ESI-MS	Electrospray ionisation mass spectrometry
ETAAS	Electrothermal atomic absorption spectrometry
ETV	Electrothermal vaporisation
EXAFS	Extended X-ray absorption fine structure
FAAS	Flame atomic absorption spectrometry
FFFF	Flow field flow fractionation
FI	Flow injection

FI-CVG	Flow injection chemical vapour generation
FTIR	Fourier transform infrared
FWHM	Full width at half maximum
GA-KELM	Genetic algorithm-kernel extreme learning machine
GC	Gas chromatography
GD-MS	Glow discharge mass spectrometry
GD-OES	Glow discharge optical emission spectrometry
GI-SAXS	Grazing incidence small angle X-ray scattering
GIXRD	Grazing incidence X-ray diffraction
GIXRF	Grazing incidence X-ray fluorescence
HG	Hydride generation
HPLC	High performance liquid chromatography
HR-CS-AAS	High resolution continuum source atomic absorption spectrometry
hTISIS	Heated torch integrated sample introduction system
IAEA	International atomic energy agency
IBA	Ion beam analysis
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-TOF-MS	Inductively coupled plasma time-of-flight mass spectrometry
ID	Isotope dilution
IL-DLLME	Ionic liquid-dispersive liquid–liquid microextraction
IP	Institute of petroleum
IRMS	Isotope ration mass spectrometry
ISO	International organisation for standardisation
LA	Laser ablation
LASIL	Laser ablation of sample in liquid
LC	Liquid chromatography
LEIS	Low energy ion scattering
LIBS	Laser induced breakdown spectrometry
LIF	Laser induced fluorescence
LIPS	Laser induced plasma spectroscopy
LOD	Limit of detection
LOQ	Limit of quantification
LTE	Local thermal equilibrium
MALDI-TOF	Matrix-assisted laser desorption ionisation time-of-flight

MALS	Multiangle light scattering
MC	Multicollector
MEIS	Medium energy light scattering
MHCD	Micro hollow glow discharge
MIP	Microwave induced plasma
MIP-AES	Microwave plasma atomic emission spectrometry
MS	Mass spectrometry
MCR-ALS	Multi curve resolution-alternating least squares
MWTN	Microwave thermal nebuliser
NAA	Neutron activation analysis
NAAR	Neutron activation autoradiography
Nd:YAG	Neodymium doped-yttrium aluminium garnet
Nd:YLF	Neodymium doped-yttrium lithium fluoride
ND	Neutron diffraction
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
PBS	Phosphate buffered saline
PCA	Principal component analysis
PCR	Principal component regression
PDA	Phase-doppler anemometry
PET	Polyethylene terephthalate
PGAA	Prompt gamma neutron activation analysis
PGM	Platinum group metals
PIGE	Particle induced gamma ray emission
PIXE	Particle-induced X-ray emission
PLS	Partial least squares
PLSDA	Partial least squares discriminant analysis
PLSDAVI	Partial least squares discriminant analysis with variable importance
PLSR	Partial least squares regression
ppb	Parts per billion
ppm	Parts per million
PSDA	Particle size distribution analysis
PVG	Photochemical vapour generation
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
RSD	Relative standard deviation
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
SEM-EDS	Scanning electron microscopy-energy dispersive spectrometry
SF	Sector field
SHRIMP	Sensitive high resolution ion microprobe
SIBS	Spark induced breakdown spectrometry
SIFT-MS	Selected ion flow tube mass spectrometry
SIMCA	Soft independent modelling of class analogy
SIMS	Secondary ion mass spectrometry
SP	Single particle
SR	Synchrotron radiation
SRM	Standard reference material
SRS	Synchrotron radiation source
SXRF	Synchrotron X-ray fluorescence
SVR	Support vector regression
STXM	Scanning transmission X-ray microscopy
TE	Trace element
TEM	Transmission electron microscopy
TGA	Thermogravimetic analysis
TIMS	Thermal ionisation mass spectrometry
TOF	Time of flight
TLC	Thin layer chromatography
TPR	Temperature programmed reduction
TXRF	Total reflection X-ray fluorescence
UOP	Universal oil products standards
USGS	United States geological survey
UV-VIS	Ultraviolet-visible
VOC	Volatile organic carbon
VUV	Vacuum ultraviolet
WC-AES	Tungsten coil atomic emission spectrometry
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

References

- 1 S. Carter, R. Clough, A. Fisher, B. Gibson, B. Russell and J. Waack, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(11), 1802-1848.
- 2 R. Clough, C. F. Harrington, S. J. Hill, Y. Madrid and J. F. Tyson, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(7), 1103-1149.
- 3 E. H. Evans, J. Pisonero, C. M. M. Smith and R. N. Taylor, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(5), 684-705.
- 4 J. R. Bacon, O. T. Butler, W. R. L. Cairns, J. M. Cook, R. Mertz-Kraus and J. F. Tyson, *Journal of Analytical Atomic Spectrometry*, 2019, **34**(1), 9-58.
- 5 A. Taylor, N. Barlow, M. P. Day, S. Hill, N. Martin and M. Patriarca, *Journal of Analytical Atomic Spectrometry*, 2019, **34**(3), 426-459.
- 6 C. Vanhoof, J. R. Bacon, A. T. Ellis, L. Vincze and P. Wobrauschek, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(9), 1413-1431.
- 7 H. B. Fu, Z. B. Ni, H. D. Wang, J. W. Jia and F. Z. Dong, *Plasma Science & Technology*, 2019, **21**(3).
- 8 R. Noll, C. Fricke-Begemann, S. Connemann, C. Meinhardt and V. Sturm, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(6), 945-956.
- 9 L. Jolivet, M. Leprince, S. Moncayo, L. Sorbier, C. P. Lienemann and V. Motto-Ros, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2019, **151**, 41-53.
- 10 H. Kim, S. H. Nam, S. H. Han, S. Jung and Y. Lee, *Optics and Laser Technology*, 2019, **112**, 117-125.
- 11 M. Singh and A. Sarkar, *Journal of Applied Spectroscopy*, 2018, **85**(5), 962-970.
- 12 J. H. Yang, X. M. Li, H. L. Lu, J. W. Xu and H. X. Li, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(7), 1184-1195.
- 13 Y. G. Mei, S. S. Cheng, Z. Q. Hao, L. B. Guo, X. Y. Li, X. Y. Zeng and J. L. Ge, *Plasma Science & Technology*, 2019, **21**(3).
- 14 X. M. Li, H. L. Lu, J. H. Yang and F. Chang, *Plasma Science & Technology*, 2019, **21**(3).
- 15 Y. M. Guo, L. B. Guo, Z. Q. Hao, Y. Tang, S. X. Ma, Q. D. Zeng, S. S. Tang, X. Y. Li, Y. F. Lu and X. Y. Zeng, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(8), 1330-1335.
- 16 J. J. Lin, X. M. Lin, L. B. Guo, Y. M. Guo, Y. Tang, Y. W. Chu, S. S. Tang and C. J. Che, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(9), 1545-1551.
- 17 S. Shin, Y. Moon, J. Lee, H. Jang, E. Hwang and S. Jeong, *Plasma Science & Technology*, 2019, **21**(3).
- 18 S. C. Xie, T. Xu, G. H. Niu, W. L. Liao, Q. Y. Lin and Y. X. Duan, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(6), 975-985.
- 19 Y. Qiu, J. Wu, X. W. Li, T. Liu, F. Xue, Z. F. Yang, Z. Zhang and H. Yu, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 48-56.

- 20 J. Wu, H. Yu, Y. Qiu, Z. Zhang, T. Liu, F. Xue, W. W. Yu, X. W. Li and A. C. Qiu, *Journal of Physics D-Applied Physics*, 2019, **52**(1).
- 21 C. Ke, Y. Li, X. Liu, F. J. Gou, X. R. Duan and Y. Zhao, *Fusion Engineering and Design*, 2018, **136**, 1647-1652.
- 22 S. Z. Lu, M. R. Dong, Q. F. Chen, J. W. Huang, Y. S. Yu and J. D. Lu, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2019, **151**, 1-11.
- 23 S. Z. Lu, S. Shen, J. W. Huang, M. R. Dong, J. D. Lu and W. B. Li, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **150**, 49-58.
- 24 J. W. Huang, M. R. Dong, S. Z. Lu, W. B. Li, J. D. Lu, C. Y. Liu and J. H. Yoo, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(5), 720-729.
- 25 B. C. Barlow, A. Situm, B. Guo, X. X. Guo, A. P. Grosvenor and I. J. Burgess, *Corrosion Science*, 2018, **144**, 198-206.
- 26 A. Situm, X. X. Guo, B. C. Barlow, B. Guo, I. J. Burgess and A. P. Grosvenor, *Corrosion Science*, 2018, **145**, 35-46.
- 27 Z. Q. Hao, L. Liu, M. Shen, R. Zhou, J. M. Li, L. B. Guo, X. Y. Li, Y. F. Lu and X. Y. Zeng, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(9), 1564-1570.
- 28 H. B. Fu, H. D. Wang, J. W. Jia, Z. B. Ni and F. Z. Dong, *Applied Spectroscopy*, 2018, **72**(8), 1183-1188.
- 29 Z. Q. Hao, L. Liu, R. Zhou, Y. W. Ma, X. Y. Li, L. B. Guo, Y. F. Lu and X. Y. Zeng, *Optics Express*, 2018, **26**(18), 22926-22933.
- 30 Q. Zeng, C. Y. Pan, T. Fei, X. K. Ding, S. B. Wang and Q. P. Wang, *Journal of Applied Spectroscopy*, 2018, **85**(5), 817-822.
- 31 L. M. Cabalin, T. Delgado, J. Ruiz, D. Mier and J. J. Laserna, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **146**, 93-100.
- 32 A. Hegetschweiler, O. Borovinskaya, T. Staudt and T. Kraus, *Analytical Chemistry*, 2019, **91**(1), 943-950.
- 33 E. S. Steenstra, J. Berndt, S. Klemme and W. van Westrenen, *Journal of Analytical Atomic Spectrometry*, 2019, **34**(1), 222-231.
- 34 A. Wada, N. Nonose, M. Ohata and T. Miura, *Talanta*, 2018, **189**, 289-295.
- 35 Q. D. Zeng, F. Deng, Z. H. Zhu, Y. Tang, B. Y. Wang, Y. J. Xiao, L. B. Xiong, H. Q. Yu, L. B. Guo and X. Y. Li, *Plasma Science & Technology*, 2019, **21**(3).
- 36 M. C. Cui, Y. Deguchi, Z. Z. Wang, S. Tanaka, Y. Fujita and S. D. Zhao, *Applied Spectroscopy*, 2019, **73**(2), 152-162.
- 37 J. M. Li, M. L. Xu, Q. X. Ma, N. Zhao, X. Y. Li, Q. M. Zhang, L. Guo and Y. F. Lu, *Talanta*, 2019, **194**, 697-702.
- 38 C. Y. Pan, J. He, G. Q. Wang, X. W. Du, Y. B. Liu and Y. H. Su, *Plasma Science & Technology*, 2019, **21**(3).
- 39 L. Y. Zhan, X. H. Ma, W. Q. Fang, R. Wang, Z. S. Liu, Y. Song and H. F. Zhao, *Plasma Science & Technology*, 2019, **21**(3).
- 40 T. O. Owolabi and M. A. Gondal, *Journal of Intelligent & Fuzzy Systems*, 2018, **35**(6), 6277-6286.
- 41 H. Sattar, L. Y. Sun, M. Imran, R. Hai, D. Wu and H. B. Ding, *Plasma Science & Technology*, 2019, **21**(3).
- 42 R. Yuan, Y. Tang, Z. H. Zhu, Z. Q. Hao, J. M. Li, H. Y. Yu, Y. X. Yu, L. B. Guo, X. Y. Zeng and Y. F. Lu, *Analytica Chimica Acta*, 2019, **1064**, 11-16.
- 43 W. J. Lu, Z. H. Zhu, Y. Tang, S. X. Ma, Y. W. Chu, Y. Y. Ma, Q. D. Zeng, L. B. Guo, Y. F. Lu and X. Y. Zeng, *Optics Express*, 2018, **26**(23), 30409-30419.
- 44 T. Takahashi, B. Thornton, T. Sato, T. Ohki, K. Ohki and T. Sakka, *Applied Optics*, 2018, **57**(20), 5872-5883.
- 45 V. N. Lednev, P. A. Sdvizhenskii, R. D. Asyutin, R. S. Tretyakov, M. Y. Grishin, A. Y. Stavertiy, A. N. Fedorov and S. M. Pershin, *Optics Express*, 2019, **27**(4), 4612-4628.

- 46 V. N. Lednev, P. A. Sdvizhenskii, M. Y. Grishin, M. A. Davidov, A. Y. Stavertiy, R. S. Tretyakov, M. V. Taksanc and S. M. Pershin, *Spectroscopy Letters*, 2018, **51**(4), 184-190.
- 47 V. N. Lednev, P. A. Sdvizhenskii, R. D. Asyutin, R. S. Tretyakov, M. Y. Grishin, A. Y. Stavertiy and S. M. Pershin, *Additive Manufacturing*, 2019, **25**, 64-70.
- 48 E. Mal, R. Junjuri, M. K. Gundawar and A. Khare, *Journal of Analytical Atomic Spectrometry*, 2019, **34**(2), 319-330.
- 49 T. Q. Li, Z. Y. Hou, Y. T. Fu, J. L. Yu, W. L. Gu and Z. Wang, *Analytica Chimica Acta*, 2019, **1058**, 39-47.
- 50 X. Y. He, R. H. Li and F. J. Wang, *Plasma Science & Technology*, 2019, **21**(3).
- 51 X. Y. He, B. Q. Chen, Y. Q. Chen, R. H. Li and F. J. Wang, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(12), 2203-2209.
- 52 Y. R. Wang, Y. H. Jiang, X. Y. He, Y. Q. Chen and R. H. Li, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **150**, 9-17.
- 53 L. Huang, D. Beauchemin and C. Dalpe, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(10), 1784-1789.
- 54 K. Ido, H. Obayashi, Y. B. Zhu, T. Hirata, A. Hokura, N. Nonose and K. Inagaki, *Analytical Sciences*, 2018, **34**(6), 693-699.
- 55 G. P. Ma, X. C. Duan and J. S. Sun, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 57-61.
- 56 N. S. Medvedev, O. V. Lundovskaya and A. I. Saprykin, *Microchemical Journal*, 2019, **145**, 751-755.
- 57 L. Fu, S. Y. Shi, X. Q. Chen and H. L. Xie, *Microchemical Journal*, 2018, **139**, 236-241.
- 58 P. Phukphatthanachai, J. Vogl, H. Traub, N. Jakubowski and U. Panne, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(9), 1506-1517.
- 59 E. Castellon, P. P. Martinez, J. Alvarez, F. Bredice, F. Borges, M. V. Muniz, C. Sanchez-Ake, V. Palleschi and R. Sarmiento, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 229-235.
- 60 A. H. Galmed, C. Steenkamp, I. Ahmed, A. du Plussis, H. von Bergmann, M. A. Harith and M. Maaza, *Applied Physics B-Lasers and Optics*, 2018, **124**(12).
- 61 T. Warchilova, V. Dillingerova, R. Skoda, T. Simo, O. Matal, T. Vaculovic and V. Kanicky, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **148**, 113-117.
- 62 A. Botto, B. Campanella, S. Legnaioli, M. Lezzerini, G. Lorenzetti, S. Pagnotta, F. Poggialini and V. Palleschi, *Journal of Analytical Atomic Spectrometry*, 2019, **34**(1), 81-103.
- 63 V. Lazic, M. Vadrucci, R. Fantoni, M. Chiari, A. Mazzinghi and A. Gorghinian, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 1-14.
- 64 S. Robotti, P. Rizzi, C. Soffritti, G. L. Garagnani, C. Greco, F. Facchetti, M. Borla, L. Operti and A. Agostino, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **146**, 41-49.
- 65 R. N. S. Sodhi, P. Brodersen, S. Boccia, A. Anastasiades and C. Zaccagnino, *Journal of Vacuum Science & Technology B*, 2018, **36**(3).
- 66 I. Ortega-Feliu, S. Scrivano, B. Gomez-Tubio, F. J. Ager, M. L. de la Bandera, M. A. Respaldiza, A. D. Navarro and C. San Martin, *Microchemical Journal*, 2018, **139**, 401-409.
- 67 F. Lopes, R. J. C. Silva, M. F. Araujo, V. H. Correia, L. Dias and J. Mirao, *Microchemical Journal*, 2018, **138**, 438-446.
- 68 S. Porcinai and M. Ferretti, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 184-189.
- 69 V. V. Zaykov, I. Y. Melekestseva, E. V. Zaykova, D. Fellenger and D. Motz, *Archaeometry*, 2018, **60**(6), 1290-1305.
- 70 I. Nemet, S. Roncevic, A. Bugar, T. Z. Ferri and L. Pitarevic, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(12), 2053-2061.
- 71 G. Balassone, M. Mercurio, C. Germinario, C. Grifa, I. M. Villa, G. Di Maio, S. Scala, R. de' Gennaro, C. Petti, M. C. Del Re and A. Langella, *Measurement*, 2018, **128**, 104-118.

- 72 S. S. Gomes, M. F. Araujo, A. M. M. Soares, J. Pimenta and H. Mendes, *Microchemical Journal*, 2018, **141**, 337-345.
- 73 M. P. Seah, R. Havelund, S. J. Spencer and I. S. Gilmore, *Journal of the American Society for Mass Spectrometry*, 2019, **30**(2), 309-320.
- 74 N. Turhan, N. Ozbek and S. Akman, *Journal of Analytical Atomic Spectrometry*, 2019, **34**(3), 577-582.
- 75 V. S. Souza, L. S. G. Teixeira, M. G. A. Korn, U. Cerqueira and M. A. Bezerra, *Fuel*, 2019, **242**, 479-486.
- 76 C. H. Wu, S. J. Jiang and A. C. Sahayam, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **147**, 115-120.
- 77 C. W. Lu, H. Y. Hung, H. C. Sung, Y. S. Sheu, W. L. Lin and S. P. Wu, *Journal of Analytical Atomic Spectrometry*, 2019, **34**(3), 570-576.
- 78 A. S. Henn, E. M. M. Flores, V. L. Dressler, M. F. Mesko, J. Feldmann and P. A. Mello, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(8), 1384-1393.
- 79 S. M. Z. Iqbal, Z. Uddin, N. Ahmed, Z. A. Umar and M. A. Baig, *Laser Physics*, 2019, **29**(3).
- 80 S. C. Yao, J. B. Zhao, Z. Z. Wang, Y. Deguchi, Z. M. Lu and J. D. Lu, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 249-255.
- 81 H. Zhu, M. Liu, T. Guo, L. Xu, J. G. Dong, J. L. Feng, P. Cheng and Z. Zhou, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(7), 1158-1167.
- 82 L. Husakova, I. Urbanova, T. Sidova and M. Safrankova, *Journal of Analytical Chemistry*, 2018, **73**(7), 650-660.
- 83 J. P. Souza, K. Kellermann, M. S. Camargo, D. P. Moraes, D. Pozebon and J. S. F. Pereira, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(8), 1284-1291.
- 84 S. G. Sama, C. Barrere-Mangote, B. Bouyssiere, P. Giusti and R. Lobinski, *Trac-Trends in Analytical Chemistry*, 2018, **104**, 69-76.
- 85 R. Sanchez, J. Lefevre and J. L. Todoli, *Journal of Analytical Atomic Spectrometry*, 2019, **34**(4), 664-673.
- 86 L. V. Vieira, T. T. B. Marchezi, E. V. R. de Castro, G. P. Brandao and M. Carneiro, *Fuel*, 2019, **244**, 352-358.
- 87 D. Ruhland, K. Nwoko, M. Perez, J. Feldmann and E. M. Krupp, *Analytical Chemistry*, 2019, **91**(1), 1164-1170.
- 88 N. Fetter, J. Blichert-Toft, P. Telouk and F. Albarede, *Chemical Geology*, 2019, **511**, 112-122.
- 89 J. S. Silva, A. S. Henn, V. L. Dressler, P. A. Mello and E. M. M. Flores, *Analytical Chemistry*, 2018, **90**(11), 7064-7071.
- 90 A. P. M. Michel, A. E. Morrison, C. T. Marx and H. K. White, *Environmental Science & Technology Letters*, 2019, **6**(1), 34-37.
- 91 E. C. Lourenco, E. Eyng, P. R. S. Bittencourt, F. A. Duarte, R. S. Picoloto and E. L. M. Flores, *Talanta*, 2019, **199**, 1-7.
- 92 K. R. N. da Silva, A. D. Greco, M. Z. Corazza and J. L. Raposo, *Analytical Methods*, 2018, **10**(26), 3284-3291.
- 93 J. O. Vinhal and R. J. Cassella, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2019, **151**, 33-40.
- 94 L. A. Meira, J. S. Almeida, F. D. Dias, P. P. Pedra, A. L. C. Pereira and L. S. G. Teixeira, *Microchemical Journal*, 2018, **142**, 144-151.
- 95 P. S. Barela, J. P. Souza, J. S. F. Pereira, J. C. Marques, E. I. Muller and D. P. Moraes, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(6), 1049-1056.
- 96 Y. Z. Liu, Z. H. Wang, J. Xia, L. Vervisch, K. D. Wan, Y. He, R. Whiddon, H. Bahai and K. F. Cen, *Proceedings of the Combustion Institute*, 2019, **37**(3), 2681-2688.
- 97 J. Viljanen, H. Zhao, Z. Zhang, J. Toivonen and Z. T. Alwahabi, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 76-83.
- 98 P. Pohl, A. Bielawska-Pohl, A. Dzimitrowicz, P. Jamroz and M. Welna, *Trac-Trends in Analytical Chemistry*, 2018, **101**, 43-55.

- 99 M. Bernardin, F. Bessueille-Barbier, A. Le Masle, C. P. Lienemann and S. Heinisch, *Journal of Chromatography A*, 2018, **1565**, 68-80.
- 100 B. Klencsar, S. W. Li, L. Balcaen and F. Vanhaecke, *Trac-Trends in Analytical Chemistry*, 2018, **104**, 118-134.
- 101 T. G. Kazi, H. I. Afridi, M. Bhatti and A. Akhtar, *Ultrasonics Sonochemistry*, 2019, **51**, 40-48.
- 102 E. Koosha, M. Ramezani and A. Niazi, *International Journal of Environmental Analytical Chemistry*, 2018, **98**(6), 506-519.
- 103 M. A. Speranca, D. F. Andrade, J. P. Castro and E. R. Pereira, *Optics and Laser Technology*, 2019, **109**, 648-653.
- 104 J. White, A. Celik, R. Washington, V. Yilmaz, T. Mitchum and Z. Arslan, *Microchemical Journal*, 2018, **139**, 242-249.
- 105 S. M. Ansar and T. Mudalige, *International Journal of Pharmaceutics*, 2019, **561**, 283-288.
- 106 Q. Xu, Z. H. Wang, L. H. Jin, P. Liu, Y. Tian, S. X. Zhang and C. Q. Zhang, *Analytical Methods*, 2018, **10**(18), 2144-2150.
- 107 E. Kamilari, K. Farsalinos, K. Poulas, C. G. Kontoyannis and M. G. Orkoula, *Food and Chemical Toxicology*, 2018, **116**, 233-237.
- 108 P. Kikongi, C. Fauteux-Lefebvre, J. Salvas and R. Gosselin, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **147**, 59-70.
- 109 A. F. Oliveira, M. H. Gonzalez and A. R. A. Nogueira, *Microchemical Journal*, 2018, **143**, 326-330.
- 110 E. Parhizkar, H. Saeedzadeh, F. Alunadi, M. Ghazali and A. Sakhteman, *Iranian Journal of Pharmaceutical Research*, 2019, **18**(1), 72-79.
- 111 H. Rebiere, A. Kermaidic, C. Ghyselincq and C. Brenier, *Talanta*, 2019, **195**, 490-496.
- 112 I. Costantini, K. Castro and J. M. Madariaga, *Analytical Methods*, 2018, **10**(40), 4854-4870.
- 113 M. Cotte, A. Genty-Vincent, K. Janssens and J. Susini, *Comptes Rendus Physique*, 2018, **19**(7), 575-588.
- 114 A. Re, M. Zangirolami, D. Angelici, A. Borghi, E. Costa, R. Giustetto, L. M. Gallo, L. Castelli, A. Mazzinghi, C. Ruberto, F. Taccetti and A. Lo Giudice, *European Physical Journal Plus*, 2018, **133**(9).
- 115 A. Martinez-Hernandez, M. Oujja, M. Sanz, E. Carrasco, V. Detalle and M. Castillejo, *Journal of Cultural Heritage*, 2018, **32**, 1-8.
- 116 N. H. Cheung, *Journal of Analytical Atomic Spectrometry*, 2019, **34**(3), 616-622.
- 117 K. Rzecki, T. Sosnicki, M. Baran, M. Niedzwiecki, M. Krol, T. Lojewski, U. R. Acharya, O. Yildirim and P. Plawiak, *Sensors*, 2018, **18**(11).
- 118 R. C. Machado, A. B. S. Silva, G. L. Donati and A. R. A. Nogueira, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(7), 1168-1172.
- 119 T. Delgado, J. M. Vadillo and J. J. Laserna, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(9).
- 120 P. Mattiazzi, D. Bohrer, E. Becker, C. Viana, P. C. Nascimento and L. M. Carvalho, *Talanta*, 2019, **197**, 20-27.
- 121 L. M. Smieska, J. Twilley, A. R. Woll, M. Schafer and A. M. DeGalan, *Microchemical Journal*, 2019, **146**, 679-691.
- 122 C. Germinario, I. Francesco, M. Mercurio, A. Langella, D. Sali, I. Kakoulli, A. De Bonis and C. Grifa, *European Physical Journal Plus*, 2018, **133**(9).
- 123 E. Pospisilova, K. Novotny, P. Porizka, D. Hradil, J. Hradilova, J. Kaiser and V. Kanicky, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **147**, 100-108.
- 124 H. Zhang, S. Wang, K. K. Chang, H. F. Sun, Q. Q. Guo, L. Z. Ma, Y. T. Yang, C. H. Zou, L. Wang and J. D. Hu, *Applied Spectroscopy*, 2018, **72**(6), 913-920.
- 125 A. H. Rezaei, M. H. Keshavarz, M. K. Tehrani and M. R. Darbani, *Central European Journal of Energetic Materials*, 2019, **16**(1), 3-20.
- 126 K. Liu, D. Tian, C. Li, Y. C. Li, G. Yang and Y. Ding, *Trac-Trends in Analytical Chemistry*, 2019, **110**, 327-334.

- 127 K. Liu, D. Tian, H. X. Wang and G. Yang, *Analytical Methods*, 2019, **11**(9), 1174-1179.
- 128 Y. M. Guo, Y. Tang, Y. Du, S. S. Tang, L. B. Guo, X. Y. Li, Y. F. Lu and X. Y. Zeng, *Plasma Science & Technology*, 2018, **20**(6).
- 129 Y. Tang, Y. M. Guo, Q. Q. Sun, S. S. Tang, J. M. Li, L. B. Guo and J. Duan, *Optik*, 2018, **165**, 179-185.
- 130 H. Jull, J. Bier, R. Kunzemeyer and P. Schaare, *Spectroscopy Letters*, 2018, **51**(6), 257-265.
- 131 S. B. Roh, S. B. Park, S. K. Oh, E. K. Park and W. Z. Choi, *Journal of Material Cycles and Waste Management*, 2018, **20**(4), 1934-1949.
- 132 E. Kim and W. Z. Choi, *Journal of Material Cycles and Waste Management*, 2019, **21**(1), 176-180.
- 133 M. V. Dastjerdi, S. J. Mousavi, M. Soltanolkotabi and A. N. Zadeh, *Iranian Journal of Science and Technology Transaction a-Science*, 2018, **42**(A2), 959-965.
- 134 R. M. T. Madiona, S. E. Bamford, D. A. Winkler, B. W. Muir and P. J. Pigram, *Analytical Chemistry*, 2018, **90**(21), 12475-12484.
- 135 R. M. T. Madiona, N. G. Welch, S. B. Russell, D. A. Winkler, J. A. Scoble, B. W. Muir and P. J. Pigram, *Surface and Interface Analysis*, 2018, **50**(7), 713-728.
- 136 A. Villasenor, M. Bocconcelli and J. L. Todoli, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(7), 1173-1183.
- 137 K. Vogel, A. Wegener, M. Pursch, P. Luschas and M. Wiesmann, *Spectroscopy*, 2019, **34**(1), 38-46.
- 138 R. Ledesma, F. Palmieri, B. Campbell, W. Yost, J. Fitz-Gerald, G. Dillingham and J. Connell, *Applied Spectroscopy*, 2019, **73**(2), 229-235.
- 139 P. Chen, X. L. Wang, X. Li, Q. S. Lyu, N. X. Wang and Z. D. Jia, *Sensors*, 2019, **19**(5).
- 140 K. Bezemer, R. Woortmeijer, M. Koeberg, W. Wiarda, P. Schoenmakers and A. van Asten, *Forensic Science International*, 2018, **290**, 336-348.
- 141 M. Bonta and A. Limbeck, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(10).
- 142 P. Wachulak, M. Duda, A. Bartnik, A. Sarzynski, L. Wegrzynski and H. Fiedorowicz, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **145**, 107-114.
- 143 M. Pardede, T. J. Lie, J. Iqbal, M. Bilal, R. Hedwig, M. Ramli, A. Khumaeni, W. S. Budi, N. Idris, S. N. Abdulmadjid, A. M. Marpaung, I. Karnadi, I. Tanra, Z. S. Lie, H. Suyanto, D. P. Kurniawan, K. H. Kurniawan, K. Kagawa and M. O. Tjia, *Analytical Chemistry*, 2019, **91**(2), 1571-1577.
- 144 C. Devouge-Boyer, S. Mouda, O. Gueguen and S. Marcotte, *Talanta*, 2018, **189**, 568-572.
- 145 R. F. Santos, S. M. Cruz, S. R. Krzyzaniak, F. A. Duarte, P. A. Mello and E. M. M. Flores, *Microchemical Journal*, 2019, **146**, 492-497.
- 146 V. Lazic, M. Filella and A. Turner, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(11), 1917-1924.
- 147 E. J. Dos Santos, G. F. Zagonel, A. B. Herrmann, E. B. Fantin and R. E. Sturgeon, *Analytical Methods*, 2018, **10**(41), 5047-5050.
- 148 R. Manjusha, R. Shekhar and S. Jaikumar, *Microchemical Journal*, 2019, **145**, 301-307.
- 149 L. Fu, H. L. Xie, S. Y. Shi and X. Q. Chen, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **144**, 1-6.
- 150 O. E. Bezrukova, S. D. Kirik, S. G. Ruzhnikov, I. S. Yakimov and P. S. Dubinin, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2019, **152**, 52-58.
- 151 E. Begu, B. Snell and Z. Arslan, *Microchemical Journal*, 2019, **145**, 412-418.
- 152 V. Bodnar, A. Ganeev, A. Gubal, N. Solovyev, O. Glumov, V. Yakobson and I. Murin, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **145**, 20-28.
- 153 C. P. de Moraes, A. I. Barros, M. A. Bechlin, T. V. Silva, D. Santos, G. S. Senesi, M. S. Crespi, C. A. Ribeiro, J. A. G. Neto and E. C. Ferreira, *Talanta*, 2018, **188**, 199-202.
- 154 S. Millar, C. Gottlieb, T. Gunther, N. Sankat, G. Wilsch and S. Kruschwitz, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **147**, 1-8.
- 155 S. Millar, S. Kruschwitz and G. Wilsch, *Cement and Concrete Research*, 2019, **117**, 16-22.

- 156 T. Dietz, J. Klose, P. Kohns and G. Ankerhold, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2019, **152**, 59-67.
- 157 P. Bran-Anleu, F. Caruso, T. Wangler, E. Pomjakushina and R. J. Flatt, *Microchemical Journal*, 2018, **141**, 382-387.
- 158 M. M. Elfaham, M. Okil and N. M. Nagy, *Optics and Laser Technology*, 2018, **106**, 69-75.
- 159 M. M. Elfaham and U. Eldemerdash, *Optics and Laser Technology*, 2019, **111**, 338-346.
- 160 Z. W. Guo, L. X. Sun, P. Zhang, L. F. Qi, H. B. Yu, P. Zeng, Z. H. Zhou, W. Wang and Y. Z. Shi, *Spectroscopy and Spectral Analysis*, 2019, **39**(1), 278-285.
- 161 H. Morillas, C. Garcia-Florentino, I. Marcaida, M. Maguregui, G. Arana, L. F. O. Silva and J. M. Madariaga, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **146**, 28-35.
- 162 M. Ramacciotti, S. Rubio, G. Gallelo, M. Lezzerini, S. Columbu, E. Hernandez, A. Morales-Rubio, A. Pastor and M. de la Guardia, *Journal of Spectroscopy*, 2018.
- 163 C. Garcia-Florentino, M. Maguregui, M. Romera-Fernandez, I. Queralt, E. Margui and J. M. Madariaga, *Analytical Chemistry*, 2018, **90**(9), 5795-5802.
- 164 C. Garcia-Florentino, M. Maguregui, E. Margui, L. Torrent, I. Queralt and J. M. Madariaga, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **143**, 18-25.
- 165 M. Kasamatsu, T. Igawa, S. Suzuki and Y. Suzuki, *Analytical Sciences*, 2018, **34**(6), 729-733.
- 166 E. V. Yakubenko, O. V. Tolmachyeva, Chernikova, II and T. N. Ermolaeva, *Inorganic Materials*, 2018, **54**(14), 1392-1396.
- 167 T. Y. Alekseeva, Y. A. Karpov, O. A. Dal'nova, V. V. Es'kina, V. B. Baranovskaya and L. D. Gorbatova, *Inorganic Materials*, 2018, **54**(14), 1421-1429.
- 168 J. Kim, J. Anawati and G. Azimi, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(8), 1310-1321.
- 169 J. E. Jaine and M. R. Mucalo, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **145**, 58-63.
- 170 F. Trichard, F. Gaulier, J. Barbier, D. Espinat, B. Guichard, C. P. Lienemann, L. Sorbier, P. Levitz and V. Motto-Ros, *Journal of Catalysis*, 2018, **363**, 183-190.
- 171 P. Jovanovic, F. Ruiz-Zepeda, M. Sala and N. Hodnik, *Journal of Physical Chemistry C*, 2018, **122**(18), 10050-10058.
- 172 A. Pavlisic, P. Jovanovic, V. S. Selih, M. Sala, N. Hodnik and M. Gaberscek, *Journal of the Electrochemical Society*, 2018, **165**(6), F3161-F3165.
- 173 R. K. Ahluwalia, D. D. Papadias, N. N. Kariuki, J. K. Peng, X. P. Wang, Y. F. Tsai, D. G. Graczyk and D. J. Myers, *Journal of the Electrochemical Society*, 2018, **165**(6), F3024-F3035.
- 174 D. Gonzalez-Flores, K. Klingan, P. Chernev, S. Loos, M. R. Mohammadi, C. Pasquini, P. Kubella, I. Zaharieva, R. D. L. Smith and H. Dau, *Sustainable Energy & Fuels*, 2018, **2**(9), 1986-1994.
- 175 A. A. Guda, A. L. Bugaev, R. Kopelent, L. Braglia, A. V. Soldatov, M. Nachtegaal, O. V. Safonova and G. Smolentsev, *Journal of Synchrotron Radiation*, 2018, **25**, 989-997.
- 176 C. W. Lopes, J. L. Cerrillo, A. E. Palomares, F. Rey and G. Agostini, *Physical Chemistry Chemical Physics*, 2018, **20**(18), 12700-12709.
- 177 M. Agote-Aran, I. Lezcano-Gonzalez, A. G. Greenaway, S. Hayama, S. Diaz-Moreno, A. B. Kroner and A. M. Beale, *Applied Catalysis a-General*, 2019, **570**, 283-291.
- 178 A. Martini, E. Alladio and E. Borfecchia, *Topics in Catalysis*, 2018, **61**(14), 1396-1407.
- 179 Y. Zhou, D. E. Doronkin, Z. Y. Zhao, P. N. Plessow, J. Jelic, B. Detlefs, T. Pruessmann, F. Studt and J. D. Grunwaldt, *Acs Catalysis*, 2018, **8**(12), 11398-11406.
- 180 L. Mino, E. Borfecchia, J. Segura-Ruiz, C. Giannini, G. Martinez-Criado and C. Lamberti, *Reviews of Modern Physics*, 2018, **90**(2).
- 181 C. H. Park, I. H. Kim, C. M. Choi, J. S. Jin, M. C. Choi and Y. D. Kim, *International Journal of Mass Spectrometry*, 2018, **433**, 47-54.
- 182 R. Muller, I. Kuznetsov, Y. Arbelo, M. Trottmann, C. S. Menoni, J. J. Rocca, G. R. Patzke and D. Bleiner, *Analytical Chemistry*, 2018, **90**(15), 9234-9240.
- 183 A. Dona-Fernandez, I. de Andres-Gimeno, P. Santiago-Toribio, E. Valtuille-Fernandez, F. Aller-Sanchez and A. Heras-Gonzalez, *Forensic Science International*, 2018, **292**, 167-175.

- 184 C. Vander Pyl, O. Ovide, M. Ho, B. Yuksel and T. Trejos, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2019, **152**, 93-101.
- 185 D. Merli, A. Amadasi, D. Mazzarelli, A. Cappella, E. Castoldi, S. Ripa, L. Cucca, C. Cattaneo and A. Profumo, *Journal of Forensic Sciences*, 2019, **64**(2), 558-564.
- 186 A. McKenzie-Coe, S. Bell and F. Fernandez-Lima, *Analytical Methods*, 2018, **10**(35).
- 187 R. D. Heringer and J. F. Ranville, *Forensic Science International*, 2018, **288**, E20-E25.
- 188 M. A. Comanescu, T. J. Millett and T. A. Kubic, *Journal of Forensic Sciences*, 2019, **64**(2), 565-569.
- 189 K. G. Myhre, M. J. Mehta, M. Z. Martin and M. T. Du, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 30-34.
- 190 S. J. Pandey, R. Locke, R. M. Gaume and M. Baudelet, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **148**, 99-104.
- 191 H. Takahara, A. Ohbuchi and K. Murai, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 276-280.
- 192 C. L. Zong, Z. A. Bao, W. L. Ran, X. Ling, L. Chen, K. Y. Chen and H. L. Yuan, *Analytical Methods*, 2018, **10**(21), 2456-2463.
- 193 D. Sakate, Y. Iwazaki, Y. Kon, T. Yokoyama and M. Ohata, *Analytical Sciences*, 2018, **34**(6), 739-742.
- 194 Y. Tang, L. B. Guo, S. S. Tang, Y. W. Chu, Q. D. Zeng, X. Y. Zeng, J. Duan and Y. F. Lu, *Applied Optics*, 2018, **57**(22), 6451-6455.
- 195 M. Bouza, L. Lobo, R. Muniz, R. Pereiro, J. Esparza and J. A. Garcia, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(3), 502-507.
- 196 A. G. Nord and K. Billstrom, *Heritage Science*, 2018, **6**.
- 197 V. Panchuk, I. Yaroshenko, A. Legin, V. Semenov and D. Kirsanov, *Analytica Chimica Acta*, 2018, **1040**, 19-32.
- 198 J. Qi, T. L. Zhang, H. S. Tang and H. Li, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 288-293.
- 199 P. Singh, E. Mal, A. Khare and S. Sharma, *Journal of Cultural Heritage*, 2018, **33**, 71-82.
- 200 A. De Bonis, I. Arienzo, M. D'Antonio, L. Franciosi, C. Germinario, C. Grifa, V. Guarino, A. Langella and V. Morra, *Journal of Archaeological Science*, 2018, **94**, 51-59.
- 201 R. A. Ikeoka, C. R. Appoloni, M. A. Rizzutto and A. M. Bandeira, *Microchemical Journal*, 2018, **138**, 384-389.
- 202 S. Haciosmanoglu, M. Kibaroglu, G. Sunal, E. Kozal and P. Gutsuz, *Archaeometry*, 2018, **60**(3), 471-488.
- 203 S. Stojanovic, V. Bikic, L. Milicic, I. R. Evans, N. V. Y. Scarlett, H. E. A. Brand and L. Damjanovic-Vasilic, *Microchemical Journal*, 2019, **146**, 557-567.
- 204 S. Ichikawa, T. Matsumoto, T. Nakamura and T. Kurisaki, *X-Ray Spectrometry*, 2019, **48**(2), 110-128.
- 205 M. A. C. Ontiveros, E. Tsantini, L. Fantuzzi and J. Ramon, *Archaeological and Anthropological Sciences*, 2019, **11**(2), 627-649.
- 206 E. De Pauw, P. Tack, E. Verhaeven, S. Bauters, L. Acke, B. Vekemans and L. Vincze, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 190-196.
- 207 B. Gehres and G. Querre, *Archaeometry*, 2018, **60**(4), 750-763.
- 208 W. P. Xu, L. C. Niziolek and G. M. Feinman, *Journal of Archaeological Science*, 2019, **103**, 57-71.
- 209 H. Aoyama, K. Yamagiwa, S. Fujimoto, J. Izumi, R. Ishikawa, S. Kameshima and T. Arakaki, *X-Ray Spectrometry*, 2018, **47**(4), 265-272.
- 210 A. Rodrigues, S. Fearn, T. Palomar and M. Vilarigues, *Corrosion Science*, 2018, **143**, 362-375.
- 211 A. Rodrigues, S. Fearn and M. Vilarigues, *Corrosion Science*, 2018, **145**, 249-261.
- 212 J. D. Zhang, Y. Y. Zhang, M. Collin, S. Gin, J. J. Neeway, T. S. Wang and Z. H. Zhu, *Surface and Interface Analysis*, 2019, **51**(2), 219-225.

- 213 K. E. Seyfang, H. J. Kobus, R. S. Popelka-Filcoff, A. Plummer, C. W. Magee, K. E. Redman and K. P. Kirkbride, *Forensic Science International*, 2018, **293**, 47-62.
- 214 J. Skruibis, O. Balachninaite, S. Butkus, V. Vaicaitis and V. Sirutkaitis, *Optics and Laser Technology*, 2019, **111**, 295-302.
- 215 C. Sanchez-Ake, T. Garcia-Fernandez, J. L. Benitez, M. B. de la Mora and M. Villagran-Muniz, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **146**, 77-83.
- 216 G. X. Zhang, Q. Li, Y. Zhu and Z. Wang, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **145**, 51-57.
- 217 A. Ceglia, P. Cosyns, N. Schibille and W. Meulebroeck, *Archaeological and Anthropological Sciences*, 2019, **11**(1), 279-291.
- 218 E. Gliozzo, E. Braschi, F. Giannetti, A. Langone and M. Turchiano, *Archaeological and Anthropological Sciences*, 2019, **11**(1), 141-170.
- 219 A. K. Detcheva and J. Hassler, *Comptes Rendus De L Academie Bulgare Des Sciences*, 2018, **71**(4), 476-482.
- 220 S. Krizova, G. Blazkova and R. Skala, *Microchemical Journal*, 2018, **142**, 236-250.
- 221 T. Purowski, L. Kepa and B. Wagner, *Archaeological and Anthropological Sciences*, 2018, **10**(6), 1283-1302.
- 222 N. Zacharias, M. Kaparou, A. Oikonomou and Z. Kasztovszky, *Microchemical Journal*, 2018, **141**, 404-417.
- 223 N. Schibille, B. Gratuze, E. Ollivier and E. Blondeau, *Journal of Archaeological Science*, 2019, **104**, 10-18.
- 224 E. Neri, B. Gratuze and N. Schibille, *Archaeological and Anthropological Sciences*, 2019, **11**(3), 1107-1122.
- 225 A. Van Ham-Meert, P. Claeys, S. Jasim, B. Overlaet, E. Yousif and P. Degryse, *Archaeological and Anthropological Sciences*, 2019, **11**(4), 1431-1441.
- 226 A. Carter, L. Dussubieux, M. Polkinghorne and C. Pottier, *Archaeological and Anthropological Sciences*, 2019, **11**(3), 1013-1027.
- 227 R. Balvanovic, M. M. Stojanovic and Z. Smit, *Journal of Radioanalytical and Nuclear Chemistry*, 2018, **317**(2), 1175-1189.
- 228 A. Quemet, A. Ruas, V. Dalier and C. Rivier, *International Journal of Mass Spectrometry*, 2019, **438**, 166-174.
- 229 A. Quemet, A. Ruas, V. Dalier and C. Rivier, *International Journal of Mass Spectrometry*, 2018, **431**, 8-14.
- 230 M. L. Baruzzini, H. L. Hall, K. J. Spencer and F. E. Stanley, *International Journal of Mass Spectrometry*, 2018, **430**, 57-62.
- 231 J. M. Mannion, C. R. Shick, G. A. Fugate, B. A. Powell and S. M. Husson, *Talanta*, 2018, **189**, 502-508.
- 232 A. L. Ronzani, A. Hubert, F. Pointurier, O. Marie, N. Clavier, A. C. Humbert, J. Aupiais and N. Dacheux, *Rapid Communications in Mass Spectrometry*, 2019, **33**(5), 419-428.
- 233 M. Krachler, Z. Varga, A. Nicholl, M. Wallenius and K. Mayer, *Microchemical Journal*, 2018, **140**, 24-30.
- 234 Z. Varga, M. Krachler, A. Nicholl, M. Ernstberger, T. Wiss, M. Wallenius and K. Mayer, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(6), 1076-1080.
- 235 W. Wang, S. Fang, J. Xu, Z. M. Li, X. L. Yuan and X. P. Shen, *Chinese Journal of Analytical Chemistry*, 2018, **46**(8), 1245-1252.
- 236 E. Chamizo and M. Lopez-Lora, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2019, **438**, 198-206.
- 237 M. A. C. Hotchkis, D. P. Child, M. B. Froehlich, A. Wallner, K. Wilcken and M. Williams, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2019, **438**, 70-76.

- 238 J. J. Song, G. C. Y. Chan, X. L. Mao, J. D. Woodward, R. W. Smithwick, T. G. Schaaff, A. C. Stowe, C. D. Harris, R. E. Zheng, V. Zorba and R. E. Russo, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **150**, 67-76.
- 239 F. Wang, Y. Zhang, Y. G. Zhao, D. F. Guo, S. K. Xie, J. Tan, J. Y. Li and J. Lu, *Measurement Science and Technology*, 2018, **29**(9).
- 240 E. K. Fenske, B. D. Roach, D. C. Glasgow, R. H. Ilgner and J. M. Giaquinto, *Journal of Radioanalytical and Nuclear Chemistry*, 2019, **320**(1), 153-163.
- 241 B. D. Roach, E. K. Fenske, R. H. Ilgner, C. R. Hexel, T. J. Haverlock and J. M. Giaquinto, *Journal of Chromatography A*, 2019, **1587**, 155-165.
- 242 B. Martelat, H. Isnard, L. Vio, E. Dupuis, T. Cornet, A. Nonell and F. Chartier, *Analytical Chemistry*, 2018, **90**(14), 8622-8628.
- 243 D. A. Childs and J. G. Hill, *Journal of Radioanalytical and Nuclear Chemistry*, 2018, **318**(1), 139-148.
- 244 S. Xing, W. C. Zhang, J. X. Qiao and X. L. Hou, *Talanta*, 2018, **187**, 357-364.
- 245 M. Penkin, S. Boulyga, B. Dabbs, D. Fischer, M. Humphrey, A. Kochetkov, A. Koepf and M. Sturm, *Journal of Radioanalytical and Nuclear Chemistry*, 2018, **316**(2), 791-798.
- 246 S. Richter, C. Venchiarutti, C. Hennessy, U. Jacobsson, R. Bujak, J. Truyens and Y. Aregbe, *Journal of Radioanalytical and Nuclear Chemistry*, 2018, **318**(2), 1359-1368.
- 247 B. A. Dittmann, R. Buompane, E. Chamizo, M. Christl, A. Dewald, T. Dunai, C. Feuerstein, K. Fifield, M. Frohlich, S. Heinze, F. Marzaioli, C. Munker, A. Petraglia, C. Sirignano, E. Strub, H. A. Synal, F. Terrasi, S. Tims and A. Wallner, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2019, **438**, 189-192.
- 248 K. J. Mathew, C. Ottenfeld, R. Keller and A. Slemmons, *Journal of Radioanalytical and Nuclear Chemistry*, 2018, **318**(1), 395-400.
- 249 T. Parsons-Davis, J. Wimpenny, C. B. Keller, K. Thomas, K. M. Samperton, P. R. Renne, R. Mundil, K. Moody, K. Knight, M. J. Kristo and R. Williams, *Journal of Radioanalytical and Nuclear Chemistry*, 2018, **318**(1), 711-721.
- 250 M. Enachescu and C. Stan-Sion, *Radiocarbon*, 2019, **61**(2), 435-444.
- 251 B. Z. Cvetkovic, G. Salazar, D. Kunz, J. Tits, S. Szidat and E. Wieland, *Radiocarbon*, 2018, **60**(6), 1711-1727.
- 252 B. Z. Cvetkovic, G. Salazar, D. Kunz, S. Szidat and E. Wieland, *Analyst*, 2018, **143**(13), 3059-3067.
- 253 S. Hosoya, K. Sasa, T. Takahashi, T. Matsunaka, M. Matsumura, H. T. Shen, Y. Ota, K. Takano, Y. Ochiai and K. Sueki, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2019, **438**, 131-135.
- 254 Y. C. Fu, W. J. Zhou, P. Cheng and L. Y. Zhang, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2019, **438**, 162-165.
- 255 F. Quinto, C. Busser, T. Faestermann, K. Hain, D. Koll, G. Korschinek, S. Kraft, P. Ludwig, M. Plaschke, T. Schafer and H. Geckeis, *Analytical Chemistry*, 2019, **91**(7), 4585-4591.
- 256 L. Y. Zhang, X. L. Hou, Y. C. Fu, M. Fang and N. Chen, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(10), 1729-1736.
- 257 S. Pavetich, A. Carey, L. K. Fifield, M. B. Froehlich, S. Halfon, A. Kinast, M. Martschini, D. Nelson, M. Paul, A. Shor, J. H. Sterba, M. Tessler, S. G. Tims, L. Weissman and A. Wallner, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2019, **438**, 77-83.
- 258 K. Hain, B. Deneva, T. Faestermann, L. Fimiani, J. M. Gomez-Guzman, D. Koll, G. Korschinek, P. Ludwig, V. Sergeeva and N. Thiollay, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2018, **423**, 42-48.
- 259 S. Asai, Y. Hanzawa, M. Konda, D. Suzuki, M. Magara, T. Kimura, R. Ishihara, K. Saito, S. Yamada and H. Hirota, *Talanta*, 2018, **185**, 98-105.
- 260 S. J. Goldstein, K. A. Hinrichs, A. J. Nunn, D. W. Gurganus, R. S. Amato and W. J. Oldham, *Journal of Radioanalytical and Nuclear Chemistry*, 2018, **318**(1), 695-701.

- 261 K. Kolacinska, Z. Samczynski, J. Dudek, A. Bojanowska-Czajka and M. Trojanowicz, *Talanta*, 2018, **184**, 527-536.
- 262 M. Furukawa, M. Matsueda and Y. Takagai, *Analytical Sciences*, 2018, **34**(4), 471-476.
- 263 W. T. Bu, L. Tang, X. M. Liu, Z. T. Wang, M. Fukuda, J. Zheng, T. Aono, S. Hu and X. L. Wang, *Journal of Analytical Atomic Spectrometry*, 2019, **34**(2), 301-309.
- 264 T. Sakamoto, M. Morita, K. Kanenari, H. Tomita, V. Sonnenschein, K. Saito, M. Ohashi, K. Kato, T. Iguon, T. Kawai, T. Okumura, Y. Satou and I. Wakaida, *Analytical Sciences*, 2018, **34**(11), 1265-1270.
- 265 S. Mishra, S. Kasar, A. Takamasa, N. Veerasamy and S. K. Sahoo, *Journal of Environmental Radioactivity*, 2019, **198**, 36-42.
- 266 C. Stan-Sion, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2019, **438**, 107-112.
- 267 T. Matsuyama, Y. Izumoto, K. Ishii, Y. Sakai and H. Yoshii, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 35-41.
- 268 H. Yoshii, Y. Izumoto, T. Matsuyama, K. Ishii and Y. Sakai, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **148**, 183-187.
- 269 D. Obada, A. S. Mamede, N. Nuns, A. C. Gregoire and L. Gasnot, *Applied Surface Science*, 2018, **459**, 23-31.
- 270 J. Song, B. Min, S. Hong, S. An and S. Hong, *Progress in Nuclear Energy*, 2018, **106**, 345-356.
- 271 D. G. Fobar, X. Xiao, M. Burger, S. Le Berre, A. T. Motta and I. Jovanovic, *Progress in Nuclear Energy*, 2018, **109**, 188-194.
- 272 B. T. Manard, E. M. Wylie and S. P. Willson, *Applied Spectroscopy*, 2018, **72**(11), 1653-1660.
- 273 K. Sanyal, S. Dhara and N. L. Misra, *Analytical Chemistry*, 2018, **90**(18), 11070-11077.
- 274 S. Dhara, K. Sanyal, S. Paul and N. L. Misra, *Journal of Analytical Atomic Spectrometry*, 2019, **34**(2), 366-374.
- 275 A. Pandey, S. Dhara, F. A. Khan, A. Kelkar, P. Kumar, R. B. Bhatt and P. G. Behere, *Journal of Radioanalytical and Nuclear Chemistry*, 2019, **319**(3), 775-781.
- 276 B. K. Nagar, M. K. Saxena and B. S. Tomar, *Atomic Spectroscopy*, 2018, **39**(5), 185-192.
- 277 D. D. Reilly, M. T. Athon, J. E. Corbey, Leavy, II, K. M. McCoy and J. M. Schwantes, *Journal of Nuclear Materials*, 2018, **510**, 156-162.
- 278 R. Plukiene, E. Lagzdina, L. Juodis, A. Plukis, A. Puzas, R. Gvozdaite, V. Remeikis, Z. Revay, J. Kucera, D. Ancius and D. Ridikas, *Radiocarbon*, 2018, **60**(6), 1861-1870.
- 279 H. L. Wu, F. Carotti, R. Gakhar, N. Patel and R. O. Scarlat, *Journal of Fluorine Chemistry*, 2018, **211**, 159-170.
- 280 G. Maddaluno, S. Almaguira, L. Caneve, F. Colao, V. Lazic, L. Laguardia, P. Gasior, M. Kubkowska and F. T. U. Team, *Nuclear Materials and Energy*, 2019, **18**, 208-211.
- 281 D. Y. Zhao, C. Li, Z. H. Hu, C. L. Feng, Q. M. Xiao, R. Hai, P. Liu, L. Y. Sun, D. Wu, C. L. Fu, J. M. Liu, N. Farid, F. Ding, G. N. Luo, L. Wang and H. B. Ding, *Review of Scientific Instruments*, 2018, **89**(7).
- 282 P. Paris, J. Butikova, M. Laan, A. Hakola, I. Jogi, J. Likonen, E. Grigore and C. Ruset, *Nuclear Materials and Energy*, 2019, **18**, 1-5.
- 283 Y. Li, C. Ke, X. Liu, F. J. Gou, X. R. Duan and Y. Zhao, *Fusion Engineering and Design*, 2018, **136**, 1640-1646.
- 284 J. M. Liu, D. Wu, C. L. Fu, R. Hai, X. Yu, L. Y. Sun and H. B. Ding, *Plasma Science & Technology*, 2019, **21**(3).
- 285 P. Liu, D. Y. Zhao, L. Y. Sun, C. L. Fu, J. M. Liu, C. Li, R. Hai, C. F. Sang, Z. H. Hu, Z. Sun, J. S. Hu, L. Wang, J. L. Chen, Y. F. Liang, G. N. Luo, H. Ding and E. Team, *Plasma Physics and Controlled Fusion*, 2018, **60**(8).
- 286 Z. H. Hu, N. Gierse, C. Li, J. Oelmann, D. Y. Zhao, M. Tokar, X. Jiang, D. Nicolai, J. Wu, F. Ding, S. Brezinsek, H. B. Ding, G. N. Luo and C. Linsmeier, *Fusion Engineering and Design*, 2018, **135**, 95-101.

- 287 J. Oelmann, C. Li, S. Brezinsek, M. Rasinski, C. P. Dhard, R. Konig, V. Winters and C. Linsmeier, *Nuclear Materials and Energy*, 2019, **18**, 153-158.
- 288 P. Dinca, V. Tiron, I. L. Velicu, C. Porosnicu, B. Butoi, A. Velea, E. Grigore, C. Costin and C. P. Lungu, *Surface & Coatings Technology*, 2019, **363**, 273-281.
- 289 L. Zhang, S. Morita, Z. W. Wu, Z. Xu, X. D. Yang, Y. X. Cheng, Q. Zang, H. Q. Liu, Y. Liu, H. M. Zhang, T. Ohishi, Y. J. Chen, L. Q. Xu, C. R. Wu, Y. M. Duan, W. Gao, J. Huang, X. Z. Gong and L. Q. Hu, *Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment*, 2019, **916**, 169-178.
- 290 J. D. Zhang, W. L. Jiang, Z. H. Zhu, L. Shao, L. Price, J. T. Zhao and T. S. Wang, *Journal of Nuclear Science and Technology*, 2018, **55**(7), 703-708.
- 291 S. Fazinic, T. Tadic, M. Vuksic, M. Rubel, P. Petersson, E. Fortuna-Zalesna and A. Widdowson, *Analytical Chemistry*, 2018, **90**(9), 5744-5752.
- 292 V. C. Costa, J. P. Castro, D. F. Andrade, D. V. Babos, J. A. Garcia, M. A. Speranca, T. A. Catelani and E. R. Pereira, *Trac-Trends in Analytical Chemistry*, 2018, **108**, 65-73.
- 293 G. Gamez and K. Finch, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **148**, 129-136.
- 294 K. Sakurai and A. Kurokawa, *X-Ray Spectrometry*, 2019, **48**(1), 3-7.
- 295 P. A. W. van der Heide, *Journal of Vacuum Science & Technology B*, 2018, **36**(3).
- 296 P. Honicke, M. Kramer, L. Luhl, K. Andrianov, B. Beckhoff, R. Dietsch, T. Holz, B. Kanngiesser, D. Weissbach and T. Wilhein, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **145**, 36-42.
- 297 A. Mejstrik, P. Kregsamer, M. Fugger and C. Strel, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 163-166.
- 298 M. L. Polignano, G. Borionetti, A. Galbiati, S. Grasso, I. Mica and A. Nutsch, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 313-321.
- 299 R. Jakiela, A. Barcz, J. Sarnecki and G. K. Celler, *Surface and Interface Analysis*, 2018, **50**(7), 729-733.
- 300 S. A. Davari, P. A. Taylor, R. W. Standley and D. Mukherjee, *Talanta*, 2019, **193**, 192-198.
- 301 A. Maderitsch, D. Ingerle, T. Bretschneider, M. Rauwolf, C. Pflumm, H. Buchholz, H. Borchert, C. Strel and J. Parisi, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **148**, 188-192.
- 302 W. Pessoa, A. Roule, E. Nolot, Y. Mazel, M. Bernard, M. C. Lepy, Y. Menesguen, A. Novikova, P. Gergaud, F. Brigidi and D. Eichert, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 143-149.
- 303 T. Yamada, H. Takahara, A. Ohbuchi, W. Matsuda and Y. Shimizu, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 256-260.
- 304 J. Hermann, E. Axente, F. Pelascini and V. Craciun, *Analytical Chemistry*, 2019, **91**(3), 2544-2550.
- 305 D. Kaser, L. Hendriks, J. Koch and D. Gunther, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 176-183.
- 306 J. H. Choi, H. J. Lee, S. H. Lee, J. H. In and S. Jeong, *Thin Solid Films*, 2018, **660**, 314-319.
- 307 J. S. Xiu, S. M. Liu, S. G. Fu, T. Wang, M. X. Meng and Y. Y. Liu, *Applied Optics*, 2019, **58**(4), 1040-1047.
- 308 J. Colwell, P. Hsiao, W. Zhang, X. Wang, R. Akter and A. Lennon, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(3), 422-430.
- 309 Y. J. Jang, J. Lee, K. B. Lee, D. Kim and Y. Lee, *Journal of Analytical Methods in Chemistry*, 2018.
- 310 J. Oelmann, N. Gierse, C. Li, S. Brezinsek, M. Zlobinski, B. Turan, S. Haas and C. Linsmeier, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **144**, 38-45.
- 311 S. Imashuku, H. Taguchi, S. Fujieda, S. Suzuki and K. Wagatsuma, *Electrochimica Acta*, 2019, **293**, 78-83.
- 312 S. Imashuku, H. Taguchi, T. Kawamata, S. Fujieda, S. Kashiwakura, S. Suzuki and K. Wagatsuma, *Journal of Power Sources*, 2018, **399**, 186-191.

- 313 P. Smyrek, T. Bergfeldt, H. J. Seifert and W. Pfleging, *Journal of Materials Chemistry A*, 2019, **7**(10), 5656-5665.
- 314 P. Harte, M. Evertz, T. Schwieters, M. Diehl, M. Winter and S. Nowak, *Analytical and Bioanalytical Chemistry*, 2019, **411**(3), 581-589.
- 315 M. Evertz, T. N. Kroger, M. Winter and S. Nowak, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 118-123.
- 316 B. Bookhagen, W. Obermaier, C. Opper, C. Koeberl, T. Hofmann, T. Prohaska and J. Irrgeher, *Analytical Methods*, 2018, **10**(31), 3864-3871.
- 317 D. F. Andrade, F. M. Fortunato and E. R. Pereira, *Analytica Chimica Acta*, 2019, **1061**, 42-49.
- 318 J. P. Castro and E. R. Pereira, *Talanta*, 2018, **189**, 205-210.
- 319 E. Nolot, B. Caby, R. Gassilloud, M. Veillerot and D. Eichert, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 71-75.
- 320 C. W. Lu, H. Y. Hung, W. L. Lin and S. P. Wu, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2018, **149**, 243-248.
- 321 N. X. Wang, X. L. Wang, P. Chen, Z. D. Jia, L. M. Wang, R. H. Huang and Q. S. Lv, *Sensors*, 2018, **18**(8).
- 322 M. H. Wang, M. J. Zhao, S. Ye, M. Zhu, R. X. Yi, L. W. Liu and J. L. Qu, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(5), 713-719.
- 323 S. Lopez-Sanz, F. J. G. Bernardo, R. C. R. Martin-Doimeadios and A. Rios, *Analytica Chimica Acta*, 2019, **1059**, 1-15.
- 324 A. R. M. Bustos, K. P. Purushotham, A. Possolo, N. Farkas, A. E. Vladar, K. E. Murphy and M. R. Winchester, *Analytical Chemistry*, 2018, **90**(24), 14376-14386.
- 325 S. Naasz, S. Weigel, O. Borovinskaya, A. Serva, C. Cascio, A. K. Undas, F. C. Simeone, H. J. P. Marvin and R. J. B. Peters, *Journal of Analytical Atomic Spectrometry*, 2018, **33**(5), 835-845.
- 326 T. Hirata, S. Yamashita, T. Suzuki and M. Ishida, *Bunseki Kagaku*, 2019, **68**(2), 81-88.
- 327 L. Hendriks, B. Ramkorun-Schmidt, A. Gundlach-Graham, J. Koch, R. N. Grass, N. Jakubowski and D. Gunther, *Journal of Analytical Atomic Spectrometry*, 2019, **34**(4), 716-728.
- 328 F. H. Lin, S. Miyashita, K. Inagaki, Y. H. Liu and I. H. Hsu, *Journal of Analytical Atomic Spectrometry*, 2019, **34**(2), 401-406.
- 329 L. A. Rush, M. C. Endres, M. Liezers, J. D. Ward, G. C. Eiden and A. M. Duffin, *Talanta*, 2018, **189**, 268-273.
- 330 A. Kana, M. Loula, R. Koplik, M. Vosmanska and O. Mestek, *Talanta*, 2019, **197**, 189-198.
- 331 M. Loula, A. Kana, R. Koplik, J. Hanus, M. Vosmanska and O. Mestek, *Analytical Letters*, 2019, **52**(2), 288-307.
- 332 D. Bouzas-Ramos, J. I. Garcia-Alonso, J. M. Costa-Fernandez and J. R. Encinar, *Analytical Chemistry*, 2019, **91**(5), 3567-3574.
- 333 H. M. Neu, S. A. Alexishin, J. E. P. Brandis, A. M. C. Williams, W. J. Li, D. J. Sun, N. Zheng, W. L. Jiang, A. Zimrin, J. C. Fink, J. E. Polli, M. A. Kane and S. L. J. Michel, *Molecular Pharmaceutics*, 2019, **16**(3), 1272-1281.
- 334 S. Lopez-Sanz, N. R. Farinas, R. D. R. Martin-Doimeadios and A. Rios, *Analytica Chimica Acta*, 2019, **1053**, 178-185.
- 335 J. J. Tan, Y. Yang, H. El Hadri, M. D. Li, V. A. Hackley and M. R. Zachariah, *Analyst*, 2019, **144**(7), 2275-2283.
- 336 I. Rujido-Santos, L. Naveiro-Seijo, P. Herbelo-Hermelo, M. D. Barciela-Alonso, P. Bermejo-Barrera and A. Moreda-Pineiro, *Talanta*, 2019, **197**, 530-538.
- 337 P. Anekthirakun and A. Imyim, *Microchemical Journal*, 2019, **145**, 470-475.
- 338 A. Radtke, M. Grodzicka, M. Ehlert, T. M. Muziol, M. Szkodo, M. Bartmanski and P. Piszczek, *International Journal of Molecular Sciences*, 2018, **19**(12).
- 339 A. Rahman, S. Kumar, A. Bafana, S. A. Dahoumane and C. Jeffryes, *Molecules*, 2019, **24**(1).
- 340 S. Oliver, H. Wagh, Y. L. Liang, S. Yang and C. Boyer, *Journal of Materials Chemistry B*, 2018, **6**(24), 4124-4138.
- 341 S. Yamashita, T. Suzuki and T. Hirata, *Bunseki Kagaku*, 2019, **68**(1), 1-7.

- 342 D. Lomeli-Marroquin, D. M. Cruz, A. Nieto-Arguello, A. V. Crua, J. J. Chen, A. Torres-Castro, T. J. Webster and J. L. Cholula-Diaz, *International Journal of Nanomedicine*, 2019, **14**, 2171-2189.
- 343 R. P. Luo, L. N. Zheng, L. Li, J. Wang, W. Y. Feng, X. H. Yu and M. Wang, *Chinese Journal of Analytical Chemistry*, 2018, **46**(6), 925-930.
- 344 R. Saenmuangchin and A. Siripinyanond, *Analytical and Bioanalytical Chemistry*, 2018, **410**(26), 6845-6859.
- 345 N. Anjuthaprabha and R. Manimekalai, *Journal of Coordination Chemistry*, 2019, **72**(1), 83-101.
- 346 M. Chigondo, H. K. Paumo, M. Bhaumik, K. Pillay and A. Maity, *Journal of Molecular Liquids*, 2019, **275**, 778-791.
- 347 U. Dalal and S. N. Reddy, *Environmental Science and Pollution Research*, 2019, **26**(11), 10631-10640.
- 348 S. G. Lanas, M. Valiente, M. Tolazzi and A. Melchior, *Journal of Thermal Analysis and Calorimetry*, 2019, **136**(3), 1153-1162.
- 349 T. Preller, D. Menzel, S. Knickmeier, J. C. Porsiel, B. Temel and G. Garnweitner, *Nanomaterials*, 2018, **8**(5).
- 350 C. Tang, A. W. York, J. L. Mikitsh, A. C. Wright, A. M. Chacko, D. R. Elias, Y. D. Xu, H. K. Lim and R. K. Prud'homme, *Macromolecular Chemistry and Physics*, 2018, **219**(11).
- 351 M. Bartosiak, J. Giersz and K. Jankowski, *Microchemical Journal*, 2019, **145**, 1169-1175.
- 352 N. L. Zufah and A. Siripinyanond, *Journal of Analytical Science and Technology*, 2018, **9**.
- 353 M. Ghaffari, F. Mortarzadeh and M. Safavi, *Ceramics International*, 2019, **45**(1), 1179-1188.
- 354 D. Marsan, H. Sengul and A. M. A. Ozdil, *Environmental Science-Nano*, 2019, **6**(3), 879-891.