

ATOMIC SPECTROMETRY UPDATE—INORGANIC MASS SPECTROMETRY AND X-RAY FLUORESCENCE SPECTROMETRY

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This is the second Update covering Inorganic MS and XRF exclusively. The ICP-MS and XRF sections cover a full year and are based upon comprehensive abstracts. The sections other than ICP-MS in Inorganic MS are less well covered but should be fully abstracted during the coming year in readiness for the 1990 ASU. In the Inorganic MS field an increasing interest in the environmental field, particularly on radionuclide pollution, is evident. This trend seems certain to continue in an increasingly Green, post-Chernobyl Europe. In ICP-MS, the increasing popularity of the technique is clear and much attention has turned to solution of problems surrounding introduction of "real world" samples. Slurry nebulisation and ETV techniques show promise in this area. In XRF, the main instrumental developments in the review period centre around the use of synchrotron radiation (SR). The use of SR in conjunction with the increasingly popular techniques of X-ray microfluorescence (XRMF) and total reflection XRF (TXRF) is particularly interesting. A wide application base continues to be developed, with notable interest evident in speciation and workplace monitoring.

1. INORGANIC MASS SPECTROMETRY

1.1. Introduction

It has not been possible to cover fully all areas of inorganic MS in this update. Stable isotope ratio MS (SIRMS) and the microprobe techniques, laser microprobe mass spectrometry (LMMS) and secondary ion MS (SIMS), have only been covered partially. Accelerator MS has not been covered at all. It is hoped to be able to expand coverage for future updates.

The wide coverage of the papers in this Update underlines the fact that inorganic mass spectrometry or, as preferred elsewhere, atomic mass spectrometry (89/241), is making considerable advances, not only in the newer methods but also in the older established methods. There is now considerable interest in the applications of these newer techniques, as highlighted by the rapid growth of inductively coupled plasma mass spectrometry (ICP-MS), and the usefulness of each technique is the criterion by which it should be judged. Although most of the newer techniques have now moved from the stage of pure method development to evaluation of their applicability, few can be considered routine procedures. The number of workers in such areas is limited due to the major problems of instrument cost and availability. Few, if any, of the instruments used can be considered cheap and in choosing a technique for a particular operation, the researcher is usually constrained by what is available rather than what is the best or most applicable method. Most of the techniques, especially the solid sampling methods, are being developed for as wide a range of applications as possible even though not ideally suited for all of them. In the following sections the advances are considered in terms of the mass spec-

trometric technique. Most of the applications recur in several of the sections and a summary of the broad areas of applications is given in Table 1.

The most comprehensive review of atomic mass spectrometry is that of Koppenaal (89/241) but, by its very nature, it has probably already been superseded. Another wide ranging review (89/2692) covers advances and new perspectives, while the summaries of abstracts of the American Society for Mass Spectrometry (ASMS) annual conference give coverage to all aspects of mass spectrometry (Proceedings of the 36th ASMS Conference on Mass Spectrometry and Allied Topics, San Francisco, CA, USA, 5th-10th June, 1988). The applications of time-of-flight (TOF) mass spectrometry have also been reviewed (89/2667). Reviews on specific areas of application have included the trace analysis of refractory metals (88/1927, 89/1974), the determination of the lanthanide elements, Th and U in geological samples (89/2584), mass spectrometry in nuclear science (89/2573), agriculture (89/C594) and the study of Pb in the atmosphere (89/2685). These reviews cover the range of inorganic mass spectrometry techniques and it is clear that each technique has a potential contribution to each area of study.

Two trends become apparent in the range of applications. Firstly, environmental studies are increasing with the concern on contamination and pollution, especially by radionuclides. Secondly, the use of isotope dilution analysis is increasing for accurate determination of elemental concentrations. Isotopic studies in general are increasing with a growing use of stable isotope tracers in nutrition and environmental studies.

Table 1. Reported applications (x) of mass spectrometric methods

Application	GDMS	ICP-MS	Microprobe	RIMS	SSMS	SIRMS	TIMS	Other
High-purity solids—								
Metals	x	x	—	x	x	—	—	—
Semiconductors	x	x	x	x	x	—	—	—
Insulators	x	x	x	x	x	—	—	—
Geological	—	x	x	x	x	x	x	x*
Environmental	—	x	x	x	x	x	x	—
Nuclear	—	x	x	x	—	x	x	—
Isotope analysis	—	x	x	x	x	x	x	x†,‡

* Laser MS.
† FAB-MS.
‡ GC - MS.

1.2. Glow Discharge Mass Spectrometry (GDMS)

The *glow discharge* has been used as an ion source for mass spectrometry for many years but recently it has been refined and developed to become a viable alternative for solids analysis and indeed could be considered as the natural successor to SSMS. However, it is noticeable that much of the ever increasing output on GDMS is in the form of reviews of the technique and potential applications or of conference abstracts, and that these are from a limited number of groups, which include the manufacturers of the sole commercial instrument (the VG 9000). Hopefully these preliminary reports will become full papers so that the true potential of the technique can be assessed objectively.

The pioneering group of Harrison and co-workers has presented some excellent reviews of GDMS (89/387, 89/551, 89/C762, 89/C1289) and to quote from one (89/C762) "GDMS has come close to meeting the advantages claimed for it, such as excellent sensitivity, relatively uniform elemental response and minimal matrix effects." Other review articles also cover the development and current status of GDMS for solids analysis (89/C1302, 89/2568, 89/2644, 89/2700) and the Instrumentation Atomic Spectrometry Update (88/2091) considers developments in the glow discharge.

The interesting point about GDMS is that the development of the technique appears to be mirroring that of SSMS and indeed the above quote could have been written about SSMS some two decades ago. Many of the analytical advantages and disadvantages of SSMS are shared by GDMS. One of the last problems to be addressed in the development of any new MS technique is often that of *molecular interferences* but the occurrence of these in GDMS is now being acknowledged and methods investigated to reduce or even overcome them. A study of the formation of metal - argon ions, $M\text{Ar}^+$ and $M\text{Ar}^{2+}$ where $M = \text{Cu}, \text{Ni}$ or Zn , found that, whereas CuAr^+ and NiAr^+ were readily formed, almost no ZnAr^+ was generated (89/C778). It was suggested that molecular ions were formed by associative ionisation involving metastable argon atoms and a harpooning type of reaction mechanism. The resolution required to separate elemental and molecular interference ions is, in many instances, beyond the capability of the instruments used and approaches for the reduction of commonly encountered interferences have been considered by King *et al.* (89/554). The introduction of getters or matrix modifiers influences the chemistry of the plasma and may allow custom-designed plasma environments for specific applications. Alternatively, a collision cell between the ion source and mass analyser induces dissociation of the polyatomic ions and results in fewer interference lines in the spectrum. Reduction of molecular interferences is especially important if cheaper instrumentation, based on quadrupole analysers, is to find a market. An example of the complexity of spectra is to be found in the determination of the lanthanide elements which, in a mass range of 40 u, produces over 100 ions consisting of elemental ions and, mainly, oxide and carbide molecular ions (89/C1942). An ultra-high resolution (>40 000) mass spectrometer (VG-ZAB) was used to separate the interfering lines but such instrumentation is only available to a few users.

Studies on the *processes of ion formation* have concentrated mainly on the role of sputter atomisation, a model for which has been proposed by Harrison and co-workers (89/C1303, see also Harrison, W. W., King, F. L., Tong, S. L., and Barshick, C. M., "Secondary Ion Mass Spectrometry SIMS VI," John Wiley, Chichester, 1988, pp. 825-828). Sputter activity was found to increase with incident ion energy and discharge pressure and across the rows of the Periodic Table. Sputter yields appeared to

be influenced by the presence of fast neutral atoms which can contribute to sample ablation. The efficiency of sputter ionisation has been studied theoretically in terms of spatial distribution of species and probability of extraction into the ion beam in order to predict various effects (89/764). To observe the effect on ion formation, Hess and Harrison (88/1996) used a tunable laser to de-populate metastable atom populations and they concluded that Penning ionisation plays a role.

The independence of GDMS from *matrix effects* has been discussed (see Hall, D. J., Sanderson, N. C., and Charalambous, P. M., "Secondary Ion Mass Spectrometry SIMS VI," John Wiley, Chichester, 1988, pp. 829-832) but this is always a relative judgement and the formation of molecular ions, for example, is highly dependent on the matrix and can markedly affect the analysis. Indeed, quantitative aspects of GDMS have been addressed and the use of relative sensitivity factors considered (89/2669, 89/2671).

Applications of GDMS are confined almost entirely to trace analysis and quality control of high-purity materials (metals, semiconductors and insulators). The newer areas of application which illustrate the wider potential of the technique have been summarised as: the detection of Th and U in materials at the 10 pg g⁻¹ level; the determination of C, N and O in semiconductor materials below µg g⁻¹ levels; analysis of non-conducting powders; direct analysis of insulating glasses and depth profiling (89/C1302). The use of high resolution (89/2569) and low resolution (89/2570) has been discussed for the analysis of metals. Despite the use of GDMS instruments in industry for quality control very few published reports exist. An example of this type of use is the analysis of high-purity Ga (89/2567). The analysis of high-purity electronic grade chemicals has been described for the determination of U and Th to control the levels of alpha-emitters (89/2670). Hall *et al.* have compared GDMS and SIMS for applications in surface analysis (see Hall, D. J., Sanderson, N. E., Hoodless, R. C., and Charalambous, P. M., "Secondary Ion Mass Spectrometry SIMS VI," John Wiley, Chichester, 1988, pp. 477-480).

The analysis of *insulators* presents a greater problem of sample preparation. Impurities in Y₂O₃ powder were determined by using high-purity Ga powder as a conducting binder to give detection limits of about 5 ng g⁻¹ for a 1-min acquisition time (89/C775). For an insulator in the form of a solid block an alternative to grinding is to use a high-purity counter electrode to produce continuous sputtering (89/C795). A new source for the analysis of insulators uses a high frequency (13.56 MHz) voltage pulse to produce a pseudo-continuous discharge (89/C1304). This study used a quadrupole analyser and in the past the combination of spark source and quadrupole analyser never proved successful because of the high energy spread of ions.

It is apparent that the only *commercially available instrument*, the VG 9000, has found a niche in the analysis of high-purity materials for which the matrix is extremely simple and high resolution is required to achieve low detection limits. There has, however, been no reported analyses of more complex materials such as rocks, soils or biological samples and the area of surface analysis is only now being investigated. This instrument is complex and expensive, which must limit the potential application of the technique beyond that of high-purity, high-value analyses. It is notable that most of the non-commercial instruments employ quadrupole analysers and it could be that the future availability of cheaper quadrupole-based instruments will determine the future growth of GDMS. The alternative to new instruments would be the availability of glow-discharge sources which could be fitted to existing instruments.

1.3. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

1.3.1. General reviews

It is clear from papers available for review this year that ICP-MS is continuing to increase in popularity. Although the technique is being used in the analysis of many types of sample, a significant part of the fundamental research has been devoted to studies on alternative methods of sample introduction, particularly in using ICP-MS as a detector for liquid chromatography.

Up to the end of this review year there were several refereed general summary papers on ICP-MS. Houk and Thompson (89/982) presented a useful review with 211 references, covering most aspects of the technique. Kawaguchi (89/1763) described instrumental developments, analytical performance and applications of the technique in a review containing 43 references. Luck and Siewers (89/1744) presented a summary of sample preparation, detection limits and interferences in ICP-MS for multi-element analysis. An atomic spectroscopy bibliography (89/1841) of some 14000 references, including entries for ICP-MS is available. The following Atomic Spectrometry Updates which cover minerals and refractories (88/945), environmental analysis (88/1749), clinical and biological materials (88/1993) and instrumentation (88/2091) include ICP-MS development and applications.

There have been a number of "current status" conference reports; Horlick (89/C1239) reviewed the current status and future trends of ICP-MS, highlighting its versatility. Hutton *et al.* (89/C1517) emphasised the applicability of the technique to trace analysis of biochemical systems, for both elemental and isotope ratio determinations. Gray (89/C159, 89/C791) outlined the history of ICP-MS, together with potential future developments.

1.3.2. Fundamental studies

1.3.2.1. Interference effects. Despite the potential problems that can arise from *matrix effects*, few studies on these effects have been reported. Gillson *et al.* (89/246) proposed a mechanism to explain the greater susceptibility of ICP-MS to non-spectroscopic interferences, relative to ICP-OES. Changes in analyte sensitivities in the presence of some matrix elements (e.g., uranium) were attributed to space charge effects in the skimmer and ion optics. However, Kawaguchi *et al.* (88/2330) in their study of matrix effects of easily ionisable elements such as Na, found that suppression of analyte signal increased with increasing relative atomic mass of the matrix elements and attributed the signal reduction to scattering of the analyte ion by collision with matrix atoms.

Solids deposition on the extraction interface is a problem unique to ICP-MS. Douglas and Kerr (89/533) investigated the rate of deposition of solids resulting from the analysis of solutions with 0.1–1% *m/v* dissolved solids under various operating conditions. They concluded that deposition decreased with both increasing power and decreasing aerosol flow-rates. In addition, it was observed that a pseudo-steady-state could be achieved between deposition and erosion of matrix material after a period of time. Williams and Gray (89/1845) showed that disparate plasma operating conditions led to different rates of solids deposition and that individual elemental determinand signals decay at different rates when cone blockage occurs, making correction with internal standards difficult. They also found that rates of solids deposition and erosion reached a steady state.

Spectral interference problems are now well documented for ICP-MS and it is generally recognised that adjustment of plasma operating conditions can provide a way of avoiding some interferences. Houk and co-workers (89/1788), by increasing the distance of the sampling cone from the plasma, decreasing forward

power and increasing aerosol flow-rate, suppressed the intense interfering background peaks at *m/z* 39, 40 and 41, which correspond to Ar^+ and ArH^+ . These interfering ions would normally prevent the determination of K^+ isotope ratios. Jarvis (89/C756) overcame the problem of refractory oxide and hydroxide interference from barium in the determination of the REE, by optimising the plasma to produce high levels of doubly charged REE species, which would occur at half their mass in the mass spectrum. By increasing the resolution of the mass spectrometer to resolve half masses, the REE were determined free from spectral interference as doubly charged oxide species are not observed.

The use of the *negative ion mode* for ICP-MS was demonstrated (88/1676) in the determination of Br^- and Cl^- in standard solutions. The effect of high salt and acid concentrations on the determinand signals were discussed. Although limits of detection of $<1 \mu\text{g ml}^{-1}$ were achieved, very high background counts from secondary electrons reaching the detector, make this method of ion detection impractical.

1.3.2.2. Operating parameters. Very few studies on the effects of operating parameters on determinand signals have been reported. Kawaguchi *et al.* (89/1520) studied factors affecting continuum background levels in a laboratory-constructed ICP-MS instrument. Optimisation of the sizes of an optical baffle plate and lens cap cone was found to minimise background intensity. Increasing the voltages applied to the ion lenses was found to yield increased background which was attributed to a weak discharge in the lens elements. Richardson *et al.* (89/C758) studied optimisation of various physical and chemical parameters on Os isotopic analysis using both nebuliser and OsO_4 generator techniques. Ting and Janghorbani (88/1678) also studied the optimisation of instrumental parameters for the precise measurement of isotope ratios, including both plasma parameters and data acquisition parameters (e.g., dwell time). For maximum precision, optimisation had to be carried out for each individual element of interest.

In nearly all ICP-MS instruments, *ion detection* is carried out with a channel electron multiplier. As an alternative, Houk and co-workers (88/2326) investigated the performance of a scintillation ion detector and compared it with that of the multiplier. The performance of the scintillation detector was generally superior to that of the multiplier. Unfortunately the initial cost of the detector was much greater than that of a multiplier and installation of the device was complex.

Puchelt and Noeltner (89/1790) investigated the *stability of highly diluted multi-element calibration solutions* ($<1 \mu\text{g ml}^{-1}$) for ICP-MS and found acidic solutions (pH 1) of most elements, except Ag, Au and Ta, were stable for 30 d.

Although the *interface region* lies at the heart of the ICP-MS instrument, physical and chemical processes in this region are not fully understood. Douglas and French (89/532) presented a useful summary of some of the gas dynamics thought to take place in the ICP-MS interface and concluded that provided the free jet behind the sampling cone is skimmed properly, a representative sample of ions from the ICP can be obtained.

Zhu and Browner (89/538) studied the *influence of water loading* on ion counts for singly- and doubly-charged ions as well as oxide and hydroxide species of a number of elements on two different commercial ICP-MS instruments. The authors concluded that, although vapour loading affected each system differently, it was an important parameter in the optimisation of ICP-MS systems. Findings were compared with an analogous study carried out on an ICP-OES system.

Interest continues in the use of *microwave-induced plasmas* (MIP) as ion sources for MS. Wilson *et al.* (88/2280) compared the performance of a N_2 MIP with an Ar ICP as an ion source and found interferences from oxide and hydroxide ions and from

concomitant elements were significantly greater with the MIP source. Poussel *et al.* (89/505) used a low-power, low-pressure MIP operated with Ar, Kr or Xe as a soft ionisation source for molecular analysis of organic compounds by MS. Adjustment of the power and pressure was found to modify the fragmentation of organic compounds. Brown *et al.* (89/535) used a He MIP as an ion source for the determination of Br^+ , Cl^+ , F^+ and I^+ in standard gas mixtures and presented data on the background mass spectrum of the He MIP and the effect of plasma sampling parameters on the background. Satzger *et al.* (88/1677) presented data which demonstrated an inhomogeneous distribution of determinand ions throughout a moderate power Ar MIP, indicating the necessity for sampling of the plasma in a position where oxide and hydroxide formation was favoured. Interference effects were found to be more severe with an Ar MIP than with an Ar ICP.

Koppenaal and Quinton (89/84) continued their investigations into the feasibility of using a *He ICP ion source* for MS. Although thought to be a promising ion source, offering simpler background and higher sensitivities for elements with high ionisation potentials, an intense ICP to sampling cone discharge together with a low plasma gas temperature constitute major impediments to the use of this source.

1.3.2.3. Sample introduction. Interest in alternative sample introduction techniques continues to grow, although more noticeably so in some areas than others. Despite the potential of laser ablation ICP-MS for rapid sample analysis, often with minimum sample preparation, very few reports have appeared. Use of high-repetition rates (10 Hz) with a highly focused beam (1.06 μm) were claimed to improve precision and duty cycle for data acquisition while quantitative analysis was achieved by internal standardisation (88/2274).

Slurry nebulisation ICP-MS was used to determine trace elements in eight coal certified reference materials (89/534). Results, which showed good agreement with certified values, were obtained in both semi-quantitative and quantitative mode, using rhodium as an internal standard. Ebdon (89/C7) reviewed the use of slurry nebulisation in ICP-OES, DCP-OES and ICP-MS, pointing out both the ease of sample preparation and the importance of sample particle size. Jarvis and Williams (89/C749) used slurry nebulisation ICP-MS to determine mainly trace REE successfully, in a range of geological sample types including Barytes.

Sample introduction by *electrothermal vaporisation* (ETV) for ICP-MS has a number of advantages which have been responsible for its increased use. Park *et al.* (88/2323) reported the use of a previously described ETV device (88/346) for the analysis of various biological RMs. Detection limits were ten times better than those obtained by nebulisation ICP-MS. The system was also applied to the determination of Tl in geological materials (88/1682), but spectral interferences caused by high concentrations of Pb necessitated chemical separation of Tl. In the determination of the platinum group metals by ETV-ICP-MS (88/1675), addition of 500 $\mu\text{g ml}^{-1}$ of Ni as nitrate provided a maximum ten-fold enhancement in analyte ion count rate.

Hall *et al.* (89/539) compared the relative merits of an ETV and a *direct sample insertion device* (DSID) for ICP-MS sample introduction. It was found that analyte transport efficiency was much better with the DSID than with the ETV, but that the DSID was more susceptible to problems from solutions containing high salt concentrations. In addition, impurities of Fe, Mo and Ni in the wire loop precluded their determination using the DSID.

Inductively coupled plasma MS has become popular as a rapid, sensitive and element specific on-line detector for *chromatography*. Beauchemin *et al.* (89/1456) using HPLC - ICP-MS,

identified 84% of total As present in a dogfish muscle RM as arsenobetaine. Bushee (89/202) determined methylmercury in a reference tuna sample and thimerosal, a mercury containing preservative, in contact lens solution using HPLC - ICP-MS with post-column cold vapour generation.

Jiang and co-workers (89/220) used chromatographic retention to remove complexes of Mo^{VI} and Ti^{IV} from samples of standard reference sediments and Ni-base alloys to allow Cd, Cu and Zn to be determined without interference from MoO^+ or TiO^+ . The process was also used to remove excess of U^{VI} , thereby preventing non-spectral interference in the determination of REE. This group also separated P and S in inorganic and organic samples prior to detection by ICP-MS (89/528). Lyon *et al.* (88/2090) used desalination by chromatographic separation to avoid the problem of chloride interference in the determination of Se in serum samples. A He MIP-MS system coupled to a gas chromatograph was used to detect separated Br and I compounds (89/561).

Gustavsson (89/1516) described a *membrane interface* for removal of organic solvent from solution prior to analysis by spectrometric methods. Interfacing flow injection analysis or HPLC with ICP techniques was claimed to be of particular value.

Solutions used for analysis by ICP-MS are often restricted to those containing low levels of dissolved solids (0.2% *m/V*), because of the problems associated with sampling cone blockage. By using *flow injection techniques*, Hutton and Eaton (88/2079) showed that samples of brine and aluminium digests could be analysed by ICP-MS at up to 2% *m/V* of total dissolved solids. Dean *et al.* (88/1681) applied the technique to the determination of biological reference materials, with external calibration and by isotope dilution analysis (IDA).

Hydride generation (89/544) was used in conjunction with IDA calibration to improve sensitivity and precision in the determination of trace amounts of Pb in various sample types. Serious interference on the generation of PbH_4 by Fe and Cu was eliminated by the use of sulphosalicylic acid and sodium cyanide dissolved in sodium tetrahydroborate(III) solution.

1.3.3. Applications

1.3.3.1. Geochemistry. Sansoni and co-workers (89/891) compared the performance of ICP-MS with that of ICP-OES, ICP-AFS and FAAS for the multi-element analysis of *natural waters from a granite region* and generally found good agreement between the techniques. Of the 36 elements investigated, 34 elements could be determined simultaneously by ICP-MS, compared with 13 by ICP-OES, 12 by ICP-AFS and 14 sequentially by AAS.

The late Alan Date and co-workers (89/82) compared *digestion procedures* for iron-rich RMs and studied the influence of polyatomic ion interferences in relation to both the dissolution media and sample matrix. Cheung and Coote (89/C761) compared three decomposition methods for cassiterites (hydrogen decomposition, ammonium iodide fusion and lithium metaborate fusion), pointing out the advantages and drawbacks of each. Hall *et al.* (89/C1444) compared a series of fusion flux mixtures to establish an efficient method by which Hf, Nb, Tb and Zr could be determined routinely in a variety of geological matrices by ICP-MS. High dissolved solids concentration was reduced by precipitation with cupferron. For the multi-element analysis of quartz sand by ICP-MS, a chemical pre-treatment procedure to dissolve the sample and to evaporate the matrix was developed (88/C1520) using a mixture of acids and H_2O_2 .

Jarvis (89/2554) described the use of ICP-MS for the determination of *REE and Y* in eight geological RMs. The elements of interest were determined with good accuracy and precision

down to $10\times$ chondrite abundances (2760 ng g^{-1} of Gd) and to $0.01\times$ chondrite (2.760 ng g^{-1} of Gd) following an ion-exchange separation and pre-concentration procedure.

The determination of *Re:Os ratios* presents a unique opportunity to study the age and origin of base and noble metal ore deposits (88/1679). Inductively coupled plasma MS is ideally suited to the task of determining precise Os isotope ratios, as the high ionisation potential of Os precludes isotopic analysis by TIMS. The OsO_4 from a pure Os solution and a natural sulphide ore standard were directly distilled into the plasma. Isotope ratio precision of 0.3% RSD (1σ) were obtained with an accuracy of 0.1–0.2%, relative to the standard, from samples with low ng ml^{-1} concentrations.

1.3.3.2. *Environmental*. The *halides* are generally regarded as difficult elements to determine by optical spectrometric techniques. With the exception of F, all can be relatively easily determined by ICP-MS. Date and Stuart (89/83) determined Br, Cl and I in NIST SRM 1648 Urban Particulates following investigation of a number of dissolution procedures. Results were considered in the light of possible polyatomic ion interferences from chemicals used in sample fusion procedures.

Hall *et al.* (88/2210) illustrated the relative merits of analysing fresh and saline *water samples* for Mo and W by ICP-OES and ICP-MS. In order to determine 0.4 ng ml^{-1} Mo or 1.2 ng ml^{-1} W by ICP-OES, pre-concentration via adsorption of analytes on to activated charcoal was mandatory. This pre-concentration procedure was also necessary for ICP-MS analysis where waters contained high levels of dissolved solids.

Hollenbach and Grohs (89/C1420) overcame the problem of memory effects from iodine in the analysis of *brines*. Oxidation of I^- to IO_3^- with NaOCl was found to reduce memory effects significantly.

Beauchemin *et al.* (88/1674), in applying ICP-MS to the particularly difficult problem of *sea water analysis*, utilised a 50-fold pre-concentration procedure. This involved adsorbing several trace metals in NRCC saline reference material UASS-2 on to silica-immobilised quinolin-8-ol, separating the elements of interest from the bulk of the alkali and alkaline earth elements.

Information on the levels of trace elements in *marine biological material* can indicate much to marine scientists about the food web status in the ocean environment. Ridout *et al.* (89/531) accurately determined 16 elements in marine reference material TORT-1. Non-spectral interferences were overcome by using sample dilution and standard additions. Mathematical correction for polyatomic interferences arising from Cl in the matrix were successfully made. Beauchemin and co-workers (88/1995, 89/537) determined 13 elements in NRCC marine reference materials DOLT-1 and DORM-1 and 12 elements in cod liver tissue and shellfish tissue by standard additions or isotope dilution techniques. With the exception of Cr in DOLT-1, accurate results were obtained for all elements.

McLaren *et al.* (89/529) determined 16 elements in a *marine sediment* RM PACS-1 by a combination of external calibration and isotope dilution. The use of $^{40}\text{Ar}_2^+$ as an internal standard in the calibration method was effective when concomitant element concentrations were high enough to cause sensitivity changes or calibration drift. However, owing to the unpredictable nature of polyatomic species such as $^{40}\text{Ar}_2^+$, their routine use as internal standards would not be prudent.

1.3.3.3. *Biological materials*. As the medical relevance of more trace elements becomes understood, the demand for more versatile multi-element analysis grows. Inductively coupled plasma MS is now generally regarded as a useful tool to meet this challenge. Mulligan *et al.* (88/C1527) assessed the potential of ICP-MS as a means of directly screening *urine* for heavy metals. Samples were prepared by a ten-fold dilution, which allowed

continuous analysis for 24 h without appreciable accumulation of material at the sampling cone. The determination of As and Se was compromised by polyatomic interferences.

Emmett (89/1674) described the development of a wet-oxidation method for full cream *liquid milk* which avoided the use of sulphuric acid for the destruction of organic matter, as the use of this acid causes severe polyatomic interferences in ICP-MS analysis. The recovery of the digestion method was assessed with a relevant RM.

Isotope ratio determinations by ICP-MS for *medical tracer studies* using stable isotopes have become more commonplace. Schutte *et al.* (89/1625) described a method for the accurate determination of Mg stable isotopes in a variety of biological materials. Precision of analysis was found to be 0.1–1% with a mean accuracy for the isotope ratios of about 1.5%. Accuracy of the determination of Mg was assessed using several biological RMs.

Delves and Campbell (88/1680) determined total Pb concentrations and Pb isotope ratios in *whole blood* by ICP-MS. Samples were prepared by a simple 1+24 dilution of blood using a diluent that contained ammonia solution and Triton X-100, which allowed prolonged pneumatic aerosol generation without nebuliser blockage. Results for total Pb analysis showed excellent agreement between the AAS and ICP-MS methods. Isotope ratio precisions for 15-min analyses were generally better than 0.5%, with a bias of -0.412% for ^{206}Pb , ^{207}Pb and $+0.055\%$ for ^{208}Pb , compared with those obtained by isotope dilution MS. Janghorbani *et al.* (88/1473) measured stable isotopes of Br in various biological fluids. Samples were prepared according to their matrix, using either simple dilution or cation exchange.

In a pilot study to verify the applicability of stable isotope tracers (^{65}Cu , ^{58}Fe and ^{70}Zn) to *nutritional studies*, Koirtjohann (89/C1717) achieved isotope precisions of 0.5–1%, with good accuracy for Cu and Zn. However, interferences from ArO^+ and ArOH^+ on ^{56}Fe and ^{57}Fe , respectively, prevented accurate isotope ratio determination. Whittaker *et al.* (89/C737) in their study of *iron adsorption* during normal human pregnancy overcame this problem by using ICP-MS with sample introduction by electrothermal vaporisation. This enabled rapid determination of the ^{54}Fe : ^{56}Fe and ^{57}Fe : ^{56}Fe isotope ratios in blood serum with no sample preparation, following simultaneous oral and intravenous administration of enriched iron(II) sulphate to female patients.

1.3.3.4. *Industrial materials*. Despite the number of ICP-MS instruments in industry, relatively few papers have been produced. Beck *et al.* (89/536) reported on the determination of the ratio of ^{235}U to total U in military zirconium and hafnium *alloys*. A more direct route to determining Gd, Sm, Th and U in these alloys following a digestion - separation procedure was provided by ICP-MS than the various time-consuming methods previously employed.

In the analysis of *gold*, Oguaro and co-workers (88/1619) determined Th and U down to several ng ml^{-1} , following digestion in aqua regia. To avoid $^{197}\text{Au}^{35}\text{Cl}^+$ polyatomic interference on monoisotopic $^{232}\text{Th}^+$, Th and U were separated from the gold matrix using an anion-exchange resin.

Inductively coupled plasma MS was used by Suzuki *et al.* (89/1225) as an additional method of discrimination of the source of impurities in 0.1% *m/v* solutions of *methyl amphetamine crystals*. Large variations in Br, Na and Pd concentrations were observed between samples collected from the surface and interior of the same large crystal.

Chemical and ICP-MS procedures developed by Paulsen *et al.* (89/504) enabled the analysis of ultra-pure acids and similar materials to be made for trace elements at concentrations of a few pg g^{-1} . Sample throughput compared with SSMS was dra-

matically improved and methods were reported in which elements were simultaneously quantified either by IDA or external standard calibration.

1.4. Microprobe Techniques

These continue to be popular for both multi-element and isotopic *microanalysis of solids* and the reported applications cover a wide range of sample types. A general review of laser microprobe mass spectrometry (LMMS) and its applications has been given (89/2593). The use of SIMS has been discussed for isotope and elemental ratio measurements (see Newbury, D. E., and Bright, D. S., "Secondary Ion Mass Spectrometry SIMS VI," John Wiley, Chichester, 1988, pp. 389–392), isotope ratio measurement in geo- and cosmochemistry (see Lorin, J. C., and Havette, A., "Secondary Ion Mass Spectrometry SIMS VI," John Wiley, Chichester, 1988, pp. 927–936), ultratrace analysis of surfaces (see Virag, A., Friedbacher, G., and Grasserbauer, M., "Secondary Ion Mass Spectrometry SIMS VI," John Wiley, Chichester, 1988, pp. 561–564) and the trace analysis of refractory metals (89/2572). Vertes *et al.* (89/2718) discussed the role in ionisation of transfer of energy from the incident laser beam to the sample and they presented a hydrodynamic model to define the process. Clear distinction could be made between laser desorption, based mainly on classical absorption at low power densities (1×10^5 to 1×10^7 W cm⁻²), and laser plasma ionisation, ignited by resonant plasma absorption at higher irradiances (1×10^8 to 1×10^{11} W cm⁻²). The latter condition is accompanied by heavy fragmentation of ions and wide energy distributions.

The strength of the microprobe techniques lies in its ability to focus on a chosen and well defined discrete part of the sample and this finds wide application in the isotopic and elemental study of specific grains or crystals in *geochemistry*. Sulphur isotope heterogeneity in the Earth's mantle was investigated by measuring the isotopic composition in sulphide inclusion in diamonds (89/2563), while instrumental mass fractionation effects were discussed for ion microprobe studies of S isotope ratios (see Chausisidon, M., and Demange, J. C., "Secondary Ion Mass Spectrometry SIMS VI," John Wiley, Chichester, 1988, pp. 937–940). The determination of lanthanides in apatite has been discussed (see Reed, S. J. B., "Secondary Ion Mass Spectrometry SIMS VI," John Wiley, Chichester, 1988, pp. 965–968). Selected trace element (Ba, Hf, Nb, Sc, Sr, V, Y, Hf and lanthanides) abundances and Mg, Si and Ti isotopic abundances were measured in calcium and aluminium rich inclusions (89/2610). Considerable detail is given for the methods used in the latter study, especially for the isotopic measurements. A mass resolving power of 13 000 was required for reliable measurement of Ti isotopes, but corrections were still necessary for the interference of ⁴⁶Ca on ⁴⁶Ti and of ⁵⁰V and ⁵⁰Cr on ⁵⁰Ti. Interferences were also a major consideration in a similar study of calcium and aluminium rich inclusions in the Allende meteorite (89/2609). No evidence was found for isotopic anomalies in Fe, Mg, Ru or W but possibly for Mo. Other isotopic studies have been of Mg in olivine minerals in the Allende chondrite (89/2640), of Pb in the U–Pb dating of pitchblende (see Reed, S. J. B., Trueman, N. A., and Long, J. V. P., "Secondary Ion Mass Spectrometry SIMS VI," John Wiley, Chichester, 1988, pp. 945–948) and in studies of zircons (89/2603, 89/2605). The attraction of the microprobe techniques is their ability to perform *in situ* analyses with little, if any, sample preparation but this is offset by the difficulty in quantification and problems of interferences.

Environmental studies include the characterisation of ambient air contaminants from hot-dip galvanising plants (89/1057), the determination of Cu, Fe, Mn, Pb and Zn in samples of Mmytili-

dae (ash mixed with glycerol and applied to a silver substrate) (89/230) and the laser-microprobe determination of Al in the gills of rainbow trout exposed to Al dissolved in their water (89/2717).

1.5. Resonance Ionisation Mass Spectrometry (RIMS)

This technique, which uses resonant laser *photoionisation* for selective ionisation of previously atomised sample material, is receiving much attention. The ability to select the element, or indeed isotope, of interest, combined with high sensitivity, opens up numerous possibilities, especially for ultratrace analysis and the measurement of small isotope ratios. Much of the work reported relates to development of the technique but a range of applications is beginning to appear. As resonance ionisation mass spectrometry (RIMS) defines the ionisation process alone, various types of atomisation and analyser systems have been investigated and several combinations are possible. The ionisation process itself is complex and the data required to set up a resonance ionisation scheme for a given element are now available from a data service (89/C1821) which provides data sheets giving the relevant ionisation information. General reviews of RIMS are not common, as specific aspects of the procedure are usually discussed but the reader is referred to the papers of Hurst and Payne (89/715) and Young *et al.* (89/2634) which give good general overviews. Fundamental information to be obtained about the excited states of neutral molecules has been considered (89/1631). Other more general reports have also appeared (89/C170, 89/2143, 89/2647, 89/2706).

Several types of atomisation are fairly widely used, including thermal atomisation, either in a conventional thermal ionisation mass spectrometry (TIMS) source or in an electrothermal graphite furnace, as well as laser ablation and ion sputtering. Originally the thermal ionisation source was the most common, as modified TIMS instruments were used but currently more attention is being given to the other types of atomisation. Walker and co-workers (89/C1823, 89/2595) measured the isotopic composition of Os and Re in a number of silicate rocks by atomisation of extracted determinands on a miniaturised pulse-heated tantalum filament. The Os and Re were selectively photoionised with a Nd:YAG tunable dye laser with an isobaric selectivity of $>10^3$ at m/z 187 and $<pg$ sensitivities. At these levels of determinand (<1 ng g⁻¹ of rock) a chemical separation was necessary and procedures using distillation and solvent extraction techniques have been described (89/507). A pulsed thermal atomic beam has been used to improve the efficiency of RIMS (89/2596).

Electrothermal atomisation in a graphite furnace has been used for the determination of Ba, Ga and Rh. Bekov and co-workers (89/2574) used a two-step ionisation to determine Ga in a dilute aqueous solution of gallium or in germanium samples which were heated in steps to 1650 °C. Higher temperatures were not used to avoid loss of Ga in the form of clusters. The calibration graph was linear in the concentration range 0.1 ng g⁻¹ to 1 µg g⁻¹ of Ga and detection limits were 5×10^7 atoms cm⁻³ in pure gallium samples and 3×10^{10} atoms cm⁻³ in germanium samples. Reproducibility, however, was only 15% ($n=27$) for 50 pg in 50-µl samples. The same workers have used a similar procedure to determine Rh in environmental water samples (10–100 µl) with a detection limit of 5 pg g⁻¹ in 100-µl samples (89/705). Bushaw and co-workers (88/2062, 89/C1826) have demonstrated isotopic selectivities of $>10^5$ and isotopic abundance sensitivities of $>10^{10}$ for Ba atomised in a graphite furnace, ionised by double-resonance excitation to Rydberg states, and analysed with a quadrupole mass spectrometer. The instrumental detection limit was about 10^{-17} g. Barium has been determined by Yamada *et al.* (89/2714). To cope with the rapid pulse rate produced by

multiphoton excitation, Green *et al.* (89/2631) developed a gated pulse counter with AND logic circuitry for use with their TOF mass spectrometer and microchannel plate detector. Precision for determination of Ba was 0.3–1% RSD.

Laser ablation has been investigated by some workers in an attempt to improve the efficiency of RIMS. In a continuous atomisation source only a small proportion of the specimen (*ca.* 1×10^{-5}) is actually ionised by the ionising laser. Pulsed atomising lasers can improve this proportion by a factor of 10^4 but introduce problems of overheating, which may be overcome through the use of thin films (50 Å) of Ag, C, Mn, Pt and Ta on quartz substrates (89/C1819). Optical damage in selected commercial optics was characterised by laser ablation due to carbon contamination of the Al_2O_3 - SiO_2 multi-layer coating on a silicon substrate or as iron contamination of Sc_2O_3 - SiO_2 multi-layer coated substrates (89/C1836). A scheme was also presented for mixed Al - Fe alloys vaporised by laser desorption. Laser ablation has been used for the analysis of bulk samples of silicon (0.5–58 p.p.m. of Ga) and steel (7–2400 p.p.m. of Al) but the problem of interference from ions generated by the ablation process was encountered (89/C1822).

Laser ablation is seen to have analytical potential but still raises certain problems, such as those associated with the plasma processes close to the sample. An alternative is *sputter-initiated RIMS* which is used especially for the analysis of high-purity solids (89/2699, see also Gobert, O., Dubreuil, B., Gelin, P., Debrun, J. L., and Inglebert, R. L., "Secondary Ion Mass Spectrometry SIMS VI," John Wiley, Chichester, 1988, pp. 845–848). Direct sputtering of silicon containing salts on a high-purity gold substrate yielded nanogram sensitivities for interference-free measurement of Si isotopes in a sodium salt matrix ($\text{Na:Si} > 10^4$) but a double-focusing mass spectrometer was used suggesting a wide energy spread or the need for high resolution (89/C1828). The importance of the matrix effect has been considered for the trace analysis of semiconductor materials (89/C1827) and of uranium containing solids (89/2597) while the analysis of semiconductors and other solids using sputtering has also been described (89/2673, 89/2701, see also Parks, J. E., Spaar, M. T., and Cressman, P. J., "Secondary Ion Mass Spectrometry SIMS VI," John Wiley, Chichester, 1988, pp. 813–816).

It is apparent that no matter how efficient the ionisation step is, the atomisation stage is critical in the achievement of reasonable analytical precision and the issues of matrix effect, spectral interferences and selective sampling at the atomisation stage must be addressed. For solids analysis RIMS will have to follow the same path as other, more established techniques.

The *mechanism of resonance ionisation* of atoms under non-resonant excitation has been investigated (89/2651) and multiphoton ionisation processes have been predicted and identified (89/2686). Combination of a CW laser and a secondary ionising laser has been used to achieve both high-duty cycle and high-ionisation efficiency and has been applied to the determination of Lu for which a simple ionisation scheme is available (89/C1835).

The high selectivity and sensitivity of RIMS is finding particular application in the determination of low-abundance or short-lived isotopes or rare earth elements (89/2621, 89/2632, 89/2633, 89/2635). A report on the potential as a radioanalytical technique has been presented (see Baxter, M. S., Scott, R. D., and Ledingham, K. W. D., "Resonance Ionisation Mass Spectrometry. A Review of its Status and Potential as a Radioanalytical Technique," Report, DOE-RW-87.075, July 1987, 58 pp.) and determination of the actinides (89/2586, 89/2672) and U (89/2597) and the analysis of uranium for trace elements (see Cristy, S. S., "Analyses of Carbon, Silicon and Iron in Uranium by Sputter-initiated Resonance Ionisation Spectrometry and Sec-

ondary Ion Mass Spectrometry," Report Y/DW-734, 23 June 1987, 21 pp., Oak Ridge Y-12 Plant, Oak Ridge, TN, USA) have been discussed. Short-lived gold isotopes (^{195}Au , $T_{1/2} = 183$ d), implanted into graphite, at 60 keV in a mass separator have been determined by pulsed laser-induced desorption, photoionisation and TOF-MS (89/C1831). About 60% of the 1.5 pg were released with 200–300 laser shots at a pulse power density of about 10 MW cm^{-2} . A similar scheme has been used to study the isotope shifts and hyperfine structure of radioactive Au and Pt isotopes but, in contrast to the previous study, only 4% of Au ions implanted at 45 keV were desorbed with a 30 MW cm^{-2} pulse (89/C1820). Large isotope ratios in Bi and the small ^{210}Pb isotope in lead have been measured using a pulsed laser to achieve elemental selectivity and the elimination of isobaric interferences (89/2693).

The possibilities for RIMS in a *broader area of applications* is shown by its use to characterise a Be isotopic solution standard reference material (89/C1829) and investigations into the determination of trace elements and isotopes in medical and biological studies (89/C1825, 89/2668).

1.6. Spark Source Mass Spectrometry (SSMS)

The MS7 spark source mass spectrometer became available commercially in about 1960. This gives a clear indication of the longevity of spark source mass spectrometry (SSMS). There is little doubt that the use of SSMS is on the decline but the technique still provides many users with simultaneous and direct determination of nearly all elements at low detection limits. The advantages of a *panoramic semiquantitative survey* can outweigh the disadvantages of poor precision and SSMS still finds use for bulk and surface analysis of high-purity materials. A comparison of SSMS with other MS techniques for bulk analysis has been presented (89/2645).

Studies are still carried out on *fundamental aspects* of spark ionisation such as ion formation (89/2630), matrix effects (89/2594) and production of heteronuclear clusters (89/2585). Tyurin *et al.* (89/2565) showed that relative sensitivity factors (RSFs) are a function of the chemical form of the determinand but not of the composition of the matrix and they discussed consequent systematic errors.

For *quantitative analyses*, RSFs must be determined for each type of analysis and for each individual procedure. A statistical evaluation of results obtained on an MS7 instrument for analysis of iron- and low-alloy steel reference materials showed that matrix group specific RSFs gave acceptable results and varied only within one order of magnitude for singly-charged ions (89/518). Often, however, reference standards are not available and must be prepared in-house, which is a major exercise. A comprehensive range of standards containing up to 34 elements, each with Y as the internal reference, has been prepared for the analysis of U_3O_8 in a graphite matrix (89/C1941). Accuracy was reported to be better than 20% at the $10 \mu\text{g g}^{-1}$ concentration level.

Spark source MS is still mainly used as a quality check of *high-purity materials*. The technique has been used for the characterisation of high-purity gallium (89/2567), alumina powders and sintered corundum products (89/2620), zircalloy-2 and tellurium (89/2715) and $\alpha\text{-HgI}_2$ crystals (89/1953). For the analysis of highly pure GaAs, effectively an insulator, the need for pelletising, which would introduce high levels of contamination, was removed by depositing a thin layer of 99.999% pure gold on one surface of the GaAs electrodes in a chamber mounted on the ion source (89/2702). No contamination was introduced and C could be detected at the $1\text{--}2 \mu\text{g g}^{-1}$ level. These developments show that SSMS still has much to offer in such applications.

Pattern recognition analysis of about 40 elements determined in indium metal with detection limits of $10\text{--}30 \text{ ng g}^{-1}$ and accu-

racies of 20–40% showed a strong spatial correlation for some elements (88/817). The contribution of individual sources of error were evaluated from the data obtained. Spark source MS has been evaluated for the analysis of refractory metals (89/2571) and used for the analysis of South Indian bronzes (89/2564). Materials with more complex matrices, such as soils (89/C594) and plants (88/1960, 88/2069), have also been analysed.

One surprising area in which to find SSMS used is *isotope dilution mass spectrometry* which one normally associates with high-precision analysis, not the low-precision of SSMS. Several applications have been reported and confirm that SSMS can be used where, possibly, all else fails. This is probably so for highly volatile elements which require special preparation methods. Selenium and Te have been determined in copper standard RMs following acid digestion of the sample, coprecipitation with gold as carrier and reduction to the zero oxidation state (88/1961). However, the levels of Se and Te were relatively high at 0.58–479 $\mu\text{g g}^{-1}$ and 0.295–196 $\mu\text{g g}^{-1}$, respectively. Mercury has been determined in biological samples using a quartz combustion tube and a liquid nitrogen trap (88/2069). The combustion tube was modified to include a side-arm to supply a secondary source of oxygen for samples which were difficult to combust. Electrodes were prepared from high-purity silver and Mg was determined at the 0.1 $\mu\text{g g}^{-1}$ concentration level with a precision of about 4%. Isotope dilution SSMS has also been reported for the multi-element determination of Nb, Th, U, Y and Zr (89/2642), for the determination of sub-ng amounts of trace elements (89/2643) and the quantitative analysis of plant samples (88/1960).

1.7. Stable Isotope Ratio Mass Spectrometry (SIRMS)

This section refers to the determination of *isotopic abundances* of C, H, N, O and S in the gaseous form (CO_2 , H_2 , N_2 , O_2 and SO_2) using electron impact ionisation. Applications can be divided into two main areas: (i) the use of enriched stable isotope tracers in mainly agricultural, environmental and nutritional studies and; (ii) the measurement of natural variations in isotopic abundances in geological, environmental and related studies. In the second type of study, very small changes in isotopic composition are significant and the demands for rigorous sample preparation and precise instrumental techniques are greater than in tracer studies in which large isotopic enrichment factors are often employed. It has not been possible to give a comprehensive coverage to this section and consideration will not be given to H and O studies, in particular.

Stable isotope ratio mass spectrometry (SIRMS) is probably the most widely used of all the mass spectrometric techniques discussed in this Update and yet it is so firmly established as a routine procedure that it seldom receives a reference, especially in biological and clinical studies. For these areas of study there is a marked trend towards *direct coupling* of an elemental analyser to the mass spectrometer, as introduced for the determination of N by the VG ANASIRA and continued in their ISOMASS instrument and also adopted by Europa Scientific in the TRACERMAS (89/2723). The automated, directly coupled instruments offer simple sample preparation and high sample throughput. A typical precision of <0.1% RSD for the determination of N at the natural abundance is sufficient for biological tracer applications. The MAT 251 has also been coupled to a Carlo Erba Elemental Analyser for the determination of C isotope ratios in lake sediments (see Pichlmayer, F., "On-line Coupling of the MAT 251 with a Carlo Erba Elemental Analyser for Carbon Isotope Ratio Measurements," Techn. Rept. OEFZS-4366, 1986, 19 pp., Inst. Landwirtsch., Oesterr. Forschungszent. Seibersdorf GmbH, A-2444 Seibersdorf, Austria) and for the iso-

topic abundance analysis of C, N and S (89/2655). Instrument modifications reported are the use of a trapping box for N and C isotope ratio determination (89/2687) and modification of the mass spectrometer source electronics to allow high precision determination of N stable isotope ratios at the sub-nanomole level (89/2690).

Sample preparation continues to receive attention. A rapid method for the preparation of combustion samples for the determination of stable C has been reported (89/2705) and new and conventional evaporation systems were compared for the concentration of N from soil samples (89/2710). Sulphide and sulphate minerals have been converted directly into SO_2 for the determination of S isotopes by reduction of SO_3 with copper in the analysis of small samples, including single grains (89/2624). Existing methods for the extraction of particular forms of S in rocks and sediments have been evaluated and used to devise a chemical scheme to recover S as either Ag_2S or BaSO_4 precipitates for isotopic analysis (88/1935). The species distinguished include "acid soluble" sulphides and sulphates, elemental S, pyrite, barite and various categories of organically bound S. The prospect of isotopic speciation studies is opened up and is an interesting development.

Only an indication of the *applications* of SIRMS can be presented. The C isotopic composition has been studied in different carbonaceous components in enstatite chondrites (89/2601) and in two splits of the Allende meteorite reference sample (89/2697). Carbon isotope ratios in atmospheric and soil CO_2 and traces of gaseous hydrocarbons absorbed in sedimentary rocks can give information for environmental studies and exploration geochemistry (89/C615). The hydrocarbons were desorbed from drill cores and the components separated by gas chromatography before combustion to CO_2 for analysis. The ^{13}C distribution in the sequence of hydrocarbons gives information on their generation and migration pathways. Nitrogen isotope contents have been used as an indicator of the origin of nitrate (89/2579) and the formation of polymict ureilites (89/2581), while fractionation has been identified in synthetic diamonds (89/2589). Study of the N isotope ecology in southern Africa has implications for environmental and dietary tracing (89/2580).

1.8. Thermal Ionisation Mass Spectrometry (TIMS)

One of the first of the mass spectrometric techniques, TIMS, is well established as the technique of choice for measuring *precise isotopic ratios* in geochemical, environmental and nuclear materials. The role of this technique in establishing the relative atomic masses of the elements is paramount and a new list has been published recently (89/2720). De Laeter and Hosie (89/2625) have studied the isotopic composition of Sb. Unsurpassed precision combined with isotope dilution analysis has given TIMS the status of a definitive method for elemental determination, especially for certifying RMs. Examples include the determination of B in a rye grass CRM (BCR 281) (88/C2021, 89/2713), Se in human blood RMs (88/C2002), Pb in rock standard materials (89/2591), Pb and Tl (89/2641) and the lanthanides (89/2698) in Allende meteorite reference sample, heavy metals in sedimentary RMs (89/2712) and Sr in GSJ rock reference sample (89/2704). The expense of purchasing and maintaining a TIMS instrument, however, has always been a major drawback to the general availability of the method and it is noticeable that the two major manufacturers are offering cheaper instruments with somewhat poorer performance for applications in the areas of tracer studies and isotope dilution analysis. The MAT ThermoQuad employs a quadrupole analyser whereas the VG 336 retains the conventional magnetic analyser. It remains to be seen how these developments are accepted in the market place and whether competition from ICP-MS proves too strong for the pro-

posed applications. Use of the quadrupole instrument has already been reported for isotopic analysis of Fe (89/2626), I, Nd and Sr (89/2656), Mo, Ti, V and Zr in water samples (89/2661) and Cr (89/2663).

The fundamental features of the TIMS technique have remained unchanged and there have been few advances or innovations in the *instrumentation* reported other than by the manufacturers. A new filter supplement for a quadrupole instrument (89/2660) and sensitivity calibration of multi-collector instruments have been described.

Most effort in TIMS is being put into developing new or refined procedures for the determination of individual elements by *isotope dilution*. An assessment of the errors in the technique led to suggestions for its optimisation (89/2708). Purity of chemicals is of critical importance in isotope dilution analysis and analytical reagents have been purified by sub-boiling distillation (89/2722). Attention is being given to the determination of B, either as the Cs_2BO_2^+ ion (89/2636, 89/2675) or as the BO_2^- ion (88/C2021, 89/2713), the latter method giving an accuracy of $\pm 10\%$ at the $5 \mu\text{g g}^{-1}$ level. Lithium has been measured both as lithium tetraborate (89/2576) and as dilithium fluoride ions (88/1462). Low-temperature (900 °C) ionisation of Cu gave smaller time variations and errors than high-temperature ionisation but an extremely high loading of $50 \mu\text{g}$ of Cu per filament was used which could limit its applicability for realistic Cu loadings (89/2694). Negative thermal ionisation has been used in speciation studies of Se in water samples (89/2650, 89/2716). Use of a mixed spike has allowed simultaneous determination of the ^{235}U : ^{238}U isotope ratio and of the U concentration at ng levels (89/2674). Neodymium and Sm have been determined simultaneously using a fixed multi-collector mass spectrometer (89/2653).

Isotope dilution has found particular importance in the analysis of *environmental samples*. Waters have been analysed for Se (89/2650, 89/2716) and for Mo, Ti, V and Zr (89/2661) while ion chromatography and negative ionisation was used to determine nitrate in fruit juices (88/2165) and Antarctic snow samples (89/2646). Some 12 elements in oyster tissue were measured using a multi-element scheme (89/2662) while B, Br, Cl and I were determined simultaneously in water samples (89/2566). Chromium has been determined in a range of samples (89/2663). The interest in heavy metal pollution is reflected by the determination of eight metals at the pg g^{-1} level in Antarctic snow by DPASV and isotope dilution MS (89/2648) and of Pb in contaminants in Monterey Bay (89/2592), in airborne particulate matter from the Atlantic Ocean (89/2684) and in cases of childhood lead poisoning (89/2707). One area of environmental work seeing increased interest and for which TIMS is ideally suited is the detection of radionuclides or heavy metals associated with nuclear materials which follows on from the extensive use of TIMS in the nuclear industry. Atmospheric I, including the long-lived radioisotope ^{129}I , can be measured by negative ionisation (89/2658, 89/2721). The distribution and determination of U and the transuranic elements in the environment (89/2665, see also Chastagner, P., "Determination of the Distribution of Uranium and the Transuranic Elements in the Environment by Thermal Ionisation Mass Spectrometry," Rept. DP-MS-86-204, 1987, 6 pp., Savannah River Lab., Aiken, SC 29808, USA) and the geochemistry of fallout Pu in the North Atlantic (89/2577, 89/2578) have been discussed while Pu has been determined in marine samples (89/2587).

Two areas of study for which high-precision analysis remains essential are in the nuclear industry and in isotope geology. The first tends, by its very nature, to be secretive but *nuclear analytical* applications have been discussed (89/2654). Details have been reported for the simultaneous determination of Eu, Gd and

Sm in U_2O_3 (89/2711), trace U in residual solutions from the electroplating of U targets (89/2666), of trace levels U and Pu [see Romkowski, M., Franzini, S., and Koch, L., *Euro Abstr. Sect. 1*, 1988, **26**(1), 5, Eur. Inst. Transuranium Elem., Comm. Eur. Communities, D-5700 Karlsruhe, FRG] and of the analysis of spent fuel solutions by resin bead MS (see Hayashi, N., Terekado, S., and Kuno, Y., "JASPAS Programme Task JC-4: Isotopic and Isotope Dilution Analysis of Spent Fuel Solutions by Resin Bead Mass Spectrometry. Results of the Sixth Inter-laboratory Experiment," Rept. IAEA-AL-003, May 1988, 33 pp., Power React. and Nucl. Fuel Dev. Corp., Tokai 319-11, Japan). Spent nuclear fuels have been characterised by the determination of nanogram amounts of the stable fission product Ru (89/2560, 89/2683) by use of Zr and Ru isotope correlations (89/2637) and by use of Nd isotopes (89/2628).

Isotope geology continues to be the main area of application for TIMS and a considerable number of studies are reported each year, especially for the established methods using U - Pb, Sm - Nd and Rb - Sr isotope relationships. A review of the development and present status of the Rb - Sr dating method has been presented (89/2688). In most studies, however, TIMS is relegated to the status of a routine analytical procedure and few analytical details are given. A list of references indicating the isotopic analysis made is given in Table 2. As an indication of the high sensitivity of the techniques developed, Pb isotope ratios have been determined in a single zircon by evaporation combined with Pb^+ emitter bedding (89/2703). Such analyses demand the ultimate in terms of contamination-free conditions and precise instrumental procedures. Reports of the isotopic analysis of other elements are limited. The Li isotopic abundance ratio has been studied in a few minerals of pegmatite (89/2695) and Mn - Cr isotope systematics have been used to discuss the development of the early solar system (89/2588). Interest in Ti isotope anomalies continues but analysis of chondrules from carbonaceous chondrites showed possible isotope anomalies for only ^{50}Ti even though one terrestrial standard was run per sample to maintain close control of the analysis (89/2613). No correlation was observed between Al, Ca and Ti contents and the Ti anomalies.

Thermal ionisation mass spectrometry generally requires *sample preparation* procedures to produce the determinand in a form pure enough for analysis and the established procedures of

Table 2. Reported applications of TIMS in isotope geology

Element	Reference			
Nd	89/2590	89/2606	89/2607	89/2608
	89/2611	89/2612	89/2614	89/2615
	89/2616	89/2622	89/2638	89/2678
	89/2679	89/2682		
Pb	89/2562	89/2598	89/2604	89/2606
	89/2607	89/2611	89/2612	89/2617
	89/2638	89/2639	89/2676	89/2677
	89/2681	89/2682	89/2709	
Sr	89/2557	89/2558	89/2599	89/2600
	89/2606	89/2607	89/2608	89/2611
	89/2612	89/2614	89/2615	89/2616
	89/2622	89/2623	89/2629	89/2638
	89/2677	89/2679	89/2680	89/2682
	89/2696			

ion-exchange chromatography or electrodeposition are still widely used. Attempts to improve the techniques continue and a nitrate precipitate procedure for the preparation of Sr has been devised (89/2618).

The newest area of application is that of *stable isotope tracers* and this would appear to be on the verge of a marked expansion with both manufacturers aiming their cheaper instruments at this market. Strong competition from ICP-MS is expected, except in those studies where high precision is required or large ratios are to be measured. The use of Cu in animal metabolism studies and K in plant nutrition studies (89/C594) and of Fe in human nutrition studies (89/2626) have been reported. The ability to measure small changes in ratio can lead to a considerable reduction in the cost of experiments, as for K, for example, for which the use of enriched ^{39}K reduces considerably the cost of using enriched ^{41}K . Potassium is such a readily-ionised element that its analysis requires no sample preparation and no addition of ionising aids, making the analysis of plant digests very simple and easy to maintain free from contamination. The natural variation in isotopic composition can also be used to trace elements in natural systems. Neodymium isotopes have been used as tracers in marine sediments and aerosols in the North Atlantic (89/2602) and Pb isotopes to trace air mass trajectories in the Mediterranean region (89/2562). In the latter study, aerosols were collected on 47-mm cellulose filters which were digested with acid and the Pb extracted with dithione before isotopic analysis. The preliminary data suggest that the Pb isotope ratios could be used to identify the origin of airborne Pb even from a variety of emission sources in a complicated atmospheric system.

The one area in which welcome moves are being made is the production of *isotopic calibration standards*. A detailed study has been made of Pb isotope ratios in existing NIST SRM 981 and SRM 982 standards (89/2555). Using multiple collection, analysis of 15-ng samples gave external precision at the 2σ levels of $\pm 0.015\%$ for the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio and $\pm 0.08\%$ for the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio. The GSJ rock reference standards have been characterised for their $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (89/2704) and an enriched ^6Li isotopic reference material has been produced (89/2627). A CBNM isotopic reference material set (CBNM IRM 072/1-15) has been produced to test the linearity of instruments (89/2657) and the preparation and use of synthetic isotope mixtures has been discussed (89/2559).

1.9. Other Methods

Fourier transform mass spectrometry (FTMS) or ion storage MS as reviewed by Allison and Stepnowski (89/2575) would appear to have some potential for inorganic analysis but the first moves are only just being made to investigate the technique for relatively pure matrices. A system has been developed for multi-element analysis which combines a graphite furnace for atomisation of microlitre samples, electron bombardment for ionisation and a rotationally symmetric quadrupole mass spectrometer to store the ions (88/C1587). The applied r.f. voltage confines the ions spatially and temporally before selective detection by sweeping the voltage. To date the system has only been used for background

gases and volatile organic compounds. The use of a laser microprobe - FTMS combination has been investigated for the elemental analysis of surfaces 89/2652, see also Brenna, J. T., "Secondary Ion Mass Spectrometry SIMS VI," John Wiley, Chichester, 1988, pp. 327-330) and it remains to be seen whether a suitable source can be found for inorganic FTMS and whether the analysis of complex mixtures of ions is feasible.

The *graphite electrothermal atomiser* has been used as a source of ions for RIMS (88/2062) and ion trapping MS (88/C1587) but MS has been used more frequently to study the reactions taking place in a graphite furnace. The atomisation of Co in a pyrolytic graphite coated graphite furnace operating *in vacuo* was investigated by rapid scanning of a quadrupole mass spectrometer (89/722). The shift in the appearance of gaseous Pb to higher temperatures with oxygen in the gas phase or on an oxygenated graphite surface has been found not to be entirely due to oxygen in the gas phase but probably to the $\text{CO}_2:\text{CO}$ ratio, which increases to produce a less reducing environment (88/1742). Molecular-beam sampling has been used to study the mechanisms of Pd stabilisation (89/C803) and of the decomposition and atomisation of arsenic hydride in a conventional hydride generator (89/C1315). Reactions at high temperatures at the metal - graphite surface have been studied using temperature-programmed static SIMS (89/C1366).

Laser ionisation MS has never been widely adopted as it offers little advantage over SSMS, except possibly in the analysis of insulators. The technique was included with LMMS in a survey of methods for the analysis of solid surface (89/1090). A JEOL SSMS instrument has been modified by fitting a Nd:YAG laser and additional pumping to the source to allow the laser ionisation of insulator samples in addition to conventional spark operation (89/2619). The instrument was operated in the same way as for spark operation with photoplate detection and a range of materials from metals to insulators and several glasses were analysed. Ions produced by the laser had a lower energy spread than those produced by a spark, which resulted in narrower line widths and improved mass resolution. However, the laser power was insufficient and the spark method was still preferred for the analysis of metals. The analysis of geological samples on an SSMS instrument with a laser source has also been reported (89/2561, 89/2664). The only fundamental studies of laser ionisation have been of ion formation (89/2630), the production of heteronuclear clusters (89/2585) and the discovery of anomalous fractionation of heavy metal isotopes (89/2719).

The interest in the use of stable isotope tracers in *nutrition studies* is emphasised by continued investigations of fast atom bombardment (FAB) MS for the measurement of Zn (89/2582) and Ca (89/2583) isotope ratios and of gas chromatography (GC) - MS for the determination of Co, Cu, Fe and Zn (89/2649). The use of GC - MS has previously been found to suffer from serious problems in reproducibility, especially in the formation of chelates and other volatile compounds and it is unlikely that this approach will find wide acceptance. The use of the soft ionisation techniques of FAB and field desorption have been discussed for the isotopic analysis of organic compounds and for Fe isotope analysis (89/2691).

2. X-RAY FLUORESCENCE SPECTROMETRY

2.1. Reviews

The last two decades of X-ray spectrometry have been reviewed from a personal and historical viewpoint by Jenkins (89/306) who has been particularly influential in promoting the virtues of X-ray techniques throughout that period. The same author has

also reviewed the present status and future trends in XRF instrumentation (89/902). Adams has delivered a comprehensive review of elemental analysis using X-ray techniques (89/C164) which included specific sections on synchrotron radiation (SR) excitation and total reflection XRF (TXRF). Pella (88/C1572)

has reviewed the prospects for "standardless" analysis and the use of pre-concentration procedures in the application of EDXRF spectrometry to environmental analysis.

The *historical development* of EDXRF spectrometry has been presented by Kunz (89/1756). The author indicates current instrumentation characteristics of typical EDXRF analysis systems and includes an example of the way in which their instrument has been networked in a large analytical laboratory. In addition, the application of EDXRF to the analysis of research materials in the automotive industry, where very few standards are available, is discussed using such diverse examples as GaAs semiconductors, complex Al - Cu alloys and the determination of paint thickness.

A comprehensive review of the determination of noble metals by XRF spectrometry has been published (88/2342) and recent progress, emphasising instrumentation developments, has been given by Xie *et al.* (89/1576). Of the more general instrumental analysis reviews, many have included sections on XRF covering instrumentation (89/288) and application areas such as trace element analysis (88/1874, 89/252, 89/1597) and REE in geological samples (88/1475).

The Atomic Spectrometry Updates on the topics of Instrumentation (88/2091) and Minerals and Refractories (88/945, 89/1675) were published during this review period and contain sections on XRF spectrometry. The first Update on Mass Spectrometry and XRF Spectrometry (89/1659) also appeared.

2.2. Instrumentation

The principal area of new instrumentation being investigated is that of *X-ray microfluorescence (XRMF)* whose main attraction lies in its ability to determine elements deep in the specimen ($>20\text{ }\mu\text{m}$). In addition, there is no need to evacuate a specimen chamber or to render the specimen conductive as is the case in electron microscopy. The non-destructive nature of XRMF should prove interesting to those working in biology as soon as spatial resolution can be improved. Of the work reported in this review period, XRMF systems based around both low-power (50 W) (88/2393) and higher power (1 kW) (88/2392) have been claimed to image features as small as $15\text{ }\mu\text{m}$.

An *X-ray microprobe* using an SR source has been designed (89/1030) in which focusing was achieved using two concave layered synthetic microstructures (LSMs) in Kirkpatrick Baes geometry. The resulting instrument had a beam spot size of $10 \times 10\text{ }\mu\text{m}$ and was used for the analysis of biological and geological specimens. Specimens were scanned using an $x - y$ translational stage and keeping the beam in fixed position allowing two-dimensional element images to be built up rapidly using multi-element detection with a Si(Li) detector. System performance is impressive, with absolute sensitivities for elements with atomic number (Z) 19–30 in the fg range when using 60-s acquisition times. The system has been used for the analysis of fluid inclusions in minerals (89/1525).

The advantages of SR in XRMF have been clearly demonstrated (89/1031, 89/1559) in obtaining spatial resolution down to $3\text{ }\mu\text{m}$. The high forward power of the SR source allowed extremely narrow slits to be used, and, when combined with a closely coupled Si(Li) detector, yielded very high sensitivity. The intrinsic polarisation of the SR beam allowed improvements in both limits of detection and precision to be achieved due to reduced spectral background. The image data were transformed by a filtered back-projection technique which allowed spatial resolution smaller than the beam spot size to be attained.

A system in which *polarisation* in Johanssen geometry was used and which exhibited high spatial resolution has been described (89/926). In the absence of X-ray tubes which have very high power and are strongly focused, the use of SR seems man-

datory for obtaining the required sensitivity. Once SR is used, the necessity for any additional polarising element disappears.

The penetrating nature of X-rays has been used to advantage (89/C1310) for imaging of macro-specimens, such as drill cores, using the technique of *computed tomography*. Although only used as an imaging device based upon differential X-ray absorption, there exist various possibilities for obtaining additional analytical information.

One area of instrument development which EDXRF instrument manufacturers are exploiting is that of *on-line analysis* (89/C1312). The compact nature of EDXRF equipment, the penetrating power of X-rays and the ability to monitor non-invasively liquid and powder process streams are characteristics which can be usefully exploited. The greatest success is often to be obtained in the analysis of liquid streams but problems of calibration and in maintaining precision are areas of concern identified by Weakliem and Kalnicky (89/993).

An automatic 50-position *sample changer* for EDXRF analysis has been described (89/1639). The system was applied to hair analysis and used a Si(Li) detector in conjunction with an annular radioisotope source. Positional accuracy was poor and although no analytical data were quoted, there is no apparent advantage of the system over those available more than ten years ago.

Morton and Lott (88/2312) reported the modification of a *diffractometer* for the analysis of copper- and silver-based alloys. The tube radiation was dispersed by a flat crystal and then passed through two slits set so that the energy of each beam path lay on opposite sides of an absorption edge of a determinand. The two monochromatic beams were used for both transmission and fluorescence measurements. Only a single detector was required as the two slits were opened sequentially to obtain a different excitation spectrum.

A prototype XRF system has been developed (89/299) for the *measurement of blood flow*. The incident X-ray beam was polarised and the geometry of the Si(Li) detector set in such a way that the background and Compton scatter were reduced. A CaF_2 scintillation detector was operated in the anti-coincidence mode which resulted in a 10% decrease in spectral background. The element tracers used were Ag, Gd, I, La, Mo and Rb and 1 ml of a $0.2\text{--}20\text{ }\mu\text{g ml}^{-1}$ solution of these elements was required. When using $20\text{ }\mu\text{g ml}^{-1}$ solutions, count times of 10 min were necessary to obtain adequate measurement precision.

2.2.1. Excitation

Improvements in excitation in systems using both radioisotope sources and X-ray tubes continue to be reported, but the main areas of interest during this review period are related to developments in systems using SR or TXRF. The combination of SR and TXRF in a single instrument has been achieved and extremely low limits of detection are claimed.

2.2.1.1. Radioisotopes. The benefits of compact radioisotope-excited EDXRF systems for applications such as geological fieldwork, in-plant and on-stream monitoring and non-destructive analysis of large art objects have been described (89/C612). The use of a ^{71}Ge radioisotope source for EDXRF determination of low- and mid- Z elements has been suggested (88/2369). Although the authors claim simplicity of preparation of this source as an advantage, the obvious requirement for a reactor and the extremely short half-life (11.3 d) of this source would seem to make its widespread use unlikely. The practical difficulties encountered in the use of a $^3\text{H} - \text{Ti}$ source for the determination of Mg in Al alloys have been described by Szaloki (89/925). In order to reduce leakage from the source, it was covered with either epoxy resin or chromium, both of which resulted in a significant reduction in excitation flux.

The various options for *geometric arrangements* of an isotope source and a non-dispersive, proportional - scintillation type detector have been investigated by Monte Carlo techniques (88/2375). The geometry in which the source is recessed into the front surface of the detector and which allows the closest coupling and largest solid angle to be attained was found to be the optimum arrangement. This arrangement yielded a four-fold sensitivity improvement over both the "conventional" side source and the circular source geometries.

2.2.1.2. *X-ray tubes*. Broll (88/2346) has carried out a theoretical and experimental comparison of *monochromatic excitation methods* used in tube-excited EDXRF spectrometry. The methods of regenerative monochromatic filter, secondary target and crystal monochromator were compared. Results for all three methods were similar, but it was noted that the regenerative filter was the most simple and flexible method in practical use. The use of secondary target excitation was preferred to the use of detector-side filtration in an investigation of techniques for background reduction in EDXRF spectrometry (89/332).

A new end-window, *dual anode X-ray tube* has been described (88/C1557, 88/C1558). The two targets are semi-circular and are each arranged with an individual filament. A Rh - W target prototype was evaluated and showed sensitivity advantages for elements with atomic number 20–40 but anode cross-talk was evident. These workers commented that cross-talk cannot be eliminated in this design but described ways in which the effects of this spectral cross-contamination could be minimised.

2.2.1.3. *Total reflection X-ray fluorescence*. The interest in the development and application of TXRF continues to grow as more research groups acquire or build equipment. A noticeable trend is the increasing diversity of application areas being addressed by this powerful technique. The use of conventional double-reflection optics for the analysis of microtomed sections of biomaterials (89/961), onions (88/2309) and incinerator ash (88/2352) has been reported. The specimen preparation techniques used in the analysis of a variety of solid specimens such as alloy smears, environmental, geological and biological samples have been described in detail by Von Bohlen *et al.* (89/325). Results obtained from the TXRF analysis of acid digests of soils and biological materials agreed well with certified standard values and the resulting TXRF method was claimed (88/2361) to offer up to a 50% improvement in efficiency over AAS methods. General introductions to the analytical capability of TXRF have been provided by Leyden (88/C1574) and Haswell (89/C1307).

Schwenke (89/C1306) has introduced the use of TXRF for *surface analysis* where the first few nm of a surface, such as that of a silicon wafer, are probed. The technique was found to yield limits of detection down to 10^{11} atoms cm^{-2} for impurities on metallic surfaces.

The appearance of papers from *Japan* from a number of workers in the field of TXRF is evident during this review period. The determination of catalyst traces and pigment in polymers (89/1016) and trace elements in TiO_2 pigments (89/1015) have been reported, although the justification for the use of TXRF over conventional XRF instrumentation is not clear. In general, the Japanese instrumentation uses a single reflection from the analytical surface, compared with the European equipment which uses a primary beam reflector to reduce the high-energy Bremsstrahlung background emanating from the reflection at the analytical surface. Limits of detection in the single reflection mode are reported (89/C1640) to be in the region of 10^{-10} g, whereas double reflection generally yields limits of detection of 10^{-12} g.

Interest in the application of TXRF methods to the analysis of *biomedical materials* has increased during the review period and these applications are discussed in the Biological materials sec-

tion (2.4.6). Of particular interest is the combination of the powerful techniques of both SR excitation and TXRF which has been applied to the analysis of human serum samples (88/1994).

The need for clear statement of the counting times employed and the equation used for *calculating limits of detection* in TXRF papers would, as in conventional XRF, be of immense use. This would reduce the uncertainty for workers new to the field intending to compare limits of detection quoted from different instrumentation or specimen preparation and presentation techniques.

2.2.1.4. *Synchrotron radiation*. The principles of SR-XRF have been described by Chevallier *et al.* (89/979) who indicated the clear benefits of the technique for analysis at levels <10 p.p.b. in a variety of materials. A review of specimen preparation techniques for SR-XRF has been presented by Khvostova and co-workers (88/2336).

A study by Jaklevic and co-workers (88/1639) into the optimisation of tunable monochromatic SR for XRF analysis demonstrated the importance of *resonant Raman X-ray scattering* in establishing limits of detection in certain types of trace analysis. The high degree of polarisation and the monochromatic nature of the SR beam should result in the minimisation of scattered background radiation and should therefore yield extremely high peak to background ratios. However, in instances where trace element peaks lie immediately on the low energy side of a major peak, the use of a highly monochromatic SR beam immediately below the absorption edge of the major (matrix) element will yield high sensitivity for the trace element, but the background under the trace peak is significantly increased due to resonant Raman X-ray scattering. As an example of the effect, the authors quote a 10-fold deterioration of the limit of detection for trace amounts of Cu in GaAs.

The possibility of using narrow collimation and the high forward power of the SR beam for *X-ray imaging* is an area of increasing interest with strong prospects which have been reviewed by Rivers *et al.* (89/C1103). An X-ray microprobe using a focused SR beam has been described in detail (89/1030) and its application to the analysis of fluid inclusions in natural minerals has been published in full (89/1525). A second system (89/1031, 89/1559) has been reported to achieve a spatial resolution of 3 μm and was used for the analysis of material from space. The application of SR-XRF to the analysis of extraterrestrial materials such as meteorites has been described by Sutton *et al.* (88/2379) who included a description of techniques for optimising sensitivity.

Although there are only a few synchrotron installations throughout the World, there is considerable interest in the improved limits of detection which can be obtained as a result of the high tunability and intrinsic polarisation of the incident SR beam. The use of the Soviet VEPP-4 storage ring for SR-XRF work has been described in a series of accessible papers (88/2334, 88/2335, 88/2337, 88/2338). The instrumentation for SR-XRF is unlikely to become generally available for the foreseeable future but is currently being used in applications such as biomedical and environmental where the detection power of SR-XRF is particularly valuable.

2.2.2. Dispersing devices

Some 5 years after the introduction of *layered synthetic microstructures* (LSM) to replace the Langmuir - Blodgett films for determination of the elements with Z from 5 to 12, development work continues and improved devices are now commercially available. Nicolosi and colleagues (89/991) have reported quantitative determination of elements in the Z range 5–12, using LSM devices and indicate the problems confronting the analyst who would attempt analysis of B by XRF. Limits of detection for B

were reported to be 0.3% in borosilicate glass and 0.14% in borophosphosilicate passivation layers on silicon wafer substrates. Larger interplanar spacings have been produced which can yield such data for B, but the susceptibility to electronic noise and high detector window absorption contribute major limitations. Perhaps the greatest limitation is in specimen preparation where very clean, highly polished surfaces are necessary and this may explain the obvious preference for analysis of glasses. The problems confronting the analyst searching for methods for determining B and C are also discussed by Anzelmo and Boyer (89/992). The low reflectivity of LSM devices prompts the authors to recommend wider collimation than normal with which they obtained a limit of detection of $300 \mu\text{g g}^{-1}$ of C using a 100-s counting time.

Sperling (89/1767) has described a simple method for the accurate calibration of goniometer angles which compensates for the slight differences between tabulated and actual crystal d-spacings. A relationship between $\delta 2\theta$ and $\tan \theta$ is determined for each crystal which then allows compensation for crystal d-spacing differences and for goniometer dial offset in older, manual systems.

2.2.3. Detectors

The search for improved energy resolution in EDXRF systems continues and Sadoulet (89/1638) has presented a review of possibilities for the next generation of devices which might be used. The author's principal area of interest was in the detection of particles and photons in the 100 eV to 100 keV energy range and a variety of devices were presented as being useful. Resolutions (full width at half maximum, FWHM, at 5.9 keV) of 50.5 eV for an Sn tunnel junction detector and of 17.4 eV for a Si calorimeter indicate the large improvements over the 120-eV resolution of the state of the art Si(Li) detector conventionally used in EDXRF work. These very low noise devices are particularly small and generally need cooling to liquid argon temperatures, as opposed to Si(Li) detectors which may be over 100 mm^2 in area and which require liquid nitrogen or electrothermal cooling. However, the emergence of the Si(Li) and Ge detector technologies more than 25 years ago was from a very similar background and it is wise to remember the efforts of physics research in bringing new detectors to the service of analytical science.

Although interest in mercuric iodide detectors for inclusion in EDXRF spectrometers has not been revived, their use in a detector array has been described (89/1588). The aim of this development was to produce high-resolution HgI_2 detector sub-modules consisting of several detector elements. A detector element module consisting of five $7.3 \times 0.7 \text{ mm}$ individual crystals was successfully produced and was demonstrated to yield 335-eV FWHM resolution at 5.9 keV. Pulsed optical feedback charge restoration of the field effect transistor was achieved by guiding the light pulse along a fibre optic to minimise electronic cross-talk between adjacent detector elements. The incorporation of 100–400 individual detector elements into a large detector array is expected to allow high spatial resolution and energy resolution sufficient for the study of anomalous scattering effects in SR X-ray spectroscopy.

The extension of EDXRF spectrometry into the lower energy range through the use of high transmission detector windows has not yet been reported fully in the literature although the importance of excitation in light element analysis has been recognised (89/C174). The formation of an ice layer on the front surface of the Si(Li) detector was reported (88/2387, 88/2388) to constitute a significant limitation to the energy dispersive measurement of low energy X-rays. This effect has been confirmed by Bombelka and Richter (Bombelka, E., and Richter, F.W., *X-ray Spectrom.*, 1988, 17, 23) who estimated the rate of ice growth to be 0.004

μm per month resulting in a 0.15- μm ice layer after 3 years. Such an ice layer depressed the Na and Al signals by 17 and 11%, respectively, and may easily remove any advantage gained from the use of high transmission windows unless ice growth is properly controlled or methods for *in situ* ice removal are developed. The authors recommended a detector regeneration by bake-out when 10% loss of detector efficiency was experienced.

2.3. Calibration and Data Processing

Despite the continuing growth in application of fundamental parameter (FP) and fundamental coefficient (FC) correction procedures, XRF spectrometry remains largely a comparative technique which requires accurate calibration standards. Dzubyay *et al.* (89/1612) have reported the preparation of thin polymer film standards, containing up to 18 elements of environmental importance, whose long-term storage stability was reported to be good. Heinrich (89/C80) has described the problems encountered in certifying NIST SRMs for homogeneity, particularly when they are to be used for microanalysis.

Before any calibration model can be used to relate analyte line intensity to concentration it is essential that due care be exercised in the extraction of intensities from spectra. The correction of the severe line overlap of Pb $L\alpha$ and As $K\alpha$ has been addressed (89/203) in the determination of As in the presence of Pb in a ZnS matrix. The loss of sensitivity precluded the use of the non-overlapped As $K\beta$ line for quantitation but a simple overlap correction was found to be successful for measurement using the As $K\alpha$ line. These workers recommended that the chemical state of the Pb standard be identical to that in the unknowns. Overlap factor calculations have also been applied to the complex spectra obtained in the analysis of REE mixtures (89/C1653). A computer program for spectrum processing and, in particular, the correction of pile-up effects in energy dispersive X-ray spectra has been developed (89/1487). A method for the calculation of limit of detection from X-ray spectra has been proposed by Yap and Anicin (89/1466).

The problems of background estimation and peak smoothing in automatic peak identification in wavelength dispersive XRF (WDXRF) spectrometry have been considered by Jordanov *et al.* (88/2378) who designed a computer program which accounted for several of the problems encountered.

A calibration procedure which uses only a single mono-element standard for the multi-element analysis of thin film specimens produced from industrial waste water by pre-concentration methods has been described by Coetzee (88/2362). An FP calculation was used to produce a calibration relationship of relative sensitivity versus atomic number (Z) and the actual sensitivity from the single calibration point was then used to convert the relative sensitivities with absolute values which could then be used for the analysis of unknowns. The method yields data which show excellent agreement with AAS data, but another method (Wegscheider, W., Ellis, A. T., Goldbach, K., Leyden, D. E., and Mahan, K. I., *Anal. Chim. Acta*, 1986, 188, 59) in which $\log(\text{sensitivity})$ versus $\log(\text{energy})$ plots are constructed could be used and would obviate the need for complex FP calculations.

Potts *et al.* (89/326) have made a comparison of linear least-squares regression and Theil's incomplete method for the generation of calibration coefficients for use in the determination of trace elements in silicate rocks. The conventional least-squares method was able to yield reliable calibrations only when outliers and isolated data were rejected whilst Theil's incomplete method gave a robust and reliable calibration directly.

A novel automated quantitative analysis procedure based upon pattern recognition has been reported (89/316). A suite of

FORTRAN programs allowed the XRF system to be "trained" to recognise spectral patterns taken from soda lime glass. After the spectral features and associated chemical data had been entered into the program, the software automatically determined the elemental composition of similar unknown glasses. A pattern recognition method for the analysis of ores has also been recommended (88/2315) for use in industrial analyses where the standards and unknown specimens have very similar compositions.

A so-called "limit dilution method" has been introduced for the analysis of clays when using $\text{Li}_2\text{B}_4\text{O}_7$ glass fusion beads (89/724). Seven dilutions of a reference clay were used to allow a linearisation of the calibration graph of intensity *versus* dilution ratio.

Plesch (89/1872) has studied the calculation of *standard error* of calibration and concluded that a bivalent estimate of error must be used for all calibration methods other than simple linear regression.

A series of four papers entitled "Novel theoretical analyses of some features of X-ray spectrometry" has been published by Kuczumow and co-workers. Part I of the series (89/511) considers tertiary effects in XRF and how the concentration correction equations of Lachance and Traill can be modified to so-called Kuczumow - Holland equations which take tertiary effects into account in a simple manner. The equations were developed mainly for monochromatic excitation and the notion of an apparent mass absorption correction was introduced although the notations used are not entirely clear. The interesting possibility of "analysis by matrix effects" is proposed in Part II (89/512). The effect which an "unexcited" element has upon the measured relative intensities of a number of lines (*e.g.*, K and L series) of a second element may be used to determine the unexcited element. To be successful the method requires that the unexcited element exerts strong differential absorption upon the measurable analyte lines and so is very limited in application and only suitable for major element determinations. Part III of the series contains a derivation of concentration correction equations for scattered radiation (89/717) whilst Part IV (89/718) presents a semi-empirical method for the calculation of the limit of detection in XRF spectrometry. A route for deriving the LOD from concentration correction equations for fluorescent, Compton scattered and Rayleigh scattered radiations is proposed, but the practical complexity of the method makes it unlikely that it will supplant existing methods.

A new empirical procedure for the correction of *loss on ignition* (LOI) in silicate rock analysis by the glass fusion bead technique has been developed (89/1495). The procedure required a large number of standards with known LOI but was found to be particularly effective at higher (5% or greater) LOI where existing correction methods fail due to the non-linear effect of LOI on measured peak intensity. An empirical correction for LOI and gain on ignition, which typically occurs during preparation of glass fusions of iron ore for the determination of Fe, has been proposed (89/391). The method required different correction factors for the different sample:flux ratios (of 10:1 and 7:1) to be used.

The performance of two *empirical correction methods* has been compared (88/2356) for the difficult determination of Cr in Fe - Ni - Cr ternary alloys. The Japanese Industrial Standard (JIS) model and the Rasberry - Heinrich model were compared and the former model was reported to give accuracies of 0.08% Cr in high-alloy steel and 0.14% Cr in Ni alloys. The utility of the empirical intensity correction procedure has been presented by Ehrhardt (89/C611). Variations of empirical correction methods have been reported for correction of enhancement effects (89/335) and for restricting the range of calculated influence coefficients in the analysis of clays (89/1478).

Yap *et al.* (89/329) used *transmission measurements* to determine the absorption correction required for the correction of trace element intensities in a low-Z matrix.

Lancosz (89/1496) has proposed a new method for the correction of *particle size effects* in the XRF analysis of ore slurries. The method was suitable for a wide range of particle sizes and was successful in the analysis of Zn - Pb and Cu ore slurries.

2.3.1. Fundamental parameter (FP) calculations

A popular *introduction and historical perspective* to the development of FP procedures for the correction of absorption-enhancement (a-e) effects (often referred to as matrix or inter-element effects) in XRF spectrometry has been provided (Leyden, D.E., and Gilfrich, N.L., *Trends Anal. Chem.*, 1988, 7, 321). The authors show the ability of FP methods to reduce the number of standards required to obtain accurate analysis in a number of applications in the petrochemical industry and indicate the range of software currently available for FP calculations. They conclude that FP calculations are best used for problem solving and research tasks where typically one similar standard is available. Empirical methods employing a suite of in-type standards should still be used for accurate analysis in quality control applications where the analytical problem is well defined.

A *comprehensive survey* of five FP programs which are either commercially available or in the public domain has been presented (89/921). The authors assessed accuracy, versatility and ease of use of two programs which use an equivalent wavelength approximation (CORSET and DATAPLUS) and three programs which use a tube output model (XRF-11, NBSGSC and PCXRF). The features of each program were presented in detail and the relative accuracies were assessed using analysis of low-alloy steels, Ni-base alloys, Portland cements, rocks and tobacco. A single, similar standard from each matrix type was used for calibration purposes. Overall, the programs employing tube output modelling produced the better accuracy (2.5% relative or better for a composition range of 5-100% in metals and cements) and, for programs in which normalisation was allowed, data were reported to be improved.

In a key paper on *fundamental correction procedures*, Tertian (89/1768) showed that, in principle, the "competing" a-e correction methods of FP and FC are equivalent. The author presented a brief historic review of the development of a-e correction procedures and quoted the fundamental equations with a comprehensive description of the symbols and terminology used in this important field. The methodology of FP calculations was outlined and an extremely comprehensive description of influence coefficients, their physical meaning and their determination or calculation was presented. The difficulties of including terms for tertiary fluorescence and for scattering within the specimen, the need for more accurate fundamental parameters themselves (mass absorption coefficients, fluorescent yield, etc.) and the difficulty of determining exact tube spectra, all constituted major limitations to accuracy in both FP and FC calculation procedures. Practical mathematical and experimental procedures for compensating for these inaccuracies between the theory and real life were discussed and the author proposed a new binary coefficients approach which was described in detail.

The use of a proprietary FP program in which the calculated elemental composition was normalised to 100% total has been reported to be successful in the analysis of *irregular specimens* such as drill turnings (89/330). Elements present at >1% m/m were determined with accuracy better than 1% relative but levels <1% showed poor agreement with certified values mainly due to poor counting statistics. The authors did not investigate the attainable accuracy or difficulties expected from the determination of low-Z elements such as Al and Si in such specimens.

The search for *standardless analysis* in XRF still continues, but the claims of standardless software are usually based on the use of one similar standard in conjunction with FP calculations. Glynn *et al.* (88/C1559) despite having reported "standardless" FP analysis of cements, coal fly ash and oils made a comparison of accuracy based on single, similar standards.

The *fundamental algorithm* of Rousseau (88/2386), which is available in the public domain NBSGSC program, has been assessed for the analysis of silicate and carbonate rocks, sulphide minerals (89/308) and for major and trace analysis of silicate rocks using glass fusion bead specimens (89/1896).

As the power of laboratory computers increases, the application of *Monte Carlo methods* to the solution of a-e correction and spectral deconvolution problems is becoming possible. Wegscheider (89/C1308) has proposed that the inverse Monte Carlo (MC) method could hold the key to the next generation of FP software and Yacout and co-workers have described (89/968) a forward MC technique which has been used to generate complete EDXRF spectra of both homo- and heterogeneous specimens. In a study (89/309) using their MC program for the generation of spectra from a 304 stainless steel and a Cu - Ni alloy, the accuracy of the fluorescent peak data for the generated stainless-steel spectra was 1–2% relative for the majors on the basis of 10 000 histories, but the tube backscatter lines were less-accurate even after 20 000 histories. The authors gave a complete description of the methods used and indicated ways in which the execution times of their MC program (NCSMCXF) was improved.

2.3.2. Matrix correction using scattered radiation

The level of interest in using Compton (C) and Rayleigh (R) scatter corrections for compensation of a-e effects remains high. Nielson (88/C1573) has presented a summary of the advantages and characteristics of the *backscatter fundamental parameter* (BFP) or complete element matrix analysis from scatter (CEMAS) technique. The technique uses the C and R scatter spectral information to determine the light element content of specimens and so to correct the fluorescent intensities for a-e effects using FP calculation procedures. The application of the CEMAS method to the analysis of food materials (89/1613) yielded accuracy of 2.5% relative or better and showed excellent agreement with AAS data. Bogert *et al.* (89/311) have used CEMAS to analyse ion-exchange filter-papers which had been used to collect dissolved cations from water systems in an electricity generating plant. Although a simple Compton-corrected linear regression method gave the most accurate data, the CEMAS method required only one sensitivity standard, was insensitive to filter distortion and yielded acceptable accuracy at a lower cost per analysis than AAS. A program called MARS, which is a slight variation of the CEMAS program has been used by O'Reilly and King (89/988) for the analysis of a number of geological and biological RMs. The MARS procedure required the determination of the linear relationship between mean atomic number and C/R ratio using a series of standards. This calibration was then used to calculate the mean Z in an unknown and two light elements bracketing this mean Z (or two selected by the user) were then used in an iterative FP procedure to correct the analysed elements for a-e effects. Providing the selected light elements actually existed in the specimen, accuracy was generally similar to the CEMAS procedure.

Orlic *et al.* (89/1769) have proposed a *simplification of the full BFP method* of Nielson in which calibration procedures were used to eliminate reliance on all fundamental parameters other than mass absorption coefficients. It is not evident whether the method is better than simple Compton correction and the greater

flexibility and calibration simplicity of the full BFP method is lost.

Rachetti and Wegscheider (89/310) have presented a description of the *nature and origins of the spectral background* in EDXRF spectrometry. The authors indicate that polychromatic scattered incident radiation constitutes the main source of spectral background in secondary target EDXRF spectrometry. Using a similar approach to that used in the BFP method, the authors selected a light element (typically O) to describe a "residual matrix" which was calculated from the intensity of spectral background at 5 keV and which allowed a-e corrections to be made via an iterative procedure. The application of the model to NIST biological SRMs showed good agreement with certified values for elements with Z values 30–82.

Bui *et al.* (88/2313) have described the limitations of applying methods using *C/R ratios* and made several recommendations for improvement of accuracy. Liu *et al.* (89/315) have used a Compton correction technique in which standards were used to determine apparent absorption factors which were then used in the determination of trace amounts of Cu and Zn in a variety of sample types. Accuracy better than 5% relative was obtained. Ui *et al.* (89/1878) have proposed a modified Compton correction for the determination of Fe in low-Z matrices with an absolute accuracy of 3%.

Kuczumow *et al.* (89/717) have derived equations which are referred to as "*concentration correction equations for scattered radiation*" and which are analogous to the Kuczumow - Holland equations which the same authors have derived for fluorescent radiations. Although the resulting equations are claimed to offer simplicity, their solution requires twice the number of calibration standards used for "normal" concentration correction of fluorescent radiation.

In order to carry out FP scatter corrections it is obviously necessary to have accurate and accessible data for scatter cross-sections. An analytical approximation for the coherent (Rayleigh) scatter cross-section for all elements with atomic number in the range 30–80 has been described (Massaro, E., and Matt, G., *Nucl. Instrum. Meth. Phys. Res.*, 1988, **A271**, 603). The proposed simple formula, which was quoted with a table of all the required coefficients, yielded data with an average deviation, from literature values, of 1.2%.

2.4. Applications

2.4.1. Specimen preparation

Despite the advances in instrumentation and in computer software for applying matrix corrections, the analytical limitations due to specimen preparation in XRF analysis have to be addressed with care. The ways in which specimen preparation relates to final accuracy in XRF spectrometry have been addressed by Wheeler (89/336).

The analysis of *irregular and odd-shaped specimens* has been studied by Platbrood and Van de Velde (89/987). The authors gave details of the theoretical approaches to a-e corrections in odd-shaped specimens, derived equations describing the intensity ratios expected in tilted specimens and showed the effectiveness of specimen spinning in reducing errors when analysing chip-pings. The application of an FP calculation program to the analysis of irregular specimens such as drill turnings concluded that the use of simple normalisation gave adequate accuracy (89/330). A microcomputer-controlled automatic device for holding and grinding irregular metal samples has been described (89/900). The apparatus produced specimens which allowed the XRF method to achieve very stringent analytical requirements in a steel production facility.

The problems associated with *segregation in Al alloys* have been investigated (88/1715). It was found that Si segregation could be reduced through the use of directional cooling during melt-casting and that effects upon the remaining elements could be compensated by the application of composition-dependent regression equations.

The analysis of *small masses of powder* samples has been described by Omatsu *et al.* (89/1014). The powder was dispersed in a liquid and 50 μl placed on a filter-paper which was then analysed to yield limits of detection of 0.1–2.3 μg for La, Ni, Sb, Sr, Ta, Ti and Zn. The method was simple but required particle sizes of 3 μm or less.

A method in which *asphalt or pitch* was heated to 150 $^{\circ}\text{C}$ and then melt-cast into a standard disposable plastic sample cup fitted with a 6.3- μm Mylar window has been described (89/312). To improve sensitivity for Al and Si, the Mylar window was peeled off after the specimen had solidified.

DeGroot (89/989) has used the XRF-11 software package to investigate the use of *heavy element dilution* for samples which contain 50% C. When heavy element diluents were used, dilution factors could be reduced and procedures were simplified. The reduction in scattered background is cited as an advantage of the method and the author recommended practical rules for adopting a particular dilution strategy.

The interest in *pre-concentration methods* for XRF analysis continued during this review period. Pella and Wang (89/C1311) have discussed the use of immobilised chelating groups for general trace element pre-concentration and Yamamoto (88/2311) has described an XRF method for the determination of 0.1–100 μg of Br, Cl and I in snow following precipitation as silver halide and collection on a membrane filter. Zebrev and co-workers (88/2327) have used a liquid-liquid extraction method to pre-concentrate and separate Al and Ga in waste water. The acidified sample was extracted at 60–90 $^{\circ}\text{C}$ with a C₁₇–C₂₀ mixture of carboxylic acids and analysed after the organic extract had solidified. A method in which trace amounts of Ag in natural and waste water were pre-concentrated on to a cation-exchange paper to yield a calibration range of 10–100 $\mu\text{g l}^{-1}$ of Ag and a limit of detection of 2 $\mu\text{g l}^{-1}$ of Ag has been described by Guo *et al.* (89/394). Precipitation methods for Cr (89/1066) and of eight trace heavy elements (89/1067) in natural waters have been described by Inoue and co-workers. Yamada *et al.* (89/1072) have described the use of an immobilised chelating agent for the pre-concentration of Co, Cu, Mn and Ni in natural and waste waters for subsequent EDXRF analysis. The separation, pre-concentration and XRF analysis of $\mu\text{g g}^{-1}$ levels of the REE in geological samples (89/313, 89/411), soils (89/1895) and steels (89/1877) have been described. A pre-concentration method utilising fusion followed by digestion, extraction and coprecipitation for determination of trace amounts of Zr in geological materials showed a limit of detection of 0.4 $\mu\text{g ml}^{-1}$ of Zr based on a 100-s count (89/327). A chelation and coprecipitation method has been used for the determination of 12 heavy metals in soils and sediments (88/1289). Methods for pre-concentrating Ag and Au (89/916) and Bi (89/1736) from ores and the use of hydride generation for the determination of As, Bi, Sb and Sn in solids (89/366) have also been described.

Cross and Jones (89/307) have described a completely *automated robotic specimen preparation system* which has been successfully introduced into a petrochemical industry laboratory. The system was able to load liquid into a sample cup using a variety of "hands" and the control computer was interfaced with the local laboratory management computer.

Four commercially available *automatic glass fusion bead makers* and a manual furnace technique have been compared (89/843) for their ability to carry out reproducible fusions of

sinter and slag from the steel industry. A new microprocessor-controlled, automated fusion apparatus has been designed by Flock and Ohls (88/1291). The preparation details for a heavy absorber fusion flux have been described by Eddy and Balaes (89/922) who noted a range of 17–22% *m/m* La₂O₃ in different batches of the same commercially available fluxes. Despite initial capital expenditure, the in-house flux preparation paid this investment back after making only 5 kg of flux and yielded a highly consistent and reliable product. A fusion procedure using a sample size of only 0.25 g or less in a 1:2 sample flux ratio has been reported (89/1591) for the determination of the major and 16 trace elements in a single bead prepared from archaeological samples. A conventional WDXRF instrument was used and precision of <2% for majors and detection limits of 3–6 $\mu\text{g g}^{-1}$ for the heavy traces were obtained. Beckman (89/1507) has given a definition for the calculation of limits of detection in Na₂B₄O₇-NaBO₂ glass fusions in EDXRF spectrometry and obtained typical limits of detection of 0.01–0.1% for elements with *Z* > 14. In a study comparing AAS with XRF (89/465) for the analysis of clays after preparation by fusion (and dissolution for AAS) it was concluded that the use of AAS or ICP-OES yielded a more efficient and cost-effective operation. King and Vivit (89/1493) have described an effective fusion procedure for the determination of the major elements in carbonate rocks.

2.4.2. Thin films

X-ray fluorescence spectrometry provides a rapid, non-destructive method for the analysis of *thin films* on substrates and interest in this application area continues, particularly in the analysis of semiconductor and electronic devices. Roessiger (89/1494) has presented a detailed treatise on the analysis of multi-component thin films in which the importance of correct modelling of the incident X-ray tube spectrum was stressed. An FP program for the analysis of 1-, 2- and 3-layer systems with up to 3 elements per layer was presented.

Andermann (89/319) has extensively reviewed the *instrumentation and methodology* requirements for the analysis of thin (50–5000 Å) surface films using a variety of X-ray techniques. The author described, in detail, the technique of variable angle, grazing exit XRF spectrometry for non-destructive composition depth profiling.

In-house *thickness standards* for XRF measurement of Au on Al₂O₃ have been prepared in parallel with those for AAS and profilometry (88/C1582). The two latter techniques showed good concordance of results and were used to certify the standards for calibration of the XRF instrument. The XRF method was more efficient and was used for in-plant analysis. Ernst *et al.* (Ernst, S., Lee, C.-O., and Lee, J.-J., *J. Electrochem. Soc.*, 1988, **135**, 2111) have used a simple XRF technique for the determination of the thickness of Ti, Al, Ti silicide and W silicide films on Si wafers. No attempt was made to determine concentration but the method was used for in-plant quality control.

Schuster *et al.* (89/1783) have used an LSM "crystal" for the determination of B in thin layers of *borophosphosilicate glass*. The LSM gave a factor of 3.5 improvement in B sensitivity when compared with the use of conventional diffracting crystals. A limit of detection of 0.04% *m/m* of B in a 1- μm film (which acts as an infinitely thick, bulk specimen for B K X-rays) was obtained with a 600-s count time.

Arai (89/1453) reported the construction of a new instrument for the analysis of *thin films on Si wafers*. The instrument was able to accommodate 200 mm diameter Si wafers and 300 mm diameter magnetic discs and was specifically designed for the determination of B using curved LSM "crystals." The determination of B in B-PSG glass passivation layers gave a precision of

0.07% B and an accuracy of 0.15% B using a simplified FP calculation method.

Huang (89/1782) has developed an FP calculation method for the analysis of *multi-layer films* containing "difficult" combinations of elements. For an Fe - Ni single layer on a silica substrate, accuracy of 0.7% relative for composition and 2.3% for thickness was obtained. Similar accuracy was obtained for a Cr - Cu - Ni+Fe three-layer system in which large inter-layer corrections were necessary.

Cross and Wherry (Cross, B.J., and Wherry, D.C., *Thin Solid Films*, 1988, **166**, 263) have described the use of a new *XRMF instrument* for the analysis of thin films using FP calculations. The equipment incorporated a 50-kV, 1-mA X-ray tube and a 100- μm slit to produce a beam spot size which was adjustable from 30 μm to 10 mm. Several thin film types were studied and the generation of two-dimensional data from a non-homogeneous Y - Ba - Cu superconducting film on MgO was particularly interesting.

2.4.3. Geological materials

Although the XRF technique is considered as routine for much geological analysis, there is still some interesting work being reported. The advances in pre-concentration and glass fusion bead techniques are covered in the Specimen preparation section above.

Frantz *et al.* (89/1525) have published in full their work on the use of an SR X-ray microprobe in the analysis of natural mineral fluid inclusions. A thin section was moved in 1- μm steps by an *x - y* micropositioner whilst being irradiated by a focused 10-keV SR beam of 5–10 μm diameter. The composition of the fluid inclusions was determined after correction for absorption effects. The authors were able to generate two-dimensional elemental maps from inclusions which were only 2–5 μm thick and 2–75 μm across. Limits of detection of <10 fg were obtained for Ni, Mn and Ti and the absorption of fluoresced X-rays by the host mineral was found to be the limiting factor for sensitivity.

The problems of correcting for high *loss on ignition* (LOI) in carbonate rocks have been addressed (89/1493) in a method using calcination then fusion with $\text{Li}_2\text{B}_4\text{O}_7$ (10:1). The method allowed accurate analysis of majors to be made without the need for an explicit LOI correction. A simple method for LOI correction in silicate rock fusions has also been described (89/1495).

The use of a *low dilution* (5:1) fusion allowed the determination of both major and trace elements using the same fusion bead (89/1577). The trace element data were corrected for a-e effects using the data previously collected from the majors analysis on the same bead. The Cr $K\alpha$ or W $L\beta$ Compton peak has been used successfully for the correction of a-e effects in the analysis of seven trace elements in silicate rocks (88/2318).

In two comparisons (88/2158, 88/2353) of digestion - AAS and XRF methods for the determination of *Pb in soils*, the AAS method was found to be preferable mainly for its limits of detection which were 20–50 times lower than those obtained by XRF.

The use of a *high-accuracy* XRF method has shown the reference values for an iron ore RM to be incorrect by +0.14% for Fe and -0.046% for SiO_2 (88/2359). For a practical in-house analysis service for REE in geological materials, Juras *et al.* (88/1936) have recommended pre-concentration and ETA-AAS for Dy, Er, Eu, Sm and Yb and conventional XRF analysis for the light REE (Ce, La and Nd).

The incorporation of XRF data into a national geochemical *data bank* has been described by Smith (89/990). The forensic use of multi-element XRF data (Fe, K, Rb and Sr) and principal

component analysis has been reported to allow identification of the original location of a soil sample (89/1578).

2.4.4. Industrial materials

The analysis of *metals* remains an important application area for XRF spectrometry. The use of an exponential intensity correction procedure in EDXRF analysis of cast iron and steels has been shown to yield accurate results for 13 elements (88/2317). The determination of platinum group elements, Fe and Cr in corrosion-resistant steels has been described by Eddy *et al.* (89/328). Thin film specimens were prepared from digest solutions and the method gave limits of detection for Pt and Ru of 12 and 6 $\mu\text{g g}^{-1}$, respectively. A separation and pre-concentration method which yielded thin film specimens has been proposed for the determination of five trace elements in high-purity Ta metal (89/1875). Limits of detection of 0.05–0.7 μg in the thin film were obtained. The determination of trace amounts of Ce down to 0.005% in steel has been carried out after separation of Ce as the oxalate (89/1589). In an effort to compensate for the poor energy resolution of the Si(Li) detector employed, Szaloki (89/925) has used a Se absorption edge filter on the detector to suppress the Al K line which interfered in the determination of 0.5–3% Mg in Al alloys. A ^3H - Ti source was used in conjunction with a 1.5- μm thick Se filter to yield a typical analysis of $0.57 \pm 0.14\%$ Mg in a 1000-s acquisition time. The difficulties of using this type of radioisotope source are considerable and the use of an ^{55}Fe source in conjunction with a detector of contemporary resolution should allow improved data to be obtained with no requirement for the Se edge filter.

Synthetic hydrocarbon mixtures were used by Denoyer and Siegel (88/2345) to prepare calibration standards for the determination of Ni, S and V in *oils*. Corrections for the effect of S on Ni and V were required and limits of detection of 20 $\mu\text{g ml}^{-1}$ for S and 0.8 $\mu\text{g ml}^{-1}$ for Ni and V were obtained using He flush and a Cr anode. The use of Zr as heavy absorber and of Compton scatter correction has been utilised in the determination of S in mineral oils (88/2307). Synthetic calibration standards were prepared from dibenzyl disulphide in liquid paraffin and a limit of detection of 5 $\mu\text{g ml}^{-1}$ of S was obtained. Two sample preparation techniques for the analysis of used lubricating oils have been described (89/C687). One method recommended absorption of the oil on to MgO powder then ashing while the other involved converting the oil into a solid by mixing with a wax at >100 °C.

Using an in-house EDXRF spectrometer, Rasteger *et al.* (89/390) have determined *U in enrichment plant process liquids*. The liquid (100 μl) was placed on 4- μm thickness polypropylene film for analysis and a limit of detection of 30 $\mu\text{g l}^{-1}$ of U was obtained using a 1000-s acquisition time. An internal standard (20 $\mu\text{g ml}^{-1}$ of Pb) was used for calibration and the use of U $L\alpha/\text{Pb } L\alpha$ ratios compensated for a-e effects. A method using internal standardisation has also been recommended for the determination of U in ores (89/1624).

In the difficult determination of *trace REE in REE oxides*, Chandola *et al.* (89/293, 89/453) have used a method in which the REE oxalate was prepared before being pelletised on to a boric acid back. Limits of detection of 20 $\mu\text{g g}^{-1}$ of Er and Yb in high-purity lutetium oxide and 20 $\mu\text{g g}^{-1}$ of Ho and Lu in high-purity thulium oxide were demonstrated.

In the analysis of treated *wood products*, EDXRF spectrometry was used to determine the spatial distribution of the absorbed preservative liquid which contained Cu, Cr and As (89/333).

The Atomic Spectrometry Update on Minerals, Refractories, Chemicals and Metals (89/1675) covers a number of industrial applications where XRF techniques are used.

2.4.5. Environmental

A general review, containing 15 references, on the determination of trace elements in environmental samples has been given by Ruch *et al.* (88/2344). The Atomic Spectrometry Update on Environmental Analysis (88/1749) also contains a section on developments in XRF spectrometry.

In a study on long-range transport of *air pollution*, Spitzer *et al.* (89/C68) used a WDXRF spectrometer to determine S on air filters. Standards were prepared from filters on to which known amounts of an aqueous sulphate solution had been dried. The calibration range extended up to 500 μg per filter and a detection limit of 0.24 μg of S was obtained with a 40-s count on each side of the filter.

A comparison of AAS and XRF techniques for the determination of up to 1.5% *m/m* Pb in garbage incinerator fly ash has been reported by Andersson *et al.* (89/211). Aqueous standard additions were made to the dry powder samples before being pelletised for XRF analysis. The absorption correction needed in the standard additions calculation was based upon an equivalent wavelength algorithm and agreement between AAS and XRF results was good. For future work, the authors recommended use of matrix-matched standards to simplify the XRF procedure further in order for it to become the preferred method for rapid monitoring of Pb in fly ash.

The determination of 12 elements in *workplace air* around welding operations has been described by North and Haswell (89/88). The welding fume was collected on a filter and analysed directly as a thin-film specimen using a sequential WDXRF spectrometer. A simple calibration procedure was developed in which dibenzylthiocarbamate precipitates were filtered from multi-element aqueous standards on to membrane filters. The fume samples were analysed against the straight line calibration which extended up to 900 μg per filter and the results showed excellent agreement between the XRF and an ICP-OES method. The XRF method was claimed to offer a simple and rapid method for monitoring occupational exposure of welders to toxic elements such as As, Cr, Pb and V. Tolgyessy *et al.* (88/2310) have also studied the levels of Cr, Fe, Mn and Mo in workplace aerosols around welders. Pilz *et al.* (88/2357) have determined the levels of Th and U in their own laboratory air using a 10 mCi ^{57}Co radioisotope source and a Ge detector to excite and measure the high-energy K emission lines. The limit of detection obtained was 20 μg per filter and the authors recommended reduction of this limit by means of a rather hazardous 1 Ci ^{57}Co source.

The use of pre-concentration methods allows $\mu\text{g l}^{-1}$ detection limits to be achieved in the analysis of *natural waters* by XRF techniques. A limit of detection of 4 $\mu\text{g l}^{-1}$ of Cr was obtained when using coprecipitation with Fe (89/1066) and a dithiocarbamate precipitation method allowed determination of many important heavy elements present in the 10–1000 $\mu\text{g l}^{-1}$ range (89/1067). An extensive study into the combination of TXRF and pre-concentration methods demonstrated detection limits below 1 $\mu\text{g l}^{-1}$ for the determination of up to 25 elements in river and rain water (88/2329). The method of choice used chelation with dibenzylthiocarbamate followed by reversed-phase separation on a column. The chelates were eluted with CHCl_3 -methanol solution and evaporated on to quartz specimen substrates.

Imakita *et al.* (89/1017) have reported the use of TXRF for the determination of trace elements in aqueous solutions at the 1 ng ml^{-1} level using a multi-drop specimen preparation technique.

The non-destructive nature of XRF spectrometry makes it ideal for the analysis of works of art and *archaeological* specimens. Hoffmann and Lieser have presented a review of EDXRF

analysis of a variety of archaeological materials (89/459). X-ray fluorescence methods have been used in the non-destructive elemental analysis of weathered medieval stained glass (89/1022), gold ornaments (89/996), gold antiquities (89/1027) and bronze hoards (89/C71). Yap (88/2376) has used a simple EDXRF system to determine trace amounts of As and Zn in Oriental porcelains in order to confirm their authenticity. A calibration of $\ln(\text{sensitivity})$ versus $\ln(\text{energy})$ was used to simplify the set-up procedure.

2.4.6. Biological materials

Maier *et al.* have reviewed the application of EDXRF spectrometry in *biomedical science* (89/890) and described the use of EDXRF for the simultaneous determination of Cu, Fe, Ni, Pb, Rb, Ti and Zn in human bronchio-alveolar lavage fluids (88/1488). The same group have also developed a method for the determination of Br, Ca, Cu, Fe, Pt, Rb, Se and Zn in μl volumes of human plasma (89/456). The effect of cis-platin treatment on the trace element levels was discussed. Shenberg *et al.* (89/1028) have reported an impressive technique for the accurate determination of Br, Cu, Rb, Se and Zn in very small volumes of human serum. The attainable limits of detection using the cited technique were quoted as 0.05–0.13 $\mu\text{g ml}^{-1}$ for a 100-s counting time. The determination of Se in blood serum after separation and pre-concentration by APDC precipitation has been described (89/1218) while direct determination of Br in serum, hair and urine has been reported by Cuenca and co-workers (89/1223). An FP EDXRF method has been used successfully for the determination of Ca, Cu, Fe, Mn, Pb and Zn in human gallstones (89/1013) and a review by Savory *et al.* (89/471) included XRF methods in its coverage of instrumental techniques for the increasingly important determination of Al in medical fluids and tissues. The use of a radioisotope-excited EDXRF system for the determination of Au in tissues from humans who have been treated for rheumatoid arthritis with Au solutions has been described (89/997). The analysis of the dried and pelletised tissues revealed considerably higher levels of Au in tissues from treated patients than in tissue from a control patient. A correlation between tissue Au content and Zn in major organs was noted.

The analysis of *biomaterials using TXRF* has been described by von Bohlen *et al.* (89/961) who used a microtome for the preparation of specimens 10–20 μm thick. Full practical details of the microtome procedures were presented and limits of detection of 1–5 $\mu\text{g g}^{-1}$ were obtained for elements with $Z > 22$ when using a double-reflection instrument and 1000-s acquisition times. Qualitative comparisons of lung tissue from normal and occupationally exposed workers were made and clear evidence of Pb exposure was seen in the lung tissue from a painter but no quantitative data were produced. The combination of TXRF and monochromatic SR excitation has been used for the determination of Se in human blood serum (88/1994). The tunability of the SR source radiation enabled very high excitation sensitivity to be obtained by positioning the SR beam energy on the immediate high-energy side of the Se K absorption edge whilst the use of TXRF optics gave the combined benefits of high sensitivity, low scattered spectral background and minimisation of matrix effects. The limit of detection for Se in a 30- μl specimen volume was 8 $\mu\text{g l}^{-1}$. Lenglet and co-workers (88/2328) have compared PIXE and 15-keV SR excitation SR-XRF for the analysis of freeze-dried human blood serum and concluded that the SR-XRF method gave better reproducibility and accuracy.

The utility of XRF techniques in *medical forensic analysis* has been demonstrated in a study by Winstanley and co-workers (88/2308). Soup was spiked with known amounts of toxic elements to prepare calibration standards which were then used in

the multi-element analysis of stomach contents. The effectiveness of the method was shown in a case of acute Hg poisoning.

A particularly unusual application of XRF is the *in vivo* measurement of Pb which has been reported by Chettle *et al.* (88/1692). Human tibia Pb was measured *in vivo* using the penetrating excitation from a ^{109}Cd source and the high-energy Pb K series analyte lines. The Pb K lines were ratioed to the source Compton peak in order to correct for geometric and density effects. A limit of detection of $10\text{ }\mu\text{g g}^{-1}$ of Pb was obtained and Pb levels were positively correlated with age or occupational exposure to Pb.

The determination of trace elements in human hair strands by XRF spectrometry has been reviewed by Torihara (89/314) who showed examples of data which were used in toxicological, forensic, dietary, environmental, medical and archaeological studies. The determination of F and 21 other elements in hair using a special specimen holder has been described (89/485). The mean F content of hair for a local adult population was found to be $15.6\text{ }\mu\text{g g}^{-1}$.

The multi-element capability, simple sample preparation and wide calibration range were presented as advantages of the use of XRF methods in reconnaissance marine pollution studies (88/1728). Oyster and cockle tissues were successfully analysed for Ba, Br, Cu, Fe, Mn, Pb, Rb, Sr and Zn, but the limits of detection for As, Cd, Cr and Ni were too close to "low" levels of these elements. The limit of detection for Hg ($8\text{ }\mu\text{g g}^{-1}$) was inadequate for analysis of edible marine biota.

A new method for radioisotope-excited analysis of biological materials in which only one standard is required has been introduced by Uzonyi (89/483) and the determination of I in a variety of biological materials has been described by Pavel *et al.* (89/889).

2.4.7. Chemical effects

Reports which indicate that different chemical combinations of an element show differences in fluorescent line shape and position are not new. However, until comparatively recently, it was expected that such effects should only be observable for elements with $Z < 20$.

In a comprehensive study, the observation of chemical effects in the Cr K series emission lines has recently been reported (88/1980) for the speciation of Cr^{III} and Cr^{VI} in welding fume.

Measurements of line shape, energy shift and intra-series line ratios were made using a PW1410 WDXRF spectrometer equipped with either a rubidium acid phthalate (RbAP) or an ethylenediamine-D-tartrate (EDDT) dispersing crystal. The 10th order reflection from the RbAP crystal was used for measurement of Cr $\text{K}\alpha_{1,2}$ and Cr $\text{K}\beta_{2,3}$ and the 4th-order reflection from EDDT was used for the Cr $\text{K}\beta_{2,5}$ line. In order to determine the Cr^{VI} content of fume samples the intensity ratio of the Cr $\text{K}\beta'$ to Cr $\text{K}\beta_{1,3}$ peaks was found to yield the best results and led to the introduction of a rapid routine method for the determination of Cr^{VI} in welding fume.

Tham and Preiss (89/1670) have investigated how various ligands affect the $\text{K}\beta/\text{K}\alpha$ intensity ratios of the transition elements. These workers measured the $\text{K}\beta/\text{K}\alpha$ ratios for a large number of compounds of transition elements with ligands containing the elements with $Z = 17-35$. The measurements were made using an in-house EDXRF system which incorporated a ^{109}Cd radioisotope source and a Si(Li) detector. The measured line ratios were compared with those calculated by Scofield (Scofield, J.H., *Phys. Rev., Sect. A*, 1974, **9**, 1041) and those reported from similar photoionisation studies in the literature. Definite differences from the theoretical and observed ratios in the pure element were measured for a number of compounds. The authors offered no detailed assessment of the reasons for these differences other than to relate the line ratio changes to the degree of pairing and unpairing of d-orbital bonding electrons. The potential problems of using theoretical $\text{K}\beta/\text{K}\alpha$ ratios in peak deconvolution for EDXRF, where intra-series ratios change from reference spectrum to analyte spectrum, were noted.

The use of high-resolution, double crystal XRF instruments for the determination of S species in hair (89/1582) and plant material (89/371) has been reported. An analytical expression for the shape of long wavelength X-ray lines (C K, Cu L and Si K) has been developed (89/C1654) for use in peak deconvolution and assessment of line shape changes in speciation studies. The observed peak shifts were found to be strongly related to electronegativity of the combined element.

Absorption edge shift measurements have been employed to determine chemical species of the first row transition elements (89/1569 and Sakurai, K., and Gohshi, Y., *Anal. Sci.*, 1988, **4**, 37) where the high intensity and tunability of a synchrotron source allowed speciation of 0.1 ng of determinand.

LOCATION OF REFERENCES

The full references cited in this Update have been published as follows:

88/1469–88/1943, *J. Anal. At. Spectrom.*, 1988, **3**(7), 187R–202R.
 88/1944–88/2393, *J. Anal. At. Spectrom.*, 1988, **3**(8), 255R–270R.
 89/C1–89/529, *J. Anal. At. Spectrom.*, 1989, **4**(1), 29R–45R.
 89/530–89/1227, *J. Anal. At. Spectrom.*, 1989, **4**(3), 88R–110R.
 89/1228–89/C1658, *J. Anal. At. Spectrom.*, 1989, **4**(4), 137R–150R.
 89/1659–89/C1944, *J. Anal. At. Spectrom.*, 1989, **4**(6), 188R–197R.
 (89/2555–89/2723 which are also cited in this Update can be found in the present issue.)

Abbreviated forms of the literature references quoted (*excluding* those to Conference Proceedings) are given below for the convenience of readers. The full references, names and addresses of authors and details of the Conference presentations can be found in the appropriate issues of *JAAS* cited above.

Abbreviated List of References Cited in Update

- 88/346. *Can. J. Spectrosc.*, 1987, **32**, 29. 88/817. *Fresenius Z. Anal. Chem.*, 1987, **327**, 659. 88/945. *J. Anal. At. Spectrom.*, 1987, **2**, 211R. 88/1289. *Fresenius Z. Anal. Chem.*, 1987, **328**, 469. 88/1291. *Fresenius Z. Anal. Chem.*, 1987, **328**, 560. 88/1462. *Anal. Chem.*, 1988, **60**, 34. 88/1473. *Analyst*, 1988, **113**, 405. 88/1488. *Clin. Chem.*, 1987, **33**, 2234. 88/1619. *Bunseki Kagaku*, 1988, **37**, 25. 88/1639. *Anal. Chem.*, 1988, **60**, 482. 88/1674. *J. Anal. At. Spectrom.*, 1988, **3**, 305. 88/1675. *J. Anal. At. Spectrom.*, 1988, **3**, 309. 88/1676. *J. Anal. At. Spectrom.*, 1988, **3**, 315. 88/1677. *J. Anal. At. Spectrom.*, 1988, **3**, 319. 88/1678. *J. Anal. At. Spectrom.*, 1988, **3**, 325. 88/1679. *J. Anal. At. Spectrom.*, 1988, **3**, 337. 88/1680. *J. Anal. At. Spectrom.*, 1988, **3**, 343. 88/1681. *J. Anal. At. Spectrom.*, 1988, **3**, 349. 88/1682. *J. Anal. At. Spectrom.*, 1988, **3**, 355. 88/1692. *Biol. Trace Elem. Res.*, 1987, **13**, 191. 88/1715. *Zh. Anal. Khim.*, 1987, **42**, 861. 88/1728. *Sci. Total Environ.*, 1987, **66**, 213. 88/1742. *Anal. Chem.*, 1988, **60**, 578. 88/1749. *J. Anal. At. Spectrom.*, 1988, **3**, 1R. 88/1874. *Chem. Anal. (N. Y.)*, 1987, **90**(Induct. Coupled Plasma Emiss. Spectrosc., Pt. 2), 421. 88/1927. *Mikrochim. Acta*, 1987, **1**, 233. 88/1935. *Chem. Geol.*, 1988, **67**, 35. 88/1936. *Chem. Geol.*, 1987, **64**, 143. 88/1953. *J. Cryst. Growth*, 1988, **87**, 117. 88/1960. *Fenxi Huaxue*, 1987, **15**, 831. 88/1961. *Anal. Chem.*, 1988, **60**, 733. 88/1974. *Mikrochim. Acta*, 1987, **1**, 291. 88/1980. *Analyst*, 1988, **113**, 779. 88/1993. *J. Anal. At. Spectrom.*, 1988, **3**, 45R. 88/1994. *Anal. Chem.*, 1988, **60**, 684. 88/1995. *Anal. Chem.*, 1988, **60**, 687. 88/1996. *Anal. Chem.*, 1988, **60**, 691. 88/2062. *Laser Focus*, 1988, **24**, 88. 88/2069. *Analyst*, 1988, **113**, 923. 88/2079. *J. Anal. At. Spectrom.*, 1988, **3**, 547. 88/2090. *J. Anal. At. Spectrom.*, 1988, **3**, 601. 88/2091. *J. Anal. At. Spectrom.*, 1988, **3**, 89R. 88/2158. *Commun. Soil Sci. Plant Anal.*, 1988, **19**, 107. 88/2165. *Fresenius Z. Anal. Chem.*, 1988, **329**, 795. 88/2210. *J. Geochem. Explor.*, 1988, **30**, 63. 88/2274. *Anal. Chem.*, 1987, **59**, 1437. 88/2280. *Anal. Chem.*, 1987, **59**, 1664. 88/2307. *Chem.-Ztg.*, 1987, **111**, 346. 88/2308. *Forensic Sci. Int.*, 1987, **35**, 181. 88/2309. *Fresenius Z. Anal. Chem.*, 1987, **328**, 492. 88/2310. *J. Radioanal. Nucl. Chem.*, 1987, **114**, 101. 88/2311. *Bunseki Kagaku*, 1987, **36**, 592. 88/2312. *Microchem. J.*, 1987, **36**, 9. 88/2313. *Nucl. Instrum. Methods Phys. Res., Sect. B*, 1987, **B28**, 88. 88/2315. *Zh. Anal. Khim.*, 1987, **42**, 1407. 88/2317. *Spectroscopy (Eugene, Oreg.)*, 1987, **2**(11), 32. 88/2318. *Talanta*, 1987, **34**, 1027. 88/2323. *Anal. Chem.*, 1987, **59**, 2191. 88/2326. *Anal. Chem.*, 1987, **59**, 2316. 88/2327. *Anal. Chim. Acta*, 1987, **195**, 357. 88/2328. *Anal. Chim. Acta*, 1987, **195**, 153. 88/2329. *Anal. Chim. Acta*, 1987, **195**, 275. 88/2330. *Anal. Sci.*, 1987, **3**, 305. 88/2334. *Nucl. Instrum. Methods Phys. Res., Sect. A*, 1987, **A261**, 279. 88/2335. *Nucl. Instrum. Methods Phys. Res., Sect. A*, 1987, **A261**, 290. 88/2336. *Nucl. Instrum. Methods Phys. Res., Sect. A*, 1987, **A261**, 295. 88/2337. *Nucl. Instrum. Methods Phys. Res., Sect. A*, 1987, **A261**, 292. 88/2338. *Nucl. Instrum. Methods Phys. Res., Sect. A*, 1987, **A261**, 283. 88/2342. *Zh. Anal. Khim.*, 1987, **42**, 965. 88/2344. *Analyst*, 1987, **115**, 159. 88/2345. *Anal. Chim. Acta*, 1987, **192**, 361. 88/2346. *Analyst*, 1987, **115**, 325. 88/2352. *Fresenius Z. Anal. Chem.*, 1987, **327**, 293. 88/2353. *Fresenius Z. Anal. Chem.*, 1987, **327**, 304. 88/2356. *Fresenius Z. Anal. Chem.*, 1987, **327**, 474. 88/2357. *Fresenius Z. Anal. Chem.*, 1987, **329**, 581. 88/2359. *Fresenius Z. Anal. Chem.*, 1987, **327**, 684. 88/2361. *Fresenius Z. Anal. Chem.*, 1987, **327**, 690. 88/2362. *Fresenius Z. Anal. Chem.*, 1987, **328**, 23. 88/2369. *J. Radioanal. Nucl. Chem.*, 1987, **118**, 217. 88/2375. *X-Ray Spectrom.*, 1987, **16**, 217. 88/2376. *X-Ray Spectrom.*, 1987, **16**, 229. 88/2378. *X-Ray Spectrom.*, 1987, **16**, 255. 88/2379. *Nucl. Instrum. Methods Phys. Res., Sect. B*, 1987, **24**, 405. 88/2386. *X-ray Spectrom.*, 1987, **16**, 103. 88/2387. *X-ray Spectrom.*, 1988, **16**, 237. 88/2388. *Nucl. Instrum. Methods Phys. Res.*, 1986, **A248**, 393. 88/2392. *Adv. X-ray Anal.*, 1987, **30**, 39. 88/2393. *Adv. X-ray Anal.*, 1987, **30**, 45. 89/82. *J. Anal. At. Spectrom.*, 1988, **3**, 653. 89/83. *J. Anal. At. Spectrom.*, 1988, **3**, 659. 89/84. *J. Anal. At. Spectrom.*, 1988, **3**, 667. 89/88. *J. Anal. At. Spectrom.*, 1988, **3**, 687. 89/202. *Analyst*, 1988, **113**, 1167. 89/203. *Analyst*, 1988, **113**, 1325. 89/211. *Talanta*, 1988, **35**, 337. 89/220. *Anal. Chim. Acta*, 1987, **200**, 559. 89/230. *Zh. Anal. Khim.*, 1988, **43**, 292. 89/241. *Anal. Chem.*, 1988, **60**, 113R. 89/246. *Anal. Chem.*, 1988, **60**, 1472. 89/252. *Bunseki*, 1988, (1), 37. 89/288. *Spectrochim. Acta, Part B*, 1988, **43**, 203. 89/293. *J. Radioanal. Nucl. Chem.*, 1988, **121**, 53. 89/299. *IEEE Trans. Nucl. Sci.*, 1988, **35**(1, Pt. 1), 691. 89/306. *Adv. X-Ray Anal.*, 1987, **30**, 29. 89/307. *Adv. X-Ray Anal.*, 1987, **30**, 89. 89/308. *Adv. X-Ray Anal.*, 1987, **30**, 105. 89/309. *Adv. X-Ray Anal.*, 1987, **30**, 113. 89/310. *Adv. X-Ray Anal.*, 1987, **30**, 143. 89/311. *Adv. X-Ray Anal.*, 1987, **30**, 153. 89/312. *Adv. X-Ray Anal.*, 1987, **30**, 243. 89/313. *Adv. X-Ray Anal.*, 1987, **30**, 273. 89/314. *Adv. X-Ray Anal.*, 1987, **30**, 293. 89/315. *Adv. X-Ray Anal.*, 1987, **30**, 309. 89/316. *Adv. X-Ray Anal.*, 1987, **30**, 325. 89/319. *Appl. Surf. Sci.*, 1988, **31**, 1. 89/325. *Anal. Chem.*, 1987, **59**, 2551. 89/326. *Chem. Geol.*, 1987, **63**, 345. 89/327. *Analyst*, 1988, **113**, 197. 89/328. *Appl. Spectrosc.*, 1987, **41**, 1442. 89/329. *Appl. Spectrosc.*, 1987, **41**, 1335. 89/330. *Appl. Spectrosc.*, 1987, **41**, 1455. 89/333. *Spectroscopy (Eugene, Oreg.)*, 1988, **3**(1), 37. 89/335. *J. Radioanal. Nucl. Chem.*, 1988, **120**, 161. 89/336. *Spectroscopy (Eugene, Oreg.)*, 1988, **3**(3), 24. 89/366. *Fenxi Huaxue*, 1987, **15**, 350. 89/371. *Fenxi Huaxue*, 1987, **15**, 679. 89/387. *Prog. Anal. Spectrosc.*, 1988, **11**, 53. 89/390. *Analyst*, 1988, **113**, 197. 89/391. *Bunseki Kagaku*, 1988, **37**, T50. 89/394.

- Jilin Daxue Ziran Kexue Xuebao*, 1988, (1), 98. **89/411**. *Yankuang Ceshi*, 1987, 6, 245. **89/453**. *Indian J. Pure Appl. Phys.*, 1987, 25, 157. **89/456**. *J. Trace Elem. Electrolytes Health Dis.*, 1987, 1, 99. **89/459**. *GIT Fachz. Lab.*, 1988, 32, 75. **89/465**. *Commun. Soil Sci. Plant Anal.*, 1988, 19, 471. **89/471**. *Methods Enzymol.*, 1988, 158 (Metallobiochemistry, Pt. A), 289. **89/483**. *Isotopenpraxis*, 1988, 24, 79. **89/485**. *Fluoride*, 1987, 20, 162. **89/504**. *Anal. Chem.*, 1988, 60, 971. **89/505**. *Anal. Chem.*, 1988, 60, 973. **89/507**. *Anal. Chem.*, 1988, 60, 1231. **89/511**. *Spectrochim. Acta, Part B*, 1988, 43, 227. **89/512**. *Spectrochim. Acta, Part B*, 1988, 43, 233. **89/518**. *Spectrochim. Acta, Part B*, 1988, 43, 287. **89/528**. *Spectrochim. Acta, Part B*, 1988, 43, 405. **89/529**. *Spectrochim. Acta, Part B*, 1988, 43, 413. **89/531**. *Analyst*, 1988, 113, 1383. **89/532**. *J. Anal. At. Spectrom.*, 1988, 3, 743. **89/533**. *J. Anal. At. Spectrom.*, 1988, 3, 749. **89/534**. *J. Anal. At. Spectrom.*, 1988, 3, 753. **89/535**. *J. Anal. At. Spectrom.*, 1988, 3, 763. **89/536**. *J. Anal. At. Spectrom.*, 1988, 3, 771. **89/537**. *J. Anal. At. Spectrom.*, 1988, 3, 775. **89/538**. *J. Anal. At. Spectrom.*, 1988, 3, 781. **89/539**. *J. Anal. At. Spectrom.*, 1988, 3, 791. **89/544**. *J. Anal. At. Spectrom.*, 1988, 3, 821. **89/551**. *J. Anal. At. Spectrom.*, 1988, 3, 867. **89/554**. *J. Anal. At. Spectrom.*, 1988, 3, 883. **89/561**. *J. Anal. At. Spectrom.*, 1988, 3, 923. **89/705**. *Spectrochim. Acta, Part B*, 1988, 43, 491. **89/715**. *Spectrochim. Acta, Part B*, 1988, 43, 715. **89/717**. *Spectrochim. Acta, Part B*, 1988, 43, 737. **89/718**. *Spectrochim. Acta, Part B*, 1988, 43, 743. **89/722**. *Spectrochim. Acta, Part B*, 1988, 43, 789. **89/724**. *Spectrochim. Acta, Part B*, 1988, 43, 811. **89/843**. *Anal. Proc.*, 1988, 25, 224. **89/889**. *Fresenius Z. Anal. Chem.*, 1988, 331, 51. **89/890**. *Fresenius Z. Anal. Chem.*, 1988, 331, 58. **89/891**. *Fresenius Z. Anal. Chem.*, 1988, 331, 154. **89/900**. *Stahl Eisen*, 1988, 108, 499. **89/902**. *ChemSA*, 1988, 14, 105. **89/916**. *Zavod. Lab.*, 1988, 54(4), 33. **89/921**. *X-Ray Spectrom.*, 1988, 17 (2), 63. **89/922**. *X-Ray Spectrom.*, 1988, 17 (1), 17. **89/925**. *X-Ray Spectrom.*, 1988, 17 (2), 75. **89/926**. *Adv. X-Ray Anal.*, 1987, 30, 77. **89/961**. *Fresenius Z. Anal. Chem.*, 1988, 331, 454. **89/968**. *Adv. X-Ray Anal.*, 1987, 30, 121. **89/979**. *Analisis*, 1988, 16, 261. **89/982**. *Mass Spectrom. Rev.*, 1988, 7, 425. **89/987**. *Adv. X-Ray Anal.*, 1987, 30, 133. **89/988**. *Adv. X-Ray Anal.*, 1987, 30, 165. **89/989**. *Adv. X-Ray Anal.*, 1987, 30, 175. **89/990**. *Adv. X-Ray Anal.*, 1987, 30, 281. **89/991**. *Adv. X-Ray Anal.*, 1987, 30, 183. **89/992**. *Adv. X-Ray Anal.*, 1987, 30, 193. **89/993**. *Adv. X-Ray Anal.*, 1987, 30, 303. **89/996**. *Appl. Radiat. Isot.*, 1988, 39, 331. **89/997**. *Appl. Radiat. Isot.*, 1988, 39, 323. **89/1013**. *X-sen Bunseki no Shinpo*, 1988, 19, 263. **89/1014**. *X-sen Bunseki no Shinpo*, 1988, 19, 201. **89/1015**. *X-sen Bunseki no Shinpo*, 1988, 19, 217. **89/1016**. *X-sen Bunseki no Shinpo*, 1988, 19, 227. **89/1017**. *X-sen Bunseki no Shinpo*, 1988, 19, 237. **89/1022**. *Glastech. Ber.*, 1988, 61(3), 75. **89/1027**. *Gold Bull.*, 1988, 21, 29. **89/1028**. *Biol. Trace Elem. Res.*, 1988, 16, 87. **89/1030**. *Nucl. Instrum. Methods Phys. Res., Sect. A*, 1988, A266(1-3), 318. **89/1031**. *Nucl. Instrum. Methods Phys. Res., Sect. A*, 1988, A266(1-3), 308. **89/1057**. *Ann. Occup. Hyg.*, 1988, 32, 179. **89/1066**. *Kenkyu Hokoku - Himeji Kogyo Daigaku*, 1987, (40, A), 100. **89/1067**. *Kenkyu Hokoku - Himeji Kogyo Daigaku*, 1987, (40, A), 106. **89/1072**. *X-sen Bunseki no Shinpo*, 1988, 19, 209. **89/1090**. *Anal. Proc.*, 1988, 25, 328. **89/1218**. *J. Radioanal. Nucl. Chem.*, 1988, 127, 243. **89/1223**. *Biol. Trace Elem. Res.*, 1988, 16, 151. **89/1225**. *J. Chromatogr.*, 1988, 437, 322. **89/1453**. *Adv. X-Ray Anal.*, 1987, 30, 315. **89/1456**. *Anal. Chem.*, 1988, 60, 2209. **89/1466**. *Appl. Spectrosc.*, 1988, 42, 729. **89/1478**. *Quim. Anal. (Barcelona)*, 1988, 7, 66. **89/1487**. *Nucl. Instrum. Methods Phys. Res., Sect. B*, 1988, B34, 118. **89/1493**. *X-Ray Spectrom.*, 1988, 17, 85. **89/1494**. *X-Ray Spectrom.*, 1988, 17, 107. **89/1495**. *X-Ray Spectrom.*, 1988, 17, 145. **89/1496**. *X-Ray Spectrom.*, 1988, 17, 161. **89/1507**. *GIT Fachz. Lab.*, 1988, 32, 799. **89/1516**. *Spectrochim. Acta, Part B*, 1988, 43, 917. **89/1520**. *Spectrochim. Acta, Part B*, 1988, 43, 955. **89/1525**. *Chem. Geol.*, 1988, 69, 235. **89/1559**. *J. Res. Natl. Bur. Stand. (US)*, 1988, 93, 379. **89/1576**. *Fenxi Huaxue*, 1988, 16, 279. **89/1577**. *Shimane Daigaku Chishitsugaku Kenkyu Hokoku*, 1987, (6), 161. **89/1578**. *X-sen Bunseki no Shinpo*, 1988, 19, 251. **89/1582**. *Zhongguo Kexue Jishu Daxue Xuebao*, 1988, 18, 89. **89/1588**. *IEEE Trans. Nucl. Sci.*, 1988, 35, 93. **89/1589**. *Neue Huette*, 1988, 33, 234. **89/1591**. *Archaeometry*, 1988, 30, 227. **89/1612**. *J. Trace Microprobe Tech.*, 1987, 5, 327. **89/1613**. *J. Agric. Food Chem.*, 1988, 36, 1211. **89/1624**. *J. Phys., Colloq.*, 1987, 1, C9-103. **89/1625**. *Analyst*, 1988, 113, 1837. **89/1631**. *Spectrochim. Acta, Part B*, 1988, 43, 679. **89/1638**. *IEEE Trans. Nucl. Sci.*, 1988, 35, 47. **89/1639**. *Isotop. En. Praxis*, 1988, 24, 72. **89/1659**. *J. Anal. At. Spectrom.*, 1988, 3, 175R. **89/1670**. *J. Anal. At. Spectrom.*, 1988, 3, 1127. **89/1674**. *J. Anal. At. Spectrom.*, 1988, 3, 1145. **89/1675**. *J. Anal. At. Spectrom.*, 1988, 3, 203R. **89/1736**. *Zh. Anal. Khim.*, 1988, 43, 1247. **89/1744**. *Fresenius Z. Anal. Chem.*, 1988, 331, 129. **89/1756**. *Spectroscopy (Eugene, Oreg.)*, 1988, 3(8), 16. **89/1763**. *Anal. Sci.*, 1988, 4, 339. **89/1767**. *X-Ray Spectrom.*, 1988, 17, 155. **89/1768**. *X-Ray Spectrom.*, 1988, 17, 89. **89/1769**. *X-Ray Spectrom.*, 1988, 17, 139. **89/1782**. *Thin Solid Films*, 1988, 157, 283. **89/1783**. *Thin Solid Films*, 1988, 157, 325. **89/1788**. *Anal. Chem.*, 1988, 60, 1217. **89/1790**. *Fresenius Z. Anal. Chem.*, 1988, 331, 216. **89/1841**. *At. Spectrosc.*, 1988, 9, 119. **89/1845**. *Anal. Proc.*, 1988, 25, 385. **89/1872**. *Fresenius Z. Anal. Chem.*, 1988, 332, 232. **89/1875**. *X-Ray Spectrom.*, 1988, 17, 195. **89/1877**. *Bunseki Kagaku*, 1988, 37, 503. **89/1878**. *Bunseki Kagaku*, 1988, 37, 538. **89/1895**. *Dokl. Bolg. Akad. Nauk*, 1988, 41(6), 59. **89/1896**. *Lihua Jianyan, Huaxue Fence*, 1988, 24, 76. **89/2143**. *Fresenius Z. Anal. Chem.*, 1988, 331, 133. **89/2554**. *Chem Geol.*, 1988, 68, 31. **89/2555**. *Int. J. Mass Spectrom., Ion Processes*, 1987, 77, 155. **89/2556**. *Earth Planet. Sci. Lett.*, 1987, 85, 356. **89/2557**. *Earth Planet. Sci. Lett.*, 1987, 85, 343. **89/2558**. *Geochim. Cosmochim. Acta*, 1987, 51, 2527. **89/2559**. *Int. J. Mass Spectrom., Ion Processes*, 1987, 79, 61. **89/2560**. *J. Radioanal. Nucl. Chem.*, 1987, 118, 225. **89/2561**. *Microbeam. Anal.*, 1986, 21, 471. **89/2562**. *Nature (London)*, 1987, 330, 154. **89/2563**. *Nature (London)*, 1987, 330, 242. **89/2564**. *Eur. Spectrosc. News*, 1987, (76), 10. **89/2565**. *J. Anal. Chem. USSR*, 1987, 42, 318. **89/2566**. *Fresenius Z. Anal. Chem.*, 1987, 328, 485. **89/2567**. *Mikrochim. Acta*, 1987, 1, 269. **89/2568**. *Mikrochim. Acta*, 1987, 1, 275. **89/2569**. *Mikrochim. Acta*, 1987, 1, 295. **89/2570**. *Mikrochim. Acta*, 1987, 1, 302. **89/2571**. *Mikrochim. Acta*, 1987, 1, 309. **89/2572**. *Mikrochim. Acta*, 1987, 1, 313. **89/2573**. *Mass Spectrom. Rev.*, 1988, 7, 71. **89/2574**. *Anal. Chem.*, 1987, 59, 2472. **89/2575**. *Anal. Chem.*, 1987, 59, 1072A. **89/2576**. *Anal. Chem.*, 1987, 59, 2662. **89/2577**. *Geochim. Cosmochim. Acta*, 1987, 51, 2605. **89/2578**. *Geochim. Cosmochim. Acta*, 1987, 51, 2623. **89/2579**. *Geochim. Cosmochim. Acta*, 1987, 51, 2699. **89/2580**. *Geochim. Cosmochim. Acta*, 1987, 51, 2707. **89/2581**. *Nature (London)*, 1988, 331, 321. **89/2582**. *Anal. Chem.*, 1987, 59, 2034. **89/2583**. *Anal. Chem.*, 1987, 59, 2570. **89/2584**. *Inorg. Chim. Acta*, 1987, 140, 215. **89/2585**. *Zfi-Mitt.*, 1987, (134), 163. **89/2586**. *Inorg. Chim. Acta*, 1987, 140, 277. **89/2587**. *J. Environ. Radioact.*, 1987, 5, 425. **89/2588**. *Nature (London)*, 1988, 331, 579. **89/2589**. *Nature (London)*, 1988, 331, 604. **89/2590**. *Nature (London)*, 1988, 331, 705. **89/2591**. *Bunseki Kagaku*, 1988, 37, 1. **89/2592**. *Environ. Sci. Technol.*, 1987, 21, 1075. **89/2593**. *Appl. Surf. Sci.*, 1988, 31, 103. **89/2594**. *Acta Chim. Hung.*, 1987, 124, 931. **89/2595**. *Earth Planet. Sci. Lett.*, 1988, 87, 1. **89/2596**. *Appl. Phys.*, 1987, A44, 339. **89/2597**. *Anal. Chem.*, 1988, 60, 345. **89/2598**. *Acta Chim. Hung.*, 1987, 124, 923. **89/2599**. *Earth Planet. Sci. Lett.*, 1988, 87, 249. **89/2600**. *Earth. Planet. Sci. Lett.*, 1988, 87, 273. **89/2601**. *Earth Planet. Sci. Lett.*, 1988, 87, 293. **89/2602**. *Earth Planet. Sci. Lett.*, 1988, 87, 367. **89/2603**. *Earth Planet. Sci. Lett.*, 1988, 87, 13. **89/2604**. *Earth Planet. Sci. Lett.*, 1988, 87, 29. **89/2605**. *Earth Planet. Sci. Lett.*, 1988, 87, 45. **89/2606**.

Earth Planet. Sci. Lett., 1988, **87**, 59.

89/2607. *Earth Planet. Sci. Lett.*, 1988, **87**, 73. **89/2608.**

Earth Planet. Sci. Lett., 1988, **87**, 100. **89/2609.** *Geochim.*

Cosmochim. Acta, 1987, **51**, 3175. **89/2610.** *Geochim.*

Cosmochim. Acta, 1987, **51**, 3215. **89/2611.** *Geochim.*

Cosmochim. Acta, 1988, **52**, 1. **89/2612.** *Geochim.*

Cosmochim. Acta, 1988, **52**, 209. **89/2613.** *Geochim.*

Cosmochim. Acta, 1988, **52**, 309. **89/2614.** *Geochim.*

Cosmochim. Acta, 1988, **52**, 319. **89/2615.** *Geochim.*

Cosmochim. Acta, 1988, **52**, 449. **89/2616.** *Geochim.*

Cosmochim. Acta, 1988, **52**, 461. **89/2617.** *Nature (London)*,

1988, **332**, 429. **89/2618.** *Isot. Geosci.*, 1988, **8**, 173. **89/2619.**

Spectroscopy, 1988, **3**, 27. **89/2620.** *Silikattechnik*, 1986, **37**,

420. **89/2621.** *Springer Ser. Opt. Sci.*, 1987, **55**, 167. **89/2622.**

Earth Planet. Sci. Lett., 1988, **88**, 47. **89/2623.** *Earth Planet.*

Sci. Lett., 1988, **88**, 93. **89/2624.** *Geochem. J.*, 1986, **20**, 209.

89/2625. *Int. J. Mass Spectrom., Ion Processes*, 1988, **83**, 311.

89/2626. *Int. J. Mass Spectrom., Ion Processes*, 1988, **83**,

319. **89/2627.** *Int. J. Mass Spectrom., Ion Processes*, 1988, **83**,

135. **89/2628.** *Isotopenpraxis*, 1988, **24**, 85. **89/2629.** *Kexue*

Tongbao (Foreign Lang. Ed.), 1988, **33**, 221. **89/2630.** *J. Anal.*

Chem. USSR, 1987, **41**, 1275.

89/2631. *Anal. Instrum.*, 1988, **17**, 195. **89/2632.** *Trans. Am.*

Nucl. Soc., 1986, **52**, 359. **89/2633.** *Trans. Am. Nucl. Soc.*,

1986, **52**, 360. **89/2634.** *Anal. Instrum.*, 1988, **17**, 41. **89/2635.**

Anal. Instrum., 1988, **17**, 69. **89/2636.** *J. Radioanal. Nucl.*

Chem., 1986, **107**, 215. **89/2637.** *J. Radioanal. Nucl. Chem.*,

1988, **121**, 385. **89/2638.** *Nature (London)*, 1988, **333**, 623.

89/2639. *Nature (London)*, 1988, **333**, 760. **89/2640.** *Shitsuryo*

Bunseki, 1988, **36**, 1. **89/2641.** *Smithson. Contrib. Earth Sci.*,

1987, **27**, 26. **89/2642.** *Fresenius Z. Anal. Chem.*, 1988, **331**,

104. **89/2643.** *Fresenius Z. Anal. Chem.*, 1988, **331**, 140.

89/2644. *Fresenius Z. Anal. Chem.*, 1988, **331**, 145. **89/2645.**

Fresenius Z. Anal. Chem., 1988, **331**, 150. **89/2646.** *Fresenius*

Z. Anal. Chem., 1988, **331**, 170. **89/2647.** *Fresenius Z. Anal.*

Chem., 1988, **331**, 182. **89/2648.** *Fresenius Z. Anal. Chem.*,

1988, **331**, 174. **89/2649.** *Fresenius Z. Anal. Chem.*, 1988, **331**,

202. **89/2650.** *Fresenius Z. Anal. Chem.*, 1988, **331**, 268.

89/2651. *Sov. Phys. Tech. Phys.*, 1987, **32**, 845. **89/2652.** *Rapid*

Commun. Mass Spectrom., 1988, **2**, 146. **89/2653.** *Fresenius Z.*

Anal. Chem., 1988, **331**, 114. **89/2654.** *Fresenius Z. Anal.*

Chem., 1988, **331**, 189. **89/2655.** *Fresenius Z. Anal. Chem.*,

1988, **331**, 196. **89/2656.** *Fresenius Z. Anal. Chem.*, 1988, **331**,

205. **89/2657.** *Fresenius Z. Anal. Chem.*, 1988, **331**, 214.

89/2658. *J. Radioanal. Nucl. Chem.*, 1988, **127**, 59. **89/2659.**

Fresenius Z. Anal. Chem., 1988, **331**, 209. **89/2660.** *Int. J.*

Mass Spectrom., Ion Processes, 1988, **84**, 231. **89/2661.**

Fresenius Z. Anal. Chem., 1988, **331**, 118. **89/2662.** *Fresenius*

Z. Anal. Chem., 1988, **331**, 111. **89/2663.** *Fresenius Z. Anal.*

Chem., 1988, **331**, 123. **89/2664.** *Fresenius Z. Anal. Chem.*,

1988, **331**, 136. **89/2665.** *Trans. Am. Nucl. Soc.*, 1987, **54**, 35.

89/2666. *Yuanzineng Kexue Jishu*, 1987, **21**, 97. **89/2667.**

Analisis, 1988, **16**, 147. **89/2668.** *J. Res. Natl. Bur. Stand.*

(U.S.), 1988, **93**, 328. **89/2669.** *J. Res. Natl. Bur. Stand.*

(U.S.), 1988, **93**, 392. **89/2670.** *J. Res. Natl. Bur. Stand.*

(U.S.), 1988, **93**, 398. **89/2671.** *J. Res. Natl. Bur. Stand.*

(U.S.), 1988, **93**, 426. **89/2672.** *Isotopenpraxis*, 1988, **24**, 217.

89/2673. *J. Res. Natl. Bur. Stand. (U.S.)*, 1988, **93**, 383.

89/2674. *Int. J. Mass Spectrom., Ion Processes*, 1988, **85**, 137.

89/2675. *Int. J. Mass Spectrom., Ion Processes*, 1988, **85**, 203.

89/2676. *Isot. Geosci.*, 1988, **8**, 311. **89/2677.** *Isot. Geosci.*,

1988, **8**, 337. **89/2678.** *Isot. Geosci.*, 1988, **9**, 1. **89/2679.** *Isot.*

Geosci., 1988, **9**, 15. **89/2680.** *Isot. Geosci.*, 1988, **9**, 109.

89/2681. *Isot. Geosci.*, 1988, **9**, 125. **89/2682.** *Nature*

(London), 1988, **335**, 62.

89/2683. *Radiokhimiya*, 1987, **29**, 397. **89/2684.** *Atmos.*

Environ., 1988, **22**, 1169. **89/2685.** *Mass Spectrom. Rev.*, 1988,

7, 503. **89/2686.** *Appl. Spectrosc.*, 1988, **42**, 1057. **89/2687.**

Appl. Radiat. Isot., 1988, **39**, 603. **89/2688.** *Isotopenpraxis*,

1988, **24**, 282. **89/2689.** *Kexue Tongbao (Foreign Lang. Ed.)*,

1988, **33**, 1027. **89/2690.** *J. Phys. E*, 1988, **21**, 865. **89/2691.**

Appl. Radiat. Isot., 1988, **39**, 530. **89/2692.** *Comments Inorg.*

Chem., 1987, **6**, 145. **89/2693.** *Anal. Chem.*, 1988, **60**, 1786.

89/2694. *Anal. Chem.*, 1988, **60**, 1812. **89/2695.** *Bull. Univ.*

Osaka Prefect., Ser. A, 1987, **36**, 61. **89/2696.** *Kexue Tongbao*

(Foreign Lang. Ed.), 1988, **33**, 1632. **89/2697.** *Smithson.*

Contrib. Earth Sci., 1987, (27), 25. **89/2698.** *Smithson.*

Contrib. Earth Sci., 1987, (27), 38. **89/2699.** *J. Cryst. Growth*,

1988, **89**, 4. **89/2700.** *J. Cryst. Growth*, 1988, **89**, 16. **89/2701.**

Scanning Microsc., 1988, **2**, 1353. **89/2702.** *Talanta*, 1988, **35**,

822. **89/2703.** *Contrib. Mineral. Petrol.*, 1987, **96**, 63. **89/2704.**

Yankuang Ceshi, 1988, **7**, 297. **89/2705.** *Biomed. Environ.*

Mass Spectrom., 1988, **16**, 269.

89/2706. *Spectrochim. Acta, Part B*, 1988, **43**, 1409. **89/2707.**

Biol. Trace Elem. Res., 1987, (12), 223. **89/2708.** *Geokhimiya*,

1987, (7), 1024. **89/2709.** *Izv. Akad. Nauk. Kaz. SSR, Ser.*

Geol., 1986, (6), 75. **89/2710.** *Soil Sci. Soc. Am. J.*, 1987, **51**,

951. **89/2711.** *Youkuangye*, 1986, 5(4), 22. **89/2712.** *Fresenius*

Z. Anal. Chem., 1988, **332**, 640. **89/2713.** *Fresenius Z. Anal.*

Chem., 1988, **332**, 645. **89/2714.** *J. Nucl. Sci. Technol.*, 1988,

25, 641. **89/2715.** *J. Radioanal. Nucl. Chem.*, 1988, **125**, 467.

89/2716. *Fresenius Z. Anal. Chem.*, 1988, **332**, 880. **89/2717.**

Int. J. Environ. Anal. Chem., 1988, **34**, 227. **89/2718.** *Scanning*

Microsc., 1988, **2**, 1853. **89/2719.** *Izv. Vyssh. Uchebn. Zaved.*,

Fiz., 1988, **31**, 89. **89/2720.** *J. Phys. Chem. Ref. Data*, 1988,

17, 1791. **89/2721.** *Int. J. Mass Spectrom., Ion Processes*, 1988,

85, 301. **89/2722.** *Nippon Kagaku Kaishi*, 1988, (5), 735.

89/2723. *Int. Labmate*, 1989, **XIV**, 27.