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Recent Advances in Analytical Spark Source Mass Spectrometry [and Discussion]

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Recent advances in analytical spark source mass spectrometry

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Spark source mass spectrometry is an established technique for the chemical analysis of trace and minor inorganic constituents in many types of material. Its merits are its inherent high sensitivity with detection limits down to a few nanograms per gram and an extremely wide elemental coverage, i.e. essentially all the elements present in the sample. Drawbacks that explain its lesser popularity compared with other techniques result from (1) the complexity and cost of the apparatus, (2) the time-consuming operation when detection is performed with an ion emulsion, and (3) inaccuracies inherent in ion formation and the measurement process.

A review will be given of the basic theory, the instrumentation and a few representative applications. Special reference will be made to recent advances in methodology (e.g. the development of multi-element isotope dilution) and instrumentation: the development of the understanding of the r.f. spark ion formation process, alternative mechanisms for ionization, and the exploitation of ion detectors other than the photographic plate (electrical detection with electron multipliers and position-sensitive detectors).

Introduction

Inorganic analysis by spark source mass spectrometry (s.s.m.s.) is typically performed with a radiofrequency spark source using two sample electrodes and a double focusing mass spectrometer of Mattauch–Herzog geometry. The entire mass spectrum is then simultaneously measured with an ion emulsion (photo plate) detector at a resolving power of up to $M/\Delta M = 10000$. There are variants of this particular instrumentation. The r.f. spark is in some designs replaced by a triggered low-voltage d.c. arc discharge (the d.c. arc). Frequently there is an electrical detection (electron multiplier) mode available as an option.

The technique is now well established for the determination of trace and minor constituents in many different types of material (semiconductors, metals, environmental, geological and biological samples). At present the method has failed to establish itself as a routine analytical technique, principally because the instrumentation is present only in a few well equipped research laboratories.

The merits of s.s.m.s. can be summarized as follows:

(i) simultaneous detection capability of nearly all elements and the availability of isotopic information;

(ii) extremely wide concentration range: major, minor and trace constituents down to concentration levels of *ca.* 10 ng g^{-1} can be detected;

(iii) simple sample preparation: solid conducting materials can be analysed directly, while non-conducting samples need only be mixed with a conducting material. Amounts of sample down to a few milligrams can be analysed.

On the other hand, statements are frequently made in the literature about the insufficient accuracy of the results for many purposes, on large costs of the apparatus and its maintenance, and on the time-consuming character of the method.

In this paper I shall give an up-to-date but in no way exhaustive status report on instrumentation, methodology and analytical characteristics. Other reviews of the technique have been published (e.g. Honig 1970; Ahearn 1972; Cornides 1978; Morrison 1980; Working Group Spark Source Mass Spectrometry 1979, 1982).

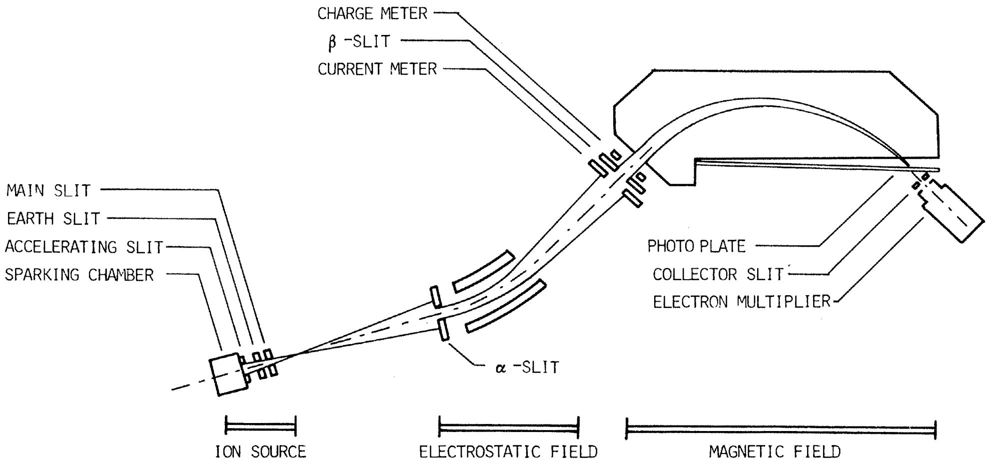

FIGURE 1. Spark source mass spectrometer.

INSTRUMENTATION

The spark source mass spectrograph is shown schematically in figure 1. The basic components date from before World War II: the double focusing mass spectrograph according to Mattauch & Herzog (1934) and the spark discharge of Dempster (1936). They were first made commercially available in 1958 (Craig *et al.* 1959).

The r.f. spark process provides a repetitive series of single high-voltage breakdowns in which the ions are generated. It makes use of an oscillating potential difference of 20–100 kV at *ca.* 1 MHz, which is generated in short pulse trains of variable length (20–200 μs) and with a repetition frequency of $1–10^4$ s^{-1}. In this way, spark parameters may be adapted to the characteristics of the sample, e.g. to prevent overheating of the electrodes while maintaining a high effective electron temperature of the spark.

The spark ion source was originally selected because of its prolific production efficiency of singly charged atomic species with comparable ionization efficiency, and therefore similar sensitivity, for all elements. Also, it puts much less stringent requirements on the conductivity of the sample than the d.c. arc. There are, however, a number of inherent drawbacks:

(i) the r.f. spark is a discontinuous and quite erratic ion source;

(ii) the ionized species are formed with a considerable energy spread, typically 1 keV or more, which may vary according to the spark parameters;

(iii) although spark source mass spectra are considerably simpler than spark atomic emission spectra, several other ionized species complicate the measurement of the singly charged atomic species (M^+): multiply charged ions (M^{n+}), cluster ions (M_n^+) and complex (molecular) ions (e.g. MO^+, MC^+).

These features require the use of a double focusing mass spectrometer of high mass resolution with simultaneous integrating detection of the entire mass spectrum, which is performed with a spectrograph of the Mattauch–Herzog design. After acceleration (20–30 kV), part of the energy distribution is selected (200–600 eV) with the electrostatic sector. These ions then enter the magnetic field and follow a path with a radius of curvature proportional to the square root of ion mass. They are brought to focus along a flat plane onto the photo plate.

Taking into account the low dynamic range of the photographic plate, one analysis consists of a series of sequential exposures. High sensitivity measurements require up to 1 μC of total charge, as measured with the charge monitor (figure 1) at the exit of the electrostatic sector analyser. Ion beam gating circuity can be used to increase sample consumption during measurements at small exposures. Typically, 15 exposures are used to cover the entire concentration range.

Two different operation modes are possible with the electron multiplier detector:

(i) scanning of the mass spectrum with simultaneous selection of the total ion current to permit account to be taken of variations of total ion production;

(ii) switching to specifically chosen m/z values to measure the ion current until a preset total ion charge level is reached.

Mass resolution with electrical selection is in general considerably worse than photo plate detection because the slit widths need to be increased to obtain stable measurement conditions. Advantages are the increased precision with peak switching compared with the photo plate detection mode, and the speed with which data become available.

In the first years of its exploitation, spark source mass spectrometry was often considered as a high-sensitivity substitute for emission spectrography for the analysis of high-purity industrial materials such as semiconductors and metals. The method was then applied primarily as a semi-quantitative survey method for multi-element analysis. If it is assumed that the sensitivity is unity for all elements, a visual comparison between faint lines on the photo plate due to trace elements (at high exposures) and matrix lines (at low exposures) is sufficient for the derivation of analytical information. Such a procedure provides accuracies to within roughly a factor of five, partly due to the crude visual way in which the analytical information is obtained. Most analytical and instrumental developments are concerned with increasing the accuracy and precision of the method. Of special importance is the elemental specificity of the ionization process in the spark source.

The spark ion source

The high-voltage breakdown process between the electrodes and the formation mechanism of ions is still imperfectly understood. The total energy flux is about 10^9–10^{11} W cm^{-2}. This corresponds roughly with the flux in pulsed laser excitation, which explains the comparable analytical characteristics of spark source and laser mass spectra and why the ionization efficiencies of all elements are of the same order of magnitude for both methods (Ramendik *et al.* 1981). Secondary ion mass spectrometry gives rise to a much lower energy flux and the sensitivity varies between elements by several orders of magnitude.

Ramendik (1980) summarizes the rapid sequential stages of the breakdown as follows.

(i) *Atomization*: a weakly ionized plasma is formed near the sample surface with an energy spread of only a few electronvolts. Its composition reflects the sample composition quite accurately. Only about 1% of the total energy is spent in this part of the process (Dherziev *et al.* 1980).

(ii) *Ionization*: nearly all the remaining energy is spent on ionization of the atoms with an average charge of 4–5 and an energy of 200–600 eV.

(iii) *Plasma expansion*: intense recombination occurs with the eventual formation of neutral particles and of *ca.* 1% ions with a charge 1 or 2. The kinetic energy spread of the ions becomes 2–3 keV and a limited bandwidth is selected with the electrostatic sector for mass analysis.

The analytical implications of such a series of events are directly apparent. Excluding any elemental discrimination effects further on in the apparatus, absolute (standardless) analysis requires that the formation efficiencies of M^+ species and their kinetic energy distribution should be the same for all elements, and that there should be no significant variation with matrix composition, i.e. sparking conditions. Criticisms of the lack of accuracy of s.s.m.s. are frequently based on an over-optimistic view of these assumptions. It is well known that elemental sensitivities vary by a factor of roughly 0.2–5, and that they change with sparking conditions.

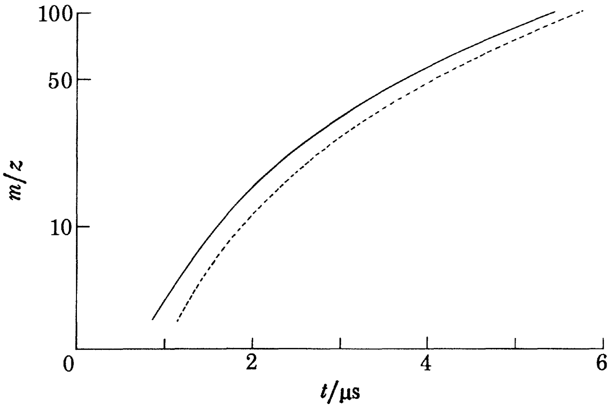

FIGURE 2. Time difference between spark and for singly charged elementary ions and molecular ions. Acceleration voltage 30 kV, Jeol JMS 01 BM-2.

Specially designed spark generators reduce the energy spread to less than 100 eV by controlling the energy liberated in the spark (Ramendik 1980). This provides nearly quantitative transmission through the mass spectrograph, thus increasing sensitivity. Another design in which control of the spark process is improved is the self-triggered mode of damped discharges (Berthod *et al.* 1978), where the spark is reproduced as a quasi-periodic succession of single discharges at one polarity (from one electrode). These improvements need further study before they can be adapted to commercially available instruments.

The formation process of molecular species and cluster ions is not entirely understood and there is some ambiguity in the literature on whether they are formed in the plasma or evaporate directly from the electrode. The spark source process explained earlier indicates the former. On the other hand, spark source mass spectra of many organic compounds are similar to, though more complex than, electron impact spectra (Buck & Hass 1973). This suggests a formation mechanism through evaporation as neutral species. Selective evaporation, probably a secondary process related to electrode heating, also occurs for metals (Van Hoye *et al.* 1979*a*). M. Viczian, J. Van Puymbroeck & R. Gijbels (unpublished results) have made accurate measurements of the formation times of various species. It appears that carbon polymers, C_n^+, appear in the ion beam about 300–500 ns later than the singly charged atomic species and that molecular ions also show a consistent, though not as well defined, delay time. The effect is shown schematically in figure 2. This could be exploited to decrease spectral complexity drastically by incorporating an electronic gate into the mass spectrometer that only transmits ions from a selected portion of the discharge.

The ion production process in the triggered d.c. arc discharge is different from that in the r.f. spark in several respects. Its reproducibility is better, but its use is more restricted to samples of good electrical conductivity. Its ionization efficiency is lower than that of the r.f. spark, but the ion energy distribution, at least if the ignition phase is discriminated against, is more restricted. The arc produces a significantly greater number of highly ionized species, doubly or even triply charged ions being frequently more abundant than singly charged ones. Radermacher & Beske (1979) showed that measurements of the average charge can be used to improve considerably the accuracy of determination.

Alternatives to the spark source

Trace element analysis by mass spectrometry has up to now been nearly exclusively performed by either s.s.m.s. or secondary ion mass spectrometry (s.i.m.s.), depending upon the analytical requirements. S.i.m.s. (Wittmaeck 1980) including microanalysis (see, for example, Morrison & Slodzian 1975; Anderson & Hinthorne 1972) is of particular use for localized surface analysis. Several other alternatives to the spark source have been proposed recently, e.g. the inductively coupled plasma, the hollow cathode discharge and laser ionization.

Inductively coupled plasma mass spectrometry: most of the characteristics of the inductively coupled plasma (i.c.p.) that have led to its use as an excitation source for atomic emission spectrometry are also desirable for mass spectrometry. A small portion of the plasma gas can be extracted, along with the ions formed, through a small orifice into a differentially pumped vacuum system containing an electrostatic lens. The ion energy distribution is small and the mass spectra are simple, which indicates that a quadrupole filter can be used. Detection limits of 0.0002–0.1 mg l^{-1} have been obtained for aqueous solutions (Houk *et al.* 1980). The technique may become a viable alternative for s.s.m.s., especially for water analysis.

Hollow cathode discharge: large neutral atom populations can be obtained that are subsequently ionized in the discharge plasma (Bruhn *et al.* 1979). Initial source models (Mattson *et al.* 1976) have been interfaced to a double focusing mass spectrometer, but the simplicity of such sources plus the stability and the low kinetic energy spread has led to simplified designs with the use of a quadrupole filter.

Both of these ion sources rely on differential pumping to overcome difficulties with high gas flows in the mass spectrometer.

Laser ionization: recent work has shown that uniform elemental sensitivities can be attained through the use of high power density (*ca.* 10^9 W cm^{-2}) laser pulses obtained by a focused Q-switched laser pulse (Consemius & Capellen 1980; Kovalev *et al.* 1978). The energy spread is large unless a particular transmission geometry is used (Wechsung *et al.* 1978; Denoyer *et al.* 1982), which implies the use of a double focusing instrument. Molecular ion intensities are low and the instrumentation is adaptable to a design that allows milliprobe capabilities (Consemius & Svec 1978). Mass resolution and detection limits are comparable with or higher than those obtainable for the r.f. spark. Further experiments will indicate whether the laser ion source can be used as a viable alternative to the r.f. spark.

Detection

Apart from its poor dynamic range, photo plate detection suffers from poor measurement precision and difficulties in extracting quantitative spectral information. Densitometry and calibration of the emulsion is necessary to achieve a precision of 5–20%. There has been an increasing tendency to use computer controlled microdensitometers. Fully implemented systems (see, for example, Millett *et al.* 1974; Burdo *et al.* 1974; Pilate & Adams 1980; Vanderborght & Van Grieken 1978) provide for the following steps: identification of the mass lines, densitometry on the exposure stages, determination of the calibration curve and the calculation of concentrations. Reading and processing of a single plate may require several hours.

The electron multiplier has a large dynamic range, an inherently superior detection efficiency and provides 'real-time' data collection. However, it is more sensitive to fluctuations of the spark process and inhomogeneities in the sample. These factors and poor ion statistics limit the precision of mass scanning to worse than 30% relative standard deviation. Several authors have determined precision of the spark switching mode to be 2–5%.

Significant improvements are possible by repetitive scanning (Mattson & Harrison 1975; De Ceuninck & Adams 1978). Signal averaging then partly corrects for the sources of error. With a fully automated magnetic step scanning system, Dale *et al.* (1981) achieved 2% standard deviation and detection limits of 0.005 μg g^{-1}, while preserving mass resolution around $M/\Delta M = 3000$.

Several recent papers (Donohue *et al.* 1980; Novak *et al.* 1980; Radermacher & Beske 1980) describe simultaneous detection systems based on the use of position-sensitive electro-optical ion detectors. These detectors are an electronic equivalent of the photo plates and they incorporate many of the desirable features of the photo plate and the electron multiplier. Currently available detectors are small, spatial (mass) resolution is still limited and there are a number of less desirable features. However, technological progress will probably make them an alternative to the other detection systems in the near future.

ACCURATE ANALYSIS

For accurate quantitative analysis, differences in ionization efficiency, selective transmission through the mass analyser and mass-dependent detector response must be taken into account. This is commonly performed by defining relative sensitivity coefficients (r.s.cs) by using a matrix element or another element whose concentration is known:

$$(\text{r.s.c.})_{\mathrm{x,\,i,\,z}} = \left\{\left(\frac{C_{\mathrm{x}}}{C_{\mathrm{i}}}\right)_{\text{determined}} \Bigg/ \left(\frac{C_{\mathrm{x}}}{C_{\mathrm{i}}}\right)_{\text{true}}\right\}_{\mathrm{z}},$$

where x, i, z refer to unknown, reference and matrix respectively. The true concentration ratio is derived from a standard sample.

Numerous authors have reported r.s.c. determinations in a number of different materials. However, published r.s.cs are often difficult to compare because of differences in definition or because they are often calculated with respect to different reference elements. In addition, they may depend on the characteristics of the instrument used and on a number of experimental parameters such as spark conditions, spark geometry with respect to entrance slit, and accelerating voltage. Finally, contradictory results may be a reflection of a general lack of reproducibility

(Pustonit & Sikharulidze 1981). In general, agreement is rather poor and there is conflicting evidence on the effect of matrix changes on sensitivity (Jackson & Whitehead 1966; Hamilton & Minski 1972; Jaworski & Morrison 1974; Bacon & Ure 1980; Van Hoye *et al.* 1980*a*, *b*). In a thorough study on the analysis of *ca.* 30 standards of iron, copper, aluminium and zinc and their alloys, Van Hoye *et al.* (1978, 1979, 1980*a*, *b*) showed the following.

(i) R.s.cs are independent of the elemental concentration.

(ii) Significant differences exist between r.s.cs determined by photographic and electrical detection (Van Hoye *et al.* 1980*a*). After correction for the response of the detectors on ion mass and for a smaller influence of ion energy distribution and slit settings, fair agreement is obtained between both detection modes.

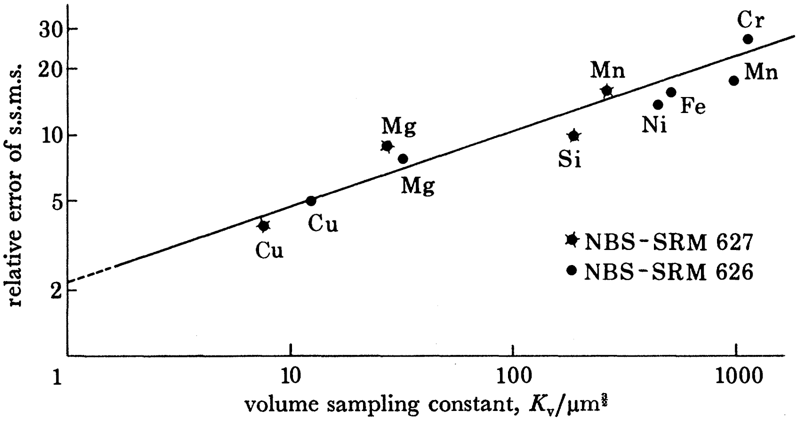

Figure 3. Relation between volume sampling constant obtained by ion microscopy and relative error of spark source mass spectrometry.

Table 1. Relative sensitivity coefficients for several metallic matrices

matrix . . . element	iron	copper	aluminium	zinc
Al	—	1.3 ± 0.2	1.08 ± 0.06	1.1 ± 0.3
Si	—	0.96 ± 0.09	0.84 ± 0.08	0.8 ± 0.2
Cr	1.7 ± 0.1	1.7 ± 0.2	1.6 ± 0.1	1.6 ± 0.6
Ni	0.82 ± 0.06	0.71 ± 0.07	0.74 ± 0.07	0.8 ± 0.2
Cu	1.6 ± 0.1	0.68 ± 0.06	0.67 ± 0.05	0.6 ± 0.1
Sn	4.2 ± 0.7	2.3 ± 0.5	2.2 ± 0.3	2.1 ± 0.5
Pb	—	2.8 ± 0.7	2.8 ± 0.4	2.7 ± 0.8

(iii) R.s.cs of elements with low boiling points (e.g. Mn, Zn and Sb) depend on sparking conditions. Electrode temperature appears to be an important parameter; selective evaporation is therefore likely to be the cause of this effect (Van Hoye *et al.* 1980*b*).

(iv) For the other elements, r.s.cs are constant from one metal matrix to another, but considerably different r.s.cs are obtained in a graphite matrix (Vanderborght & Van Grieken 1979).

A selection of r.s.cs as obtained by peak switching for different metals and alloys are shown in table 1. Except for the high sensitivity of copper in the iron matrix, which is consistent with published information, the agreement is satisfactory. The reproducibility varies considerably and depends on the homogeneity of the distribution of the impurities. This dependence is illustrated in figure 3. It shows the relative standard deviation obtained for N.B.S. steel standards SRM-626 and SRM-627 as a function of the volume sampling constant, a factor related to the heterogeneity (Scilla & Morrison 1977) and determined by ion microscopy (Van Craen *et al.* 1981). Figure 3 also shows a residual error of *ca.* 2.6% for perfectly homogeneous distribution of the impurities, a value that corresponds closely with the basic instrumental error of s.s.m.s., which is assumed to be 2.3% (Morrison *et al.* 1972).

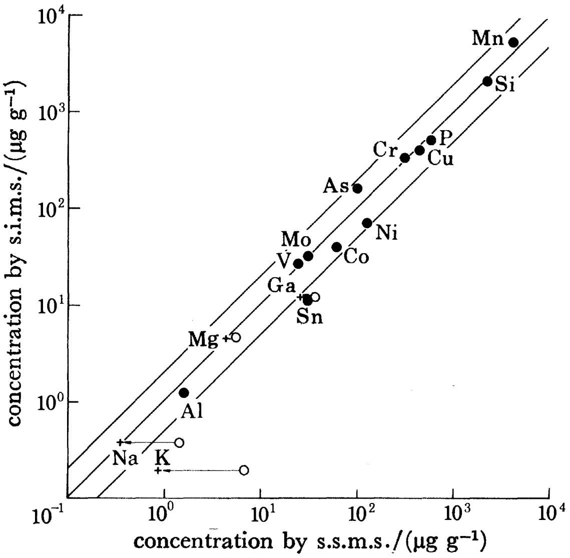

FIGURE 4. Comparison of results obtained with ion microprobe and spark source mass spectrometry for low alloy steel, using standardization with relative sensitivity coefficients (○); uncorrected results for sensitivity (●) and corrected results with the semi-empirical relation of Willardson & Socha (1965) (+).

TABLE 2. AVERAGE ABSOLUTE INACCURACY OF UNCORRECTED RESULTS, R.S.C. APPROACH AND THREE SEMI-EMPIRICAL APPROACHES

		average inaccuracy (%)				
				calculated according to		
matrix (number of samples)	number of elements	no correction	r.s.c.	Willardson & Socha (1965)	Ghosganian & Jensen (1964)	Kai & Miki (1967)
iron and steel (5)	16	220	10	48	48	93
copper and alloys (5)	21	178	13	56	50	50
aluminium and alloys (10)	11	178	10	—†	36	36

† Calculation irrelevant.

The foregoing results refute claims that other sources of poor reproducibility, such as geometrical effects of the electrodes in the spark source (Yanagihari *et al.* 1978; Pustovit & Sikharulidze 1981) cannot be eliminated. It is well known that parameters such as spark gap and spark position affect the precision and the accuracy of the method (Magee & Harrison 1973). However, results indicate that if adequate precautions are taken, relative standard deviations of the order of 5–10% can be obtained (Skogerboe *et al.* 1968). A paper by Schuy & Franzen (1967) provides an up-to-date description of sources of error for the d.c. arc and the photo plate detector.

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Multi-element standard samples are not always available with the required degree of homogeneity, and many attempts have been undertaken to derive r.s.cs from semi-empirical relations based on a number of physical constants such as boiling point, heat of sublimation, covalent radius and ionization potential or cross section for unknown and reference elements. Obviously, such procedures cannot fully take into account variations in elemental sensitivity. Table 2 compares the average absolute inaccuracy obtained with three semi-empirical approaches, with r.s.cs and with the absolute approach. When these results point to a rather dubious overall utility of the approach, it should be stressed that its use may lead to significant gain in accuracy when r.s.cs are unknown. Figure 4 shows a comparison of results obtained with s.i.m.s. and s.s.m.s. For Na, K and Ca the agreement is considerably improved by the use of the method of Willardson & Socha (1965).

TABLE 3. REPLICATE ANALYSIS OF BCR-1 BY I.D.–S.S.M.S.

	concentration/(μg g^{-1}); r.s.d. (%)		best estimate
element	photo plate	electrical det.	μg g^{-1}
Eu	2.13; 6.7	1.97; 2.4	1.95
Gd	6.17; 5.3	6.38; 2.7	6.55
Dy	6.00; 5.3	6.40; 3.6	6.39
Er	3.33; 3.6	3.80; 2.4	3.70
Yb	3.32; 5.5	3.49; 2.7	3.48

Isotope dilution mass spectrometry allows a correction for sensitivity effects for about 50 elements, and significantly it provides reliable r.s.cs without the need for homogeneous standard samples. The technique is now commonly applied, either through a process in which equilibrium is ensured between a sample solution and an isotopically enriched sample, or else by adding an isotopically enriched internal standard to powder samples. Isotopic equilibrium is then assumed to occur in the spark-plasma. Commonly, isotopically doped graphite is used as a conducting additive to the sample. In some applications up to 30 elements have been measured simultaneously. Average relative standard deviations of *ca.* 5 % are possible with photo plate detection. This figure corresponds to the typical deviation of plate uniformity, an error source that isotope dilution cannot correct. Table 3 shows a few results obtained for eight lanthanides in the standard rock BCR-1 (Van Puymbroeck & Gijbels 1982). The best estimate of the true value is shown for comparison.

CONCLUSIONS

Spark source mass spectrometry is a comprehensive analytical technique with relatively uniform sensitivity for most elements in widely diverse materials. Quantitation of the technique, however, may lead to widely divergent results, unless adequate standards are employed to correct for volatilization and ionization differences between matrices and impurities. Results indicate that relative standard deviations of the order of 10 % can be obtained with the spark source, if adequate precautions are taken in the analysis procedure.

Although current equipment is roughly equivalent to that which became available more than 25 years ago, considerable technical progress has been made recently. A better understanding of the spark ion source will probably lead in the near future to more powerful, yet simpler, spark source mass spectrometers. Position-sensitive ion detectors are now approaching the technological development level to be adaptable to spark source mass spectrometry. These detectors share with the photo plate the advantage of being simultaneously an integrating detector. They also have a considerably wider dynamic range and avoid the elaborate process of photo plate development, microdensitometry and calibration. Moreover, they may drastically increase the sensitivity.

Alternative ion sources, especially the pulser laser source and the inductively coupled plasma source, may provide alternative approaches for inorganic multi-element analysis. The laser source may find applications for localized microanalysis of solid samples, while i.c.p.–plasma excitation may be of significance for the analysis of solutions.

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Discussion

J. M. Thomas, F.R.S. (*Department of Physical Chemistry, University of Cambridge, U.K.*). The recent work of Barber & Sedgewick at U.M.I.S.T. has shown the value of the technique of fast-atom bombardment mass spectrometry in organic and biological chemistry. One wonders whether this technique can be applied to the study of inorganic systems. Would Professor Adams please elaborate?

F. Adams. The fast-atom bombardment source pioneered by Barber *et al.* at Manchester has its origins in secondary ion mass spectrometry. Fast-atom bombardment as opposed to a charged-particle beam bombardment is of advantage for obtaining mass spectral information of organic compounds not previously amenable to conventional ionization techniques. This includes high molecular mass involatile or thermally labile compounds. The source yields intense $(M+H)^+$ and $(M-H)^-$ ions. I do not see any direct advantages for inorganic analysis, except that charging effects on insulators could be eliminated.