Screaton and Seemann (17) reported detailed studies on polystyrenes from this same source while searching for reliable standards for gel permeation chromatography. Their data indicated that the nominal molecular weight values of this supplier might be incorrect in some instances. Their fractionation studies of individual polystyrenes and molecular weight results from these fractions, as well as their detection of a range in glass transitions within a given sample, showed the dissimilar composition of their material. This evidence could possibly explain our discrepancies in reproducing $\overline{M}_n$ values among our subject methods. Our results appear to indicate increases in $\overline{M}_n$ values with rise in the level of solvent temperature germane to the particular method, and an association effect appears to be demonstrated. These data illustrate the dilemma of an individual researcher facing the uncomfortable choice of which $\overline{M}_n$ value to apply to each standard when evaluating his own particular method. At this level of molecular weight, there is grave need for dependable calibration standards, particularly materials of narrow molecular weight composition.

The overall result of our adaptation of a QCT to this determination is a well standardized procedure with specifications for apparatus and technique easily duplicated. Not only is demand on sample supply minimal but, since routine determinations are accomplished with a single concentration, analysis time is greatly reduced. Precise, accurate $\overline{M}_n$ values can be obtained without resort to intricate calculations. The fortuitous achievement of a substantial reduction of solute concentration produces with a single charge of sample, an $\overline{M}_n$ value comparable to one from the results of a multiple concentration study, extrapolated to infinite dilution.

(17) R. M. Screaton and R. W. Seemann, *Appl. Polym. Symp.* **8**, 81–110, (1969).

Accuracy of Analysis by Electrical Detection in Spark Source Mass Spectrometry

R. A. Bingham and R. M. Elliott

AEI Scientific Apparatus Limited, Barton Dock Road, Manchester, England

The precision and accuracy of Spark Source Mass Spectrometry using electrical detection of the resolved ion beams has been critically examined. Rapid scanning of the spectrum using a logarithmic ratio amplifier system gives a survey of all elements present in the sample within a few minutes. The precision achieved in this rapid survey is shown to be better than 35% for concentrations down to below the 1 ppm atomic level. Precision of 2% for any chosen elements is achieved using the more accurate peak switching technique down to 1 ppm. The limits of detection are 0.001 ppm atomic for the peak switching technique and 0.01 ppm for scanning. Automatic spark discharge control has been developed permitting unattended operation for long periods and giving improved reproducibility. The absolute accuracy of the peak switching technique has been assessed using standard steel samples. The mean difference between the observed and quoted values was 4.2% for impurities in the 500–2500 ppm range.

SPARK SOURCE MASS SPECTROMETRY has been for some time an established technique for the chemical analysis of impurities where trace concentrations are involved or for a survey analysis of all possible impurities (1). The combination of extremely high sensitivity and overall element coverage makes it unique among analytical methods. In this paper significant advances in the precision and accuracy of the technique are reported.

The most widely used detector in the past has been the ion sensitive photographic plate, which effectively integrates the fluctuating ion currents produced by the spark discharge; in addition it can record all the elements from mass 7 to 240 in a single exposure. These features made the photographic plate a natural choice initially. However, its use is time-consuming and far from convenient, its linear range is only about 30 to 1, and its precision is limited. The basic precision of the emulsion itself is usually estimated to be of the order of 3–6%; Franzen and Schuy (2) have obtained relative standard deviations of 2% but under a strictly defined routine of exposure, development, and measurement.

By contrast the electron multiplier is routinely used for isotopic abundance measurements to 0.1% precision, and the output is immediately accessible in convenient electrical form. Thus, it was natural to investigate the possibility of using the electron multiplier as detector for spark source mass spectrometry; it offered not only improved precision and greater speed and convenience of analysis but also the opportunity for much easier investigation of the other remaining causes of irreproducibility.

Factors such as spark parameters and accelerating voltage had been shown by Halliday et al. (3) to affect precision, and both Bingham et al. (4) and Svec et al. (5) have shown that electrode position was critical. Once these factors were recognized and controlled, the reproducibility improved and analysis could be made with a precision of 5–20%. Removal

(1) A. J. Ahearn, "Mass Spectrometric Analysis of Solids," Elsevier, Amsterdam, 1966, p 5.

(2) J. Franzen and K. D. Schuy, *Z. Anal. Chem.*, **225**, 295 (1967).

(3) J. S. Halliday, P. Swift, and W. A. Wolstenholme, "Advances in Mass Spectrometry," Vol. 3, E. W. Mead, Ed., Institute of Petroleum, London, 1966, p 143.

(4) R. A. Bingham, R. Brown, J. S. Halliday, P. Powers, and P. G. T. Vossen, International Conference on the Characterization of Materials, Pennsylvania State University, University Park, Pa., November 1966.

(5) H. J. Svec, R. J. Conzemius, and G. D. Flesch, 15th Annual Conference on Mass Spectrometry, ASTM E14, Denver, Colo., May 1967.
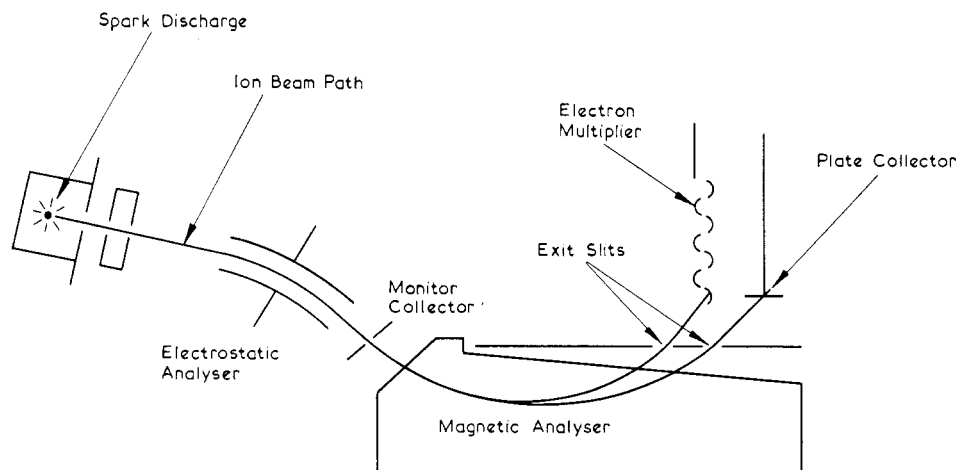
Figure 1. Schematic layout of the AEI MS702 spark source mass spectrometer with electrical detection

of the photoplate contribution to these variables should enable the remaining factors to be studied more precisely.

Several workers have published results of endeavor in the field of electrical detection of spark source mass spectra. Early papers were concerned mainly with isotope ratios [Straus (6), Fluegge (7), Dupzyk et al. (8)] or major constituents (Gorman et al. (9), Chakravarty et al. (10)] and the first systems for general use in trace analysis were reported by Capellen et al. (11) and Argyle and Bingham (12) in 1965. Svec et al. (5, 13, 14) and Bingham et al. (15–17) have subsequently described practical systems in which the key factor was the use of the ratios between individual and total ion currents. Both groups have demonstrated precisions in analytical observations of 0.5–5% (5, 13, 15, 16), and using a system similar to Bingham et al. (15), Evans, Guidoboni, and Leipziger (18, 19) have achieved similar precision.

Bingham et al. (17, 20), have also shown how the electrical output can readily be processed directly on-line by a computer which can then carry out the entire interpretation of the spectrum. Hull (21) has compared electrical detection with photoplate techniques.

The object of this paper is to describe the use of a more fully developed electrical analysis system as now fitted to the AEI MS702 spark source mass spectrometer and to analyze in detail the precision and accuracy of analytical results obtained from a number of different standard materials.

ANALYTICAL PROCEDURE

Figure 1 shows schematically how the electrical detection system is incorporated into the spark source mass spectrometer. The ion source and mass analyzer system are conventional (22). The monitor collector, between the analyzers, collects a fixed fraction of the total ion beam before mass separation. The electron multiplier behind the exit slit is used to collect the individual ion species. The alternative plate collector is normally used only for major constituents.

The ratio between the specific ion current at the electron multiplier and the fraction of the total ion current collected at the monitor is a measure of the concentration of that specific element. This ratio has to be corrected for relative sensitivity (1, 23), isotopic abundance, and other factors in the same way as for photographic plate detection. However, comparison with a standard sample eliminates the need for all of these corrections. Owing to the linearity of the method (3), a single standard can be used even though the concentration of the elements in the standard may differ by several orders of magnitude from the concentrations being measured. This greatly eases the problem commonly encountered in spectrographic techniques of providing closely similar standards.

Scanning. Two techniques for comparing the individual ion currents with the total ion current have been used. Scanning is generally used for rapid surveys of impurity content

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(7) R. A. Fluegge, 9th Annual Conference on Mass Spectrometry, ASTM E-14, Chicago, Ill., June 1961.
(8) R. J. Dupzyk, G. W. Barton, R. D. Carver, and R. A. Thomas, 12th Annual Conference on Mass Spectrometry, ASTM E-14, Montreal, Quebec, June 1964.
(9) J. S. Gorman, J. A. Hipple, and J. E. Jones, ANAL. CHEM., **23**, 438 (1951).
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(13) H. J. Svec and R. J. Conzemius, "Advances in Mass Spectrometry," Vol. 4, E. Kendrick, Ed., Institute of Petroleum, London, 1968, p 457.
(14) R. J. Conzemius and H. J. Svec, *Talanta*, **16**, 365–375 (1969).
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(16) R. A. Bingham and P. Powers, 16th Annual Conference on Mass Spectrometry, ASTM E-14, Pittsburgh, Pa., May 1968.
(17) R. A. Bingham, P. Powers, and W. A. Wolstenholme, 17th Annual Conference on Mass Spectrometry, ASTM E-14, Dallas, Texas, May 1969.
(18) C. A. Evans, R. J. Guidoboni, and F. D. Leipziger, 17th Annual Conference on Mass Spectrometry, ASTM E-14, Dallas, Texas, May 1969.
(19) C. A. Evans, R. J. Guidoboni, and F. D. Leipziger, *Appl. Spectrosc.*, **24**, 85–91 (1970).
(20) R. A. Bingham, P. Powers, and W. A. Wolstenholme, Proceedings of the International Conference on Mass Spectrometry, Kyoto, Japan, September 1969.
(21) C. W. Hull, *Int. J. Mass Spectrum Ion Phys.*, **3**, 293–307 (1969).
(22) R. M. Elliott, R. D. Craig, and G. A. Errock, "Instruments and Measurements," Vol. 1, Academic Press, New York, 1961, p 271.
(23) R. Brown, R. D. Craig, and R. M. Elliott, "Advances in Mass Spectrometry," Vol. 2, R. M. Elliott, Ed., Pergamon Press, Elmsford, N. Y., 1963, p 141.

Figure 2. Ratiometer system used in the scanning mode. The output of the summing amplifier is the logarithm of the Collector Current/ Monitor Current ratio
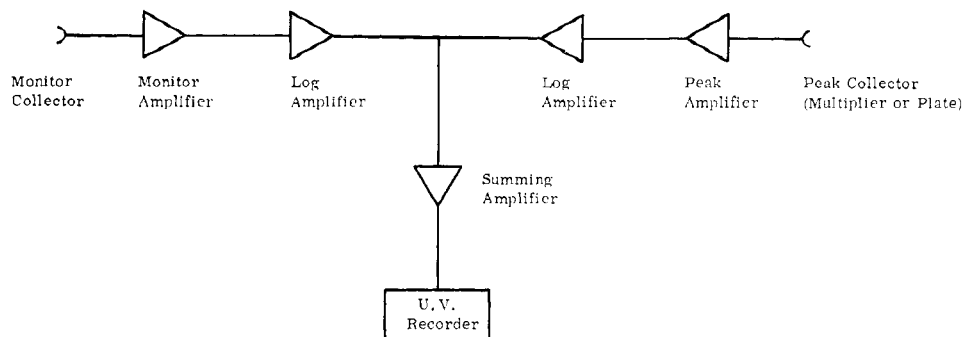
with wide element coverage. In this mode, the ion accelerating voltage is held constant and the magnet field is scanned so that ions of different mass are swept successively over the collector. A wide range of elements, e.g. ^{238}U to ^{7}Li, can be covered in a single scan, which is typically covered in a scan time of three minutes.

The ratio of the collector current to the monitor current is recorded continuously by means of the ratiometer system shown in Figure 2. Values proportional to the relative concentrations of the various elements can then be read directly from the recorder chart. A recording of the portion of the mass range from mass 112 to mass 124 is shown in Figure 3. In the example shown here, the electron multiplier and amplifier gains were set so that the concentration range 0.2–200 ppm was displayed on the three-decade logarithmic scale. By adjustment of either the multiplier or amplifier gain, any other concentration ranges covering a factor of 1000 can be recorded; by running three scans covering the ranges 0.1–100, 10–10^4, and 10^3–10^6 ppm the entire concentration range from 0.1 ppm up to the major elements can be covered in a time of about ten minutes. Thus two important advantages of the logarithmic ratiometer system are that it produces the desired ratio of collector current to monitor current directly, and that it has a wide dynamic range covering concentrations differing by up to a factor 1000. A third important advantage is that it compensates for the fluctuations in the spark discharge.

Amplifiers with a logarithmic characteristic are used because the ratio of the two individual currents is given very conveniently by the difference between the two logarithmic signals. In practice the collector current from the electron multiplier is of opposite sign to the monitor current, and the two logarithmic signals therefore have to be added by the summing amplifier to give the logarithm of the ratio. If the plate collector is used, the signal is inverted before the log amplifier.

The most valuable feature of the scanning mode is the ease with which a rapid qualitative survey of all elements in an unknown material can be made from the recorder chart. Comparison with an internal standard or the matrix then permits semi-quantitative determinations of concentration to be made with a precision better than that achieved by visual photoplate analysis, and direct comparison with a standard leads to quantitative determinations of concentration. As already described elsewhere (17, 20), the output signal can also be taken directly to a computer for on-line data acquisition and automatic interpretation of the data by the computer.

The precision and detection limit achieved depend on the scan time. In a later section it will be shown that the precision for a single three minute scan is of the order of 35%, which is at least as good as the analogous readings from a series of exposures on a photographic plate and attained far more conveniently. This precision may be improved to 10% by averaging. The detection limit is of the order of 0.01 ppm for a ten-minute scan over a mass range 7–238 or a three-minute scan covering a narrower mass range, e.g. 105–210.

Peak Switching. Peak switching is employed where high precision is required on the few selected elements of interest. In this mode, a number of channels are provided so that the ion accelerating voltage can be switched to preset values at which the ion beams of the elements of interest are tuned on to the exit slit and detected by the electron multiplier. This technique is similar to that used in direct reading emission spectrometers, but is more flexible in that any channel can be quickly tuned in to a different element.

For each mass of interest the collector current is integrated while a predetermined charge is collected at the monitor (see Figure 4), the ion beam then being automatically switched off; the value of integrated peak collector charge is recorded before switching to the next peak. The knowledge of the integrated charge obtained from each peak allows an estimation of the relative concentrations to be made; similar analy-

Figure 3. A portion of the ultra-violet recorder chart of the mass spectrum of copper sample CA2 using the scanning mode

The spectrum was scanned at 18 minutes per decade in mass and the portion shown occupied about 1 minute. The intensity scale is logarithmic with X1 corresponding to a concentration level of 0.2 ppm atomic
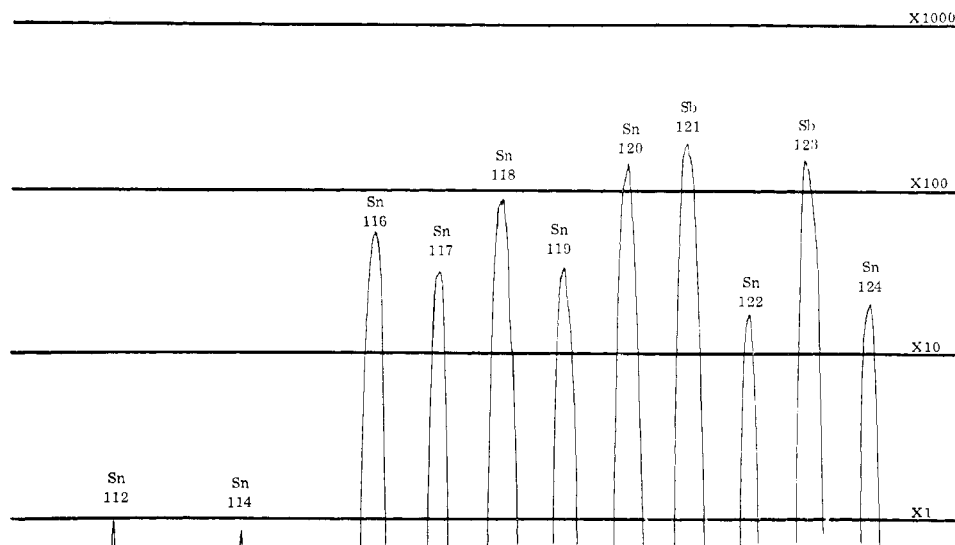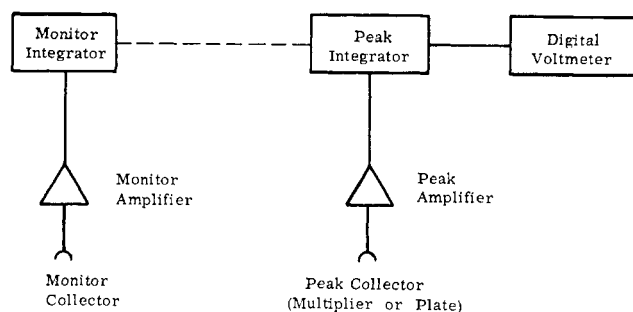
Figure 4. Integration system used in the peak switching mode

The digital voltmeter is read when the monitor integrator has reached a predetermined charge

sis of a standard leads to accurate quantitative analysis of all the elements under consideration. The precision is greatly improved over the scanning mode due to the longer time for which each ion beam is observed.

The choice of integrated monitor charge, and hence of analysis time per element, is governed by the precision required and the concentration level. Figure 5 shows how the reproducibility of the collected charge varies with integrated monitor charge for a wide range of elements in copper. For a monitor charge between 0.3 and 1 nanocoulomb, as normally used, Figure 5 indicates that a precision of the order of 2% or better is achieved for all components greater than 1 ppm. Analytically useful values of precision are still achieved at even lower concentrations. One hundred repeat integrations on ^{204}Pb in copper CA8 at the 0.014-ppm concentration level showed a standard deviation of 9.6%. A detection limit of 0.001 ppm can be achieved for the typical 1-nanocoulomb exposure.

With a 1-nanocoulomb monitor charge, elements can normally be determined at a typical rate of one every ten seconds. Any number of elements may be examined at this rate provided the mass range covered is within a factor 2, e.g. ^{209}Bi to ^{107}Ag or ^{100}Mo to ^{50}Cr. To cover masses outside the factor of 2, the magnet current is reset to a new value and another series of elements can then be examined.

Detection Limits and Precision at Low Concentrations. At very low concentrations, the number of ions collected during the observation of a particular peak may be quite small and part of the variations between successive observations is due to the random rate of arrival of these ions. The precision which could be expected under various conditions can be obtained from Table I which indicates the theoretical number of ions to be expected per peak at different concentrations, assuming continuous ion production and perfect sample homogeneity.

The minimum number of ions required for the existence of a peak to be positively established is about 5 (21, 24), pro-

(24) B. N. Green, T. O. Merren, and J. G. Murray, 13th Annual Conference on Mass Spectrometry, ASTM E-14, St. Louis, Mo., May 1965.
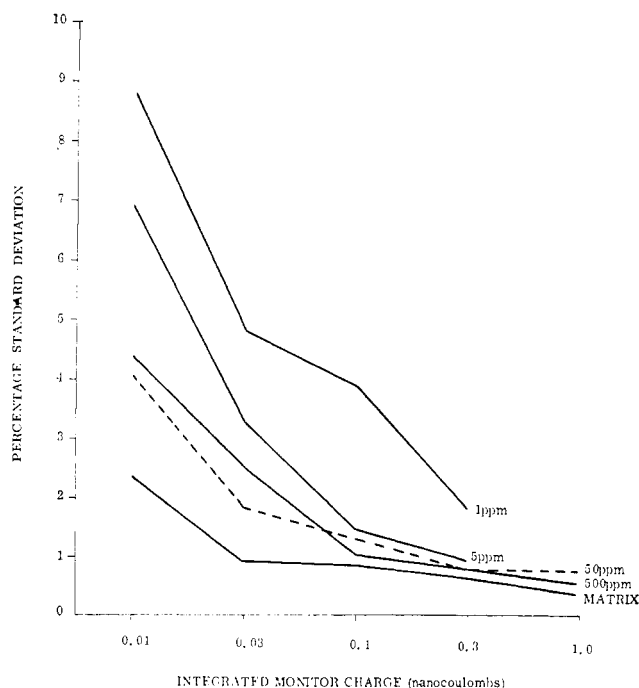
Figure 5. Reproducibility of integrated collector charge measurements for elements in copper present at various concentrations

Data for several elements at similar concentrations are grouped together, viz, Ag and Fe at 5 ppm, Ni and Ag at 50 ppm, and Mn, Ag, and Co at 500 ppm. Each estimate of standard deviation is based on 10 or more determinations

vided single ions can be readily detected by the electron multiplier. In practice a single ion gives a signal many times higher than the noise, and the background signal is negligible (except near the matrix lines) under any of the conditions shown in the Table. The conditions in Table I for which 6 ions are observed, therefore, represent realistic detection limits. When one considers an example from the Table, 600 ions would be observed for a 1-ppm impurity and a 0.1-nanocoulomb monitor charge, and the standard deviation for successive observations would be $100\%/\sqrt{N}$ or 4.1%. This is in good agreement with the experimentally observed value in Figure 5.

A sensitivity of 0.001 ppm for peak switching or 0.01 ppm for scanning is achievable even when the impurity line is close to a major line of the matrix elements. Figure 6 shows the intensity of the background close to the major lines in a copper spectrum. The impurity peaks due to ^{60}Ni$^+$, ^{61}Ni$^+$, ^{62}Ni$^+$, ^{64}Zn$^+$, ^{66}Zn$^+$, ^{121}Sb^{2+}, ^{123}Sb^{2+} can be detected at very low levels since the background is equivalent to less than 0.02 ppm at any of these mass positions, and is indeed less than 0.005 ppm for masses more than 1.5 mass units from the matrix peaks. With photoplate detection the background

Table I. Number of Ions Observed per Peak

| Mode	Monitor signal	Ions collected at monitor	Number of ions observed per peak at concentration, ppm					
			100	10	1	0.1	0.01	0.001
	Integrated charge (nanocoulombs)	Total						
Peak	1	6×10^9	6×10^6	6×10^4	6×10^3	6×10^2	60	6
switching	0.1	6×10^8	6×10^4	6×10^3	6×10^2	60	6	...
	Current (Amperes)	Ions/second						
Scanning[a]	10^{-9} (High)	6×10^9	6×10^4	6×10^3	6×10^2	60	6	...
	10^{-10} (Typical)	6×10^8	6×10^3	6×10^2	60	6	...	...
	10^{-11} (Low)	6×10^7	6×10^2	60	6	...	...	...

[a] Three minute scan over mass range 238–7 at 500 resolution.
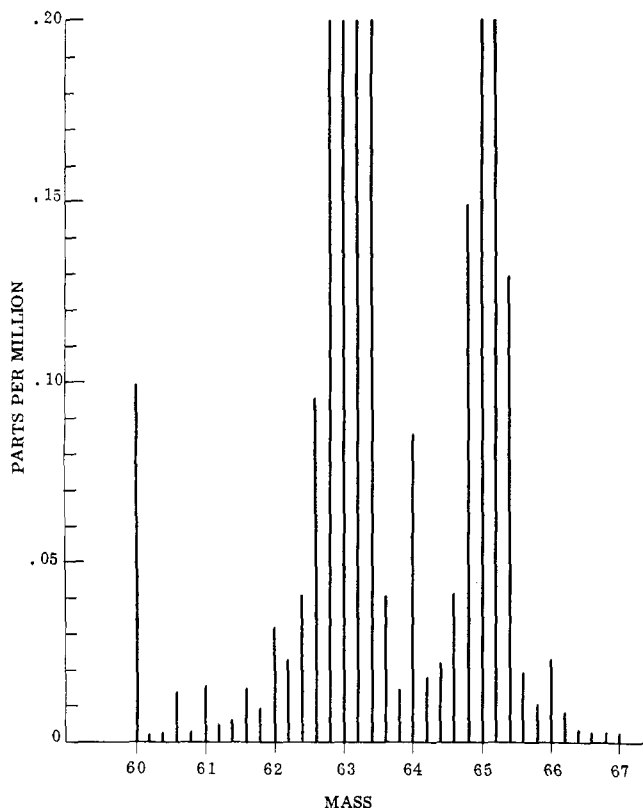
Figure 6. A portion of the spectrum of copper CA2 in the vicinity of the matrix peaks $^{63}Cu^+$ and $^{65}Cu^+$ showing the detectability of trace impurities at the 0.1 ppm level and below

Integrations were made at intervals of 0.2 mass unit. Resolution was 400

level in this region would be of the order of 10 ppm, because of the halation formed around the matrix lines due to secondary particles striking the emulsion.

Automatic Spark Control. In practice, sequential scanning of the peaks in the spectrum will produce quantitative analyses only if the inherent variations in the rf spark discharge are compensated. Although the ratiometer system does compensate for fluctuations, the system would still fail if the spark discharge were not maintained throughout the scan.

The automatic spark control system ("Autospark") developed in our laboratories (25) controls the operation of an rf spark discharge in which one electrode is continuously vibrated with respect to the other. A sensing element close to the rf generator detects the magnitude of the electrode gap, and a feedback circuit then causes the mean position of the vibrated electrode to be adjusted accordingly. The discharge will run unattended for long periods, certainly for times corresponding to a large number of scans. A further advantage of this control system is that the characteristics of the discharge are maintained more constant because of the automatic control of the electrode positions.

Both these features can be seen from the traces in Figure 7. Tungsten is normally a difficult material to spark and in the one-hour run under manual conditions, the ion current fell to zero 67 times and the electrode gap needed adjustment 28 times. Under Autospark control no manual electrode adjustment was needed and the signal never fell to zero for a period long enough for the recorder to respond. The limits of fluctuation of the monitor current are also generally reduced. Many other materials including graphite show
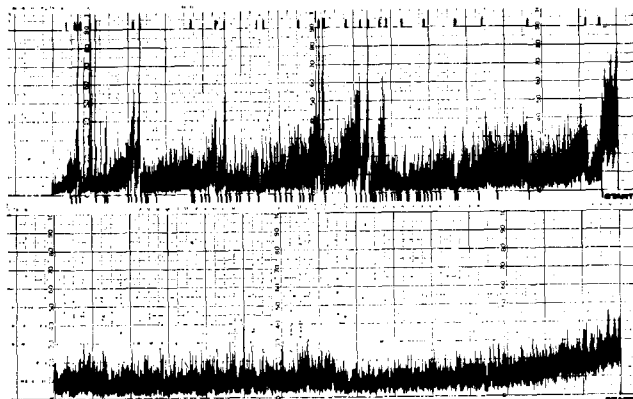
(25) P. Powers, R. Graham, and R. A. Bingham, British Patent applied for.

Figure 7. Traces of monitor signal during sparking of a tungsten sample

Upper trace is for manual control, lower trace for Autospark control. Each trace is for a 1-hour run and is recorded from right to left. Vertical ticks above the trace show points where electrode adjustment was needed, below the trace points where the signal fell to zero

similar behavior; samples of copper and steel have been sparked for more than eight hours without operator intervention.

The automatic spark control is clearly an essential requirement for the scanning technique and is also of great advantage for peak switching. While the mean gap is maintained constant, the instantaneous value is continuously varied over a fixed range, typically from close to zero to twice the mean. Although it has been observed in this laboratory, when manual control was used, that the apparent concentration of chromium in a copper standard can vary by a factor of two between a very narrow gap and the widest gap over which breakdown can occur, with Autospark control these variations are controlled and averaged out. During observation of any impurity the entire range of gap widths is covered a number of times, and the signal observed represents an average of all electrode gap conditions. This enables analytical precision to be improved to 1–2%, as shown later.

RESULTS

A number of series of steel, aluminum, and copper standards have been analyzed and the results of the analyses are presented and analyzed below. The purpose of these experiments was to evaluate systematically the basic limits of the technique, which could then serve as a guide to the performance that might be expected for other materials.

Peak switching results on all three materials are described first, since this is the more precise technique and the basic accuracy of the spark source method can therefore be more readily assessed. Scanning results are then presented for some copper standards in order to indicate the performance to be expected in rapid survey analysis.

The BCS Steel standards employed, with concentrations in the range 0.015 to 0.25% by weight, have been extensively examined by analysts using X-ray and emission spectrometry and chemical methods of analysis. The Johnson Matthey aluminum and copper standards used cover a wider concentration range, from 0.00004 to 1% by weight, and have been extensively studied by emission spectrometry.

Analysis of Peak Switching Results on BCS Steels. The chosen spectral peaks were tuned in to their selected channels using the reference standard sample and the channels adjusted in turn for maximum signal. The resolution was set at 500 (10% valley definition). The multiplier gain was adjusted so that for the selected integrated monitor charge of 0.3 nC the

Sample	Load-ing	Inte-gration	Concentration (% wt) observed			
			Ni	Co	Cr	V
SS12	1	1	0.0420	0.265	0.0250	
		2	0.0431	0.265	0.0238	
		3	0.0431	0.260	0.0234	
	2	1	0.0403	0.230	0.0230	
		2	0.0409	0.232	0.0234	
		3	0.0409	0.226	0.0234	
	Mean observed value		0.04168	0.2462	0.02369	
	Mean quoted value		0.03229	0.2470	0.02671	a
SS14	1	1	0.134	0.173	0.215	0.0143
		2	0.134	0.173	0.214	0.0143
		3	0.134	0.175	0.206	0.0143
	2	1	0.131	0.176	0.204	0.0138
		2	0.127	0.177	0.204	0.0141
		3	0.128	0.172	0.202	0.0138
	Mean observed value		0.1314	0.1742	0.2076	0.01409
	Mean quoted value		0.1270	0.1887	0.1833	0.01457
SS15	1	1	0.0939	0.0631	0.191	0.0499
		2	0.0939	0.0631	0.185	0.0495
		3	0.0950	0.0631	0.183	0.0499
	2	1	0.0933	0.0631	0.182	0.0545
		2	0.0939	0.0622	0.175	0.0552
		3	0.0927	0.0627	0.180	0.0535
	Mean observed value		0.09376	0.06290	0.1828	0.05208
	Mean quoted value		0.07871	0.05855	0.1641	0.05050
SS16	1	1	0.176	0.0266	0.118	0.0503
		2	0.183	0.0271	0.113	0.0516
		3	0.178	0.0275	0.113	0.0524
	2	1	0.170	0.0262	0.110	0.0562
		2	0.166	0.0262	0.106	0.0562
		3	0.172	0.0266	0.105	0.0547
	Mean observed value		0.1741	0.02668	0.1108	0.05358
	Mean quoted value		0.1819	0.02660	0.1000	0.05650
Ref SS17	Mean quoted value		0.2334	0.1258	0.02843	0.1053

a The scatter in the quoted values for V in SS12 was so great (standard deviation 41%) that the observations were excluded from the analysis.

collector integrator reading did not exceed full scale deflection.

The reference sample was then re-set in the ion source so that new surfaces could be sparked. Integrations were performed on each element three times taking the elements in rotation, i.e., Ni—Co—Cr—V, Ni—Co—Cr—V, etc., the integrated values being read directly from a meter. The other standards were then run in the same manner, and each "sample" standard was loaded in the ion source twice. The integrated values obtained were compared with the average of 9 integrations for the reference standard, which was loaded three times.

The samples were positioned in the source as carefully as possible. One electrode was clamped to the 20-kV accelerating plate to maintain a fixed position, with the discharge point on the axis of the slit system. Not more than 1 mm of electrode overlap was allowed to ensure that the discharge occurred within the limits of the slits. The position of the

discharge was thus controlled as carefully as possible in all directions.

Each integration reading took about ten seconds with source conditions of 20-kV rf spark voltage, 1000 pulses per second, and 200 microseconds pulse length. The discharge was maintained using the manually controlled vibrator.

VARIATIONS AND POSSIBLE CAUSES OF ERROR. The analytically determined values are shown in Table II. Each value is determined by comparing the element/monitor ratio for the particular integration with the corresponding average ratio derived from all three runs on the reference standard.

The variations between successive integrations were estimated from the variations within each group of 3 values for a particular sample loading. The mean standard deviation thus calculated (see Appendix) for variations between successive integrations is 1.6%.

Although care was taken in visually aligning the electrodes, it was expected that some analytical errors from this cause might remain. Analysis of the differences between the two sets of values corresponding to different sample loadings (see Appendix) indicates that the mean standard deviation for variations between sample loadings is 4.1%. Evans et al. (19) have shown that this variation can be reduced to 1.9% by positioning the electrodes using a telescope and this procedure will be adopted for future analyses.

Thus there are two separate sources of variation in the values shown in Table II, namely random variations of $\pm1.6\%$ between one integration and the next, and variations of $\pm4.1\%$ due to changes in sample loading position. Since three integrations and two sample positions have been used for each standard sample, one would expect variations in the mean value to be of the order of $\pm\sqrt{\dfrac{1.6^2}{3} + \dfrac{4.1^2}{2}} = \pm3.0\%$. An additional error is contributed by the reference standard, in this case $\pm\sqrt{\dfrac{1.6^2}{3} + \dfrac{4.1^2}{3}} = \pm2.5\%$ since there were three loading positions. The expected errors in the absolute values of concentrations would therefore be of the order of $\sqrt{3.0^2 + 2.5^2} = 3.9\%$ if only random errors were present. The expected mean error in the absolute values would then be $3.9\sqrt{\dfrac{2}{\pi}} = 3.1\%$ (see Appendix).

ABSOLUTE ERRORS OBSERVED. The actual differences between the measured mean values and the quoted concentrations for the 15 elements examined in steel have a mean value (irrespective of sign) of 7.9%. Since the random errors considered in the last section amounted to 3.1%, there is some additional source of error either in the measurements or in the quoted values.

The variations in the values quoted by the referee analysts (26) using chemical techniques have therefore been examined. The standard deviations of the reported values were calculated together with the overall spread, and these are plotted against concentration in Figure 8. It is clear that in the reported values the scatter increased markedly as the concentration decreased, which must indicate either larger errors in the techniques used, or increased inhomogeneity, at the 0.01–0.05% concentration level.

The percentage standard deviation of these reported values has an average value of 5.8% for the 15 concentration levels involved. Each spark source determination is compared

(26) Certificates of Analysis, Bureau of Analysed Samples Limited, Newham Hall, Middlesbrough, England.

PERCENTAGE STANDARD DEVIATION

15

10

5

0

0.01   0.02   0.05   0.1   0.2

CONCENTRATION (% Wt)

Figure 8. Standard deviations calculated from the analytical values recorded by referee analysts for Ni, Co, Cr, and V in steel standards SS12, 14, 15, 16 and 17
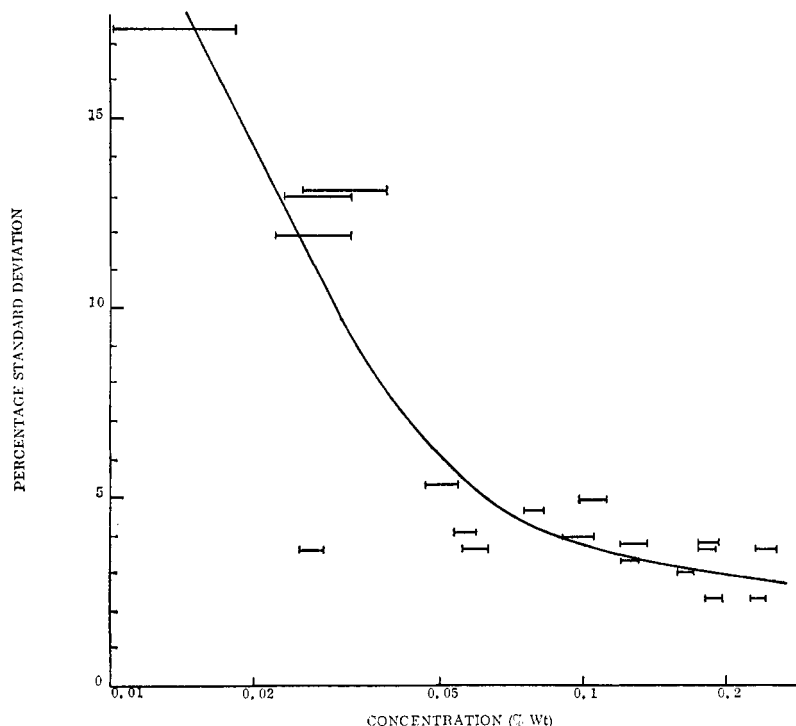
with the ratio between two of the quoted values, and the probable effect of these variations on the reliance to be placed on the ratio can be expressed as a probable mean error e. If σ_1 is the standard deviation for the reported values for the element and sample concerned, σ_2 the corresponding standard deviation for the same element in the reference standard and n_1 and n_2 the number of analysts reporting the values, the probable mean error $e = \sqrt{\dfrac{2}{\pi}\left(\dfrac{\sigma_1{}^2}{n_1} + \dfrac{\sigma_2{}^2}{n_2}\right)}$. The individual values of e are listed in Table III. The mean value is 4.4%. If any systematic errors are also present in the chemical techniques used for the reference analyses, the contribution of uncertainties in the quoted values could be higher than 4.4%.

The probable error due to the limited number of significant figures quoted by the referee analysts was also examined, but was found to be small ($\pm0.25\%$) in comparison with the other possible causes of error.

The errors and their possible sources can be summarized as follows:

Mean difference between observed and quoted values (%)   7.9

Expected mean error in the absolute value due to spark source variations (%)   3.1

Probable mean error in the quoted values (%)   4.4

Average probable error due to rounding-off quoted values (%)   0.25

It is interesting to observe the correlation between the individual values of observed percentage absolute error, which can be calculated from Table II, and the variations in the reference analyses in Table III. The calculated correlation coefficient r is 0.40 (perfect correlation, $r = 1$; no correlation, $r = 0$) which Student's "t" test shows is significant at the 15% level. One is therefore justified in suspecting that many of the higher errors may arise in part from some factor connected with the standard.

If the concentrations with the 9 lowest standard errors of the referee analysts quoted values are selected from Table III,

Table III. Expected Errors Due to Variations in Quoted Values, %

	Ni	Co	Cr	V
SS12	6.1	2.1	8.2	...
SS14	1.8	1.8	6.2	10.0
SS15	2.4	2.1	6.1	4.2
SS16	2.1	2.2	6.2	3.6

the mean difference between the observed and quoted values falls to 4.2%, and the analysis of these errors then appears as follows:

Mean difference between observed and quoted values (%)   4.2

Expected mean error in the absolute value due to spark source variations (%)   3.5

Probable mean error in the quoted values (%)   3.0

Average probable error due to rounding-off of quoted values (%)   0.14

Analysis of Peak Switching Results on Aluminum and Copper Standards. Four of the Johnson Matthey aluminum standards AA1 to AA4, and five copper standards CB0, 1, 2, 3, and 8 were analyzed in a similar way. However, comparison with the quoted values was not made in such detail because the values were quoted to only two significant figures and in many cases only to one.

For a value quoted to one significant figure, e.g., 2 or 0.002, one must assume that the true value may lie anywhere between 25 and 15 or within $\pm25\%$ of the quoted value. For a number of values quoted in this way, the errors would be evenly distributed between zero and the extreme values, so that in the example quoted here the probable average rounding-off error would be half of the extreme value of 12.5%.

Calculating these rounding-off errors for each quoted elemental concentration in the aluminum standards AA1-3 used as samples, combining these values with the corresponding rounding-off error value for the reference standard

Sample	Loading	Integration	Concentration (% wt) observed				
			Mn	Fe	Ni	Cu	Zn
		1	0.00277	0.0532	0.00258	0.00350	0.00342
	1	2	0.00264	0.0566	0.00255	0.00319	0.00332
AA1		3	0.00249	0.0550	0.00244	0.00355	0.00332
		1	0.00277	0.0581	0.00251	0.00355	0.00300
	2	2	0.00277	0.0581	0.00248	0.00410	0.00295
		3	0.00277	0.0581	0.00251	0.00350	0.00311
	Mean observed value		0.00270	0.0565	0.00251	0.00357	0.00319
	Quoted value		0.002	0.055	0.0025	0.0015	0.002
		1	0.00709	0.105	0.00461	0.00527	0.00514
	1	2	0.00709	0.107	0.00456	0.00459	0.00488
AA2		3	0.00693	0.108	0.00456	0.00542	0.00492
		1	0.00603	0.107	0.00431	0.00510	0.00501
	2	2	0.00618	0.116	0.00409	0.00527	0.00478
		3	0.00632	0.118	0.00394	0.00542	0.00496
	Mean observed value		0.00661	0.110	0.00435	0.00524	0.00495
	Quoted value		0.007	0.10	0.004	0.006	0.005
		1	0.0190	0.199	0.0092	0.0192	0.0105
	1	2	0.0192	0.188	0.0096	0.0190	0.0106
		3	0.0188	0.197	0.0090	0.0196	0.0105
AA3		1	0.0192	0.184	0.0096	0.0176	0.0106
	2	2	0.0192	0.186	0.0094	0.0168	0.0105
		3	0.0188	0.195	0.0092	0.0165	0.0108
	Mean observed value		0.0190	0.192	0.0093	0.0181	0.0106
	Quoted value		0.018	0.19	0.010	0.02	0.010
Ref AA4	Quoted value		0.07	0.76	0.02	0.065	0.025

AA4, and taking an average, one concludes that the probable average error in an analytical determination due to the limited number of significant figures quoted is 6.2%. The corresponding probable average error for the 15 concentration values in copper would be 7.3%.

These uncertainties are themselves higher than those expected from the spark source measurements, which are shown in Table IV and explained in the following paragraphs. Furthermore we have no independent basis for assessing the accuracy of the quoted values in this case, since no list of values obtained by a panel of referee analysts is available for these standards. The analysis of the results is therefore limited to calculation of the variations between integrations and the effects of sample loading and the probable effects on the absolute errors.

The procedure for the aluminium standards was similar to that used with the BCS steels with the following exceptions:

(a) the exposure value used was 1 nanocoulomb
(b) only two integrations were made on the reference standard
(c) the rf spark voltage was 12 kV

The analytically determined values are shown in Table IV. These values were analyzed in the same way as the steel results and indicated variations between integrations of ±3.3% and sample loading variations of ±5.1%. Hence, one would expect variations in the mean value of $\pm\sqrt{\dfrac{3.3^2}{3} + \dfrac{5.1^2}{2}} =$ 4.1%. The reference standard would contribute a similar variation and the expected mean errors in the absolute values of concentrations would therefore be of the order of $4.1\sqrt{2}$.

$\sqrt{\dfrac{2}{\pi}} = 4.6\%$ if only random errors were present.

The procedure for the copper standards was similar to that for steel and aluminium except that:

(a) the exposure value used was 0.1 nanocoulomb
(b) five integrations were made on each sample but each sample was only loaded once
(c) the reference standard was run before each sample run
(d) the integrated values were read from a DVM
(e) the rf spark voltage was 40 kV

The analytically determined values are shown in Table V. Analysis of these results can only give a measure of the variations between integrations; the standard deviation is 2.9%.

A further series of measurements was made on silver in copper standard CA4. Silver, which was at a concentration level of 12 ppm atomic, mixes easily in a copper matrix, and represents a fairly homogeneous standard. The sample was loaded, measured, and removed from the source eight times, each measurement being a series of ten integrations. The standard deviation of the variations between integrations was 1.8% and between sample loading 4.0%. These variations correspond closely to those seen for the steel measurements, but in this case at a much lower concentration level.

At even lower concentrations, useful results can still be achieved as shown by the 9.6% standard deviation between successive integrations observed for 0.014 ppm of ^{204}Pb in copper CA8 mentioned earlier.

An example of the linearity of the technique can be seen in Table V where the concentration of the elements in CBO used as the standard are on average 250 times those in CB8.

Summary of Peak Switching Analyses. The sources of the variations to be expected in the values obtained by the spark source mass spectrometry technique are summarized in Table VI.

Table V. Analysis of Standard Copper Samples CB1, 2, 3, 8 Using CB0 as Reference Standard

| Sample | Integration | Concentration (% wt) observed | | | |
		Co	Ni[a]	Fe[a]	Mn
CB1	1	0.0224	0.0146	0.0147	0.0183
	2	0.0226	0.0144	0.0145	0.0178
	3	0.0228	0.0143	0.0148	0.0179
	4	0.0227	0.0144	0.0142	0.0176
	5	0.0224	0.0146	0.0146	0.0178
	Mean observed value	0.0226	0.0145	0.0147	0.0179
	Quoted value	0.02	0.015	0.011	0.018
CB2	1	0.0099	0.0064	0.0044	0.0096
	2	0.0104	0.0062	0.0044	0.0097
	3	0.0101	0.0062	0.0043	0.0095
	4	0.0100	0.0062	0.0044	0.0098
	5	0.0100	0.0066	0.0045	0.0098
	Mean observed value	0.0101	0.0063	0.0044	0.0097
	Quoted value	0.01	0.005–0.01[c]	0.005	0.009
CB3	1	0.0054	0.00147	0.0052	0.00425
	2	0.0056	0.00158	0.0048	0.00425
	3	0.0052	0.00158	0.0049	0.00431
	4	0.0053	0.00158	0.0054	0.00414
	5	0.0054	0.00147	0.0044	0.00420
	Mean observed value	0.0054	0.00154	0.00494	0.00423
	Quoted value	0.0052	0.005	0.0025	0.0035
CB8	1	0.000154	0.000185	0.000279	0.000194
	2	0.000154	0.000196	0.000283	0.000180
	3	0.000162	0.000196	0.000271	0.000180
	4	0.000145	0.000175	0.000297	0.000187
	5	0.000137	0.000169	0.000283	0.000180
	Mean observed value	0.000150	0.000184	0.000283	0.000184
	Quoted value	0.0001[b]	0.0002	0.0004	0.00004
Ref CB0	Quoted value	0.052	0.033	0.023	0.046

[a] Evidence of segregation.
[b] Not detected, analysis by dilution.
[c] Quoted range too great for inclusion in absolute error calculation.

RESULTS—SCANNING

Description of Analytical Runs of Johnson Matthey Copper Standards. The starting point of the downward exponential scan of the magnet current was set to cover the mass range 70–24 (gallium to magnesium) in one minute which would embrace the elements to be analyzed. Scans were made at a resolution of 500 (10% valley). Spark conditions used were 25 kV rf spark voltage, 1000 pulses per second, and 200 μsec pulse length with Autospark control. For these copper samples, the scale displayed on the UV recorder corresponded to an approximate concentration range of 1 ppm to 1000 ppm atomic for the samples containing higher concentrations. For the samples containing lower concentrations, the peak amplifier gain was increased by a factor 10 so that the 0.1 ppm to 100 ppm concentration range was covered. The peak height ratios were then read off the ultraviolet recorder chart using a logarithmically engraved scale.

The reference standard was the first sample loaded into the ion source and five scans were recorded. The same procedure was repeated on each of the sample standards. If any series of samples was run on different days, the reference standard was run after each one.

Variation and Possible Causes of Error. The analytically determined values, for one run of five scans on each sample, are shown in Table VII. Each value is determined by comparing the peak height ratio for the particular scan with the corresponding average peak height ratio derived from the five scans on the reference standard. Silicon was determined using the 29 and 30 isotopes since the levels of silicon were

Table VI. Sources of Variations in Peak Switching Determinations

	Steels SS12, 14, 15, 16 (reference SS17)	Aluminium AA1, AA2, AA3, (reference AA4)	Copper CB1, CB2, CB3, CB8 (reference CB0)	Copper CA4, [109]Ag at 6 ppm Concentration
Variations between integrations (standard deviation, %)	1.6	3.3	2.9	1.8
Variations between sample loadings (standard deviation, %)	4.1	5.1	. . .	4.0
Expected mean error in absolute value (%)	3.1	4.6	. . .	1.7

higher than the other elements and for some samples the silicon 28 peak was above or near the upper limit of the dynamic range.

The variations between individual scans are normally considerably greater in the scanning method than the variations between individual integrations in the peak switching mode. Figure 9 shows the standard deviations for repeat scans for all the elements listed in the Johnson Matthey copper standards CA Series (CA0 and CA2-8), CB Series (CB0-8), and CC Series (CC1-5) plotted against concentration. These standard deviations were all derived from 5 repeat scans as in

Table VII. Analysis of Standard Copper Samples CB1, 2, 3 Using CB0 as Reference Standard:
One Run of Five Scans

| Run 1 Sample	Scan	Concentration (% wt) observed				
		Co	Ni[a]	Fe[a]	Mn	Si
CB1	1	0.0200	0.0138	0.0053	0.0162	0.0133
	2	0.0375	0.0187	0.0096	0.0220	0.0245
	3	0.0265	0.0098	0.0108	0.0239	0.0194
	4	0.0221	0.0200	0.0113	0.0362	0.0227
	5	0.0210	0.0184	0.0150	0.0401	0.0076
	Mean observed value	0.02542	0.01614	0.01040	0.02768	0.01750
	Quoted value	0.02	0.015	0.011	0.018	0.02
CB2	1	0.0175	0.0076	0.0082	0.0210	0.0168
	2	0.0024	0.0066	0.0075	0.0257	0.0153
	3	0.0166	0.0109	0.0066	0.0248	0.0109
	4	0.0150	0.0076	0.0072	0.0100	0.0061
	5	0.0117	0.0081	0.0061	0.0168	0.0122
	Mean observed value	0.01264	0.00816	0.00712	0.01966	0.01226
	Quoted value	0.01	0.005–0.01	0.005	0.009	0.016
CB3	1	0.0071	0.0052	0.0048	0.0130	0.0109
	2	0.0042	0.0043	0.0042	0.0130	0.0053
	3	0.0095	0.0052	0.0030	0.0069	0.0070
	4	0.0062	0.0049	0.0036	0.0069	0.0088
	5	0.0068	0.0046	0.0038	0.0132	0.0079
	Mean observed value	0.00676	0.00484	0.00388	0.01060	0.00798
	Quoted value	0.0052	0.005	0.0025	0.0035	0.004
Ref CB0	Quoted value	0.052	0.033	0.023	0.045	0.049

[a] Evidence of segregation.
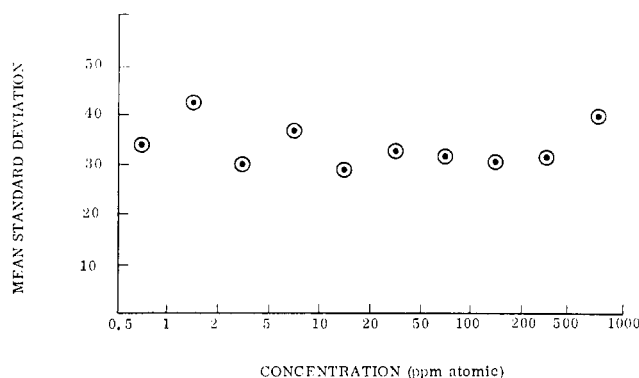
Figure 9. Standard deviations for spark source measurements made on 16 elements in the Johnson Matthey copper standards CA, CB, and CC series over a wide range of concentration using the ratio scanning mode

Table VII. The figure shows very clearly that for the scan conditions used, the reproducibility of individual scans is largely independent of concentration in the range 0.5 to 1000 ppm atomic, the standard deviation for repeat scans on individual elements being in the region of 33% throughout this range.

From the number of ions observed during a peak, given in Table I, one would expect the standard deviation to be smaller, especially at higher concentrations. For example, a 100-ppm component would give typically 6×10^3 ions, and hence on ion statistical grounds alone, one would expect a standard deviation of $100/(6 \times 10^3)^{1/2}$ or 1.3%. The larger variations observed in practice are largely a consequence of the short time (typically 0.1 second) during which each peak is being observed and of the fluctuations in the spark discharge during such short periods of time.

In the case of the CB0–3 standards on which the most de-

tailed examination was carried out, the average standard deviation for repeat scans on individual elements was in fact 42.5%.

One would expect the reliability of the mean of 5 scans to be improved by a factor $\sqrt{5}$ compared with the individual scan values. Such variability would, however, be present in the reference standard runs also, so that the expected variations in the analytical determinations derived from the average of 5 sample scans compared with the average of 5 reference standard scans would be $\frac{42.5}{\sqrt{5}} \times \sqrt{2} = 26.8\%$.

The results from several runs of 5 scans each are shown in Table VIII. In fact, the average standard deviation observed for those determinations is 28.8%, indicating that the variability encountered between runs done with different loadings of the samples, and in some cases on different days, is essentially accounted for by the variation between scans. In view of the fact that the peak switching work for the BCS steels and Johnson Matthey aluminium showed that sample loading effects contributed only a 4–5% variation, this is not surprising.

Absolute Errors Observed. Since the variations observed between runs is 28.8% one would expect the absolute errors in the mean values of the 5 runs to have a mean value of the order of $\frac{28.8}{\sqrt{5}} \times \sqrt{\frac{2}{\pi}} = 10.3\%$ if the only significant errors were random ones. The actual differences between the measured mean values and the quoted concentrations for the 14 determinations have a mean value (irrespective of sign) of 28.3%. Thus, as with the peak switching results for the same standards, there is an additional source of error apart from those due to random variations. As before, there is no list of reported values on which to base an assessment of the source of error, but the mean expected rounding-off error due to the limited number of significant figures quoted is 5.7%.

Table VIII. Analysis of Standard Copper Samples CB1, 2, 3 Using CB0 as Reference Standard: Five Runs of Five Scans Each

| Sample | Run | Concentration (% wt) observed | | | | |
		Co	Ni^a	Fe^a	Mn	Si
	1	0.0254	0.0161	0.0104	0.0277	0.0175
	2	0.0222	0.0043	0.0096	0.0251	0.0100
CB1	3	0.0217	0.0160	0.0124	0.0234	0.0190
	4	0.0265	0.0116	0.0086	0.0168	0.0282
	5	0.0170	0.0098	0.0107	0.0217	0.0315
	Mean observed value	0.02256	0.01156	0.01034	0.02294	0.02124
	Quoted value	0.02	0.015	0.011	0.018	0.02
	1	0.0126	0.0082	0.0071	0.0197	0.0123
	2	0.0122	0.0057	0.0053	0.0122	0.0059
CB2	3	0.0098	0.0128	0.0072	0.0112	0.0076
	4	0.0107	0.0050	0.0049	0.0074	0.0128
	5	0.0157	0.0038	0.0040	0.0148	0.0135
	Mean observed value	0.01220	0.00710	0.00570	0.01306	0.01042
	Quoted value	0.01	0.005–0.01^b	0.005	0.009	0.016
	1	0.0068	0.0048	0.0039	0.0106	0.0080
	2	0.0053	0.0022	0.0030	0.0083	0.0046
CB3	3	0.0046	0.0062	0.0028	0.0072	0.0054
	4	0.0055	0.0031	0.0028	0.0048	0.0035
	5	0.0049	0.0028	0.0026	0.0078	0.0080
	Mean observed value	0.00542	0.00382	0.00302	0.00774	0.00590
	Quoted value	0.0052	0.005	0.0025	0.0035	0.004
Ref CB0	Quoted value	0.052	0.033	0.023	0.046	0.049

^{a} Evidence of segregation.
^{b} Quoted range too great for inclusion in absolute error calculation.

CONCLUSIONS

The precision of the spark source mass spectrometry technique has been improved by the use of electrical detection.

By using the scanning mode, a rapid survey of all elements is obtained with a precision and accuracy of 10–35% for all concentrations down to 1 ppm, and with a detection limit of 0.01 ppm. Because the output is immediately available and easy to interpret, the technique is considerably faster and more convenient than the photoplate method even for a complete survey of the elements. Only 10 minutes is required to obtain the data for a complete analysis covering the concentration range from major elements down to 0.1 ppm.

The convenience of the technique is further improved by the use of automatic spark control; after loading the sample, the instrument can be left to run automatically during the scans. On-line interpretation of the data by computer, identifying peaks, and calculating and printing out the concentrations of all elements within a few minutes (17, 20), is also particularly convenient with the immediately accessible electrical output.

When the peak switching technique is used, the precision with which concentrations can be established relative to one another is better than 2%. When all the factors involved in a truly absolute analytical determination are taken into account, including sample loading and comparison with a known standard, the absolute accuracy should be of the order of 2–5%. For four steel standards with impurity concentrations in the range 500–2500 ppm, absolute differences of 4.2% were observed between the concentrations determined and the quoted values. More than half this error could be attributed to residual uncertainties in the quoted values.

This precision and accuracy should be maintained for concentrations down to a few ppm, rising as the concentration decreases further toward the detection limit of 0.001 ppm. This has been borne out by the routine use of the technique in our laboratories over a wide range of materials.

The precision and accuracy of the peak switching technique is thus considerably better than can be obtained using photoplates under routine analytical conditions, and the spark source mass spectrometric method now compares favorably with other analytical techniques such as emission and X-ray fluorescence spectrometry, particularly at lower concentration levels. Further improvements can be expected as the remaining factors influencing accuracy, such as sample inhomogeneity and availability of standards, are investigated and dealt with.

APPENDIX

Statistical Methods of Analysis of Sources of Variation. We can represent any of the sets of 6 values in Table II by x_{i11}, x_{i12}, x_{i13} (1st sample loading) and x_{i21}, x_{i22}, x_{i23} (2nd sample loading) where the suffix i refers to the particular combination of element and sample.

An estimate of the typical variation between successive integrations can be made from the spread in any of the groups of three values x_{ij1}, x_{ij2}, x_{ij3}. In general, where m successive integrations are run, the groups will have the form x_{ijk} ($k = 1$ to m).

The best estimate of the percentage standard deviation corresponding to this variation which can be made from any one group of m values will be

$$\left\{ \frac{\sum_{k=1}^{m} \left(x_{ijk} - \frac{1}{m} \sum_{k=1}^{m} x_{ijk} \right)^2}{m-1} \right\}^{1/2} \times \frac{100m}{\sum_{k=1}^{m} x_{ijk}} \qquad (1)$$

When $m = 3$ as in Table II, any such single estimate will be a poor one. For example, for Ni in SS14 one obtains 0.0% from sample loading 1 (0.134, 0.134, 0.134) but 2.1% from sample loading 2 (0.131, 0.127, 0.128). But an average taken over a considerable number of groups of 3 will give a good estimate of the variation. For $(n \times N)$ such groups corresponding to N combinations of element and sample and n loadings of each sample, the formula becomes:

Best estimate of percentage standard deviation between
successive integrations =

$$\left\{ \frac{1}{N.n.(m-1)} \sum_{i=1}^{N} \sum_{j=1}^{n} \sum_{k=1}^{m} \left(\frac{m x_{ijk}}{\sum_{k=1}^{m} x_{ijk}} - 1 \right)^2 \right\}^{1/2} \times 100 \quad (2)$$

For $m = 3, n = 2, N = 15$ as in Table II, this formula reduces to 100 and gives a value of 1.6%.

$$100 \left\{ \frac{1}{60} \sum^{90} \left(\frac{3 x_{ijk}}{\sum_{k=1}^{3} x_{ijk}} - 1 \right)^2 \right\}^{1/2} \quad (3)$$

In the same way an estimate of the typical variation between sample loadings can be estimated from the means of the groups, e.g. from the values $(0.134 + 0.134 + 0.134)/3 = 0.134$ and $(0.131 + 0.127 + 0.128)/3 = 0.1287$ for Ni in SS14. The best estimate of the percentage standard deviation corresponding to sample loading which can be made from a group of values, from n loadings and m integrations for each loading, is given by

$$\left\{ \frac{\sum_{j=1}^{n} \left(\sum_{k=1}^{m} x_{ijk} - \frac{\sum_{j=1}^{n} \sum_{k=1}^{m} x_{ijk}}{n} \right)^2}{n-1} \right\}^{1/2} \times \frac{100n}{\sum_{j=1}^{n} \sum_{k=1}^{m} x_{ijk}} \quad (4)$$

When $n = 2$ as in Table II this becomes

$$\sqrt{2} \cdot \frac{|X_{i1} - X_{i2}|}{X_{i1} + X_{i2}} \times 100 \quad (5)$$

where $X_{ij} = \frac{1}{m} \sum_{k=1}^{m} x_{ijk}$, for example the mean values 0.134 and 0.1287 correspond to X_{i1} and X_{i2} for Ni in SS14. The estimate of percentage standard deviation works out in that case to 2.9%.

Any such estimate from two values only will again be a poor one, but here also a statistically good estimate will be obtained by pooling the N individual estimates. We then obtain the general formula

Best estimate of percentage standard deviation between
sample loadings =

$$\left\{ \frac{1}{N(n-1)} \sum_{i=1}^{N} \left[\sum_{j=1}^{n} \left\{ \left(\sum_{k=1}^{m} x_{ijk} - \frac{\sum_{j=1}^{n} \sum_{k=1}^{m} x_{ijk}}{n} \right) \times \frac{100n}{\sum_{j=1}^{n} \sum_{k=1}^{m} x_{ijk}} \right\}^2 \right] \right\}^{1/2} \quad (6)$$

For $m = 3, n = 2, N = 15$ as in Table II this formula reduces to

$$100 \left\{ \frac{2}{15} \sum_{i=1}^{15} \left(\frac{\sum_{k=1}^{3} x_{i1k} - \sum_{k=1}^{3} x_{i2k}}{\sum_{k=1}^{3} x_{i1k} + \sum_{k=1}^{3} x_{i2k}} \right)^2 \right\}^{1/2} \quad (7)$$

and gives a value of 4.1%.

When the mean value of one of the N groups of $(n \times m)$ values is calculated, the standard error of that mean value is of course reduced compared with the variations in the individual values. If the Bessel-corrected estimates of percentage standard deviations are $\hat{\sigma}_s$ for variations between the n sample loadings, and $\hat{\sigma}_i$ for variations between the m integrations, the best estimate of the percentage standard error of the mean is given by $\hat{s} = \sqrt{\frac{\hat{\sigma}_s{}^2}{n} + \frac{\hat{\sigma}_i{}^2}{m}}$. Thus in the case of the steel results in Table II, $n = 2$, $\hat{\sigma}_s = 4.1\%$, $m = 3$, $\hat{\sigma}_i = 1.6\%$, so that $\hat{s} = \sqrt{\frac{4.1^2}{2} + \frac{1.6^2}{3}} = 3.0\%$.

It should be noted that the common expression for the standard error of the mean, $\hat{\sigma}/\sqrt{6}$, where $\hat{\sigma}^2 = \frac{\sum_{6}^{6}(x - \bar{x})^2}{5}$, gives a lower value in this case. But this formula applies only when all the samples are independently selected in a random fashion, whereas in the steel results the values in each of the two groups of three are not independent.

The value obtained is in the nature of a standard error of the mean, i.e. a Gaussian distribution of errors is implied. For a Gaussian distribution of means it can be shown that the mean deviation from the central value is $\sqrt{\frac{2}{\pi}}$ times the standard error.

Since some of the sources of error can be expressed only as mean deviations and the absolute errors are most conveniently expressed in that form, all sources of variation are expressed as actual or expected mean deviations.