

REPORT

No. 2075

**THE OPTIMIZATION OF SOME OF THE
CONDITIONS FOR ANALYSIS BY SPARK-SOURCE
MASS SPECTROMETRY**

by

D.C.G. Pearton and A. Sobiecki

**NATIONAL
INSTITUTE
for
METALLURGY**

**200 Hans Strijdom Road
RANDSBURG
South Africa**

15th October, 1980



NATIONAL INSTITUTE FOR METALLURGY

ANALYTICAL CHEMISTRY DIVISION

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BY SPARK-SOURCE MASS SPECTROMETRY**

**Investigators D.C.G. Pearton and A. Sobiecki
Director of Division T.V. Steele**

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All correspondence to the National Institute for Metallurgy, Private Bag X3015, Randburg, 2125 South Africa.

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SYNOPSIS

The need for improved precision in spark-source mass spectrometry is highlighted. Several parameters, such as photoplate-development technique, instrumental stability and focus, and sparking conditions, were optimized. Measurements made under these optimum conditions attained precisions of more than 12 per cent.

SAMEVATTING

Die behoefte aan beter presisie in vonkbronmassaspektrometrie word beklemtoon. Verskeie parameters soos die fotoplaatontwikkeltegniek, instrumentele stabiliteit en fokus en vonktoestande is geoptimaliseer. Metings wat onder hierdie optimale toestande gedoen is, het 'n presisie van meer as 12 persent bereik.

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1. INTRODUCTION

Certain difficulties have been experienced in the operation of the spark-source mass spectrometer at the National Institute for Metallurgy (NIM). These are a fluctuating and irreproducible accelerating voltage, excessive variations in the magnetic current, photoplates with high backgrounds, and poor focus of the isotope lines. In his critical assessment of vital parameters, Magee¹ showed that electrode positioning, electrode gap, and sparking parameters are also important factors.

The levels of precision and accuracy obtained with this instrument (Tables 1 to 3) are not always acceptable. For instance, the results obtained on a lead sample of high purity by the use of spark-source mass spectrometry (SSMS) and atomic-absorption spectrophotometry (AAS) show reasonable agreement for copper and nickel, but poor agreement for the other elements (Table 1). As can be seen in Table 2, only four out of fifteen elements in a steel standard showed reasonable agreement, and the precision of the results obtained on a copper sample of high purity (Table 3) varied between 10 and 28 per cent, with an average of 20 per cent.

TABLE 1

Results obtained on Sample no. FB-171/1

Element	SSMS	Atomic absorption
Bi	<1 p.p.m.	5,7 p.p.m.
Te	Not detected	98 p.p.m.
Sb	14 500 p.p.m.	3500 p.p.m.
Cu	<2 p.p.m.	<3 p.p.m.
Ni	<2 p.p.m.	<5 p.p.m.

TABLE 2

Results obtained on NBS 461 (steel)

Element	SSMS values %	Preferred values* %
Pb	0,0058	0,003
W	0,011	0,012
Sn	0,021	0,022
Ag	0,0034	0,001
Mo	0,29	0,30
Nb	0,013	0,011
As	0,020	0,028
Ge	0,0021	0,001
Cu	0,26	0,34
Ni	1,4	1,73
Co	0,22	0,26
Mn	0,27	0,36
V	0,01	0,024
P	0,095	0,053
B	0,001	0,0002

* Supplied by the National Bureau of Standards, Washington.

TABLE 3

Precision obtained on copper sample K7

Element	Value, p.p.m.	R.S.D.
⁵⁹ Co	6,10	0,24
⁶⁰ Ni	269	0,21
⁵⁸ Ni	246	0,18
⁵⁶ Fe	113	0,10
⁵⁴ Fe	107	0,18
⁵⁵ Mn	1,04	0,28

R.S.D. = relative standard deviation.

As a study of the literature indicates, better results have been obtained elsewhere. Using electrical detection and standards of steel, aluminium, and copper, Bingham and Elliott² obtained a precision of 2 per cent and an accuracy of 4,5 per cent, but stated that several groups of workers had achieved precisions of more than 5 per cent. Relative standard deviations of 2 per cent were obtained by Franzen and Schuy³ under a strictly defined routine of exposure, development, and measurement, and results on international standards indicate that analytical values with an accuracy of more than 10 per cent can be obtained³. In their

work on meteorites, Morrison and Rothenberg³ published results in which the precision obtained was 8 per cent and the accuracy 9 per cent, whereas Van Hoya *et al.*⁶, concentrating on relative sensitivity factors as a means of measuring precision, obtained a mean precision of 10 per cent.

It was therefore decided that an attempt should be made at NIM to improve the performance of the instrument by investigation and optimization of the parameters mentioned earlier. The equipment used in this investigation was a modified AEI MS702 mass spectrometer, a modified Jarrell-Ash microdensitometer, and a Texas Instruments computer. These are described in earlier reports^{7,8}.

2. QUALITATIVE INVESTIGATIONS

2.1. Electrodes

The electrodes on which an investigation of this kind is based must meet certain requirements if the investigation is to proceed at a uniform pace and the desired level of accuracy is to be achieved.

The ideal electrode is one in which the material allows for easy, reproducible sparking. A broad spectrum of trace elements must be present, their concentration being such that a set of exposures over a limited range would enable most of the elements to be measured. Because of sample consumption, which causes changes in electrode gap and, consequently, electrode position, the concentration of these elements must be such that long exposures are avoided.

Several materials were selected for analysis. Among these were copper, nickel, tin, tantalum, and steel electrodes. Copper and tin electrodes were found to have very good characteristics, although the copper electrodes contained some trace elements that were not at sufficiently high concentrations and others that were too highly concentrated. With the tin electrodes, not enough trace elements were present. The nickel electrodes tested were not homogeneous, and tantalum electrodes, whether in the form of the powder or the solid, sparked poorly, and the concentration of trace elements was so low as to necessitate long exposures. Eventually, NBS 463 steel electrodes were chosen. Of the many elements present, several could be measured for exposures ranging from 0.1 to 5.6 nC. Another reason for the choice of steel electrodes is that they can be machined to any desired shape, so that the effect of this characteristic on sparking conditions can be evaluated.

2.1.1. Shape of the Electrodes

Magee¹ used square, rectangular, or triangular electrodes; he and others have stated that the precision depends critically on the position of the electrodes in relation to the first slit and that it should therefore be kept constant. With this in mind, very flat electrodes were cut (1 mm by 3 mm by 10 mm) so that the distance between the electrode and the first slit could be set accurately and the uniform width of the electrode (1 mm) would ensure that this parameter remained constant during sparking. With cylindrical or triangular electrodes this would be impossible, since the electrodes become wider as their edges are consumed, and the distance alters accordingly.

2.1.2. Electrode Gap

As it has been reported that the position of the electrodes in relation to the first slit is critical, and since Morrison and Rothenberg³ and Magee¹ have stated that the size of the electrode gap affects the precision of analysis, a movable telescope was positioned at the source window. With this telescope, the position of the electrodes can be ascertained accurately, and the spark gap can be kept constant by the movement of either electrode or both of them as the sample is consumed. This procedure for control of the spark gap was used in all the later experiments.

2.2. Internal Standard

Taylor⁹ has published an excellent review of the use of internal standards in SSMS, in which he lists the following essential attributes of an element that is to be used as an internal standard.

1. The behaviour, volatility, and ionization potential of the element should be similar to those of the analytes.
2. It should possess at least two isotopes with an abundance ratio of 100 so that lines of readable density can be recorded on widely varying exposures.
3. The isotopes should be odd-numbered so as to minimize interference from fractional masses, and the mass of the isotopes should be sufficiently great for interference from multiple-ion lines to be avoided.
4. The element should not be one of the analytes.

Several other conditions have been laid down, but these refer to the addition of an internal standard.

Before the present work began, several elements were considered as possible internal standards, but the use of such a standard was rejected since the experiments were to be conducted on solid-steel electrodes. It was decided that a constituent of the electrodes should act as an internal standard.

Molybdenum is present at a convenient concentration in the NBS steel electrodes, and all seven isotopes can be measured. As no ruthenium could be detected at the strongest line (^{102}Ru), no interference was expected from that element on the ^{100}Mo , ^{98}Mo , or ^{96}Mo mass lines. Similarly, no interference was expected from the doubly charged mercury, platinum, and osmium lines, since these elements cannot be detected. Tungsten is present in the electrodes but at a lower intensity than the molybdenum lines, so that the $^{184}\text{W}^{2+}$ line should not interfere with the ^{92}Mo line. The zirconium lines are of the same intensity as the molybdenum lines in these electrodes, so that ^{90}Zr , ^{94}Zr , and ^{92}Zr do interfere with the corresponding molybdenum lines. The most intense molecular line is 112 from $^{56}\text{Fe}_2$, but, with the set of exposures chosen for the work, it is not visible for exposures shorter than 0.5 nC. If this line, the most intense molecular line (the electrode is 94 per cent iron), cannot be detected, all the other molecular lines (e.g., $\text{FeCa} = 100$ or $\text{FeK} = 95$) can be ignored. Hence, the interference-free lines for the internal standard are ^{100}Mo , ^{98}Mo , ^{97}Mo , and ^{96}Mo .

3. OPTIMIZATION OF THE INSTRUMENT

3.1. Magnetic Current

During one of the preliminary investigations, it became obvious that the stability of the instrument was not within the manufacturers' specifications¹⁰, and detailed investigations indicated that the most significant cause of instrument instability was the magnet current power unit.

Various attempts to improve the stability of the magnet current were made. These included the replacement of the reference batteries, the cooling of the ambient temperature, the passing of chilled water through the water-cooling system, and, finally, the blowing of cold air through the electronics unit. Although these procedures were all successful to some extent, the magnet current was still not up to specification. Eventually the entire magnet current unit was replaced by a solid-state unit that was designed and built at NIM, where it has given exceptionally good stability for extended periods¹¹ with corresponding improvements in the precision of the measurements. A variation of 0.0015 in a current of 300 mA over a two-hour period provides evidence of its stability.

3.2. Accelerating Voltage

When the new magnet current power supply was used, the stability was of such a high order that it was possible for the accelerating voltage to be identified as another area of instability.

Under conditions of stable magnet current, the accelerating voltage varied between 22 and 25 kV on the exposures collected. Visual inspection indicated that many isotope lines were badly out of focus. The experiment was repeated, the standard spectra being set at 24 kV and being varied in small increments both above and below the 24 kV level. For each position, an exposure of 2 nC was collected. Several isotopes were measured, and a linearized form ($Q(\nu)$) of each exposure for these elements was obtained. Then, each of these $Q(\nu)$ values was divided by $Q(\nu)$ for the standard spectra at 24 kV, and the percentage recovery was obtained¹¹. These are presented in Table 4, together with the variation allowed in the accelerating voltage.

TABLE 4

Percentage recovery as a function of the instabilities of accelerating voltage (V)

Variations in V (10^{-1} %)	^{186}W	^{94}Mo	^{63}Cu	Average
$\pm 1\ 000$	97	121	116	111
$\pm 2\ 000$	59	82	80	74
$\pm 4\ 000$	61	81	72	71
$\pm 7\ 000$	40	51	52	48
$\pm 10\ 000$	59	50	41	50

From a visual examination of the photoplate, it was evident that, as the accelerating voltage fluctuated, so the isotope lines became diffuse and out of focus. Quantitatively, the average percentage recovery for the three isotopes relative to the intensities at 24 kV decreases very significantly with increasing deviations

from the fixed accelerating voltage. Variations in this voltage should not exceed 1000×10^{-4} per cent. In later work, therefore, the accelerating voltage was maintained at 24 kV and the stability was continuously monitored.

3.3. Photoplate Data

3.3.1. Background on Photoplates

There was always some fogging of the photoplates, and backgrounds of about 75 to 80 per cent transmission were regularly obtained. Several conditions were therefore changed. The method recommended by the manufacturers for the development of the plates was abandoned and the procedure recommended by Franzen and Schuy³ was adopted, the changes being indicated in Table 5.

TABLE 5

Changes in developing conditions

Stage	Initial conditions	Improved conditions
Pre-cooling time, s	–	30 at 8°C
Developing temp., °C	20	8
Developing time, min	2.5 to 3	8
Rinsing time, s	60	15 at 8°C
Fixing time, s	90	60 at 8°C
Washing time, min	5	5

Previously, new plates had been evacuated in the photoplate magazine for 3 to 4 hours before they were placed in the analyser for sparking. This was changed to the following procedure:

- (1) only four plates at a time were packed, rather than six to eight plates as previously,
- (2) the four plates were placed in the magazine and pumped overnight,
- (3) a plate was introduced into the analyser and pumped there for two hours before the analysis was begun, and
- (4) as soon as the plate was exposed, it was removed from the analyser and developed immediately under the new conditions.

Under these conditions, plates with backgrounds between 90 and 96 per cent transmission are obtained regularly (Table 6). This means that the plates are much cleaner, and faint lines, which had previously been lost in the background, can be seen. Lower limits of detection can therefore be achieved.

3.3.2. Characteristics of the Photoplates

Franzen and Schuy³ emphasized the importance of the grain-distribution function and saturation transmission in the processing of photoplate data. The computer programme used for the evaluation of the results⁴ makes provision for the correction of differences in the photoplate characteristics.

4. OPTIMIZATION OF WORKING PARAMETERS

In the determination of the relative sensitivity factor (RSF) for each sample, the average of the molybdenum intercepts was used as the internal standard⁵. The precision obtained for the RSF in a series of experiments was determined, and this was used as the criterion in the determination of optimum conditions. The measure of precision is the robust coefficient of variation (ROCOV) as described by Ellis¹², which is outlined in the Appendix.

4.1. Precision Obtainable under Initial Conditions

The initial conditions, upon which all the subsequent investigations were to be based, were as follows.

- (a) NBS 463 steel electrodes were used. Their dimensions were 1 mm by 3 mm by 10 mm, the gap between the electrodes was 1 mm, and the distance to the first slit was 15 mm. These distances were measured, monitored, and adjusted with the telescope so as to compensate for gap variations as the electrodes were consumed.
- (b) The accelerating voltage and the magnetic current were set (and monitored) at 25 kV and 300 mA respectively. The spark voltage was set at 35 per cent, and the sparking parameters were a pulse

TABLE 6

Improvement in background on the photoplates

Developing conditions*	Transmission, %					
	⁶⁵ Cu		³¹ P		²³ Na	
	Back-ground	Line	Back-ground	Line	Back-ground	Line
Initial conditions	76,3	11,9	77,7	31,7	81,8	15,4
	79,9	17,6	82,4	44,5	80,5	42,2
	80,9	27,5	83,9	43,8	82,0	48,0
	84,5	40,0	85,9	55,4	83,9	43,6
	87,2	46,4	86,0	66,8	85,4	58,7
	88,8	56,9	87,2	70,8	83,0	65,9
	89,7	67,8	87,0	76,2	86,2	71,8
	90,8	80,5	-	-	85,9	78,3
Improved conditions	93,2	8,2	94,5	18,2	96,5	11,2
	94,0	12,4	94,5	33,0	96,1	8,7
	94,1	16,7	94,7	33,8	94,7	24,3
	94,7	22,8	92,8	46,4	96,2	25,4
	94,6	54,8	94,2	59,5	96,0	30,2
	95,7	76,8	93,8	62,5	95,7	52,7
	-	-	93,5	82,5	95,8	84,8

* For the first set of data, exposures were from 0,056 to 3,2 nC, and for the second from 0,032 to 1,0 nC.

frequency of 100 pulses per second and a pulse length of 100 μ s. The radio frequency was set to give a maximum beam for the steel electrodes. The parameters used for setting the focus were the same as those set previously for a copper matrix.

(c) The exposures chosen were 0,1 nC, 0,18 nC, 0,32 nC, 0,56 nC, 1 nC, 1,8 nC, 3,2 nC, and 5,6 nC. For this range of exposures, the isotopic lines selected were ²⁰⁸Pb, ²⁰⁶Pb, ¹⁸⁶W, ¹⁸⁴W, ¹²⁰Sn, ¹¹⁸Sn, ¹⁰⁰Mo, ⁹⁷Mo, ⁶²Ni, ⁶¹Ni, ³¹S, and ³²S.

(d) Photoplates were prepared, exposed, and developed by the method outlined in Section 3.3.1, and the data were processed on the computer programme described by Pearton⁴.

The precision obtained under the above conditions is shown in Table 7. The values were obtained from four photoplates, each consisting of two sets of exposures. It can be seen that the ROCOVs are very poor, especially for the lead and tungsten isotopes, which have a large mass.

A number of factors, each related to the efficiency of the sparking system, the focusing, and the collection of the atomized vapour, could have contributed to the poor performance of the SSMS system.

4.2. Focusing

An examination of the photoplate showed that the instrument was very poorly focused for many of the isotope lines, especially the lines for isotopes of high mass. Poor focusing of the instrument leads to wide, diffuse lines, rather than sharp, uniformly intense lines.

In an attempt to overcome this undesirable state of affairs, the instrument was re-focused, more attention being paid to the lines of high mass, e.g., lead lines. The procedure involved exposure of the sample for several identical exposures of 2 nC while the focus controls were varied until the sharpest lead lines were obtained. The optimum values of focus are those which were used subsequently to give the sharpest, most consistently intense lead lines.

4.3. Precision after Focusing

The previous experiment was repeated with the new focusing parameters, which were as follows: $\Delta V = 750$ and focus = 400. Table 8 shows the effect of refocusing, which resulted in a much better precision, only the variation in precision for ⁶¹Ni being higher than 20 per cent.

TABLE 7

RSF values obtained from initial precision test

Plate no.	Spectral no.	²⁰⁸ Pb × 10 ⁻¹	²⁰⁶ Pb × 10 ⁻¹	¹⁸⁶ W × 10 ⁻¹	¹⁸⁴ W × 10 ⁻¹	¹²⁰ Sn × 10 ⁻²	¹¹⁸ Sn × 10 ⁻²	¹⁰⁰ Mo × 10 ⁻²	⁹⁷ Mo × 10 ⁻²	⁶² Ni × 10 ⁻²	⁶¹ Ni × 10 ⁻²	³⁴ S × 10 ⁻²	³² S × 10 ⁻²
M99	1	16	14	42	40	59	60	98	102	64	48	47	43
	2	18	14	54	38	87	92	98	102	91	81	39	100
M96	1	8	10	39	40	72	64	101	99	97	85	53	95
	2	-	-	46	45	76	72	98	102	110	71	40	88
M912	1	-	-	52	51	68	82	99	101	140	170	73	58
	2	8	12	52	52	63	71	98	105	120	110	45	65
M913	1	21	23	79	76	97	96	103	97	91	74	48	87
	2	22	36	95	91	120	110	101	99	130	110	44	-
Median ROCOV		16	15	54	51	77	80	99	101	105	88	46	79
		42	35	34	35	22	20	1.5	1.5	16	23	14	24

Notes: 1. The average of the $Q(o)$'s for ¹⁰⁰Mo and ⁹⁷Mo was used for the determination of the RSF.

$$\text{Then RSF} = \frac{Q(o)^E}{Q(o)^{\text{Mo}}} \text{ for each isotope E.}$$

2. The RSF values were multiplied by 10 or 100 to bring them to values that would be easier to handle.

TABLE 8

RSF values obtained on six spectra from two plates after re-focusing

	²⁰⁸ Pb	²⁰⁶ Pb	¹⁸⁶ W	¹⁸⁴ W	¹²⁰ Sn	¹¹⁸ Sn	⁶² Ni	⁶¹ Ni	³⁴ S
Median	14	14	69	75	84	74	70	71	17
ROCOV	14	9	9	7	14	8	5	26	14

Notes: 1. Figures for Mo (internal standard) are not shown.
2. ³²S was discarded because the lines are too intense.

As far as is known, there is no electrical measurement that can indicate the instability in instrumental focus. Hence, the plates are examined visually, and, if the lines are out of focus, the instrument is re-focused and the experiment repeated.

4.4. Spark Voltage

The spark-voltage Variac controls the range of the radio-frequency (RF) spark voltage. The RF ranges from 0 to 80 kV, which is represented on the Variac as 0 to 80 per cent.

Changes in sparking parameters are required when electrodes that will not spark readily are being analysed, e.g., ruthenium electrodes. It was therefore essential that the effect of variations in the spark voltage in relation to the precision attainable should be investigated.

The spark voltage was changed from 30 to 45 per cent with the standard steel electrodes. The isotopes of lead, tungsten, tin, nickel, sulphur, and molybdenum were measured, graphs were drawn, and the intercepts, $Q(o)$'s, were obtained. For normalization of the results, the $Q(o)$ value for each element was divided by the average $Q(o)$ for molybdenum. Thus, the RSF values were obtained (note 1 of Table 7). A spark voltage of 35 per cent was taken as being the standard spark-voltage condition, and the RSF values for each sparking voltage were divided by those obtained at this standard condition.

The results are presented in Table 9, from which it can be seen that, although there is some scatter, the RSF values obtained for spark voltages from 30 to 40 per cent do not differ significantly, whereas a spark voltage of 45 per cent produces much lower RSF values. This means that there was an increase in sensitivity, probably obtained by extremely quick sparking due to the higher voltage. This quick sparking implies that

TABLE 9

Changes in sensitivity (RSF values) for different spark voltages*

Spark voltage %	²⁰⁸ Pb	²⁰⁶ Pb	¹⁸⁶ W	¹⁸⁴ W	¹²⁰ Sn	¹¹⁸ Sn	⁶² Ni	⁶¹ Ni	³⁴ S
45	0,22	0,24	0,83	0,76	0,45	0,54	0,48	0,41	0,34
40	0,97	0,94	0,92	1,21	1,09	1,05	1,07	0,94	0,79
35	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0
30	0,85	0,93	1,14	0,98	0,93	0,91	0,93	1,18	0,66

* RSF_vRSF₃₅ per cent

the stability of the whole sparking technique is time-dependent: the shorter the duration of the spark, the better the stability. This means that, for the same charge (nanocoulombs of exposure), narrower lines are produced, giving rise to longer peaks and greater sensitivity. This finding applies to the isotopes of both the analyte and the internal standard, and the RSF should therefore remain constant.

However, the RSF values changed, and it can be seen from Table 9 that, although the tungsten isotopes were affected only slightly, tin and nickel improved by about 2,5 times, and lead was more sensitive by a factor of 4; the values for sulphur cannot be interpreted as readily.

These results suggest that the use of a higher spark voltage is beneficial. However, it has been stated in the literature (and experience at NIM confirms this) that higher spark voltages give rise to an increase in the number of multiple-charged isotope lines, which in turn gives rise to a general blackening of the photoplate together with interference on other isotope lines. The increase in sensitivity obtained with a higher spark voltage is therefore a detrimental step (the sensitivity is usually adequate), and the spark voltage should be set at the lowest value that will maintain regular sparking. This value must be determined separately for each matrix. For steel, the spark-voltage setting would be 35 per cent.

4.5. Variations in Pulse Length and Pulse Rate

The spark voltage applied to the electrodes is pulsed, and variations in the pulse length or the pulse rate, or both, enable the analyst to maintain accurate control over the spark voltage. If very short exposures are to be used, the pulse length would be 25 μ s at 10 pulses per second (p.p.s.) For very long exposures, in which sparking is required in as short a time as possible, 200 μ s and 1000 p.p.s. would be used.

An experiment was conducted in which all possible combinations of pulse length and repetition rate were used up to 1000 p.p.s., and the accelerating voltage was monitored under different conditions.

As shown in Figure 1, it was proved conclusively that a variation of 2000×10^{-1} per cent in the accelerating voltage produced a measurable variation in the focus; hence the sharpness of the isotopic lines. The variation in the acceleration voltage is 0,2 per cent, and on 24 kV is 0,05 kV, which corresponds to three small divisions in Figure 1.

The first conclusion to be drawn from Figure 1 is that all the conditions with a pulse length equal to or less than 50 μ s (irrespective of the pulse-repetition rate) are acceptable, in that they produce small variations of less than three units in the accelerating voltage. However, the accelerating voltage for 1000 p.p.s. and 50 μ s, 1000 p.p.s. and 25 μ s, 300 p.p.s. and 100 μ s, and 300 p.p.s. and 50 μ s varies over a wide range, from 23,8 to 23,4 kV. This means that these four conditions cannot be interchanged even though, for each one of these, the voltage variations are within the required limits. Hence, for the analysis of a sample requiring a series of long exposures, one condition must be chosen and used for all the exposures.

For short exposures, the precision is good and the overall voltage does not vary significantly; any of the conditions with the series marked A in Figure 1 can be used, and these can be freely interchanged to produce quieter or more severe sparking, depending on the duration of the exposure.

5. PRECISION OBTAINED

After most of the variables had been optimized, a precision run was conducted under the following standard conditions.

- (1) The conditions relating to electrodes, electrode gap, exposure, and photoplate and instrumental stability were the same as those described in Section 4.1.

OPTIMIZATION FOR SSMS CONDITIONS

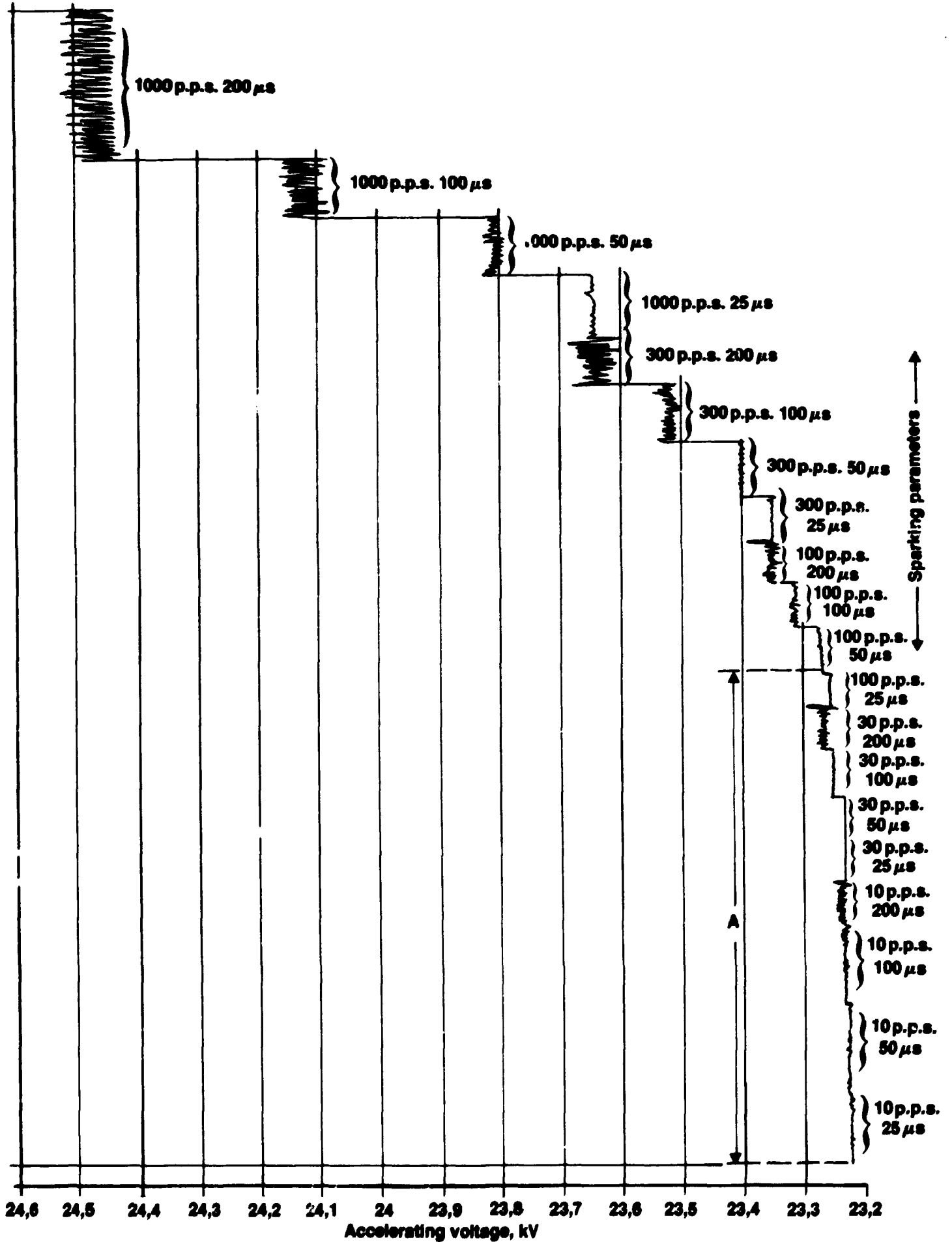


FIGURE 1. Variations in accelerating voltage resulting from changes in sparking parameters

(2) The spark voltage was set at 35 per cent, and the pulse-repetition rate and length were kept constant at 100 p.p.s. and 100 μ s respectively.

(3) The instrument was focused to give the sharpest lines for the lead isotopes.

Two photoplates were collected, each with five spectra. The ten sets of spectra were processed, the RSF values were determined, and the precision on the RSF relative to molybdenum as internal standard was calculated. The results are given in Table 10.

The average precision for these nine isotopes was 9,3 per cent, the best was 7 per cent, and all were better than 12 per cent. These results, which show a considerable improvement over the original average of 26 per cent, are, at this stage, considered satisfactory.

TABLE 10

Robust coefficients of variation for the results obtained under optimum conditions*

^{208}Pb	^{206}Pb	^{186}W	^{184}W	^{120}Sn	^{118}Sn	^{62}Ni	^{61}Ni	^{34}S
11	11	7,7	10	7	7,3	11	10	9,7

* RSF values obtained from 10 spectra on 2 plates.

6. DISCUSSION AND RECOMMENDATIONS

The optimization of any one of the parameters investigated (electronic stability of the magnetic current and the accelerating voltage, improvement in photoplate technique, focusing of the instrument, and variation in sparking parameters) was shown to have improved the analytical precision, the most significant factors being the instrumental stability and the sparking parameters.

The results of the precision run show that, with this modified mass spectrometer and under these optimum conditions, adequate precision can be obtained for several of the elements in a steel matrix.

Other matrices have not been investigated thoroughly, but preliminary results indicate that, under strictly controlled conditions, electrodes prepared from high-purity silver to which standard solutions have been added have yielded precisions of about 5 per cent. This may be because a silver matrix has better sparking characteristics or because solid electrodes are not homogeneous, or a combination of both.

Some parameters, such as distance of the electrodes from the No. 1 slit, were not investigated, and others, such as variations in pulse frequency and length, might benefit from further investigation. It is recommended that these and other parameters, such as the width of the slit at the entrance to the electrostatic analyser and the monitoring of the focus, should form the subject of further investigations so that better precision can be obtained from the mass spectrometer.

7. CONCLUSIONS

The results show that, under optimum conditions, an average precision of 9,3 per cent can be obtained in SSMS, with individual figures better than 12 per cent.

A further improvement in the precision of SSMS can be expected from the investigation of other parameters, and the use of 'doped' silver electrodes could, on the basis of the available information, make a major contribution in this direction.

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APPENDIX

THE ROBUST COEFFICIENT OF VARIATION

The word *robust* in this context denotes a lack of sensitivity in the results represented by the coefficient of variation to undesired effects such as the inclusion of data that are not truly representative or the displacement of data owing to gross error or bias.

The method used to overcome the problem in the derivation of the standard deviation in the presence of gross errors and systematically distributed data is relatively independent of data outside the dominant Gaussian peak of the histogram representing the distribution of duplicate data. This method involves rejection of one-sixth of the data at both the upper and the lower extremes, leaving four-sixths or 66,7 per cent of the total data. In a normal (Gaussian) distribution, $1 \times$ standard deviation limits on either side of the mean will enclose 68,27 per cent of the total data¹⁻³. Since 68,27 and 66,7 per cent are very close, the range of the remaining data can be considered to be a good rough approximation of twice the standard deviation of the dominant histogram peak and to be relatively independent of outliers¹⁻³.

In Table I-1, example A represents an approximately Gaussian distribution. Example B represents the same distribution with the highest value, 5,5, displaced to 25,5. The displacement causes considerable

TABLE I-1

Effect of displacement on statistics

Examples	A	B	
x_1	1,5	1,5	} Identical in both examples
x_2	2,2	2,2	
x_3	2,4	2,4	
x_4	2,6	2,6	
x_5	2,8	2,8	
x_6	3,1	3,1	
x_7	3,3	3,3	
x_8	3,4	3,4	
x_9	3,6	3,6	
x_{10}	3,7	3,7	
x_{11}	3,9	3,9	
x_{12}	4,2	4,2	
x_{13}	4,4	4,4	
x_{14}	4,6	4,6	
x_{15}	4,8	4,8	
x_{16}	5,5	25,5	Displacement
Sum	56,0	76,0	
Mean	3,5	4,75	
SD	1,0589	5,6084	
Rh	2,4 - 4,6	2,4 - 4,6	
	= 1,8	1,8	
ROSD	= 0,90	0,90	
Median	= 3,5	3,5	
COV, %	= 30,25	118,07	
ROCOV, %	= 25,7	25,7	

changes in the mean, the standard deviation, and the percentage coefficient of variation. The displacement has not changed the median, the robust standard deviation (ROSD), or the robust coefficient of variation (ROCOV). Thus, the robust coefficient of variation is regarded as definitely more robust than the coefficient of variation.

OPTIMIZATION FOR SSMS CONDITIONS

It is possible for a robust coefficient of variation to be derived that will be only slightly affected by the outliers and that can then be used in an assessment of the data without recourse to an involved rejection process.

Coefficient of variation (COV) is expressed by the formula

$$\text{COV, \%} = \frac{SD}{\bar{x}} \times 100 ,$$

where SD is standard deviation and \bar{x} is the mean value of the data.

The non-robust values SD and \bar{x} are changed to robust values by the application of the following formula where Rh is an approximation to $2 \times SD$ after rejection of one-sixth of the values on either side of the mean, and Md is the median:

$$\text{ROCOV, \%} = \frac{Rh}{2 \times Md} \times 100.$$

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