

REPORT NO. 1984

**COMMISSIONING OF THE AEI MS702
MASS SPECTROMETER**

Director of Division T.W. Steele

Investigators D.C.G. Pearton
A. Sobiecki

Date 31st August, 1978

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SYNOPSIS

The setting-up and commissioning of the AEI MS702 mass spectrometer is described. Its individual components and their use are discussed, as well as the sample preparation, analysis, and reduction of data.

A comprehensive list is given of instrumental breakdowns, and the application of the technique to several matrices is outlined. Improvements and modifications to the technique, including the use of a minicomputer, are suggested.

SAMEVATTING

Die opstelling en indienstelling van die massaspektrometer AEI MS702 word beskryf. Sy individuele onderdele en hul gebruik word bespreek asook die voorbereiding van die monster, die ontleding en die reduksie van die data.

Daar word 'n omvattende lys gegee van maniere waarop die instrument onklaar kan raak en die toepassing van die tegniek op verskeie matrikse word in hooftrekke uiteengesit. Verbeterings en wysigings van die tegniek, insluitende die gebruik van 'n minirekenaar, word aan die hand gedoen.

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1. INTRODUCTION

In 1898 Wien showed that a beam of positive ions can be deflected by electro-magnetic fields. Dempster, Hannay, and Ahearn¹⁻³ continued the development of the mass-spectrometer technique, and in 1959 the first mass spectrometer was produced commercially. Since that time, studies of trace impurities by spark-source mass spectrometry (SSMS) have experienced rapid growth.

A prime advantage of the mass-spectrometer technique is that a wide range of materials can be analysed, from biological⁴ and pollution samples^{4,5} to geological materials⁶ and metals⁴. The analysis of almost all the impurities in these samples is possible. Interferences are very rare, and mineralogical effects are non-existent. The instrument is extremely sensitive, with detection limits of as low as 1 p.p.b.^{*}, and calibrations are linear over five orders of magnitude⁸. The precision is reported to range from 20 per cent to 2 per cent with electrical detection and matched standards^{6,9}. The main disadvantage of SSMS is the long turn-around time required; for example, three samples of the same matrix can be analysed for about sixty-five elements in three days.

2. MASS-SPECTROMETRY TECHNIQUE

Spark-source mass spectrometry is a technique for the analysis of solid samples. It provides positive ions of the elements present, and separates these according to their mass-to-charge (m/e) ratios, using both electrostatic and magnetic fields. The vacuum spark is found to be the most suitable source for producing an ion beam from a solid conducting material, since the spectrum is closely representative of the composition of the sample, and the sensitivity is similar for all elements. The ions produced have a wide energy spread, and, for a sharp focus to be obtained at the detector, a double-focusing system must be used. The intensity of the spark discharge is very erratic, and a method of integrating all the mass-analysed ion beams from the sample under analysis is required. The ion-sensitive photographic plate is an ideal detector because of its unique integrating properties.

3. DESCRIPTION OF THE INSTRUMENT

Recently, the National Institute for Metallurgy (NIM) purchased a mass spectrometer — the MS702R — from AEI Scientific Apparatus Limited, Manchester, England. This model is a double-focusing spark-source mass spectrometer, with Mattauch-Hertzog ion optical geometry, giving first-order energy focusing and second-order angular focusing. The basic instrument is fitted with a pulsed radio-frequency spark source, and with a photoplate detection unit as standard equipment.

A schematic layout of the source and analyser system of the mass spectrometer is shown in Figure 1. The source is normally operated in the 10^{-7} torr (10^{-8} kPa) range, the analysers at 10^{-8} torr (10^{-9} kPa), and the photoplate magazine at 10^{-6} torr (10^{-7} kPa). So that these high vacuums (and consequently low backgrounds) can be obtained, the instrument is equipped with two rotary pumps for rough pumping, and with four diffusion pumps. The diffusion pumps operate through cold traps that must be filled with liquid nitrogen every four hours.

3.1. Source Chamber

The source chamber is illustrated in Figure 2. The metal parts that are exposed to the spark are made of tantalum (Ta), which has only one major isotope at m/e 181, thus contributing the minimum of interference to the spectrum of the sample. The sample electrodes are held in Ta clamps mounted on glass supports (isolators) that can be moved inside the source chamber by the electrode-adjusting mechanism. Thus, the electrodes can be adjusted, by means of a bellows arrangement, while the spark voltage is applied under a high vacuum. A Ta spark shield, with a slit for viewing of the spark, is mounted on the Ta kidney plate. This prevents particles of the sample from sputtering onto the source housing. The No. 1 slit, 3,175 mm in width, is mounted on the front of the kidney plate. Immediately behind it is mounted the slit housing, which contains the No. 2 and the No. 3 focusing slits. These are 0,3048 and 0,0508 mm in width, respectively (Figure 1). Alignment of the slits is achieved by stainless-steel dowels that fit into holes drilled into the kidney plate, the slits, the slit housing, and the base of the source unit.

Ions characteristic of the sample material are produced in the source by the application of a radio-frequency spark to a pair of electrodes made of the sample material. These ions are accelerated by a 25 kV potential, and pass through the defining slits into the electrostatic analyser.

*p.p.b. = parts per billion (10^{-9})

MASS SPECTROMETER

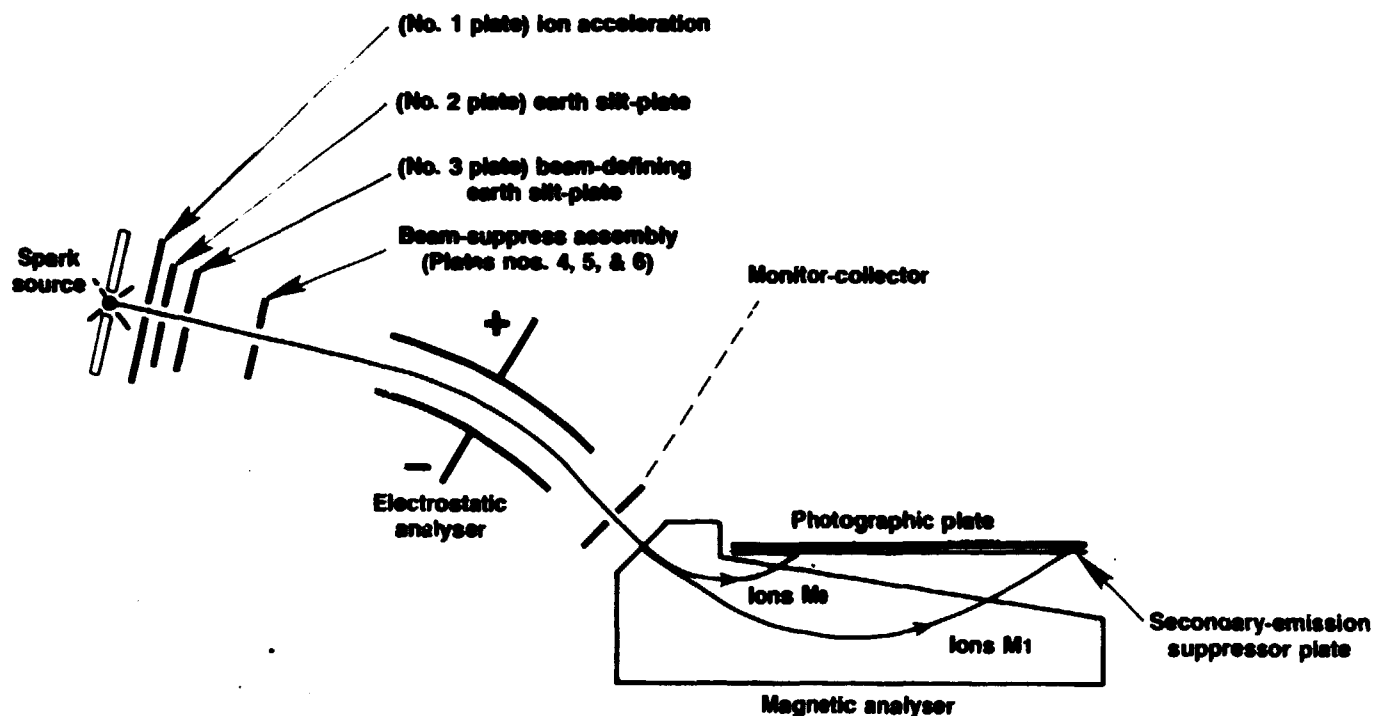


FIGURE 1. Schematic diagram of the AEI MS702 mass spectrometer (after Figure 1a in reference 11)

3.2. Electrostatic Analyser (ESA)

The analyser consists of two units: the deflector-plate assembly, and the monitor-collector assembly.

3.2.1. Deflector-plate Assembly

After entering the ESA through a plate with an adjustable, vertical slit (α slit), the ion beam passes through a hole in a glass block that prevents fringe-field effects. An earthed metal tube in the flange of the ESA housing prevents the ion beam from charging the glass. The voltage applied to the ESA deflector plates deflects the ion beam, preventing the ions from impinging on the photoplate when the beam is switched off.

3.2.2. Monitor-collector Assembly

The ion beam then passes into the monitor-collector assembly, which consists of four plates that limit the width of the beam, focus the beam, and monitor the total ion beam entering the magnetic analyser.

3.3. Magnetic Analyser

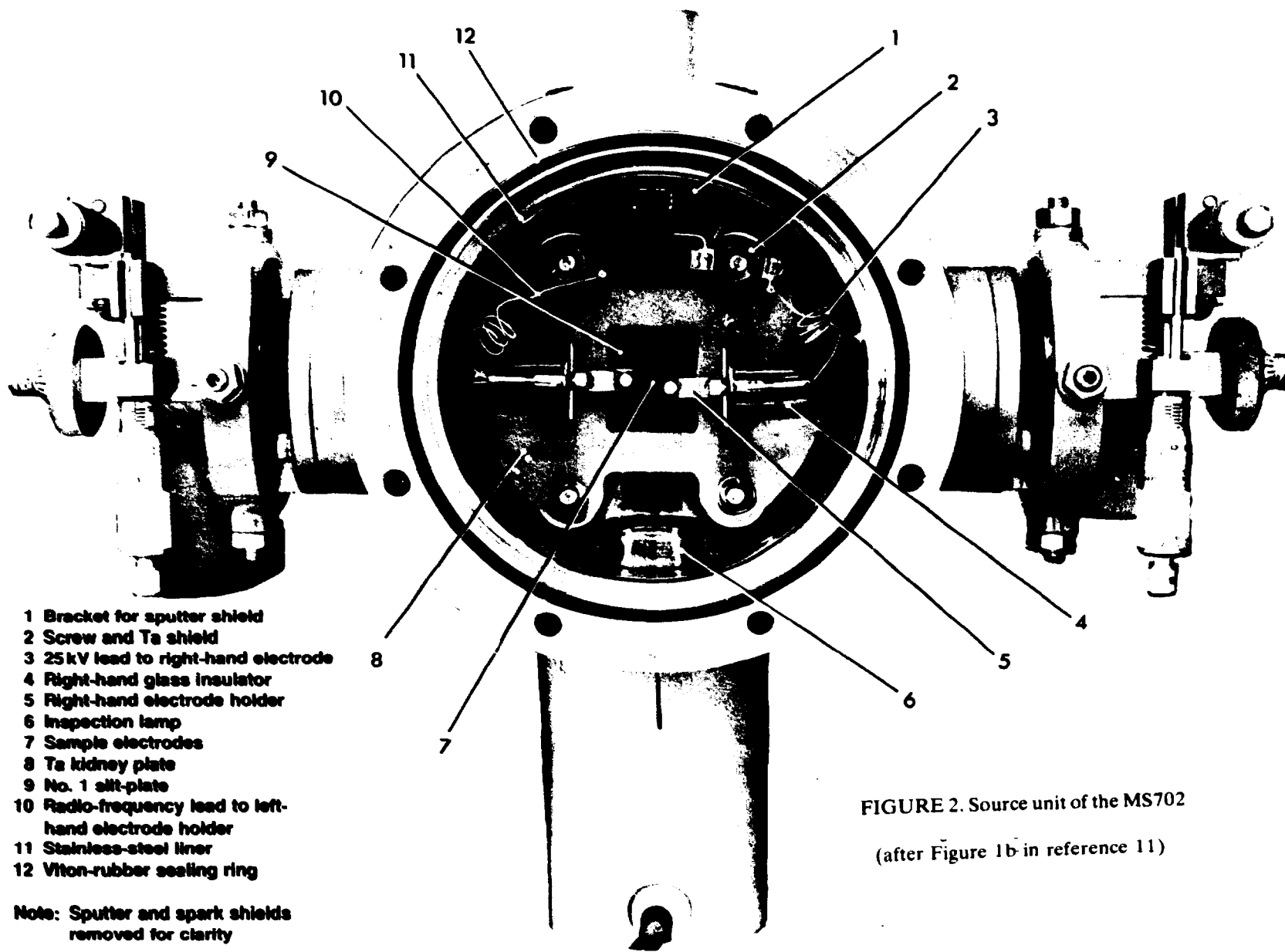
The magnetic analyser consists of gold-plated mild-steel pole pieces with stainless-steel mounting spacers and blocks. The analyser is mounted off the analyser housing, so that a low-temperature coefficient can be obtained throughout the magnetic circuit. This ensures that the effect of temperature variations on the strength of the magnetic field is minimized.

The ions of different mass follow similar paths through the ESA, but they are separated into individual beams by the magnetic analyser.

3.4. Photoplate-detection System

3.4.1. Photoplate-rack Assembly

The photoplate rack is located inside the magnetic analyser above the pole pieces, and slides across the magnetic gap on two stainless-steel rails fitted between the left- and right-side plates. The



- 1 Bracket for sputter shield
- 2 Screw and Ta shield
- 3 25 kV lead to right-hand electrode
- 4 Right-hand glass insulator
- 5 Right-hand electrode holder
- 6 Inspection lamp
- 7 Sample electrodes
- 8 Ta kidney plate
- 9 No. 1 slit-plate
- 10 Radio-frequency lead to left-hand electrode holder
- 11 Stainless-steel liner
- 12 Viton-rubber sealing ring

Note: Sputter and spark shields removed for clarity

FIGURE 2. Source unit of the MS702

(after Figure 1b in reference 11)

photoplate in its holder slides into the rack, and is supported independently of its holder by four adjustable spring-loaded pegs that ensure accurate positioning of the photoplate in the focal plane.

Either of the two photoplate controls, at the front or back of the instrument, operates a lever through a bellows assembly that moves the photoplate rack and the photoplate across the magnetic gap. The standard control dial is calibrated to give sixteen exposures on a standard 51 mm photoplate, but this instrument has been modified to give thirty-two exposures on the standard photoplate by a change in the gearing on the shaft between the photoplate-position control and the rack mechanism.

3.4.2. *Photoplate Magazine*

A polished-glass sliding valve (Figure 3) seals the end of the magnetic analyser from the tube connecting it to the photoplate magazine. When the magazine is to be vented to atmosphere for loading or unloading of the photoplates, a flap-valve between the connecting tube and the magazine is closed.

Eight cassettes can be mounted on the rotating drum, which is supported by the end walls of the magazine. The shaft for rotating the drum passes through a Wilson seal consisting of two rubber rings that are separated by a washer and pressed against the shaft. In each of the eight positions of drum rotation, a cassette is aligned with the central position of the photoplate rack in the magnetic analyser. The positions of the cassette are located by a spring-loaded ball that seats into any one of the eight holes in the drum end-plate.

Sealed into the hinged end-flange of the magazine by four rubber O-rings is the ramrod by which the photoplate holder is removed from its cassette and pushed into the magnetic analyser (Figure 3). The Engage/Release knob located at the end of the ramrod rotates the shaft through 45°, allowing the ramrod peg to engage with or clear the cassette lip. Two guide rods move parallel to and with the ramrod, which cannot be inserted or withdrawn unless the flap-valve and the glass sliding valve are opened.

3.4.3. *Photoplate Cassette*

The cassette consists of a holder that carries the photoplate into and out of the magnetic analyser, and a brass light-proof cover that encloses the photoplate holder when the cassette is not in use (Figure 4).

An Ilford-type Q2 glass photoplate, 254 by 51 by 1 mm, is held in the photoplate holder, which is rigidly constructed of aluminium alloy. The loaded cassettes are stored in the wooden case provided, and this prevents accidental fogging of the photoplate.

The ions that have been separated according to mass are collected on the photoplate. The photoplate is developed, and the intensity of the lines on the plate is measured on a microdensitometer.

3.5. *Accessories*

Fourteen accessories are available from AEI. Of these, the automatic cold-trap filler, the ion-beam chopper, and the Autospark control unit were purchased with the basic unit.

3.5.1. *Automatic Cold-trap Filler*

During operation, the instrument requires a regular supply of liquid nitrogen (LN₂) for the generation of the very low vacuum of 10⁻⁸ torr (10⁻⁹ kPa). The cold traps can be filled automatically at fixed time intervals from an LN₂ reservoir. A timer opens the LN₂ inlet, and a bi-metallic strip turns off the flow when liquid issues from the last cold trap.

3.5.2. *Ion-beam Chopper*

Jackson and Whitehead^{8,10} have demonstrated conclusively that, at short exposures, large errors may be made because of the non-homogeneity of samples, and variations in the ion beam that distort the measurement of the charge. They showed that, if the voltage supplied to the beam-suppressor plate were pulsed so that the ion beam entered the analyser region for only a fraction of the total sparking time, a relatively large amount of sample would be consumed, and a more representative sampling of the material and a more accurate measurement of the exposure would be obtained. This would improve the precision attainable at relatively high concentrations, thereby greatly extending the useful range of SSMS.

MASS SPECTROMETER

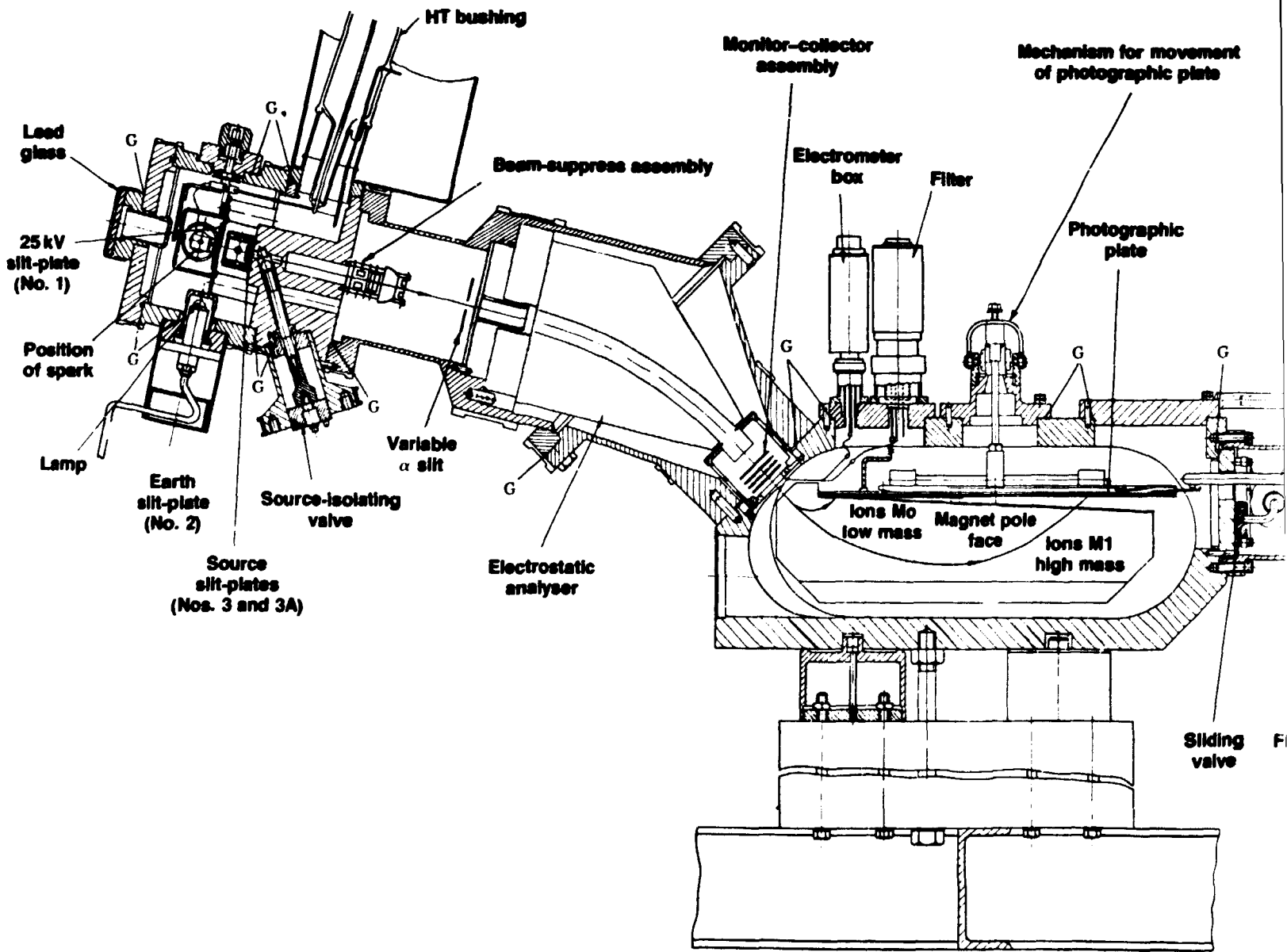
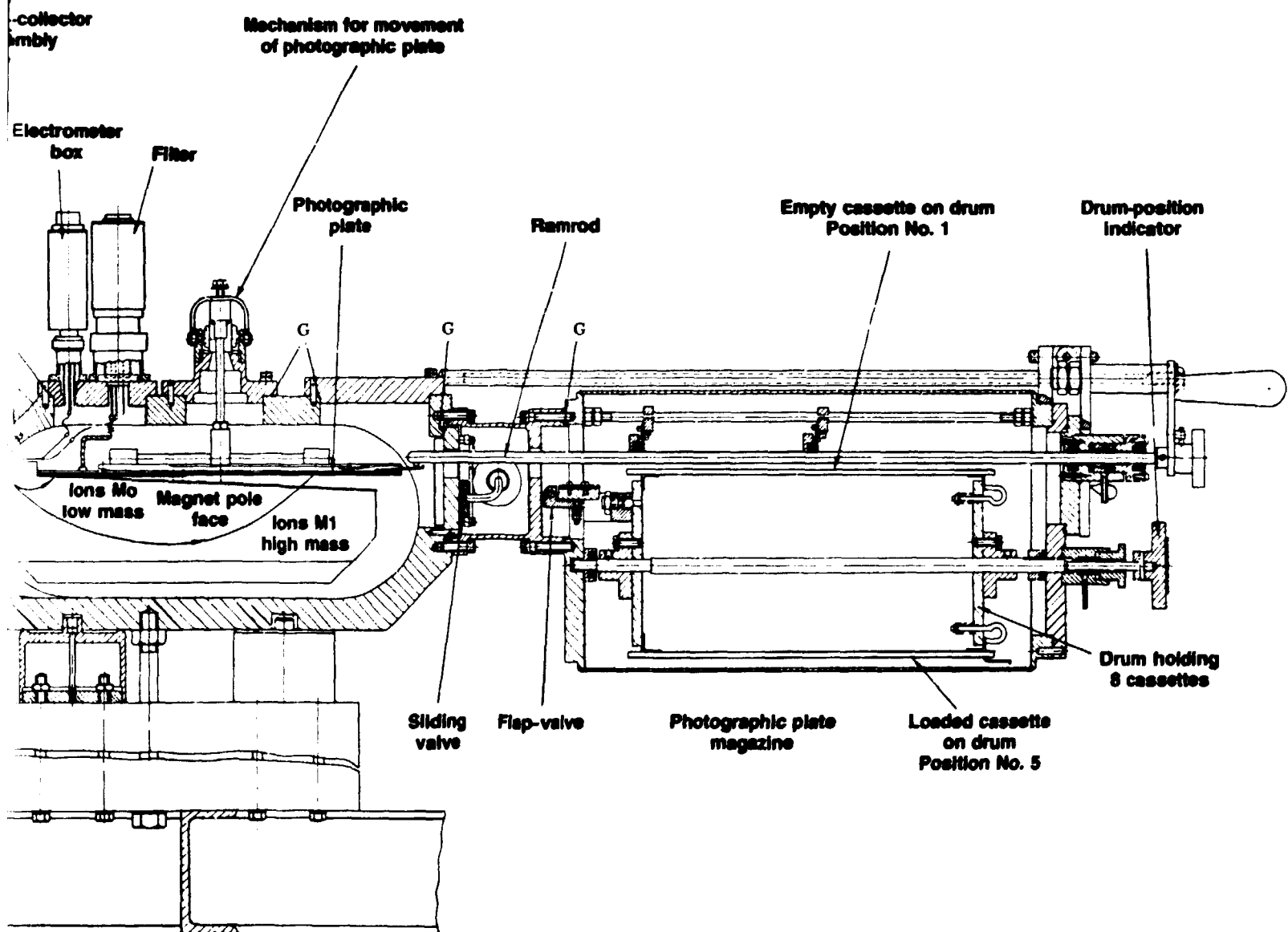
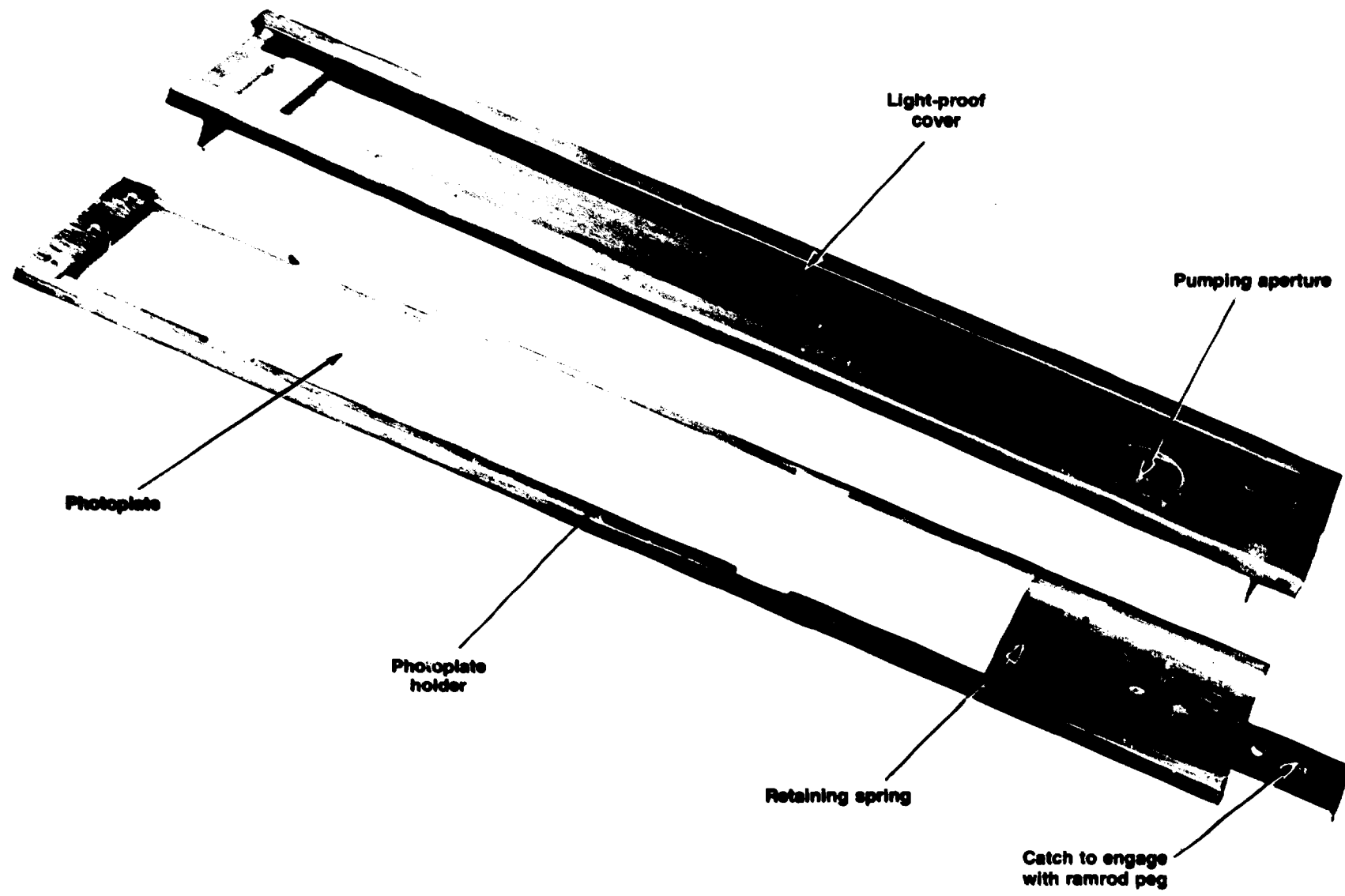


FIGURE 3. Tube assembly of the MS702 (after Figure 2p in referenc

SECTION 1



Tube assembly of the MS702 (after Figure 2p in reference 11)



6

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FIGURE 4. The cassette (after Figure 2n in reference 11)

MASS SPECTROMETER

3.5.3. Autospark Control Unit

In SSMS, precise control of the spark is essential for analytical accuracy, and much of the operator's time is spent in making adjustments to the spark. The Autospark control unit has been developed to overcome this difficulty, and provides automatic control of the spark over long periods of time.

A sensing coil, located in the spark box, monitors the discharge and provides a signal proportional to the discharge emission. If the spark gap is too large or too small, emission falls off, and the Autospark varies the electrode gap until optimum emission is restored.

4. MAJOR INSTRUMENTAL PROBLEMS ENCOUNTERED

Major breakdowns that occurred in the period during which the instrument was guaranteed, and their consequences, are listed in Table 1.

TABLE 1

Breakdowns encountered during the guarantee period of the MS702

Breakdown	Result of breakdown	Action required	Delay (days)
Accelerating voltage	Instability in voltage, breakdown of voltage, discharges during sparking	Replacement of valves, semiconductors, coils, and the plug causing arcing	48
Ion gauges	Burning out of filaments, with the result that no vacuum measurement was possible	Instrumental vacuum brought to atmosphere and new filaments installed	11
Liquid nitrogen supply	Failure of bi-metallic strip, with the result that 180 litres of liquid nitrogen was lost	Modifications to faulty switch at bi-metallic strip	5
Photoplate magazine	Jamming of mechanism, making recovery of the exposed photoplate impossible	Dismantling of magazine for the removal of the photoplate	4
Vacuum leak	Small leaks in various valves and connections, leading to loss of vacuum and fogging of photoplates	Helium-leak detector used to find leaks, which were then sealed	12
Magnetic current instability	Leading to very poor resolution, and even the production of multiple lines	Fault eventually traced to corroded switch	9
Miscellaneous	Various small faults leading to imprecision and inaccuracies	The stability of the monitor-integrator checked, and the oil in the diffusion pump changed	19

5. THE FUNCTIONS OF VARIOUS UNITS AND CIRCUITS

5.1. Fixed Parameters

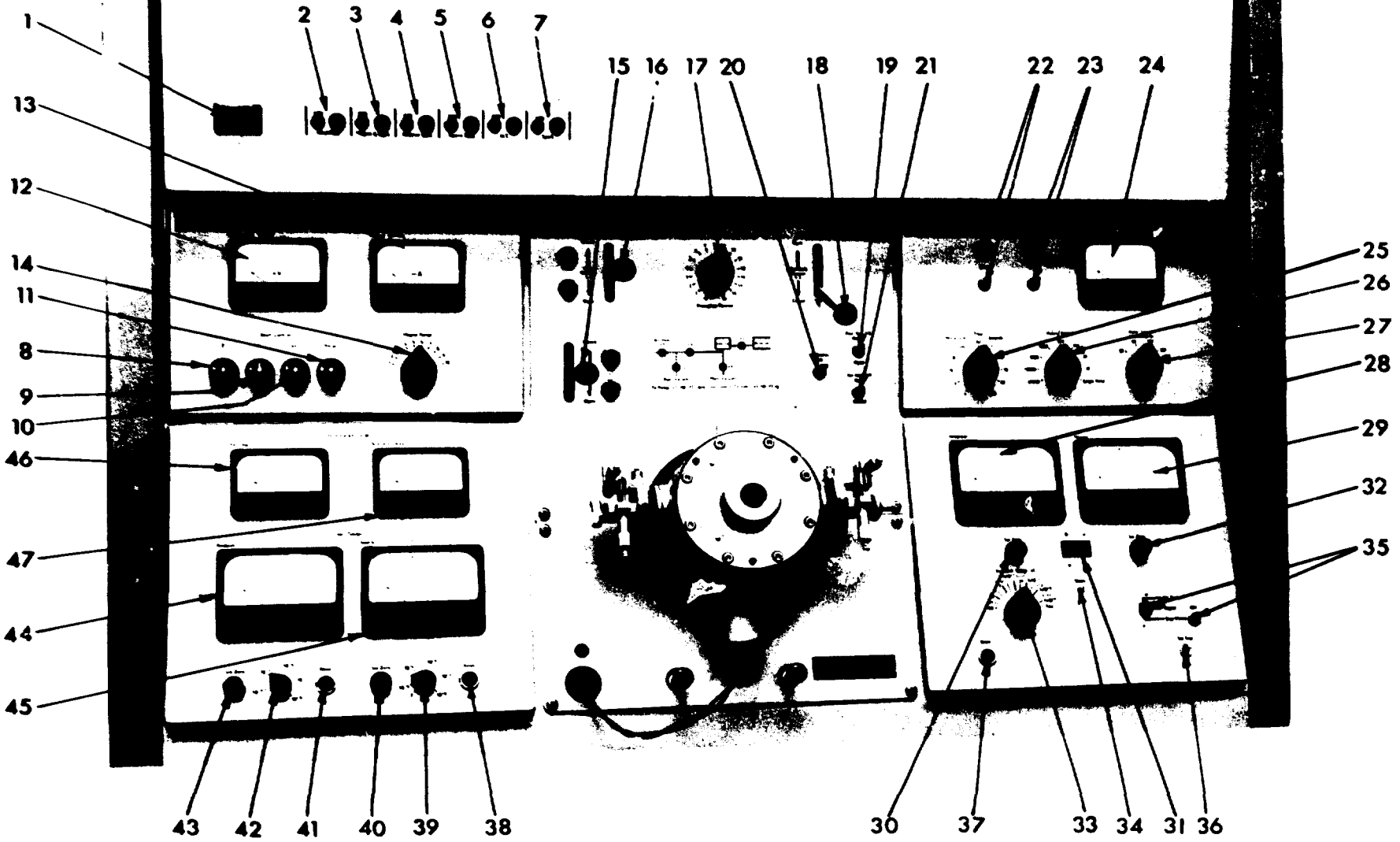
The 'amplifiers' switch and the 'magnetic and ESA' switch are normally left in the on position in order that drift can be minimized, and spurious monitor or integrator readings avoided (2 and 3 in Figure 5).

The 'analyser-bake' and 'source-bake' switches (4 and 5 in Figure 5) are used when the vacuum indicates that baking is required; otherwise, these remain in the off position.

The 'H.T.' and 'spark' switches (6 and 7 in Figure 5) are always left off until required. The 'H.T.' controls the accelerating voltage (25 kV) and the 'spark' controls the main spark voltage.

The 'spark' on-off switch (23 in Figure 5) controls the action of the spark trigger circuit and should also be left in the off position until required.

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FIGURE 5. The front control panel (after Figure 1f in reference 11)

KEY TO FIGURE 5, FRONT CONTROL PANEL

Main distribution panel

- 1 Switch, mains
- 2 Switch, amplifiers
- 3 Switch, magnet and ESA
- 4 Switch, analyser-bake
- 5 Switch, source-bake
- 6 Switch, HT
- 7 Switch, spark

Magnet control and protection unit

- 8 Z-deflector control
- 9 Y-deflector control
- 10 ΔV control (accelerating voltage)
- 11 Focus control
- 12 Meter, accelerating voltage
- 13 Meter, magnet current
- 14 Switch, magnet range

Vacuum control panel

- 15 Source isolation valve (V5 - hydraulic)
- 16 Main vacuum valve (V4 - hydraulic)
- 17 Photoplate position control
- 18 Auxiliary vacuum valve (V3 - manual)
- 19 Auxiliary vacuum valve (V2 - electromagnetic)
- 20 Switch, hydraulic pump
- 21 Air-inlet valve (V1 - electromagnetic)

Beam-control unit

- 22 Switch and indicator lamp, beam on-off
- 23 Switch and indicator lamp, spark on-off
- 24 Meter, spark voltage
- 25 Switch, time (exposure)
- 26 Switch, pulse repetition rate
- 27 Switch, pulse length

Monitor-integrator control unit

- 28 Integrator meter
- 29 Monitor meter
- 30 Integrator zero control
- 31 Numerical counter
- 32 Monitor zero control
- 33 Exposure range switch (amplifiers' sensitivity)
- 34 Re-set button for numerical counter
- 35 Zero-Repeat-Stop switch (integrator cut-out switch S6 to the right)
- 36 Set-trip control (relay circuit)
- 37 Push button, beam on-off (in parallel with item 20)

Ionization gauge control unit

- 38 Re-set protection
 - 39 Vacuum range switch
 - 40 Set zero control
 - 41 Re-set protection
 - 42 Vacuum range switch
 - 43 Set zero control
 - 44 Meter, analyser pressure
 - 45 Meter, source pressure
 - 46 Meter, main vacuum (rough pressure)
 - 47 Meter, auxiliary vacuum (rough pressure)
- } Source ionization gauge
- } Analyser ionization gauge

The 'beam' on-off switch (22 in Figure 5) controls the supply to the beam-suppress half-plates. When both the 'spark' and the 'H.T.' switches are on and the 'beam' is off, the ion beam is deflected to the side and thus does not enter the electrostatic analyser.

The 'beam' on-off push button (37 in Figure 5) is connected in parallel with the beam switch and has precisely the same action. It is normally used when very short exposures are taken, because it is easier to control than the 'beam' switch.

The 'time' switch (25 in Figure 5) controls the beam-suppress voltage, switching off the beam after a pre-selected time. However, this is normally in the ∞ (infinity) position, and the beam is switched off manually after a fixed exposure, rather than after a fixed time.

5.2. Variable Parameters

The 'magnetic range' switch (14 in Figure 5) allows any one of ten values of magnetic current to be selected. It is most commonly set at 10, giving a spectrum showing mass lines from 6 to 240. It can be adjusted to other positions if a lower mass range is required, e.g., position 1 gives a mass range from 1 to 6, and position 5 gives a range from 1 to 70.

The four beam-adjustment controls are each ten-turn potentiometers (8, 9, 10, and 11 in Figure 5). The 'Z' deflector control adjusts the direction of the beam in the horizontal plane. The 'Y' deflector adjusts the direction in the vertical plane. These two controls are normally set at 500 (corresponding to 0 V), but may vary between -250 V and $+250$ V. Variations in the ' ΔV ' control will alter the accelerating voltage over 20 per cent of its nominal range. The 'focus' control varies between -150 V and 50 V, and is used for the focusing of the beam onto the photoplate. The focus may vary with different settings for the magnetic current. These settings are changed when the lower mass range must be expanded.

A mixed fraction of the total ion beam passing through the first two monitor plates is interrupted by the third plate, whereas the remainder passes into the magnetic analyser and then to the photoplate (Figure 3). The current registered on this third plate, the monitor-collector, is amplified and displayed on the 'monitor meter' (29 in Figure 5). It is a measure of the rate at which the charge is laid down on the photoplates.

The monitor output is also fed to an integrating amplifier, so that the integrated current can be used for the quantitative determination of plate exposures. The integrator output is displayed on the 'integrator' meter (28 in Figure 5).

The 'exposure range' switch (33 in Figure 5) selects the ranges of ion current and charge (displayed respectively on the 'monitor' and 'integrator' meters), and is calibrated in terms of nanocoulomb exposure, indicated by each full-scale deflection of the integrator meter.

The 'zero/repeat/stop' switch (35 in Figure 5) controls the operations of the integrator-amplifier. When in the 'zero' position, the integrator input is short-circuited, allowing the meter to be set to zero with the set-zero control. In the 'repeat' position, the integrator-amplifier is operative. When full-scale deflection is reached, the circuit automatically resets the integrator-amplifier (which is momentarily suppressed), and continues to integrate. Each full-scale deflection is registered as a count on the numerical counter (31 in Figure 5). In the 'stop' position, only one full-scale count is obtained.

The 'pulse repetition rate' (PRR) and the 'pulse length' (PL) switches (26 and 27 in Figure 5) control the frequency and the length of the radio-frequency (RF) pulses, and are used to vary the rate and intensity of the RF pulses. The PRR and PL are kept constant during analysis so that changes in the ratio of multiply charged to singly charged ions can be avoided. The lowest values for these parameters should be used in analyses for constituents with a low melting point if selective distillation by overheating of the sample is to be prevented. The highest values should be used for long exposures because this will lay down the charge at a high rate and reduce the sparking time. This is necessary because of the instability of the electronics, including the magnetic and ESA analysers, over extended periods. Hence, for long exposures, the parameters should be set at the highest convenient values, bearing in mind the limits imposed by the heating of the electrodes. The shorter parameters (10 pulses per second, each of 25 microseconds) are used for very short exposures, and the longer parameters (1000 pulses per second, each of 200 microseconds) for long exposures.

The 'spark voltage' variac is located under the control desk and controls the range of the RF spark voltage. The RF voltage ranges from 0 to 80 kV, a stop being provided at the 80 per cent position on the variac. The percentage value of the chosen spark voltage is indicated by the spark voltage meter (24 in Figure 5).

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The 'photoplate position' indicator (17 in Figure 5) shows the position of the photoplate on the photoplate rack. The plate can be moved across the magnetic gap to give thirty-two exposures on each plate, of which fifteen would normally be used for the standard and the remainder for the sample. If the range required is so large that fifteen exposures would not suffice, short exposures should be taken on one photoplate and long exposures on another (with a convenient standard for each photoplate). Compromises must be made between the speed of analysis, the range of elements to be covered, and the space available on the photoplate. All the exposure data should be entered on the data sheets provided. Table 2 is an example of a completed exposure data sheet, and Table 3 is a guide to which PRR and PL parameters should be used for each exposure.

TABLE 2

Specimen MS7 plate data sheet

K3, K7: Cu samples	Date: 27th May, 1977	Source gasket: Viton
H6: Cu standard	Sample: K3, H6, K7	Source cleaned: Yes
	Plate number: K35	Source baked: No
	Cassette number: 8	Previous sample: Ru/Ag

Time at start and finish	Photo-plate exposure	Exposure $\times 10^{-9}$ C	Range factors		Meter or counter	Pulse repetition rate, p.p.s.*	Pulse length μ s	Spark volt %	Magnet current mA	Accelerating voltage kV	Anal. pressure torr	Source pressure torr	
			Int.	Mon.									
9h12	1	1×10^{-4}	10^{-3}		0	10	25	30	290	23,5	2×10^{-8}	5×10^{-7}	
		$1,8 \times 10^{-4}$	10^{-3}	0	10	25							
	K3	2	$3,2 \times 10^{-4}$	10^{-3}		0	10						25
		3	$5,6 \times 10^{-4}$	10^{-3}		0	10						25
			1×10^{-3}	10^{-3}	0	10	25						
10h03	4	$1,8 \times 10^{-3}$	10^{-2}		0	30	25						
		$3,2 \times 10^{-3}$	10^{-2}	0	30	25							
	5	$5,6 \times 10^{-3}$	10^{-2}		0	30	25						
		1×10^{-2}	10^{-2}	1	30	25							
		$1,8 \times 10^{-2}$	10^{-2}	1	30	50							
10h47	6	$2,2 \times 10^{-3}$	10^{-2}		0	30	50			2×10^{-8}	6×10^{-7}		
	7	$4,6 \times 10^{-3}$	10^{-2}	0	30	50							
		1×10^{-2}	10^{-2}	1	30	50							
		$2,2 \times 10^{-2}$	10^{-1}	1	30	100							
H6	8	$4,6 \times 10^{-2}$	10^{-1}		1	30	100						
		1×10^{-1}	10^{-1}	2	30	100							
	9	$2,2 \times 10^{-1}$	1		2	30	100						
		$4,6 \times 10^{-1}$	1		2	100	100						
10	1	1			3	100	100						
	11	2,2	3		3	100	100						
11h07	12	$5,6 \times 10^{-1}$	1		0	100	100			3×10^{-8}	$6,6 \times 10^{-7}$		
		1	1		1	100	100						
		1,8	10		1	100	100						
		3,2	10		1	100	100						
		5,6	10		1	100	200						
K7	14	10	10		2	100	200						
		18	100		2	100	200						
	15	32	100		2	100	200						
		56	100		2	300	200						
12h20	16	100	100		3	300	200						

* Pulses per second

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TABLE 3

Suggested spark parameters for each exposure

Photoplate exposure no.	Exposure nC	Numerical counter	Pulse repetition rate, p.p.s	Pulse length μ s
1	10^{-4}		10	25
2	3×10^{-4}		10	25
3	10^{-3}		10	25
4	3×10^{-3}		10	25
5	10^{-2}		10	25
6	3×10^{-2}		30	50
7	10^{-1}		30	50
8	3×10^{-1}		30	100
9	1		100	200
10	3		100	200
11	10		100	200
12	30		100	200
13	100		300	200
14	3×10^2	3	300	200
15	1×10^3	10	1000	200
16	3×10^3	30	1000	200

6. SPECIFICATIONS

The pressure specifications are as follows:

Source 5×10^{-7} torr ($6,665 \times 10^{-8}$ kPa)
 Analyser 10^{-8} torr (10^{-9} kPa) after baking.

These specifications have been met on several occasions after baking.

The resolving power is quoted as 3000 at mass 208, and 1100 at mass 28. A detailed procedure for the attainment of the best ΔV and focus settings is outlined in the manual¹¹. This procedure was followed at NIM, and the expected resolving power was obtained.

The sensitivity was checked on electrodes cut from samples of Johnson Matthey CA4 copper. A range of exposures was taken, and the sensitivity was defined as the exposure representing the threshold for detection of an element. For all the elements quoted, the instrument was found to be within the specifications.

The transmission, i.e., the speed with which a charge can be laid down, is obtained by the setting of the RF spark voltage at 30 per cent (approximately 30 kV), PRR at 1000 pulses per second, and PL at 200 microseconds. The time required for the collection of a charge of 300 nC with copper electrodes is then determined. This time should be less than 30 minutes. The instrument achieved this rate of transmission on several test runs.

7. POSSIBLE SOURCES OF INTERFERENCE IN SSMS

Inter-element effects are not experienced in mass spectrometry, and the interferences are confined to line-overlap effects, such as halation from matrix lines, and overlap from multiple lines and molecular lines. Interference from halation occurs in the determination of zinc in a copper matrix, when halation from ^{63}Cu and ^{65}Cu prevents the use of ^{64}Zn , the most sensitive zinc line, and halation from ^{54}Fe and ^{56}Fe prevents the determination of manganese by use of the mono-isotopic ^{55}Mn isotope.

Multiple-line interference is observed when ^{10}B is determined in the presence of large amounts of silicon, producing the isotope $^{30}\text{Si}^{2+}$ (and $^{208}\text{Pb}^{2+}$ interference with the mono-isotope ^{103}Rh line). However, it is possible for these interferences to be overcome or corrected. Interference from molecular lines is observed in the determination of tellurium, where ^{63}Cu - ^{63}Cu at line 176, ^{63}Cu - ^{65}Cu at line 129, and ^{65}Cu - ^{65}Cu at line 130 interfere with the most sensitive tellurium lines.

8. RECOMMENDED ANALYTICAL PROCEDURE

The procedure recommended for determinations by SSMS is given in Appendix I.

9. APPLICATION STUDIES

Various types of material were analysed by SSMS during the period of commissioning, and the following is a brief discussion of these investigations.

9.1. Ruthenium

High-purity ruthenium metal powder was submitted for analysis. The powder is very brittle and does not bind readily. Consequently, the electrodes pressed in the AEI die (Appendix II) had no mechanical strength and could not be used for sparking. It was decided that the sample should be mixed in a 1-to-1 ratio with silver powder (99,9999 per cent pure), and then pressed into electrodes. This procedure produced strong, durable electrodes, with good sparking characteristics owing to the presence of the silver. Results showed that twenty-seven elements could be measured in a ruthenium matrix. Agreement with the other results for this sample were good for some elements, and poor for others. The results also indicated that the sample prepared by use of the McCrone Micronizer was much more homogeneous than the sample prepared in an agate pestle and mortar¹².

The poor agreement for some elements was attributed to cross-contamination from the Micronizer mill, and the distortion of spectral lines for some elements.

9.2. Copper-Nickel Cathodes

Samples of copper-nickel cathodes in the form of turnings were submitted for analysis. These were formed into discs in an induction-coupled centrifugal furnace, and electrodes were cut from the discs. For the nickel cathodes, twenty-four elements were reported, and for the copper cathodes twenty-five elements. Included among these elements were the platinum-group metals, arsenic, selenium, and tellurium. Comparison with other techniques was not possible, but the precision of the method was obtained from the analyses of one copper sample on seven separate plates, each plate including a copper standard. The precision varied from 10 per cent for ⁵⁶Fe to 33 per cent for ⁵⁵Mn (Table 4). The lack of precision in some instances may arise from sampling unhomogeneities, or instrumental errors.

TABLE 4

Precision obtained in seven analyses of sample K7

	⁵⁹ Co	⁶⁰ Ni	⁵⁸ Ni	⁵⁶ Fe	⁵⁴ Fe	⁵⁵ Mn
K72, p.p.m.	6,7	360	270	110	100	1,8
K73, p.p.m.	5,9	320	310	110	150	0,9
K74, p.p.m.	6,2	290	250	100	120	0,8
K75, p.p.m.	9,2	240	260	140	91	1,0
K76, p.p.m.	4,7	190	260	110	93	0,9
K77, p.p.m.	4,2	230	220	100	86	0,9
K78, p.p.m.	6,2	300	210	110	120	0,8
Mean, p.p.m.	6,22	275	255	112	110	1,02
Coeff. of variation, %	27	21	13	10	20	33

9.3. Boron in Aluminium

For the determination of boron¹³, the magnetic range of the instrument was changed from a setting of 10 to 3, since this would give a better resolution of the lines from 30 to 5, and 'cleaner' or less-crowded spectra. Results¹³ were reported down to 0,1 p.p.m. of boron, and compared favourably with other results. Precision figures were not determined, but were estimated at a relative standard deviation of 20 per cent.

10. CONCLUSIONS AND RECOMMENDATIONS

The results of the application studies indicate the importance of fine particle size (less than 400 mesh) in samples for the avoidance of errors arising from the lack of sample homogeneity in view of the small mass of sample that is vaporized in the RF spark. Suitable standards can have much higher concentrations of the analytes than those of the sample because of the linearity of the calibration over several orders of magnitude. This can often lead to improved accuracy of calibration. Standards and samples should be compatible despite the fact that inter-element effects do not exist, because the sparking characteristics of the different materials lead to widely differing relative sensitivities.

Certain limitations of the equipment and in the collection and reduction of data on the plates indicate that a number of short- and long-term improvement programmes should be undertaken.

10.1. Short-term Programmes

These should involve the ion gauges and the positioning of the electrodes, and should include modifications to the electrode holders, the electrode spark shield, and the beam chopper.

Ion gauges. These have been the cause of many breakdowns and result from the burning out of the thoriated tungsten filaments. Before the filament is replaced, which is a brief operation, the liquid-nitrogen traps must be freed from nitrogen and air admitted to the analyser. After the filament has been replaced, the system must be evacuated to 10^{-8} torr (10^{-9} kPa). An instrumental bake is often required for the achievement of this. These are lengthy operations.

It is proposed that the ion gauges should be meticulously checked and cleaned, the associated electronic components cleaned, and components replaced where necessary. Operators should ensure that the protective cut-out circuits are working properly.

Electrode holders. The electrode holders supplied by the manufacturers¹¹ consist of three separate parts. They are difficult to handle, lose their shape with use, and then fail to hold the electrodes in parallel positions. New electrode holders based on a design by Jackson¹⁴ are now being made.

Positioning of electrodes. Variation in the ion beam¹⁵⁻¹⁷ would be reduced by the use of a travelling microscope, which would enable the three perpendicular positions of the electrodes to be continuously monitored and adjusted.

Use of an ion-beam chopper. Short exposures cannot be measured accurately because of variations in the discharge. Chopping of the exposure and a reduction in the charge collected per unit time result in a lengthening of the effective exposure, the consumption of more sample, and a reduction in the effects of sample unhomogeneity. A chopper is available for testing.

Spark shield. A shield with a larger aperture is to be manufactured to facilitate the setting of the electrodes with a travelling microscope. So that sputtered material will not strike the walls of the source chamber, disposable glass slides will be fixed over the larger shield aperture.

10.2 Long-term Improvements

These include improvements to the electronics of the spectrometer system, the reduction of matrix effects such as halation, and the reduction of the time required for plate reading.

Electronics. More stringent controls would be made possible by the introduction of measuring devices to key sections such as the magnetic analyser and the spark-accelerating voltage control. Modifications to the monitor-integrator circuits are expected to improve their stability. Outdated electronic components in such units as the ionization gauge control should be transistorized.

Masking of matrix lines of high intensity. Halation caused by major matrix lines, and the interference effects of multiply charged species of these matrix lines, can seriously limit the sensitivity and precision obtainable¹⁸. Various approaches to this problem have been proposed and will be investigated.

Reduction in plate-reading time. At present, consideration is being given to the feeding of manually obtained line readings into a minicomputer for the calculation of line intensities, etc. An extension of

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the computer control of the plate-reading process would involve control, via a motorized drive, of the extra coordinates of plate reading. Once an automatic plate reader has been devised, programmes will be needed to cope with repeated scans of portions of the plate and to do the required calculations on the output data, including up-dating as more information becomes available.

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APPENDIX I

RECOMMENDED ANALYTICAL PROCEDURE FOR SSMS

Certain preliminaries, such as the preparation of the sample, cleaning of the source parts, loading of the photoplates, and ensuring that an adequate vacuum (10^{-6} torr, or 10^{-3} kPa) is obtainable, must be undertaken.

1. PREPARATION OF SAMPLES

Samples may be received either as conducting or non-conducting solids, or as liquids. Because of the high sensitivity of the technique, the preparation of samples must be kept to a minimum if contamination and losses of material are to be avoided.

1.1. Metal or Conducting Materials

- a. Cut or machine the metallic sample in its bulk or ingot form into electrodes (either rectangular or cylindrical) 1.5 to 2 mm in diameter and 10 mm long.
- b. Clean the electrodes in acid, dry them, and then store them in small labelled polyvials. If the metallic or conducting material is in a finely powdered form (less than 200 Tyler mesh), press it into electrodes in the die and press supplied by AEI (see Section 1.3).

1.2. Non-conducting Materials

- a. Grind the sample to less than 200 mesh, preferably to about 400 mesh. Because ore material is consumed in microgram quantities, preservation of its homogeneity is very important⁹, and care must be taken if contaminants are not to be introduced during the grinding. Grind in a McCrone Micronizer using agate elements.
- b. Mix the finely ground sample with nine parts by mass of a suitable binder-conductor of high purity (5 to 69S pure and of known composition). Graphite is usually used for this purpose, but silver, gold, or copper will also serve.
- c. Make a slurry in absolute alcohol, evaporate the alcohol under an infrared lamp, and bake the residue at 110°C. All traces of water must be removed or undesired molecular lines will appear in the mass spectrum of the sample. If necessary, introduce an internal standard (e.g., 25 µg of lutetium, rhenium, germanium, or gallium oxides per 550 mg of sample and graphite).
- d. Press the electrodes as described in Section 1.3.

1.3. Liquids

- a. Evaporate the sample to a small volume and transfer it to graphite moistened with absolute alcohol and the internal standard mix.
- b. Evaporate the preparation as described in Section 1.2.
- c. Mix the dried sample for 20 minutes in a Wig-I-bug before packing it into two holes drilled across a polythene slug (Appendix II).
- d. Mount the slug in a stainless-steel die and subject it to a pressure of 15 tons.
- e. Remove the slug from the die, force the electrodes from the slug, and mount them in the source.

An alternative procedure involves evaporation of the solution drop by drop directly onto a high-purity electrode (e.g., gold), and then sparking this electrode against a counter-electrode of the same material. This method is quicker, easier, and more sensitive than the former, but is less precise because the electrode is not entirely homogeneous.

2. PRELIMINARY CHECKS

- a. Clean all the removable parts with suitable acids, except the screws holding the kidney plate in place and their shields, and the 25 kV Nichrome leads. (All the metallic parts are made of tantalum, and the insulators are glass.)
- b. Also clean the lead glass and viewing glass; otherwise, you may not be able to see the electrodes in the source because of the metal deposited on the viewing glass.
- c. Clean the Viton sealing ring in hot soap solution, and then dry it.
- d. Re-assemble all the parts as shown in Figure 2 of the report.

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- e. In the darkroom, insert the photoplate into its holder (Figure 4 of the report). Slide the loaded photoplate into the light-proof cover, and place a plastic cap over the open end so that fogging of the plate can be prevented. Normally, four or eight cassettes are prepared in this manner, and are placed in a light-proof box. They are then ready for insertion into the magazine.
- f. Vent the magazine to the atmosphere after it has been isolated from the analyser. Then open the end-door and insert the four (or eight) cassettes around the drum. Remove the plastic cap just before you insert the cassettes, and finally twist each cassette retainer into position.
- g. Close the end-door, and evacuate the magazine. In order that pressures of about 10^{-8} torr (10^{-9} kPa) can be obtained, it is preferable for the magazine to be pumped overnight. Each plate in the analyser should be pumped for a further two hours before being exposed.
- h. Ensure that the liquid cold-traps above the diffusion pumps are filled with LN_2 and that the analyser vacuum is about 10^{-8} torr (10^{-9} kPa). If this vacuum cannot be obtained, leak detecting or baking, or both, may be required.

3. LOADING OF THE SAMPLE

Care should be taken that none of the internal source parts are touched after being cleaned. The cleaned source parts are re-assembled as shown in Figure 2 of the report.

- a. Open the jaws of the electrode clamps, insert the electrodes, and tighten the clamps.
- b. Using the electrode-adjustment mechanism shown on either side of the source in Figure 2 of the report, adjust the position of the electrodes to a predetermined distance from the no. 1 slit plate. This is usually between 0,4 and 2 mm. Then adjust the electrodes to overlap by about 0,5 mm directly in line with the three source slits (Figure 1 of the report). For the most accurate positioning, a travelling microscope should be used¹.
- c. Cover the electrodes with the tantalum sputter shield, and, by visual inspection, ensure that the electrodes do not touch any part of the source plate or kidney plate, and that the 25 kV leads are free from contact with the sputter shield or the stainless-steel liner.
- d. Apply a small quantity of high-vacuum grease to the cleaned Viton ring, work it well into the rubber, and mount the ring in the slit provided.
- e. Place the lead glass, and then the viewing glass, in the outer clamping ring, and place this assembly over the source against the Viton ring.
- f. Close the air-inlet valve and evacuate the source. When the source vacuum is on the 10^{-7} scale, begin the analysis.

4. PROCEDURE FOR EXPOSURES

- a. Check that a photoplate has been transferred from the magazine to the analyser (Appendix III), and set the photoplate-position indicator to the zero (blank) position.
- b. Check that the required vacuum has been attained, and that the 'amplifier' and 'magnet & ESA' switches have been switched on.
- c. Select the desired setting for the magnetic current range, and check that the beam-adjustment controls 'Z', 'Y', ' ΔV ', and 'focus' are compatible with this setting.
- d. Set the 'exposure range' switch to 10^{-3} nC.
- e. Set the 'zero/repeat/stop' (ZRS) switch to 'zero', and adjust the 'monitor' and 'integrator' meters to zero.
- f. Set ZRS to 'repeat', and adjust the 'monitor' set-zero control until the 'integrator' meter is stationary. If necessary, adjust the coarse control of the 'monitor', which is located at the back of the monitor-integrator control unit. Return ZRS to 'zero'.
- g. Set the PRR to 10 p.p.s., and PS to 25 μ s.
- h. To obtain an ion beam, switch on the 'HT'. After about 1,5 minutes, the 'accelerating voltage' meter (13 in Figure 5 of the report) should indicate the voltage supplied, which must be between 22 and 25 kV dependent on the setting of ' ΔV '.
- i. Switch on the 'spark' main switch. After about a minute, you will hear the relay in the electronics cubicle clicking-in, after which RF power is supplied to the electrodes. Set the 'spark voltage', which is below the desk, to the lowest convenient value (24 in Figure 5 of the report).
- j. Switch on the 'spark' and 'beam' switches on the beam-control panel, and set ZRS to 'repeat'. Adjust the electrodes slightly if necessary, using the electrode-adjusting mechanism. If

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required, adjust the PRR and PL switches until the 'monitor' meter shows a steady value of 5 to 10 per cent FSD (full-scale deflection). If the spark cannot be maintained, increase the spark voltage by adjusting the 'spark voltage' control.

- k. When sparking can be maintained continuously, slightly adjust the gap between the electrodes, observing the monitor meter for an indication of which gap position gives the best beam. Then expose repeatedly at 10^{-3} nC, adjusting 'set trip' (36 in Figure 5 of the report) until this trips, when the integrator meter reads 'FSD'.
- l. When the most intense ion beams have been obtained, set the 'exposure range' switch to 10 nC, and adjust the PRR and PL switches to obtain 5 to 10 per cent FSD on the 'monitor current' meter. For the removal of any surface contamination, set the ZRS to 'zero' and then to 'stop', and prespark until 10 nC of charge has been collected as indicated by the integrator meter.
- m. To make an exposure, set the ZRS switch to 'zero', and switch the beam off. Reset the counter, and move the 'photoplate position' indicator to position 1. Select the lowest exposure range required, and set the exposure range switch, the PRR, and the PL to the correct values, which are determined as shown in Section 5.2 of the report.
- n. Switch the beam on, and the ZRS switch to 'repeat' for multiple exposures or to 'stop' for a single exposure. Spark until the 'integrator' meter indicates that the exposure value has been reached, and then switch the 'beam' off and the ZRS switch to 'zero'.
- o. Move the 'photoplate position' indicator to the next position, select the range and pulse parameters for the next exposure, and spark as before until the required exposure value has been reached.
- p. Continue in this manner until the required exposures have been made. Make a note of the last photoplate position, and, assuming this is at position N, return the photoplate position indicator to the 'zero' position.
- q. To change the sample, switch the ZRS to 'zero', and the 'beam' and 'spark' to off, and switch off the 'spark' and 'HT' on the distribution panel. Isolate the source, allow the source to come to atmospheric pressure, and remove the glass cover assembly. Clean the inner glass, which will have sputtered material adhering to it. Remove the spark shield. Release the electrode clamps, remove the sparked sample, and replace with the next sample (or standard). Replace the spark shield, checking as before that the electrodes and 25 kV leads are isolated. Return the cleaned and dried glass cover assembly to its position, and evacuate the source to 10^{-7} torr (10^{-2} kPa), ready for exposure. If the analyser pressure has risen above 10^{-8} torr (10^{-3} kPa), adjust it as described in steps g and h of Section 2.
- r. To make the new exposure, prespark and continue as described in steps m to p, changing the photoplate position to N+2 after the prespark.
- s. On completing the exposures, transfer the photoplate from the analyser to the magazine (Appendix III). After recovering the photoplate from the magazine, develop it according to the manufacturers' instructions², as described previously³.

5. DATA REDUCTION

- a. Measure the percentage transmission of each isotope and background, using a modified Jarrell-Ash microphotometer⁴. The percentages should be between 10 and 80, over which range the response of the photoplate can be linearized.
- b. Correct the line intensity for the background, and then linearize by using the formula

$$T_c = \frac{(B - L)(1 - S)}{B - S} \text{ and } \Delta = \log_e \left(\frac{1}{T_c} - 1 \right),$$

where B = background,
 L = line intensity, and
 S = saturation transmission for the photoplate.

- c. Then plot the line intensity (corrected) against the log of the exposure (Figure I-1). This graph should have a slope of 45° . Read and note the intercept on the X-axis (exposure axis), and record it as $\epsilon_{\Delta n} E$, where E is the isotope of interest.

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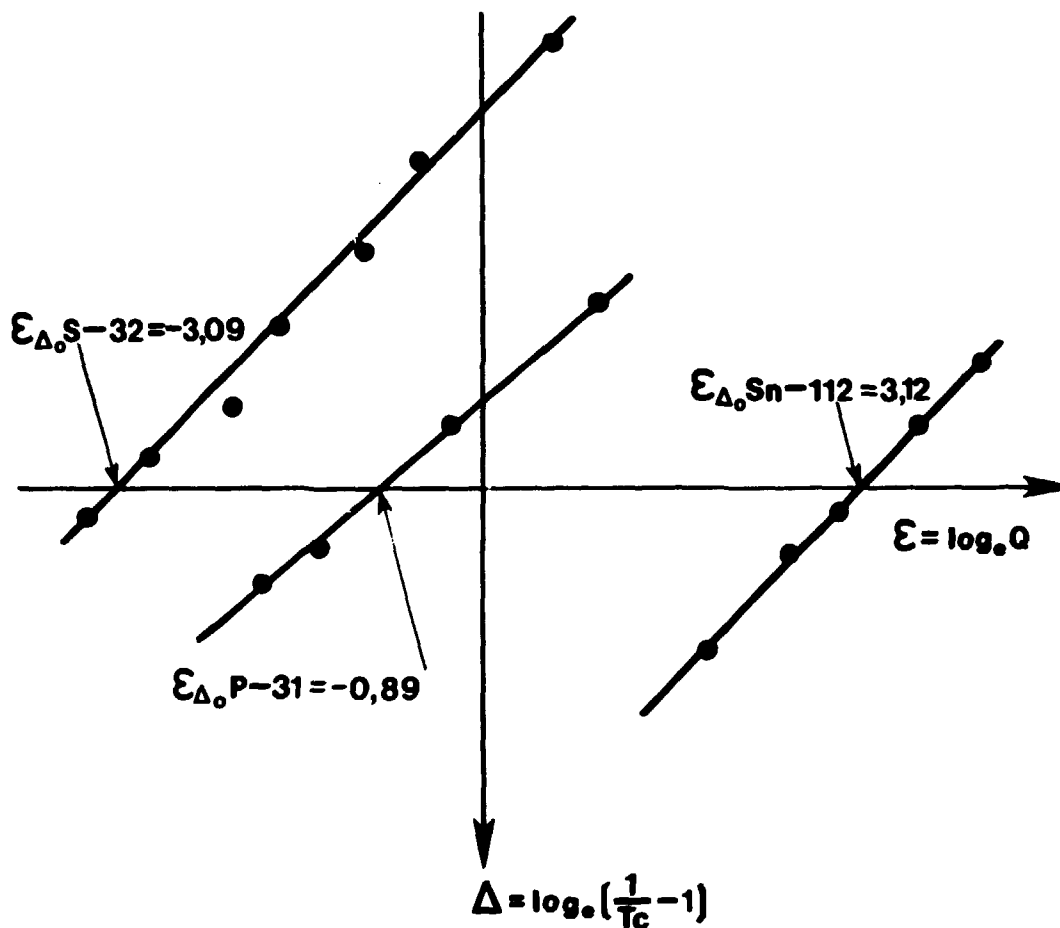


FIGURE 1-1. Calibration curves for sulphur, phosphorus, and tin

- d. When you have read and plotted all the lines, and have determined the values of ϵ_{Δ_0} , calculate the relative sensitivity factor (*RSF*) for each isotope, using the formula

$$RSF_{IS}^E = \frac{[E]}{[IS]} \cdot \frac{e^{\epsilon \Delta_0^E}}{e^{\epsilon \Delta_0^{IS}}} \cdot \frac{I_{IS}}{I_E}$$

where *E* refers to the isotope, and *IS* to the internal standard, which is usually a minor isotope of the matrix material. I_E and I_{IS} are the respective isotopic abundances, and $[E]$, $[IS]$ are the respective concentrations. This *RSF* figure is determined on the standard material.

- e. When you have obtained the *RSF* values, read and process the lines of the sample as before.
f. Determine the concentration of the element, using the formula

$$[E] = RSF_{IS}^E \cdot [IS] \cdot \frac{e^{\epsilon \Delta_0^{IS}}}{e^{\epsilon \Delta_0^E}} \cdot \frac{I_{IS}}{I_E}$$

where the *RSF* values are those determined before. The application of a minicomputer to this manipulation of data is being studied⁶.

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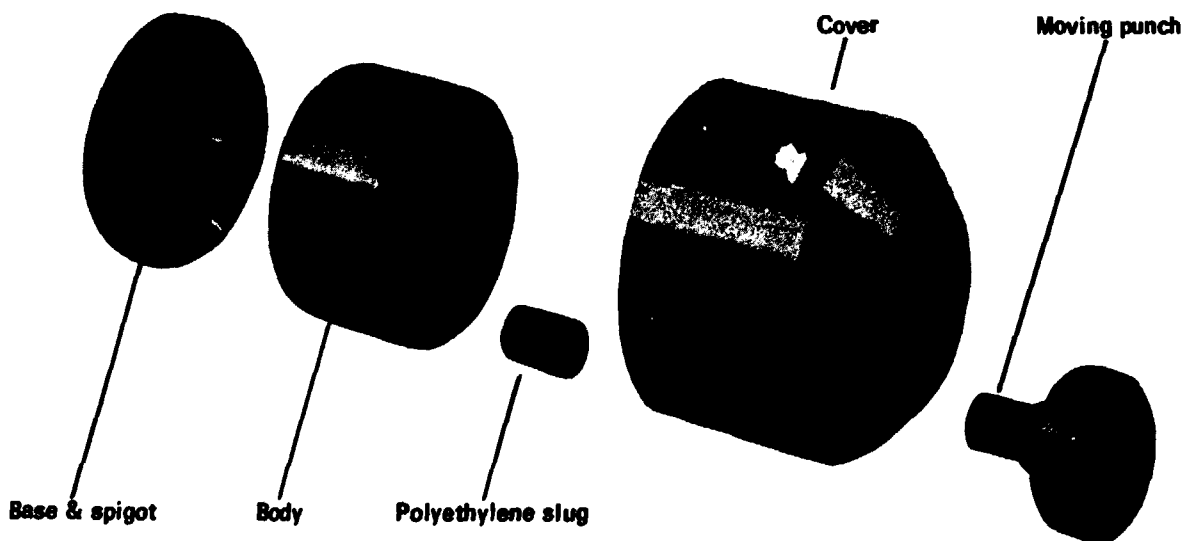
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APPENDIX II

STAINLESS-STEEL DIE FOR THE MOULDING OF SAMPLES

(Reproduced from Publication 2033-78 EDA 2500 0869 of AEI Scientific Apparatus Ltd, Manchester, England)



DESIGN OF DIE

The die consists of a steel cylinder or die body of 7/16 in. (11.1 mm) bore 2 1/4 in. (57 mm) outer diameter and 13/16 in. (20.6 mm) long. The die body stands on a separate base with a central spigot which enters the bore. The polyethylene slug is placed between the flat ends of the punch and spigot. The projecting end of the punch is enlarged to 1 1/4 in. (31.8 mm) diameter. A force of 11 tons is applied to the punch to compress the slug. During the application of this pressure the polyethylene tends to flow, allowing a near isostatic pressure to be applied to the enclosed sample powder causing it to become compacted into a rod. On release of pressure the polyethylene regains its original shape allowing easy removal of the sample rod.

ELECTRODES

The size of the finished electrodes is determined by the dimensions of the hole in the polyethylene slug. For use in the MS7 or MS702 electrodes of 7/64 in (2.78 mm) diameter and 75° cone angle are prepared. Very small electrodes of 3/64 in (1.19 mm) diameter can be pressed.

PRESS

Any hydraulic press found in the laboratory is normally suitable for use with the moulding die. The press used to form the electrodes illustrated, was the Type C-30 30 ton press manufactured by the Research, & Industrial Instrument Co., London.

SAMPLE PREPARATION

Samples for analysis are usually in the form of a powder either in its own right or as a result of grinding in an agate mortar and pestle. The sample is mixed with a quantity of pure graphite powder, or other conducting matrix, if non-conducting.

A small quantity of sample and graphite mixture is deposited in the polyethylene slug and pressed down. Pure graphite powder is then deposited on top of the sample and pressed down until the whole of the drilling is filled. The slug is then placed in the die and subjected to the pressing operation.



Tipped electrodes, described above, are generally required when limited quantities of sample are available. The process, however may be used for metal powders and most sample materials either pure or mixed with a proportion of graphite or other pure material to assist sparking.

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APPENDIX III

INSTRUCTIONS FOR THE TRANSFER OF THE PHOTOPLATE BETWEEN THE MAGAZINE AND THE ANALYSER

- a. When the magazine has been completely evacuated, the samples inserted, and the vacuum brought to the correct level, transfer a photoplate from the magazine to the analyser. To do this, open sliding valve V10, and set the photoplate position indicator to 8. Ensure that the rotating drum is at the correct position. Fully retract the ramrod in the 'Release' position, and rotate the control knob to the 'Engage' position. Gently push the ramrod in until a definite stop is felt. Rotate the control to the 'Release' position, then withdraw the ramrod. Close sliding valve V10.
- b. When the photoplate has been exposed, it is removed in a similar manner. Set the photoplate position indicator to 8 and open sliding valve V10, ensuring that the rotating drum is in the correct position. Set the control on the ramrod to 'Release' and push the ramrod fully in. Set the control to 'Engage', and withdraw the ramrod until resistance is felt. Set the control to 'Release' and fully withdraw the ramrod. The exposed plate is now enclosed in its original cassette on the rotating drum. Then isolate the magazine from the source and bring it to atmospheric pressure. Open the end door, twist the cassette retainer out of place, remove the cassette from the drum, fit the plastic cap into position, and deposit in the light-proof box.