MINTEK

REPORT

No. M125

COMMISSIONING OF AN AUTOMATED MICROPHOTOMETER USED IN SPARK-SOURCE MASS SPECTROMETRY

by

D.C.G. Pearton and C. Heron

28th November, 1983

COUNCIL FOR MINERAL TECHNOLOGY
200 Hans Strijdom Road
RANDBURG
South Africa

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(ANALYTICAL SCIENCE DIVISION)

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Investigators D.C.G. Pearton and C. Heron
Director of Division R.C. Mallett

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All correspondence to Mintek, Private Bag X3015, Randburg, 2125 South Africa

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SYNOPSIS

A description of the automated microphotometer and its operation is given, which includes measurement under computer control. Speed and precision tests indicate that the system is superior in every respect to that in which an analyst reads the photoplates in spark-source mass spectrometry.

SAMEVATTING

Hierdie verslag beskryf die geoutomatiseerde mikrofotometer en sy werking en dit sluit meting onder rekenaarbeheer in. Spoed- en presisietoetse toon dat die stelsel in elke opsig beter is as die een waarin 'n analis in vonkbronmassaspektrometrie die fotoplate lees.

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1. INTRODUCTION

The most tedious and time-consuming aspect of mass spectrometry is the reading of the photoplate produced by sparking of the sample. The photoplate contains the isotopic information on all the elements from uranium to lithium, and the analyst must read each isotopic line from each exposure for background and for line intensity. An average spectrum may contain as many as 90 isotopic lines from 16 exposures. This means that (90 + 90) × 16 = 2880 lines need to be read.

At the Council for Mineral Technology (Mintek), these lines are read on a Jarrell–Ash microphotometer, which was modified in an earlier investigation. With this equipment, an analyst requires an elapsed time of about 4 days to read all the lines on an 'average' spectrum and to store the data on disc — a monumental task that is extremely tedious and time-consuming. It was realized that the use of an automatic microphotometer would expedite the reading of photoplates since, once the instrument had been lined up and the necessary isotopic lines indicated, it would read all the lines and 'dump' the readings to disc. Therefore, it was decided that Mintek should investigate the possibility of commissioning an automatic system.

Numerous reports on automated photoplate-readers have been published. Many approaches have been suggested, from operator-interactive programmes to completely automatic systems, and several transformation formulae and means for the identification of lines have been considered. All the approaches are best summed up by Vanderborght and Van Grieken[1], Stüwer[2], Van Hoye *et al.*[3], and Conzemius *et al.*[4].

Mintek decided to follow the system of the Council for Scientific and Industrial Research (CSIR), where several automatic microphotometers have been constructed[5]. The CSIR modified Mintek's Jena microphotometer, and the Mintek system differs from the CSIR system only in that the photoplates are of different dimensions from those used at the CSIR. Also, the photoplates produced by Mintek have broader spectra and are not as uniformly located in the *Y*-(or exposure) direction. These difficulties were overcome by the design of a new photoplate holder and the modification of the software programmes to allow for inconsistent spacing in the *Y*-direction[5].

This report describes the setting-up and operation of this system, and includes the results of tests on its accuracy and precision.

2. EQUIPMENT

2.1. The Microphotometer

The microphotometer used is a Zeiss Jena II. This was modified as follows.

(a) The table previously used for holding the photoplate was replaced with a heavy chilled-brass plate, which is uniformly level. Adjustments can be made in the horizontal plane to ensure that the photoplate is perfectly level in its holder, and in the vertical plane to ensure that the photoplate is moved correctly in both the *X*- and *Y*-directions.

(b) Two accurate lead screws with anti-backlash ball nuts replace the previous drives. The *X*-drive has manipulators for the setting of the *X*-coordinates by hand; this drive was coupled to a Ferranti fringe-field system, which accurately controls the movement of the photoplate in this direction to 1 μm. The rate at which photoplates are read is 5 mm/s. The *X*- and *Y*-drives both have sewing-machine motors, and incorporate clutch systems.

(c) The tungsten lamp and holder were replaced by a 50 W quartz–iodide lamp with a matching photomultiplier tube.

(d) The measuring head was converted to a swivel type to permit easy access in the mounting and removal of the photoplate.

(e) Electronic circuits were built to drive the motors in both directions and convert the data from the photomultiplier to digital data that can be stored in the computer.

(f) Software support in ASSEMBLER and BASIC were supplied for the computer-controlling programmes. More details can be obtained from the CSIR[5].

2.2. The Computer

The whole system for the reading of photoplates operates through a Southwest Technical Products M6809 computer, with 56 K of available memory and twin floppy-disc drives.

2.3. The Photoplates

In this investigation, Ilford QII extra-thin photoplates, 10-inches by 2-inches, were used, and were produced on a modified AEI M702 spark-source mass spectrometer by the sparking of a homogeneous 'in-house' Mintek standard several times on several plates.

3. OVERALL OPERATION

The system is operated as follows.

(1) The analyst prepares the photoplate and clamps it into position.

(2) The X- and Y-coordinates of the lines of interest are then read automatically for the first exposure, from high mass to low mass.

(3) When the end of the photoplate is detected, it is moved automatically to the next exposure, and all the data from the first exposure are dumped onto the floppy disc.

(4) The second exposure is then read, this time from low to high mass, until the end of the photoplate on the high mass is detected. The third exposure is then aligned, and the data for the second exposure are dumped.

(5) In this manner, all the exposures are read for all the data required.

4. MEASUREMENT

The procedure for the measurement of a photoplate with mass-spectrometric data can be divided into three sections, as follows:

(i) setting-up of the photoplate,

(ii) entry of the relevant isotopes and calibration points, and

(iii) automatic measurement of the lines on the photoplate.

4.1. Setting-up of the Photoplate

4.1.1. Preparation of the Photoplate

The computer is provided with a cut-off point as follows. The extreme ends of the photoplate are scraped clean of emulsion so that two clear areas are produced. When these are read by the computer, a signal is sent to the motors to stop the X-drive, move the photoplate in the Y-direction to the next exposure, dump the data, reverse the X-drive, and read the next exposure. The extreme value at the high mass is chosen beyond ^{238}U, and that at the low mass exactly above ^{18}O. The clear area on the photoplate should be about 3 to 5 mm wide.

In addition to the clear areas at the extreme ends of the photoplate, a third clear area is prepared on the photoplate directly above the ^{107}Ag line, and this is read as a check on each isotope in the spectrum.

4.1.2. Placing of the Photoplate

The photoplate is placed in the recessed compartment of the table and clamped in position with 12 clamps. By use of the manual override to move the photoplate, the photoplate–holder combination is tested for flatness by the setting of the focus at the extreme right-hand corner (high-mass area) by use of the uranium or lead lines. If these are not present, the edge of the 'clear photoplate' is used for focusing. When this line is in focus (the focus control on the measuring head is used), the table is moved to the extreme left-hand corner (low-mass area) and the height is adjusted until one of the low-mass lines used in measurement is in focus. The high-mass side is checked again, brought into focus if necessary, and so is the low-mass side. This setting should be checked for the first and the last exposures. When the extreme ends are equally well in focus, the photoplate is measured for correct alignment in the X-direction.

The control on the extreme left-hand end under the table is screwed in or out so that the table will travel correctly, enabling low- and high-mass lines to be read near their centres for this setting. This is checked for the first and last exposures, and a compromise setting is chosen.

4.2. Isotopes

4.2.1. Isotopes for Measurement

All the isotopes on the photoplate can be read. However, in most investigations, only selected elements or isotopes are required. Hence, the analyst must enter a list of all the isotopes that need to be measured on that particular spectrum. For this to be done, he loads a programme called AUTOMEAS.BAS into the computer and runs it.

On the screen, MAIN MENU appears. This is depicted in Table 1.

There are various options, and these are arranged here in the most convenient order or sequence. (These options are explained in detail in Section 4.7.) Hence, the analyst enters '1...Isotopes for measurement.' The computer programme requests the name of the project. When this has been entered, the file PROJECT 1 is opened. This file includes all the isotopes required for that project, and is accessed by later programmes such as the programmes for measurement and processing. The analyst then enters each isotope (which is stored by the computer), including any special lines such as the central clear area at ^{107}Ag as a check of

TABLE I

The MAIN MENU

MAIN MENU
1...ISOTOPES FOR MEASUREMENT
2...ISOTOPES FOR CALIBRATION
3...SET Y-COORDINATES; ENTER THESE & EXPOSURES
4...TRANSMISSION LIMITS
5...MEASUREMENT

..... WHICH OPTION?

100 per cent and ^{109}Ag for saturation transmission. When the measurement programme is run, the computer measures an area of 150 units on either side of each isotope, and measures and records the line intensity and the background. When all the isotopes have been entered, the analyst enters 0,0 to return the programme to MAIN MENU.

4.2.2. Isotopes for Calibration

The isotopes are read in sequential fashion in both directions, i.e. from low mass to high mass, and from high mass to low mass. However, the computer converts the micrometer readings on the X-axis to units of mass, reads this line, and then assigns each isotope to a mass value. For the computer to do this, the photoplate must be calibrated. This is done as follows. The analyst enters several (up to eight) prominent lines across the mass range with their X-coordinates. The measurement programme then uses these lines to extrapolate and to find the relation between the isotopic lines (Section 4.2.1) and the reading on the X-scale.

From MAIN MENU, the option '2...Isotopes for calibration' is entered on the computer.

Some repeatable reference point must be chosen, i.e. a point that can relate different photoplates. The choice of the point is arbitrary, any point on the lower-mass scale being suitable. Then, with the measuring head aligned over the centre of this line, the analyst sets the X-counter to zero. In this work, ^{17}O was chosen as the zero point for several reasons.

(a) Oxygen is invariably present in the mass spectrum.
(b) ^{16}O is often far too intense, giving very diffuse lines.
(c) Lines of mass lower than ^{23}Na are seldom measured at Mintek.
(d) ^{18}O is beyond the clear area on the photoplate.

Several reference points are then chosen, e.g. ^{23}Na, ^{35}Cl, ^{48}Ti, ^{56}Fe, ^{64}Zn, ^{88}Sr, ^{120}Sn, ^{138}Ba, ^{181}Ta, ^{208}Pb, and ^{238}U. These may or may not be some of the isotopes for measurement. As the analyst moves the measuring head to a position above a line, he reads the X-counter and enters this in the programme with the name of the isotope. When he has entered all the calibration isotopes, he enters 0,0. The programme next requests the X-coordinates of the lower clear area on the photoplate, and then of the upper clear area on the photoplate.

Using these reference points, the computer then presents the X-coordinates of all the isotopes of interest on the screen. At this stage, the analyst can readily determine whether the extrapolation is correct. If it is not, it means that one of the reference points has been entered incorrectly. Provision has been made for this to be corrected. Once these coordinates are satisfactory, the programme returns to MAIN MENU.

4.3. *Y*-coordinates

Because the position of the lines in the Y-direction of the spectrum on the photoplate are not of a consistent or repeatable length and the distance between exposures can vary considerably, calibration for the Y-direction is also required. A programme routine was written from the MAIN MENU to move the photoplate accurately in the Y-direction. It starts when option '3...Set Y-coordinates' is entered. The analyst moves the photoplate to a position where the first exposure for the ^{109}Ag line is below the measuring head. He closes the slit height to between 1 and 2 mm, and accurately places the photoplate so that the top of the line is in this small slit. He then sets the Y-counter to zero, opens the slit, and sets to the maximum

height. The motor is engaged when he enters 'Y' in answer to the question 'MOVE Y-DIRECTION?' from the computer, and the photoplate moves slowly in the *Y*-direction. He notes the position corresponding to the centre of the first exposure while the motor (under computer control) moves the photoplate steadily to the second exposure, where he notes the *Y*-coordinate position.

In this manner, the analyst determines the *Y*-positions for each exposure, and jots them down so that he can enter them later.

4.4. Exposure Values

At this stage, the analyst enters *Y*-coordinates and the values for each exposure. This is done as follows. The analyst presses 'CONTROL C' on the computer terminal. When 'READY' is displayed, he enters 'RUN', and the computer programme requests the data. He then enters each *Y*-coordinate and the corresponding value for the exposure in sequence. (For each *Y*-coordinate, three values are calculated by the programme, viz $Y-2$, Y, and $Y+2$, the same exposure value being used for all three. Thus, each exposure is read three times. In the measurement programme, the median of the three readings is calculated, and this is dumped onto the floppy disc.) When these have been entered, the programme returns to the main section, and MAIN MENU is displayed again.

4.5. Transmission Limits

Before the photoplate can be measured, the analyst must set the dark current and 100 per cent transmission by the selection of option '4...Transmission limits'. The programme then commences measuring the percentage transmission. The analyst sets the slit to the correct measuring height, positions the plate with the measuring head above the clear control area on the photoplate, and notes the intensity as measured. This should read 100 per cent, and is set by use of the slit-width control on the microphotometer. The analyst physically blocks out the light (with a sheet of black paper), reads the intensity, and sets it to 0 per cent, using the small multi-turn potentiometer on the control panel, which is marked 'Set zero'. He removes the black paper, measures the reading of 100 per cent, and resets the intensity. The intensity is set alternately for 0 and 100 per cent until no further setting is required. The analyst then presses 'CONTROL C' and, when 'READY' is displayed, enters 'RUN'. The programme then returns to MAIN MENU.

4.6. Measurement

The analyst enters option '5...Measurement' on MAIN MENU and, on request from the programme, the names of the project and the spectrum. The programme prints all the isotopes to be read, as well as the *X*-coordinates, and asks whether any further isotopes are to be added. If necessary, these can be added at this stage. When all the additional isotopes have been added, the analyst enters 'N'. The display then asks whether the photoplate is in position, and the manual *X*-control and *Y*-control set to the 'AUTO' position. The photoplate should be at the extreme high-mass position, just beyond the clear area on the photoplate. Once these conditions have been met, 'Y' is entered and measurement begins. The plate is moved relatively quickly, i.e. at 5 mm/s, and the highest reading (background) and lowest reading (line intensity) for each isotope are measured for an area of 150 units on either side of the line. When the measurement of the exposure has been completed and the photoplate is at the low mass, the *Y*-motor moves the photoplate the required distance, and the *X*-drive is reversed All the line readings are dumped to the printer, which serves as a plate record and enables the analyst to check whether the correct lines are being measured. The photoplate is then scanned in the opposite direction, i.e. from low mass to high mass. As detailed in Section 4.3, each exposure is read three times. When the third reading has been completed, the median background and line are calculated, and these values, together with that for the corresponding exposure, are dumped onto the floppy disc under a file called SPECQT.DAT, where SPEC refers to the name of the spectrum being measured.

In this manner, all the exposures are read and the data dumped on disc to be processed by other programmes.

4.7. Options

MAIN MENU, as outlined in Table 1 gives the normal order for the various operations required in the measurement of photoplates. Some details on each option are given in the following sections.

4.7.1. Isotopes for Measurement

When the analyst selects Option 1, the computer loads and runs the programme called MINLO.BAS. Then he enters all the isotopes that are to be measured. He is asked how many isotopes are to be measured, and, when he has entered the correct number, the programme returns automatically to MAIN MENU.

4.7.2. Isotopes for Calibration

When the analyst selects Option 2, the computer loads and runs the programme called MINSE.BAS. Then he enters the calibration isotopes, and, when the list is complete, he enters 0,0. After this, the coordinates of all the isotopes for measurement are printed. If this is satisfactory, he enters 'Y', which indicates that the programme has ended, and the programme then returns to MAIN MENU.

4.7.3. Setting and Entry of Y-coordinates, and Entry of Exposure Values

The computer enters and runs the programme Y-COORDS.BAS, and the displa, prints 'MOVE Y-DIRECTION?'. When the photoplate is in the correct position, the analyst enters 'Y' and the photoplate starts moving slowly in the *Y*-direction. When all the spectra have been traversed (and the *Y*-values noted), he stops the programme with the 'CONTROL C' step. He then enters 'RUN', and the number of exposures and *Y*-values are requested. When he has entered all the pairs, i.e. *Y*-coordinates and exposures, the programme returns automatically to MAIN MENU.

4.7.4. Transmission Limits

For this option, the computer loads and runs the programme SCAN.BAS. The percentage transmission is measured for the portion of the photoplate under the measuring head; this is read alternately for 0 and 100 per cent until these are satisfactory. At this stage, the user presses 'CONTROL C' and the programme stops. He then enters 'RUN', and the programme returns to MAIN MENU.

4.7.5. Measurement

This is the final option. The computer enters and runs the programme called MINME-L4.BAS. The project name is required for the following reasons. After the isotopes to be measured have been entered (Option 1), they are stored on disc for use in the programmes for calibration of the isotopes and measurement. They are stored under the file name PROJECT I, where PROJECT is the name of the project. For example, if samples of South African coal are being analysed for several elements, the covering project might be called SACOAL. In this investigation, the PROJECT was AUTOPL. The disc on which the raw data are to be stored also has the name of the project (e.g. AUTOPL-A), and all the spectral data for the samples are stored on this disc. Finally, processing programmes can access all the data for these samples sequentially from the disc.

When the analyst has entered the name of the project and the spectrum, the computer displays all the isotopes to be measured. This serves as a convenient check before measurement. Also, additional isotopes can be added at this stage, e.g. elements or isotopes that were not initially required for measurement but might be required for individual spectra.

When the photoplate is in the correct position, and the analyst has selected AUTO for *X*-motor and *Y*-motor, the photoplate can be measured. Each exposure is measured three times (and printed). This enables the analyst to check on precision and reproducibility. The median should provide the most reliable reading for that exposure. When all the exposures have been read, the programme ends.

4.7.6. Variations

The order as prescribed in Table 1 is the normal order for the processing of photoplates. However, the order is entirely flexible, and any order can be used. If, for instance, a spectrum has just been read and, for reasons involving confidence limits or precision, it needs to be read again, options 1, 2, and 3 need not be executed again. All that is required is for the analyst to rename SPECQT.DAT so that the setting-up data can be used again. He can then call option '4...Transmission limits', reset the 0 and 100 per cent, and, when he has called '5...Measurement', the photoplate can be read again. Several such situations can be enumerated to illustrate that the prescribed order need not be adhered to.

Details of the individual programmes can be obtained from Mintek.

5. PRECISION AND ACCURACY

5.1. Repeated Reading of One Exposure

The required spectra would contain many isotopic lines at readable levels spread well over the entire mass range. Such an exposure was available from a photoplate containing a spectrum of several exposures from a sample called Spectromel-1. This was derived from a powdered sample (supplied by Johnson Matthey Chemicals) containing 53 elements, all at a concentration of 1,18 per cent.

The photoplate was correctly aligned in position, and the isotopes for measurement were entered into the computer programme. The *X*-coordinates of several calibration isotopes were read and entered, and the second exposure in the spectrum was read 16 times.

The 16 sets of data were processed by use of the programme for a mass spectrometer described by Pearton[6] to derive values for relative sensitivity factors (RSF) (with barium as internal standard). The precision was calculated on the 16 sets of RSF values. For this and other procedures requiring accuracy and precision, programmes based on the robust median and robust relative standard deviation were used. These are, as the names imply, robust methods for the determination of statistical quantities, and were chosen because of their lack of sensitivity to the effects of outliers. These techniques are well-documented in another Mintek report[7].

The precision obtained on the RSF figures are presented in Table 2. The poorest precisions (2,8 and 2,6) were obtained for ^{23}Na and ^{31}P; for both these isotopes, the lines were intense and thicker than other isotopic lines, which led to poorer precision. The precision for all the other lines was 2,0 or better. It should be noted that the full calibration range was covered, and that lines of poor intensity (^{207}Pb at 72 per cent transmission) and lines of strong intensity (^{48}Ti at 6 per cent transmission) were included. The precision for all of them was acceptable. As mentioned earlier, measurement is done alternately from high mass to low mass and from low mass to high mass. Hence, eight of the readings were in one direction, and eight in the opposite. The results obtained for precision indicate that there is no difference in the measurements taken in either direction; this is readily confirmed by detailed inspection of the printout of the data.

TABLE 2

Precision of values for relative sensitivity factors

Isotope	% T	Auto	Manual
^{23}Na	5,4	2,8	3,7
^{31}P	8,2	2,6	4,0
^{35}Cl	8,4	2,0	1,7
^{37}Cl	14	2,0	3,4
^{46}Ti	7,5	1,6	2,3
^{48}Ti	6,0	1,5	2,4
^{52}Cr	17	2,0	3,0
^{55}Mn	7,7	1,3	0,8
^{64}Zn	11	1,9	2,2
^{68}Zn	18	1,6	5,1
^{86}Sr	21	0,8	2,4
^{138}Ba	10	0,7	1,7
^{142}Ce	59	0,3	11
^{207}Pb	72	0,2	1,0

% T = Percentage transmission
Auto = Automated system
Manual = Manually operated

5.2. Readings Taken by the Analyst

An analyst read the same exposure on the modified system, using a variation of the SCAN programme (Section 4.7) in which the percentage transmission was displayed for each line. Using the isotopes listed in Table 1, he read the photoplate 16 times, jotted down the results, and then fed them manually into the computer programmes. The time required was 2 days, whereas the automated system took about 90 minutes. The 16 sets of data were processed by the same programmes used previously to give precision figures on the RSF values. These are given in column 4 of Table 2.

When the manual sets of data are compared with those obtained by the automated system, it can be seen that the precision of the former is not only almost invariably poorer, but that, even when the precision is very poor, e.g. 5,1 for ^{68}Zn and 11 for ^{142}Ce, the corresponding precision of the automated system is excellent.

5.3. Accuracy

A photoplate that had been read by an analyst and on which RSF values had been calculated (Spectromel) was processed on the automated microphotometer. The programmes were used to process the raw data

on disc, and the RSF values were calculated (barium being used as internal standard). A comparison of the two sets of RSF values is given in Table 3. It can be seen that the overall agreement of the results is acceptable (except for magnesium) and that the differences are within experimental error. Where there are significant differences, the results obtained with the automated system are probably more reliable.

TABLE 3

A comparison of values for relative sensitivity factors

Element	Auto	Manual
Mg	0,15	0,26
Cl	0,61	0,74
Zn	0,98	1,0
Br	2,0	2,2
Mo	0,90	0.90
Sb	8,4	7,8
Ce	1,3	1,4
W	5,1	5,4
Re	6,9	6,6
Tl	3,6	3,8
Pb	8,9	9,8

6. SPEED

The speed of operation with the automated system is far superior to what it is with manual methods. With an analyst taking the readings, the time required is 15 hours, whereas with the automated system it is 30 minutes. In addition, the data obtained from the automatic system are dumped directly onto the floppy disc, from where they can be readily manipulated. By the manual method, all the data must be entered into the computer from the table of hand-written data before they can be manipulated. This is a tedious procedure that takes about 15 hours. In addition, because of the tedium, the process is prone to error, especially in transcription.

7. DISCUSSION

The automated system possesses several advantages over the manual system.

(1) The automated system is about 60 times faster.

(2) The possibility of error (inherent in the manual system), such as electronic instability over long periods of time, errors in transcription, and other fatigue-related errors, are almost all removed or accounted for by the automated system.

(3) The precision of the automated system, based on repeated readings of the same spectrum, is superior, and its accuracy appears to be as high.

(4) Setting-up of the photoplate is a fairly tedious procedure, as is the establishment of the calibration in the X- and Y-directions. However, once these two procedures have been completed, the operation is straightforward and rapid, and the analyst is not required to give any assistance or to exercise any supervision during the measurement.

8. CONCLUSION

The automated system is far superior to the manual system in every respect, being 60 times faster and having higher precision and greater convenience. Once the photoplate has been set-up and the calibration factors have been determined, the photoplate can be measured without assistance or supervision.

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