ON LINE DATA ACQUISITION AND PROCESSING IN

A VARIAN TH-5 MASS SPECTROMETER

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ABSTRACT

Data acquisition and processing for isotopic abundance determination using mass spectrometer is reviewed. The details of the technique employed in Varian TH5 mass spectrometer are described.

INTRODUCTION

The application of computers in analytical chemistry has increased markedly in recent years, involving all aspects of analytical procedures and instrumentation. Digital electronics and laboratory scale digital computers are slowly becoming indispensible tools for analytical chemists. Manual analytical methods have been made automatic, where by speed and accury of the analyses are improved considerably and new analytical techniques have been developed.

The wide use of computers in recent years is primarily due to the significant advances in eletronic circuitry and instrumentation technology, with a large increase in the availability of computers with much greater range of memory and capability with an appreciable reduction of cost. In addition to this, the emergence of minicomputers which can be used as a built in component (on line) of analytical instruments for real time data acquisition for system control and data processing, has helped in the rapid development of analytical chemistry. Further, the application of interpretive computer languages like BASIC, FOCAL and LABTRAN has made programming an easy task.

A minicomputer may be shared by several instruments simultaneously or may be used exclusively (dedicated) for a single instrument. Examples of computer controlled instruments are discussed by Perrin[1]. According to him, it is probably more efficient if instruments with fast data collecting rates (viz. mass spectrometers and n.m.r spectrometers) have dedicated computers, where as those with slow data collection rates (such as I.R. and U.V. spectrometers, microcolorimeters and gas chromatographs) share a common central computer.

The general use of computers in mass spectrometry began a decade ago and has expanded rapidly. Much of the impetus for this has come from organic mass spectrometry, where complex mass spectra have to be acquired, reduced and analysed fast. Methods of searching mass spectral data by computer has generally been based on the successive comparison of the unknow spectrum with recorded spectrum to select the reference spectrum, which reproduces most features of the unknown. With minicomputers adequate storage may be a limitation, but this can be overcome with highly compressed spectral codes[2]. An alternative approach "reverse seaching", discussed by Abramson[1], has advantages especially where the unknown material is impure or is a mixture, because data base of the search becomes library of spectra rather than unknown species.

Minicomputers are also employed for mass spectrometric isotope abundance measurements. The function of the computer in this case is to calibrate the simple mass spectrum and measure the ratios of desired isotopes by peak switching and time integration. This aspect of the computer application in Varian TH5 Mass spectrometer is reviwed in this article.

FUNCTIONAL DETAILS OF VARIAN TH5 MASS SPECTROMETER

Varian TH5 Mass spectrometer is a single focussing thermionic instrument designed for precise isotope ratio measurements. It is fitted with a solid source and single, double and triple filament assemblies are provided for operation. The ions generated by the thermal surface ionisation are accelerated and drawn out into the analyser region by the accelerating voltage and the various ion focussing plates. The mass separation of the ions is effected in the magnetic sector field with a deflection of 90°. The ion detection can be carried out by either a faraday cup arrangement or a secondary eletron multiplier.

In general in mass spectrometers the scanning of the mass range of interest can be carried out by either varying the accelerating voltage, keeping the magnetic field value constant or by keeping the accelerating voltage constant and varying the magnetic field. These two modes of scanning have their own advantages and disadvantages and a choice of the mode of operation is made depending on the type of analysis required.

The principal advantage of the voltage scanning is the high speed of the scanning, that permits the increase of the number of cycles of repetitive scanning for a fixed time, which has, as a consequence, an improvement of signal to noise ratio by a factor of $\sqrt{K}$, where K is the number of cycles. Further the high speed of scanning also allows the possibility of investigating rapid phenomena, such as the appearence of decomposition products in high temperature thermodynamics by mass spectrometer.

On the other hand the major disadvantage of voltage scanning is the mass discrimination that is introduced in the measurement by the variation of ion extraction efficiency with variation of accelerating voltage. This discrimination is difficult to overcome, as it depends not only on the geometric, eletric and magnetic structure of the ion source, but also on the different voltages applied to the various focussing plates of the electron optics for obtaining a best extracted beam.

In the magnetic field scanning mode, the mass discrimination in the ion source disappears. But the field scanning is slow depending on the response time of the magnetic field. As the TH5 mass spectrometer is designed specifically for accurate isotope ratio determination and as a steady ion beam of the desired isotope can be maintained for long duration, speed of analysis is not the major factor to be taken into account. Further, for accurate isotopic analysis introduction of mass discrimination is not desirable. Hence magnetic field scanning mode is employed.

For accurate measurement of isotopic ratios by magnetic field switching a high reproducibility of the magnetic field setting is necessary, which cannot be achieved by conventional current regulators of the magnetic field, because of the hysteresis and heating effects. The field regulations are done in many ways by introducing hall probe motor driven coil etc. in the air gap between the pole pieces, which act as sensors and the current regulation is done using error signals from an external reference voltage. In the TH5 mass spectrometer hall probe is employed and the functional diagram of the field regulator is shown in Figure 1. The output voltage of the hall probe located in the air gap of the separating magnet is amplified and fed into one of the inputs of a differential amplifier, whose second input is driven by a reference voltage, by which the nominal value is given. The output voltage of the differential amplifier controls a servo amplifier which drives the current through the coils of the magnet. By the control circuits closed via Hall probe, the magnet current always adjusts itself such that the output voltage of the Hall probe is nearly the same as the set reference voltage. The proportionality
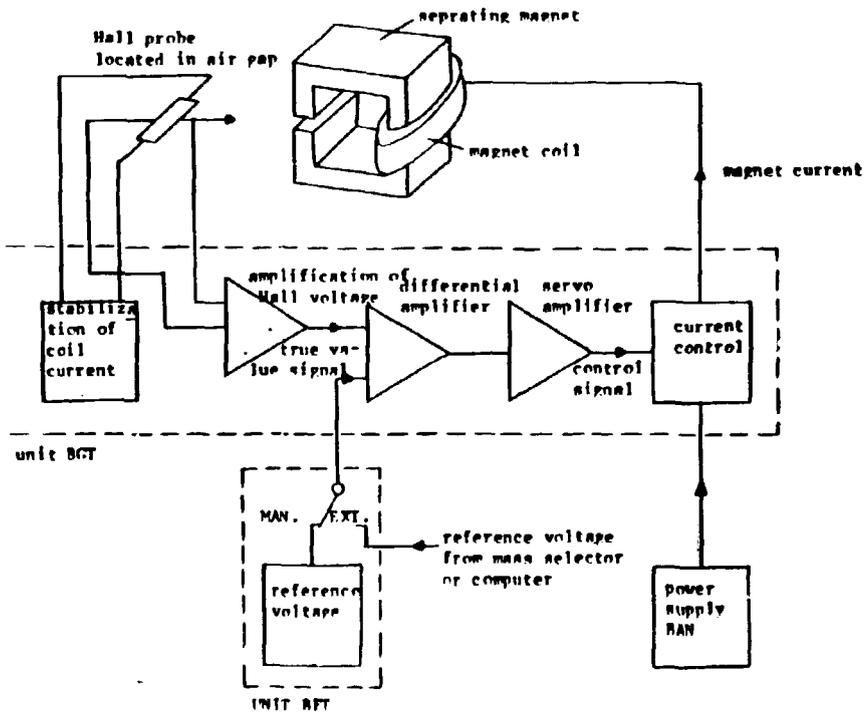
Figure 1 — Functional Diagram of Field Regulator

between the reference voltage and the field strength can be used for field scanning by the variation of the reference voltage. In the analog mode of data acquisition, partial voltage is tapped by means of step switches and potentiometers. When the operation is in the external mode (Figure 1) the reference voltage is provided by the on line computer. In this case, step switch is replaced by a relay arrangement and the potentiometers are set up by setting motors.

The ion detection can be accomplished by either a faraday collector or secondary electron multiplier. The out put current, amplified by a 100% feed back D. C. amplifier, is fed into the recording or data acquisition system through an interface unit (Range selector unit, Figure 2). The input of the Range selector unit is provided for simultaneous connections of upto eight amplifier units. One of the output is provided for connecting to a computer or tape recorder. The second out put is provided for connecting to a 10 m.v. potentiometer recorder. The output voltage from the two 100% feed back amplifiers (BDX and BDS) may range from 1 m v to 100 V. The feed back resistance that determines the current range is 10^{11} for BDX and 10^7 for BDS. The range of ion current that can be covered with BDX is between 10^{-14} A to 10^{-9} A, where as for BDS with a multiplier gain set at 10^7, this corresponds to a range of ion current 10^{-17} A to 10^{-12} A.

DATA ACQUISITION AND PROCESSING

There are two modes of data acquisition viz. analog and digital. In the analog mode of operation, the magnetic field is varied in a linear manner (manually or automatically) and the peaks recorded on a strip chart recorder. After repeated recording of the peaks the peak heights are measured for the determination of isotopic abundances. Such a procedure is slow and inefficient due to the great distance between peaks compared to their resolving power (for typical resolving power of 500). Further, the accuracy of the analysis is reduced due to slow speed of scanning and manual peak height measurements. The use of digital techniques and on line computer have resulted in considerable improvement of precision and accuracy.

Many of the new generation of computers are capable of providing analog or digital output signals, which can be used to perform control functions. In the TH5 mass spectrometer the computer is programmed to perform control functions as well as data acquisition and processing. The programme package for the data acquisition and processing comprises of two parts that are resident during operation. They are 1) operating system KOS3 with 4K memory requirement − 2) application programme package with 8 K memory.

The on line computer used is varian 620/L-100. This is a general purpose digital computer for system applications and processes 16 bit words in a full cycle execution time of 950 nanoseconds or over one million cycles per second. Core memory can be expanded in 4.096 word (4 k) increments, from a minimum of 4 K to a maximum of 32 K.

The operating system contains the following components:

a) Executive (Exc) controls the dialogue and contains error message output routine.

b) Loader (Ldr) can load both Fortran IV and Assembler via the paper tape reader. Initiation is by EXC.

c) I/O control (IOC) controls input/output exchange on the teletype and paper tape punch.

d) Interrupt Handler (INT) Schedules all interrupt signals such as Priority Interrupt Module (PIM), Real Time Clock (RTC) and power down/restart.

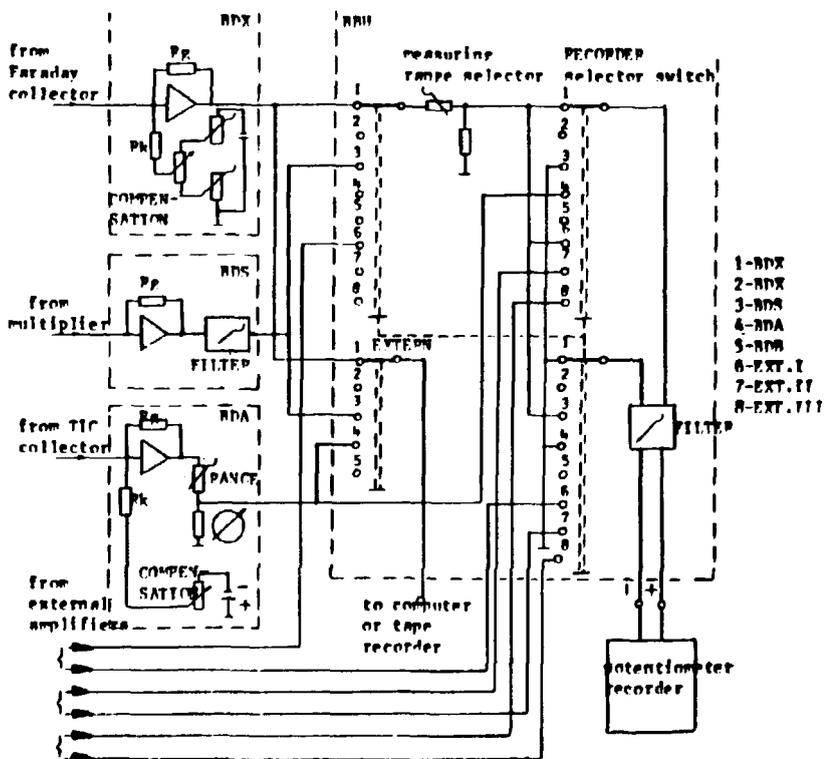e) Peripheral Device Driver (TYI, PTS) drives the teletype and paper tape reader.

Figure 2   Diagram of Range Selector Unit

APPLICATIONS SOFTWARE CONTAINS THE FOLLOWING MODULES

I) Calibration

The mass range (coarse setting of the magnetic field control unit) of interest is enquired in the dialogue. This range is scanned and the intensity and Digital Analog Converter (DAC) position are listed out. These peaks are assigned mass numbers in the dialogue. The mass numbers not found (intensity below threshold values) can be added to the input separately.

II) Data Acquisition and Evaluation

Data acquisition via peak spring is controlled by a list containing mass number and integration time for each isotope. Corrections for background and drift are applied to the data.

The output contains the isotope ratio values, relative standard deviation for isotope ratio values, and the proportion of the isotopes in weight and atom percentages. The calibration table comprises upto 30 masses and the list controlling data acquisition can contain upto 10 isotopes. The integration time for each isotope is freely selectable.

A flow chart of the programme is shown in Figure 3. Which is self explanatory. The sequence of ensuing dialogue is as follows:

After the application programme package is loaded in the computer in the teletype input START is placed. To this the system gives the following output.

SPECROSYSTEM 106 TH

The question mark indicates signalisation of a directive to be placed in the input.

The legal directives are:

STLS — Input control list

CALB — Execute calibration

ACQU — Measure (Execute data acquisition and compile list).

MSKL — List out calibration scale

LIST — List out individual values.

Illegal directives are answered with error message + + T-ERR3 (Table I lists the error messages).

. The execution of legal directives is described below.

DIRECTIVE STLS
.

The input control values of this directive are used for data acquisition by peak spring method. A graph showing the time of acquisition against ion current of the isotopes (Figure 4) demonstrates the application of this directive.
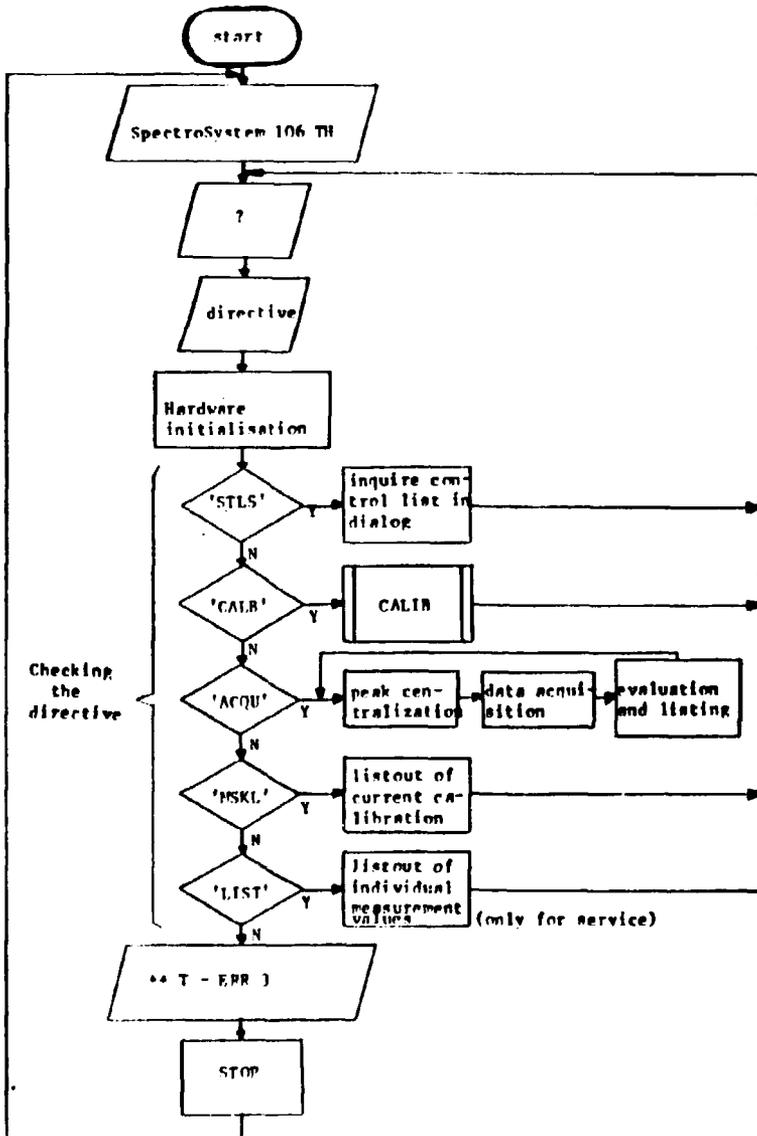
Figure 3 — Flow Chart of Computer Programme

Table I
Error Messages

X	Error	Correction
3	Illegal directive	Use only legal directives STLS, CALB, ACQU, MSKL, LIST
4	Number of isotopes greater than 9	Do not measure more than a maximum of 9 isotopes
10	Product $(N_{ISO} + 1)$ $°N_{MES} > 100$ or < 4	Reduce the number of cycles (N_{MES})
1	More than 40 masses per coarse range	Do not calibrate too many masses at the same time
11	Peak centralization: Peak does not fit into the buffer (leading peak edge)	Re-calibrate
12	As 11, trailing peak edge	Re-calibrate
2	Mass not found in calibration table	Calibrate
• •	DAC TRANSFER ERR	Hardware error of the DAC
• •	LD ERR X	
X=		
(1)	Lit overflow	
2	Reading error	Re-load; check paper tape (for dirt)
(3)	Memory overflow	
4	Checksum	Calibrate
(5)	Missing subroutine	
(6)	Illegal call up of the leader	
(7)	COMMON overflow	
(8)	Lit overflow	

The figures in brackets are relevant only when programs other than the SS 108 TF applications program are to be loaded or for the purposes of checking duplicates of paper tape No. 2.

• • ILL DIR   Illegal directive after READY

ion current
I

T = 0

M_{ST1} M_{ST2} M_{ST3} M_{ST4} M_{ST1} M_{ST2} M_{ST3} M_{ST4} M_{ST1} End   Time = T

N_{ST1} N_{ST2} N_{ST3} N_{ST4} N_{ST1} N_{ST2} N_{ST3} N_{ST4} N_{ST1}

T_{ST1} T_{ST2} T_{ST3} T_{ST4} T_{ST1} T_{ST2} T_{ST3} T_{ST4} T_{ST1}

$M_{ST1} = 0$ (Measurement of amplifier zero)
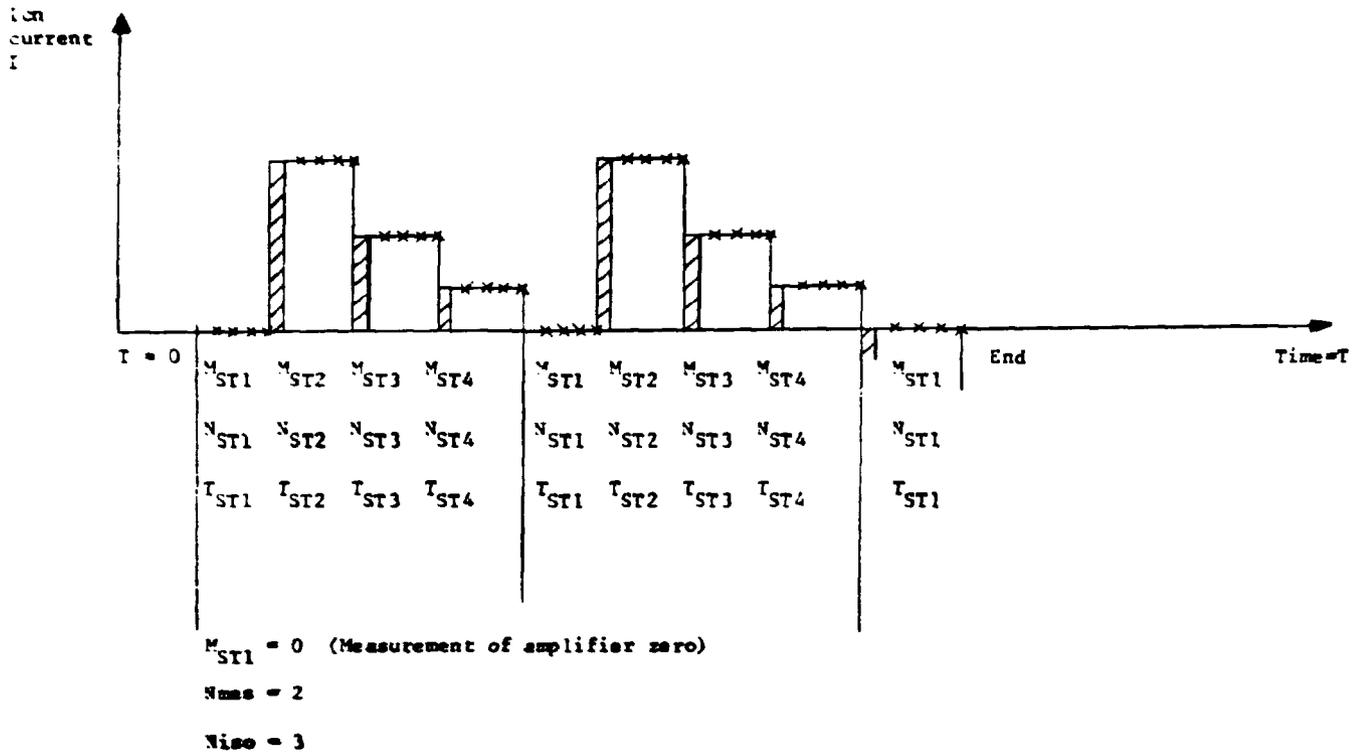
Nmas = 2

Niso = 3

Figure 4 — Graph of Time of Acquisition Against ion Currents

8

The measurement begins at $T = 0$. First the amplifier zero with an integration time of T_{ST1} and number of measurements N_{ST1} is measured (In Figure 4 $N_{ST1} = 4$).

Following the measurement of amplifier zero, the magnetic field is set to a value corresponding to a mass M_{ST2}. N_{ST2} measurements are carried out with an integration time of T_{ST2}. Similar procedure is repeated for all other masses to be measured. In Figure 4 the number of isotopes to be measured N_{ISO} is assumed to be 3, disregarding amplifier zero measurement.

After all the N_{ISO} isotopes have been measured, the cycle is started again at amplifier zero. This cycle is repeated N_{MES} times and finally the amplifier zero is measured for drift correction.

The time taken per spring is as follows: $T_P = 10 \times T_{ST} + N_{ST} T_{ST} = T_{ST} (10 + N_{ST})$.

The first term $10 \, T_{ST}$ represents time lapse necessary for the amplifier setting. The mass number of the control mass M_{ST} is to be selected in such a way that M_{ST1} represents the reference mass, which need not necessarily be the one with highest intensity.

The control data input for natural Uranium analysis carried out in the laboratory is listed in Table II were in operator input are underlined.

Table II

Control Data Input

```
┌─────────────────────────────────────────────────────────────────────┐
│ START                                                                │
│                                                                      │
│ SPECTROSYSTEM 106 TH                                                 │
│ ? STLS                                                               │
│                                                                      │
│ EINGABE DER STEUERPARAMETER        (INPUT OF CONTROL PARAMETERS)     │
│                                                                      │
│ PROBENBEZEICHNUNG - URAN           (SAMPLE DESIGNATION)              │
│ ANZAHL ISOTOPE ···· 2.             (N_ISO : 2 ISOTOPES)             │
│ ANZAHL MESSUNGEN ·· 10.            (N_MES : 10 CYCLES)              │
│                                                                      │
│ NULLPUNKT                          (AMPLIFIER ZERO)                 │
│                                                                      │
│ INT. ZEIT ·· .32                   (T_STI; in seconds)             │
│ ANZ.MESSG· 5.                      (N_STI, MEAS, POINTS)           │
│                                                                      │
│ MASSE ···· 238.                    (M_ST2, REFERENCE MASS)         │
│ INT. ZEIT ·· .32                   (T_ST2)                         │
│ ANZ. MESSG· 5.                     (N_ST2)                         │
│                                                                      │
│ MASSE ····· 235.                   (M_ST3)                         │
│ INT. ZEIT ·· 1.28                  (T_ST3)                         │
│ ANZ. MESSG· 5.                     (N_ST3)                         │
└─────────────────────────────────────────────────────────────────────┘
```

DIRECTIVE CALB

The directive CALIBRATION assigns field control unit setting and mass numbers. The procedure is best understood by the dialogue (Table III) for natural Uranium analysis.

After the directive CALB is placed in the input, coarse range for calibration is to be assigned. In Table III, coarse range 13 is assigned. The calibration module sets the field control unit to this range scans this range with Digital Analog converter (DAC). In order to reduce the time of scan, ion current is measured after every 4 DAC values and then compared with a threshold (CTHR = 0,01V). If the ion current signal is greater than this threshold, the field springs 20 steps back and scan the region in single steps untill the peak end has been obtained. The geometrical centre between the begining and the end is the peak position. It is important that amplifier zero should be adjusted to be lower than CTHR value. Otherwise peak recognition is not possible. After a peak is identified, the scanning is resumed in steps of four.

At the end of the scanning, the position list showing peak number, DAC values corresponding to peak positions and the intensity of the peaks in volts, appears in the output. In Table III two peaks and their corresponding intensities are shown. In the dialogue mass numbers 235 and 238 are assigned to them. After the input of mass numbers, specification of mass range as 0(zero) terminates the calibration measurements. If the calibrations are required in other coarse ranges, these can be entered in the input and the dialogue of mass assignment is repeated.

At the termination of the calibration measurement, the settings of magnetic field control unit are enquired for measurement of amplifier zero. The coarse range is the same one used for calibration measurement. The DAC value is calculated for a mass where it is assumed that there are no peaks. In Table III, this corresponds to value closer to mass 236.

Once the magnetic field control unit for zero measurement has been determined, field control values (coarse/DAC) for other mass numbers can be assigned. This becomes necessary when ion currents for isotopes are too small (less than CTHR values) or when measurement is to be avoided due to the circumstances relating to the nature of the sample (for eg. Pu) or calibration is already known from previous calibration. Calibration comprises a maximum of 30 calibration points. An example of the dialogue for supplementary mass U^{236} in NBS standard U 970 is shown in Table IV, along with the isotope abundance values obtained.

DIRECTIVE ACQU

Data acquisition is by peak spring procedure, where the mass numbers to be measured are sampled N_{MES} times and the ion currents thus are averaged. The ion current ip on the peak plateau is given as $ip = \sum\limits_{N_{ST}=1}^{N_{ST}}$ ip with integration time T_{ST} [5].

A drift correction for the ion currents is applied (Figure 5). It is assumed that the isotopes of one element have relatively linear drift and the time T_c represents the time when signal disappears. Drift correction is applied by extrapolating the intensity of the ip to the intensity at time T_1, thus enabling ratio values to be determined at time T_1. This is done as follows:

First the gradients of the straight lines defined by coordinates T_1, Ip, and T_4; Ip$_4$ is calculated.

$$S \quad \frac{T_{p1} - T_{p4}}{T_1 - T_4} \tag{2}$$

Table III

Calibration DATA

SPECTROSYSTEM 106 TH

? CALB

EICHUNG DER MASSENSKALA   (CALIBRATION OF MASS SCALE)

MASSENBEREICH (GROB) : <u>13.</u>   (MASS RANGE (COARSE))

POSITIONLISTE

NR.	DAC	INTENS.
1	3594	0.000
2	3630	.031
3	3806	0.000
4	3861	4.918

MASSENZUORDNUNG   (ASSIGNMENT OF MASSES)

NR.   1   MASSE : <u>0.</u>
NR.   2   MASSE : <u>235.</u>
NR.   3   MASSE : <u>0.</u>
NR.   4   MASSE : <u>238.</u>

MASSENBEREICH (GROB) : 0.

NULLPOSITION

GROB : <u>13.</u>   (COARSE)
 DAC : <u>3730.</u>

ZUSATZ .MASSEN

MASSE : <u>0.</u>

Table IV

Supplementary MASS Dialogue

MASSENBEREICH (GROB) : 0.

MULLPOSITION

GROB : 13.
  DAC : 270.

ZUSATZ MASSEN (SUPPLEMENTARY MASS)

MASSE · 236.
GROB : 18.
DAC : 196.
MASSE: 0.

? ACQU

PROBE URAN
SIGNAL 2.088 VOLT

ISOTOP	MASSE	VERH(%)	ST.ABW.(%)	GEWICHT(%)	ATOM(%)
1	235	100.00000	0.00000	97.5894	97.59000
2	234	1.73169	.95418	1.68276	1.68996
3	238	.55733	1.09234	.55084	.54390
4	236	.18047	1.95384	.17687	.17612

PROBE URAN
SIGNAL 2.101 VOLT

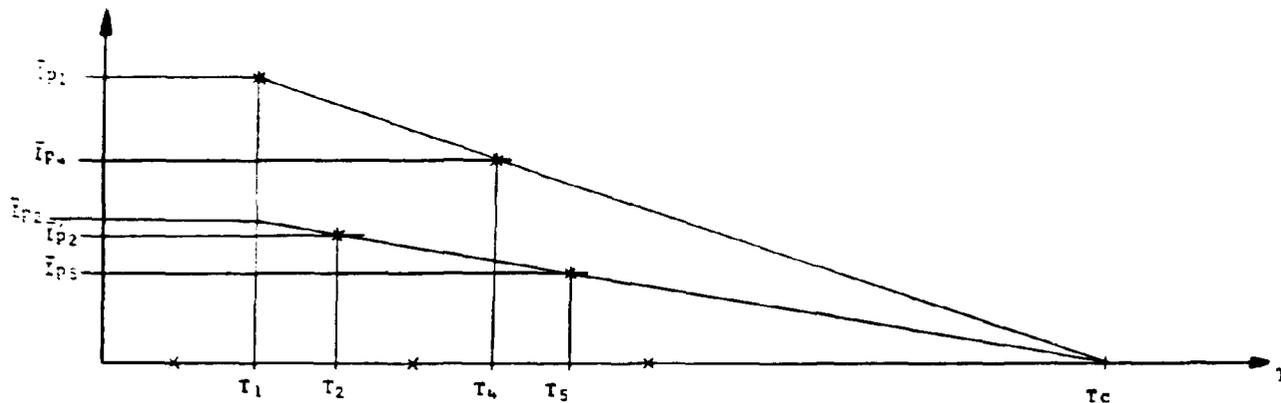| ISOTOP	MASSE	VERH(%)	ST.ABW.(%)	GEWICHT(%)	ATOM(%)
1	235	100.00000	0.00000	97.59036	97.59082
2	234	1.73295	.81846	1.68399	1.69120
3	238	.55688	1.16243	.55040	.54364
4	236	.17882	1.91487	.17526	.17452

Figure 5 — Drift Correction for Ion Currents

Hence time T_C

$$T_C = T_4 - \frac{I_{p4}}{S} \qquad (1)$$

Thus the corrected ion current I'_{p2} is

$$I'_{p2} = I_{p2} \times \frac{T_1 - T_C}{T_2 - T_C} \qquad (4)$$

and the ratio value of ion currents (I_{p2} relative to the reference mass I_{p1}) at time T_1 is

$$V = \frac{\bar{I}_{p2}}{I_{p1}} \qquad (3)$$

This procedure is repeated for all the isotopes and stored in the computer. The last cycle is omitted as the non linearity of the drift causes greater errors. When the ratio values are calculated, those relating to same mass numbers are averaged and the relative standard deviation is calculated. The listed output for each mass number are

$$\bar{V} = \sum_{i=1}^{N_{MES}-1} \qquad\qquad V_i / N_{MES} - 1$$

Where $\bar{V}$ = ratio value of isotope in percent relative to the reference mass. Standard deviation in percent is

$$\sigma = \frac{1}{\bar{V}} \left\{ \sum_{i=1}^{N_{MES}-1} \qquad (\bar{V} - V)^2 \qquad N_{MES} - 2 \right\}^{1/2} \qquad (\%)$$

atom percentage $A_i = \dfrac{\bar{V}_i}{\sum\limits_{j=1}^{N_{ISO}} V_j} \times 100 \quad (\%)$

Weight percentage $W_i = \dfrac{V_j \cdot M_i}{\sum\limits_{i=1}^{N_{ISO}} (V_j \cdot M_j)} \times 100 \quad (\%)$

In the out-put sample designation and the absolute measurement value of the ion current of the reference mass of the last cycle (in volts) is also given.

Table V gives the output for natural U sample where as in Table IV output for directive ACQU for U970 can be seen. The output values are not corrected for mass discrimination. The procedure employed for determining mass discrimination factor is described by Moraes and Rodrigues[4] and each ratio has to be corrected for mass discriminations[3].

Table V

Computer OUTPUT Values for U Natural Samples

? ACQU

PROBE URAN
SIGNAL 4.687 VOLT

ISOTOP	MASSE	VERH(%)	ST.ABW.(%)	VEWICHT(%)	ATOM(%)
1	238	100.00000	0.00000	99.28464	99.27557
2	235	.72972	.59341	.71537	.72443

PROBE URAN
SIGNAL 4.564 VOLT

ISOTOP	MASSE	VERH(%)	ST.ABW.(%)	VEWICHT(%)	ATOM(%)
1	238	100.00000	0.00000	99.29068	99.28168
2	235	.72350	.68698	.70932	.71831

PROBE URAN
SIGNAL 4.461 VOLT

ISOTOP	MASSE	VERH(%)	ST.ABW.(%)	VEWICHT(%)=	ATOM(%)
1	238	100.00000	0.00000	99.28986	99.28085
2	235	.72435	.60894	.71014	.71814

PROBE URAN
SIGNAL 4.343 VOLT

ISOTOP	MASSE	VERH(%)*	ST.ABW.(%)	VEWICHT(%)	ATOM(%)
1	238	100.00000	0.00000	99.28882	99.27979
2	235	.72542	1.00294	.71118	.72020

RESUMO

Aquisição e processamento de dados para determinações de abundância isotópica utilizando espectrômetro de massa é analisada. Os detalhes da técnica empregada no espectrômetro de massa Varian TH5 é descrita.

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