

Studies with Sector-Type Mass Spectrometers

A Thesis

**Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
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by

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PART ONE

A Mass Spectrometer Investigation of
the Equilibration of Deuterium with Deuterium Oxide.

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Part One: A Mass Spectrometer Investigation of the
Equilibration of Deuterium with Deuterium Oxide.

INTRODUCTION

During the past several years, a great deal of work has been done at McMaster University in connection with the Canadian atomic energy project. One phase of this work was the mass spectrometric determination (1) of the deuterium content of deuterium oxide (heavy water) which is used as a neutron moderator in the atomic energy pile at Chalk River. The technique of equilibration of samples of deuterium oxide with deuterium gas prior to analysis with the deuterium mass spectrometer constituted an important part of this project.

The homogeneous reaction between deuterium and water vapor occurs above 600°C. with an activation energy of about 65 kilocalories, and is complicated by a heterogeneous reaction catalyzed by the walls of the containing vessel (9). In the presence of suitable catalysts, the reaction occurs at much lower temperatures. Horiuti and Polanyi (10) showed that it occurs at room temperatures in the presence of platinum black. They suggest an ionic mechanism for the change, hydrogen being split into ions on the catalyst surface, these passing into solution and being replaced by an equivalent number of ions from the solution, leading to the exchange reaction. On unpoisoned catalysts in acid solution, they conclude that the rate is determined by the diffusion of hydrogen to the catalyst. That the ionic mechanism is not essential is

indicated by the data of Taylor and Diamond (11) in which deuterium was shown to interact rapidly with the water content of chromium oxide gel, zinc oxide, zinc chromite, alumina, and platinized asbestos catalyst at temperatures from 100° to 400°C. What the mechanism of these gas-phase catalyses is remains to be elucidated. It may involve specific activation of hydrogen or water vapor or of both.

The method of preparation of samples in the Canadian project consisted essentially of the equilibration at 25°C. of the heavy water by shaking for three hours with deuterium gas in the presence of platinum oxide as a catalyst and maleic anhydride as a peptizing agent. This method was developed in the United States (2) and has been used for some time in this laboratory by Hawkins (3).

The purpose of the present work was to determine the extent to which the procedure for the preparation of samples could be shortened and simplified without making the precision of the preparation less than the precision of the analyses with the deuterium mass spectrometer. The studies reported here involved an investigation of the necessity of shaking the samples, the use of a peptizing agent for the catalyst, and the time required for the equilibration of samples.

APPARATUS

The apparatus used in the preparation of samples consisted essentially of a dry box, equilibration and gas sample flasks (Figure I), transfer pipettes, a drying oven (150°C.), a high vacuum line (pressure 10^{-6} mm. Hg), and a shaker with a constant temperature bath (25°C.).

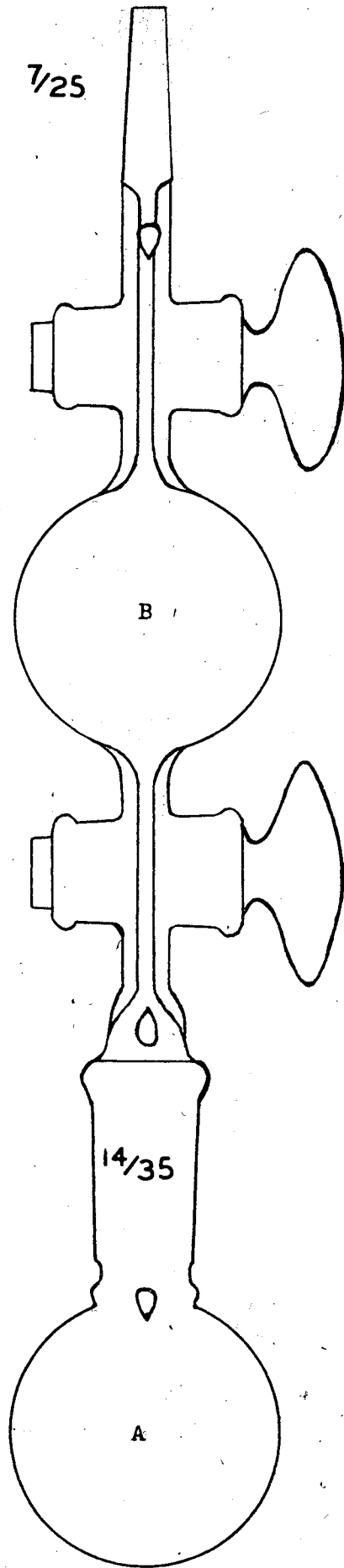


FIGURE I

All glassware which came in contact with heavy water was first cleaned in a saturated tri-sodium phosphate bath, rinsed in tap water, distilled water and heavy water (approximately 90% D), dried for four hours at 150°C., and cooled in the dry box. Stopcocks and ground glass joints were greased with Apiezon M grease. Care was taken to avoid contact of the water with the grease as much as possible. The mass spectrometer used in this investigation was a Nier 600 - deflection sector-type 3-4 deuterium mass spectrometer which has been described previously (1,5).

REAGENTS

Heavy Water - of high deuterium content was vacuum distilled into a sample tube with a glass break seal.

Platinum Oxide - Adam's Platinum Oxide Catalyst (Baker & Co., Inc., Newark, N.J.) was treated with 90% D₂O and dried at 150°C. before use.

Maleic Anhydride - The B.D.H. reagent was dried in vacuo before use.

Deuterium Gas - of over 99.0% D was prepared by the reaction in vacuo of very pure calcium metal (obtained from N.R.C. Montreal Laboratory) with 99.5% D₂O.

EXPERIMENTAL PROCEDURE

To determine the effect of peptizing agent on the equilibration analysis of heavy water, experiments were performed as outlined below, on three different samples of heavy water obtained from the Montreal Laboratory.

The sample tube containing 10 ml. of heavy water was opened in the dry box and 5 ml. portions were transferred by means of a pipette

to each of two equilibration flasks (A of Figure I) which contained 10 mg. of platinum oxide catalyst. To one flask, 2 mg. of maleic anhydride were added as a peptizing agent for the catalyst. No peptizing agent was added to the other flask. The gas sample flasks (B of Figure I) were then connected to the equilibration flasks and the units placed on the vacuum line. Each sample was then treated identically as follows.

The water in the flask was frozen by means of a dry ice and methanol bath, and the flask evacuated to a pressure of 10^{-5} mm. Hg. The water was allowed to melt so that dissolved gases could escape from the water. The water was frozen again and the flask evacuated to a pressure of 10^{-6} mm. Hg. Deuterium gas was then admitted to the equilibration flask (30 ml. volume) to a pressure of 10 cm. Hg. and closed off, after which the sample was shaken in the constant temperature bath (25°C.) for at least 5 hours. At the end of the shaking period, gas was released from the equilibration flask to the previously evacuated sample bulb, and the HD/DD ratio in the gas was measured by means of a Nier-type 3-4 deuterium mass spectrometer (5).

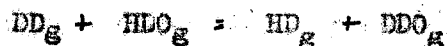
To determine the necessity for shaking the sample during the equilibration period, 5 ml. aliquot portions of a stock heavy water sample (which had been purified by one vacuum distillation) were transferred to each of ten equilibration flasks and 10 mg. of catalysts were added to each. No peptizing agent was added to these samples. The samples were degassed as above and deuterium gas admitted. Then the samples were allowed to equilibrate without shaking for 0, 1, 1.5, 2, 4, 6, 8, 10, 12 and 19 hours respectively in the constant temperature bath (25°C.).

Analysis was done as before with the deuterium mass spectrometer. As a check, another sample was prepared and allowed to equilibrate with shaking for 20 hours in the constant temperature bath, and analysed on the mass spectrometer.

CALCULATION OF RESULTS

After equilibrium had been reached in the water-gas reaction, the gas above the water was admitted to the deuterium mass spectrometer, and the HD/DD ratio in this gas was calculated from the mass spectrometer reading, taking into account the circuit constants of the instrument concerned. From the HD/DD ratio the percent deuterium in the heavy water sample was calculated as follows.

For the system



the equilibrium constant (4) is K_1 and

$$K_1 = \frac{(HD_g)(DDO_g)}{(DD_g)(HDO_g)} = 3.11 \text{ at } 25^\circ\text{C}$$

Also for the system $HDO_1 = HDO_g$ the equilibrium constant is the vapor pressure of HDO. Therefore $K_a = \frac{(HDO_g)}{(HDO_1)} = P_{HDO}$

Similarly for $DDO_1 = DDO_g$ the equilibrium constant is $K_b = \frac{(DDO_g)}{(DDO_1)} = P_{DDO}$

By extrapolation of the data of Wahl and Urey (4), we find that

$$K_a/K_b = P_{HDO}/P_{DDO} = 1.067 \text{ at } 25^\circ\text{C}.$$

However, since the ratio HD/DD is a measure of the deuterium content of the gas which is in equilibrium with DDO, we are concerned with the system



in which

$$K_2 = \frac{(HD_g)(DDO_1)}{(DD_g)(HDO_1)} = \frac{(HD_g)(DDO_g)}{(DD_g)(HDO_g)} \times \frac{(DDO_1)(HDO_g)}{(HDO_1)(DDO_g)} = K_1 \cdot K_a / K_b = 3.11 \times 1.067 = 3.318.$$

Now for the system $DD + HH = 2HD$ the $K_3 = \frac{(HD)(HD)}{(DD)(HH)} = 3.26$ at 25°C (4).

and the atom percent deuterium = $\frac{2(DD) + (HD)}{2(DD) + 2(HD) + 2(HH)} \times 100$

If we divide numerator and denominator by HD and put $HD/DD = R$, we obtain

$$\text{Atom \%D} = \frac{2/R + 1}{2/R + 2 + 2R/3.26} \times 100$$

However, it may be seen from the value of K_2 that the gas in equilibrium with the water is light by a factor of 3.318 when the water and the gas are of high deuterium content. Thus by substituting for R the corresponding value for the liquid system, (i.e. $R/3.318$) we get for the heavy water sample

$$\text{Atom \%D} = \frac{6.636/R + 1}{6.636/R + 2 + R/5.408} \times 100 = \frac{6.636 + R}{6.636 + 2R + R/5.408} \times 100$$

For samples of high deuterium content, i.e. for values of $R < 0.02$, the value of $R/5.408$ is very small and may be neglected; then for the liquid

$$\text{Atom \%D} = \frac{6.636 + R}{6.636 + 2R} \times 100$$

Also if R is less than 0.02, then R may be subtracted from both the numerator and the denominator of the atom-fraction of deuterium in the liquid, and

$$\text{Atom \%D} = \frac{6.636}{6.636 + R} \times 100$$

RESULTS

The data from the experiment on the effect of peptizing agent on the equilibration analysis of heavy water is presented in Table I.

Table I

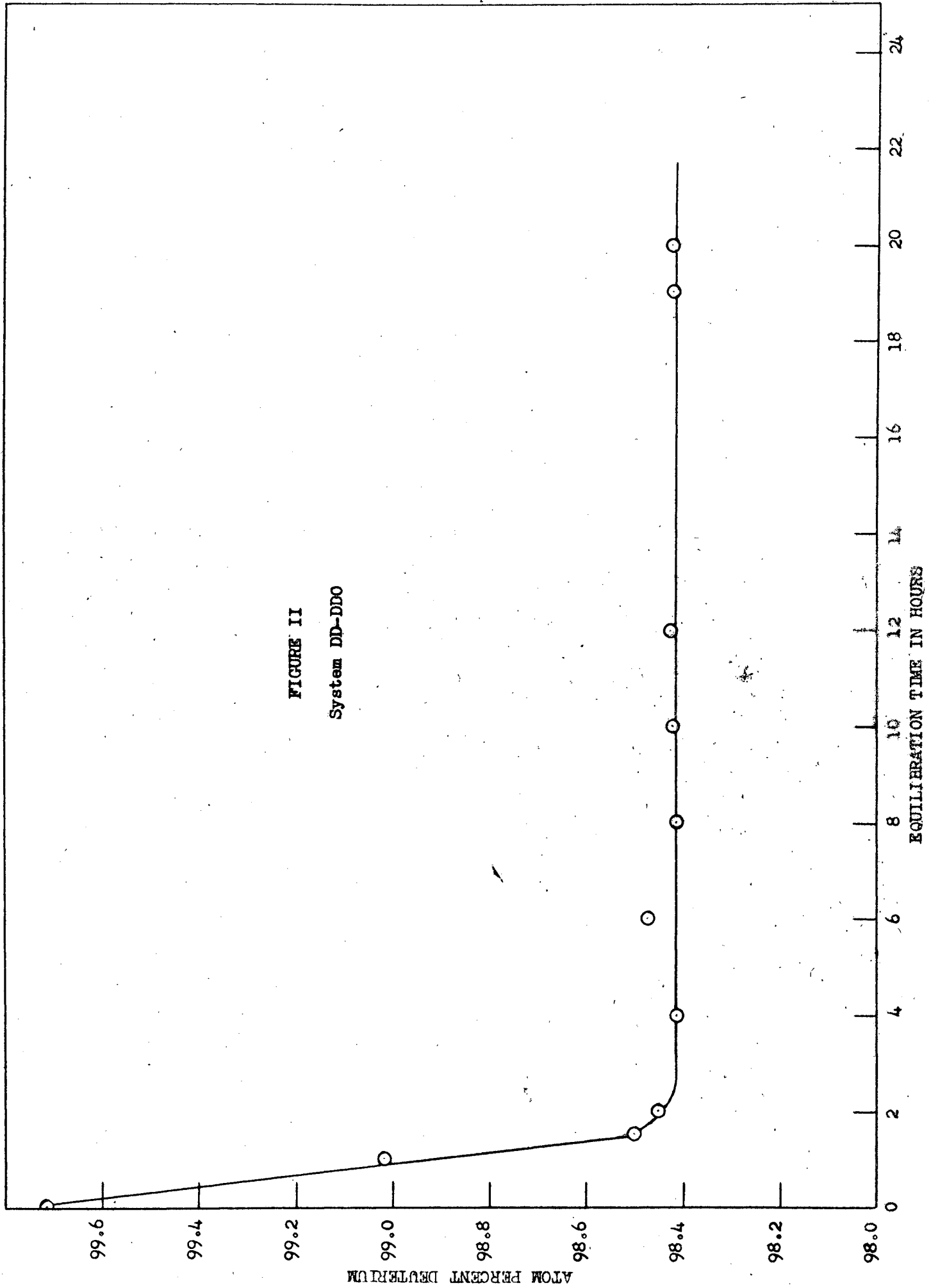
<u>Sample No.</u>	<u>Source</u>	<u>Remarks</u>	<u>Atom % Deuterium</u>
179A	Montreal #105	peptizing agent used	99.771
179B	Montreal #105	no peptizing agent used	99.777
180A	Montreal #153	peptizing agent used	99.831
180B	Montreal #153	no peptizing agent used	99.846
181A	Montreal #154	peptizing agent used	99.752
181B	Montreal #154	no peptizing agent used	99.752

The results of the experiment in which time studies were made on the equilibration process without peptizing agent and without shaking of the samples are given in Table II and are presented graphically in Figure II.

Table II

<u>Sample No.</u>	<u>Remarks</u>	<u>Equilibration time (hrs.)</u>	<u>Atom % Deuterium</u>
185E2	No shaking	0	99.72
185E2	" "	1	99.02
185D2	" "	1.5	98.50
185C2	" "	2	98.45
185E1	" "	4	98.41
185D1	" "	6	98.47
185C1	" "	8	98.41
185B1	" "	10	98.43
185A1	" "	12	98.43
185G1	" "	19	98.42
185J1	Shaking	20	98.43

FIGURE II
System DD-DDO



DISCUSSION

From the data of Table I, two conclusions are at once evident. First of all, peptizing agent seems to serve no essential purpose. This result is quite interesting in view of previous statements that peptizing agent was essential. Earlier conclusions as to its necessity were based to some extent at least upon experimental evidence. It is quite probable, however, that the earlier evidence was incorrectly interpreted for one or more of several reasons. Slow reactions when peptization did not occur may have been due to the presence of catalytic poisons, i.e. the peptizing agent and the catalyst may have been poisoned by such a thing as low pH.

It has been noticed in this work that actually the catalyst will remain suspended in the water sample for a greater length of time if no peptizing agent is used than if it is used. The catalyst in samples with peptizing agent often precipitates 15 minutes after preparation and rarely remains suspended for more than three hours. If no peptizing agent is used the catalyst never precipitates before three hours of equilibration, and has in fact remained suspended for a period of four months. Thus it is quite possible that impurities in the peptizing agent will poison the catalyst and cause its precipitation.

The second conclusion from Table I is that peptizing agent may actually do harm in that it may introduce a significant source of protium contamination. It may be of significance that two of the samples to which peptizing agent was added showed a lower atom percent deuterium than those to which no peptizing agent was added. It must be remembered, however, that the precision of the results lies within the precision of the mass spectrometer,

and there may not actually have been any protium contamination from the peptizing agent. Nevertheless, since each unnecessary step in the procedure introduces unnecessary sources of protium contamination, and since peptizing agent appears to serve no essential purpose in the equilibration procedure, its use is not recommended. Similar experiments by Voskuyl (7) have led to the same conclusion.

From the data of Table II and from a consideration of Figure II, it is apparent that shaking has no effect whatever on the time required for equilibrium to be attained, or on the final equilibrium value of the atom percent deuterium in the water sample.

According to observations made in the United States (6,7) and by Hawkings (3) in this laboratory, equilibrium is reached in this process in three hours with shaking and with peptizing agent. From Figure II it is evident that equilibrium is also reached in three hours without shaking and without peptizing agent. The final equilibrium value of the atom percent deuterium in the water sample is the same with or without shaking. It could well be expected that shaking should have no effect since the catalyzed reaction is a gaseous one, and shaking should not be expected to affect a gaseous reaction. These results are in accord with those obtained by Voskuyl (7) and his co-workers in the Metallurgical Laboratory in Chicago.

It is interesting to note that Fischer (7) reports that he has found by experience that more rapid analyses are obtained if the equilibration flasks are not cleaned, but only oven-dried, between analyses. This is likely due to the beneficial effects of catalyst imbedded on the inner upper surfaces of the flask.

Voskuyl (8) and his group at Chicago have made a study of the effect of temperature variation on the equilibration process in the analysis

of heavy water. This was done both theoretically and experimentally. They found that the error introduced by a temperature change of up to six degrees is well within the precision of the analyses of waters with isotopic composition varying from 98.0 to 99.9% deuterium, and is therefore negligible. Hence, an accurately controlled temperature bath is unnecessary for equilibrating heavy water samples with deuterium gas. From the equations used in calculating the percent deuterium in the sample, as given above, it is seen that the two factors subject to temperature variation are K_1 and the vapor pressure ratio K_a/K_b . An increase in the temperature causes a decrease in K_1 which in turn causes a decrease in the analysis obtained for atom percent deuterium. On the other hand, an increase in temperature causes a decrease in the vapor pressure ratio, which in turn causes an increase in atom percent deuterium. Thus the two factors are oppositely affected by a temperature change. However, the change in K_1 is more significant than the change in K_a/K_b for a given temperature alteration, so that the net result is a decrease in the atom percent deuterium analysis for larger temperature differences than 6°C in the 25°C range.

SUMMARY

Several radical changes, which shorten and simplify the process, have been made in the procedure for the analysis of heavy water by equilibration prior to mass spectrometric determinations. Shaking the sample has been eliminated and the use of a peptizing agent has been discarded. The shortest period of time (approximately 3 hours) required for the equilibration without shaking and without peptizing agent has been determined. Experiments were conducted to determine these factors, and the results obtained were found to

be in very close agreement with results obtained elsewhere. The real practical test of these apparently radical changes in the equilibration procedure has been provided by their successful use in routine analyses for more than a year in both the McMaster laboratory and the Chalk River laboratory where the revised method is now in use. Since the new procedure has been adopted, entirely satisfactory results have been obtained in many equilibrations. No apparent loss in reaction time has resulted. The observed precision between check analyses is as good as, or in fact better than, the precision obtained on previous equilibrations with shaking and peptizing agent. This work has all been done with heavy water, but it is anticipated that the new procedure would be equally advantageous in any range.

It is concluded, therefore, that equilibration analyses are in general best performed without peptizing agent and without shaking; and it also appears that the cleaning of flasks between analyses and close regulation of equilibration temperature is not required.

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PART TWO

A Mass Spectrometer Investigation of the Isotopes of Normal Krypton and Xenon.

ACKNOWLEDGEMENTS

It is a pleasure to record my indebtedness to Professor H. G. Thode who was the leader in this research, and whose able advice and assistance in experimental work was deeply appreciated. The assistance of Dr. F. P. Lossing with the automatic scanning and recording units has been invaluable, as was the servicing of the electronic units of the mass spectrometer by Mr. R. B. Shields. The financial assistance of the National Research Council of Canada is gratefully acknowledged.

Part II: A Mass Spectrometer Investigation of the Isotopes
of Normal Krypton and Xenon.

INTRODUCTION

A mass spectrometer investigation has been made (1) at McMaster University of the isotopes of krypton and xenon resulting from the fission of uranium 235 by thermal neutrons. This investigation was carried out with a 180° -deflection Nier-type mass spectrometer (2). It was considered that a parallel investigation, using a new 90° -deflection sector-type mass spectrometer which had been built (3) in this laboratory, would be of considerable interest and value.

It was first necessary to determine the performance of the new 90° mass spectrometer in measuring the isotopic abundances of normal krypton and xenon. In the course of this preliminary investigation, it was found that the isotopic abundance measurements for krypton and xenon were in agreement with those previously obtained by Nier (4), with the exception of that for krypton 80, which was greater by ten percent than the value given by Nier.

In the meantime, there had been built (5) in this laboratory, a unit which made possible the rapid and accurate recording of the ion currents of a given mass spectrum. This unit, used in conjunction with a linear feedback direct current amplifier, consisted of an electronic shunt-selector and a Leeds and Northrup Speedomax pen recorder. A given mass spectrum could be scanned by either manual or automatic variation of either the ion accelerating potential or the ion deflecting magnetic field of the mass spectrometer.

In view of the excellent performance of these new units, and considering the discrepancy found in the measured abundance of krypton 80,

it was decided to make a statistical study of the isotopic abundances of normal krypton and xenon. The details of this investigation are reported here.

EXPERIMENTAL PROCEDURE

Rare Gas Samples

The normal xenon samples used in this investigation were obtained from Linde Air Products Company, Tonawanda, N.Y., and the krypton samples were obtained from Linde Air Products and from Air Reduction Sales Company, New York, N.Y.

Mass Spectrometer

The mass spectrometer which was used in this investigation was a 90° -deflection sector-type instrument as shown in the photograph of Figure I. In Figure II is a block diagram which gives a general picture of the mass spectrometer tube, the electronic units, and the auxiliary apparatus. The design, construction, operation and performance of this instrument have been described in detail in a paper published by Graham, Harkness and Thode (3). The 90° mass spectrometer tube was a vacuum-tight glass and copper envelope containing an ion source system, a curved copper analyser tube and an ion collector assembly. The constructional details of this tube are shown in Figure III. In this tube, the gas to be analysed was introduced through a capillary leak to the ionization chamber of the source, and ionized by collision with an intense beam of electrons of 105-volts energy. The positive ions formed were collimated into an ion beam of 2000-volt energy by the collimating plates of the source, and directed normally into a square-shaped magnetic field of 1500 to 4500 gauss. This magnetic field resolved the ion

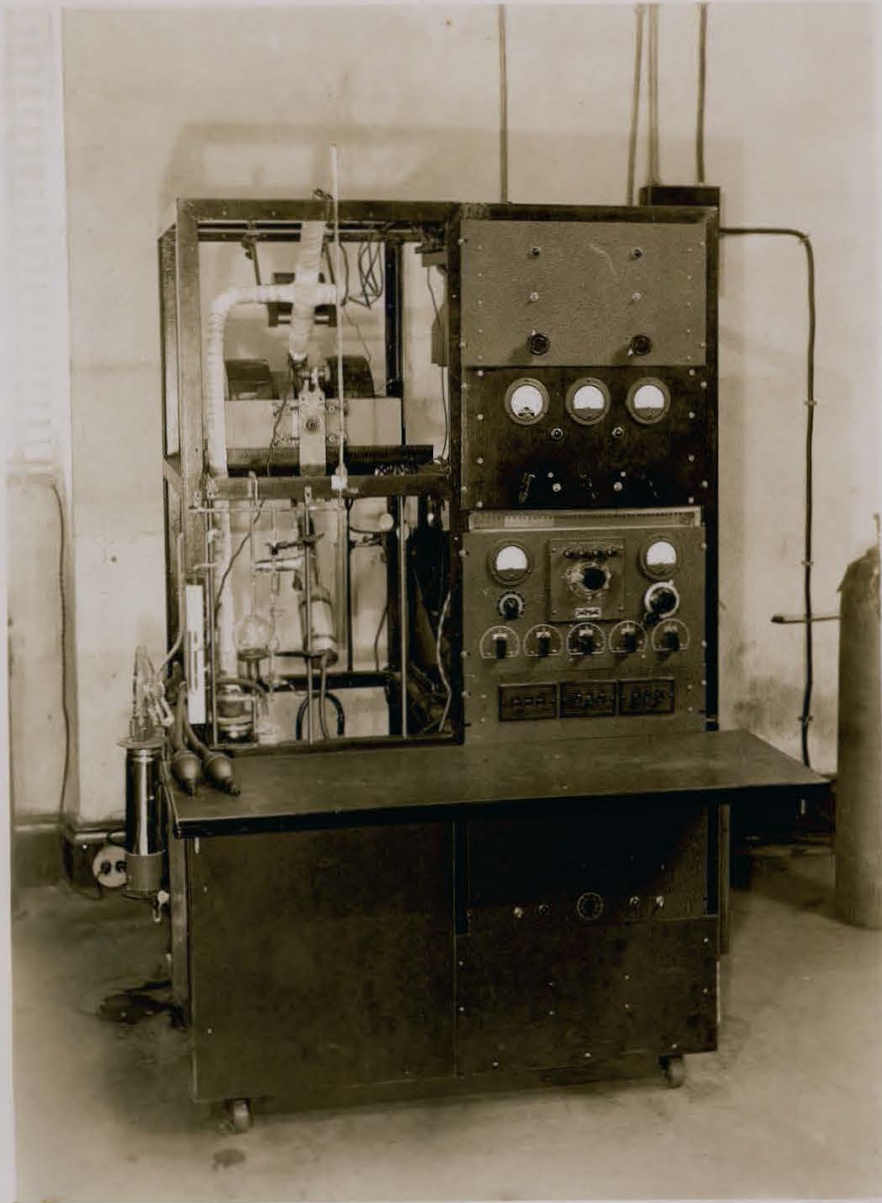


FIG. 1

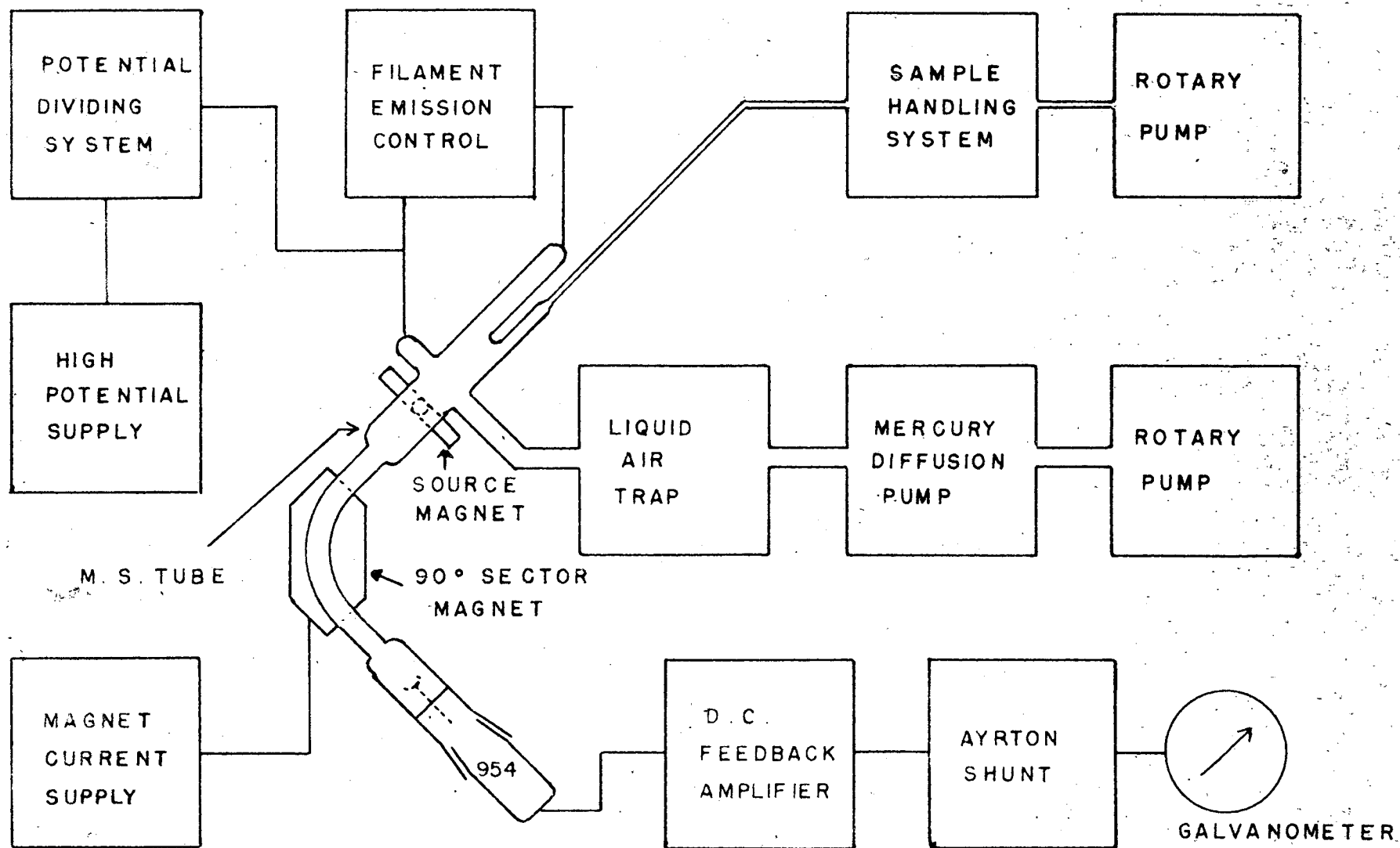


FIGURE II
BLOCK DIAGRAM
 90° MASS SPECTROMETER

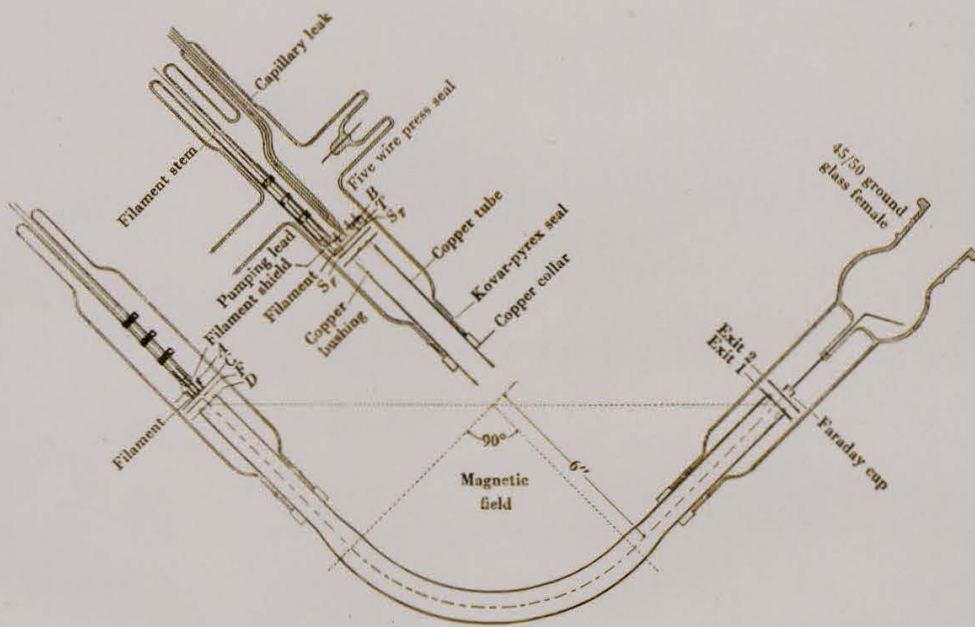


FIG. III

beam into its various mass components and refocused a beam of one mass component through the collector slits to a collector plate. The collector plate was surrounded by an electron repelling field of -45 volts (from a dry B-battery) on the second exit plate, so that secondary electrons formed at the collector plate by positive ion bombardment could not leave that plate. The ion current was applied to the grid of a 954 electrometer tube feeding a stabilized linear feedback direct current amplifier, and recorded with the automatic recording unit, which has been discussed in detail in a report published by Lossing, Shields and Thode (5). In Figure IV is a block diagram of the electronic shunt selector and recording unit (5).

Discussion of Absolute Measurements

Before discussing the results obtained in this investigation, various possible systematic errors which affect absolute measurements of isotopic abundances will be considered.

Mass Resolution: From fundamental physical principles, the familiar equation which gives the radius of curvature of an ion in a magnetic field may be derived. It is expressed as follows:

$$m/e = 4.82 \times 10^{-5} H^2 r^2 / V \quad (1)$$

In this equation, m is the mass of the ion in atomic mass units, e the number of electronic charges on the ion, H the magnetic field in gauss, r the radius of curvature of the ion in the magnetic field in cm., and V the energy of the ion in volts.

Now if $k = 4.82 \times 10^{-5} \times H^2 e / V$, then $m = kr^2$.

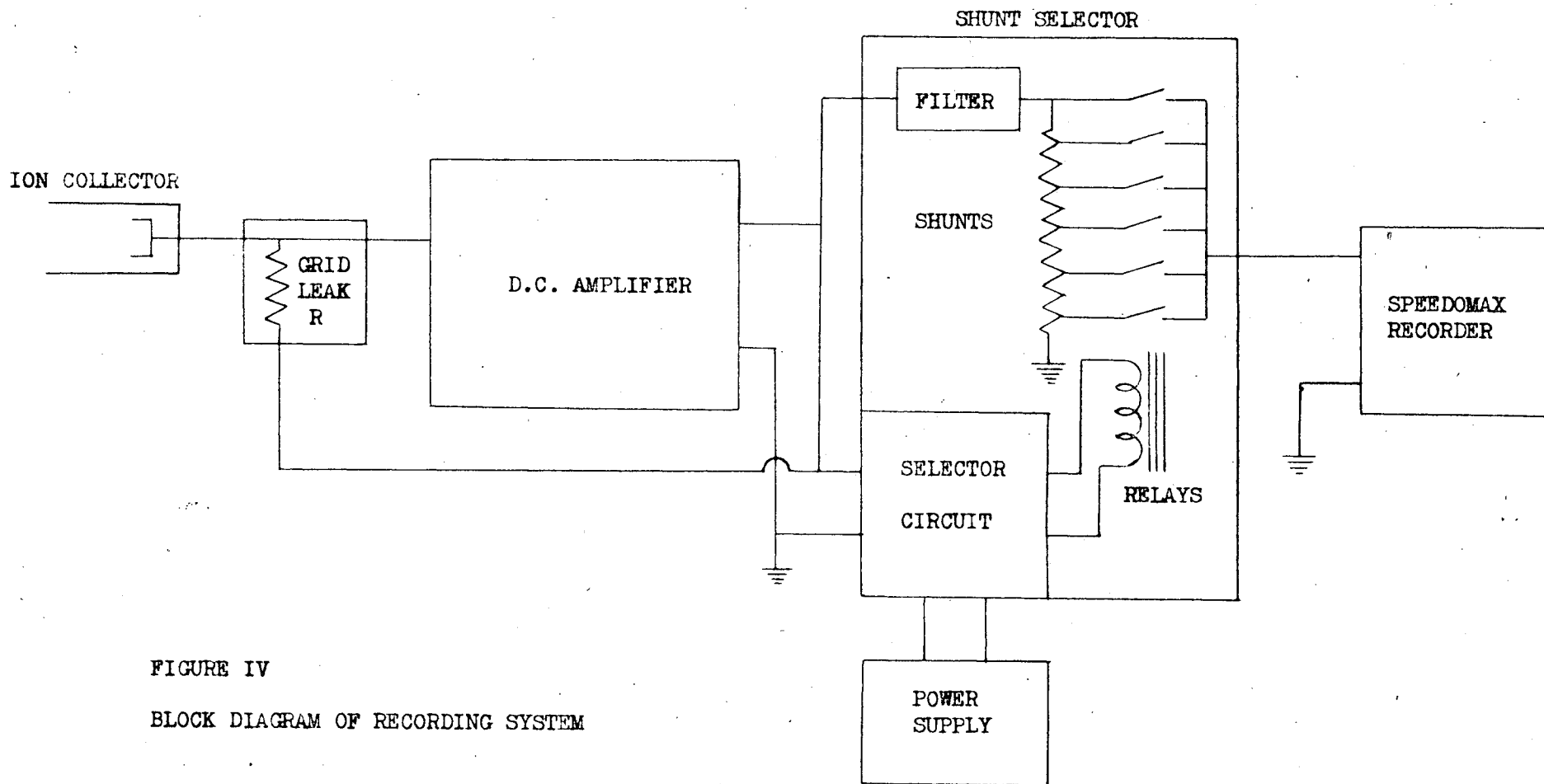


FIGURE IV
 BLOCK DIAGRAM OF RECORDING SYSTEM

By differentiation, $dm = 2 k r dr$, and then,

$$dm/m = 2 k r dr / k r^2 = 2 dr/r.$$

For finite changes in mass $\Delta m/m = 2\Delta r/r$ (2)

This last equation gives the mathematical expression for the theoretical resolving power of a mass spectrometer. The quantity Δr may be evaluated from the sum of the widths of the entrance and exit slits of the mass spectrometer tube. For the 90° instrument, $\Delta m/m = (0.25 + 1.00)/150 =$ one mass unit in 120. This instrument completely resolved the krypton isotopes but not the xenon isotopes. In the 180° mass spectrometer, $\Delta m/m = (0.25 + 0.38)/127 =$ one mass unit in 200. Therefore, the isotopes of krypton and xenon were completely resolved by the 180° instrument.

Mass Discrimination: From equation (1) given above, it may be seen that either of two basic methods can be used to bring the ion beam of desired mass to focus on the fixed collector, (i.e. with fixed r). Either H or V may be changed. When H is changed, magnetic scanning is obtained; and when V is changed, the scanning is by the electrostatic method.

The best indication that there was no mass discrimination in the 90° mass spectrometer, using magnetic scanning of mass spectra, was the fact that isotopic abundance measurements for N_2 , CO_2 , Kr, Xe, etc. did not vary, but gave reproducible results month after month under widely different operating conditions. With electrostatic scanning, abundance measurements would show variations of about 1% for a 10% difference in mass. When reproducible results were obtained, they agreed with those for magnetic scanning. This suggests that there was no mass discrimination with magnetic scanning, but that this effect was present at times with electrostatic scanning.

Similarly for the 180° mass spectrometer, consistent results were obtained with electrostatic scanning which agreed with 90° magnetic scanning. This would indicate no mass discrimination, where 180° magnetic scanning gave abundance measurements varying by about 2% for a 10% mass difference. Therefore, for absolute abundance measurements, 90° magnetic scanning and 180° electrostatic scanning were used, where mass discrimination is at a minimum.

Ion Current Discrimination: The direct current amplifier (3) was of the total feedback type to provide for handling as large an input current as possible with a given grid leak, and was of necessity a linear amplifier. In addition, the linearity of the recording of the ion currents by the Speedomax recording system was proven (5) by applying to it known voltages. A linear relation between input voltage and recorder deflection was obtained.

The major question remaining in the linearity of the measuring circuits was then the non-ohmic response of the input grid-leak resistor in the first stage of the D.C. amplifier (3). The linearity of these high resistors (10^{11} ohms) in the low voltage range may be measured by employing a circuit devised by Inghram (9). Using this circuit, Inghram found that most I.R.C. resistors are ohmic in the range 0.001 to 10 volts within $\pm 0.2\%$ of their value. The grid leak in both the 90° and 180° mass spectrometers was used well within this voltage range. That there was no non-ohmic response of the input grid leak resistors in the voltage range in which they were used, was indicated by the fact that with both the 90° and 180° mass spectrometers, consistent and accepted values of any given isotopic ratio were obtained whether high or low ion currents were measured.

Secondary Electron Emission: If there was no suppressor voltage applied to the second exit plate of the mass spectrometer tube, there was a great deal of secondary electron emission from the collector plate caused by its bombardment with positive ions of 2000-volts energy. This emission was great enough to account for one-third of the measured peak height. It was determined that below a suppressor voltage of -25 volts, only a very small fraction of a percent of the total ion current was caused by secondary electrons. Since -45 volts was used as a suppressor voltage and the potential on the collector plate never changed by more than 0.01 volts in the present measurements, it was concluded that the secondary electron contribution to the measured ion currents was negligible.

Isotopic Fractionation at the Capillary Leak: A change of isotopic abundance due to passage of the gas through the capillary leak into the ionization chamber of the mass spectrometer tube, was another factor which was considered as a source of systematic error. In this investigation it was found that there was no change in the measured isotopic abundances even after the gas had been passing through the leak for a considerable period of time (36 hours). It was concluded then that any possible fractionation at the leak was appreciably below the limit of detection of the mass spectrometer, and thus negligible.

Isotopic Fractionation in Preparation: The errors resulting from the method of preparation of the rare gas samples were negligible because no differences in isotopic abundances of normal gases from different sources were detected.

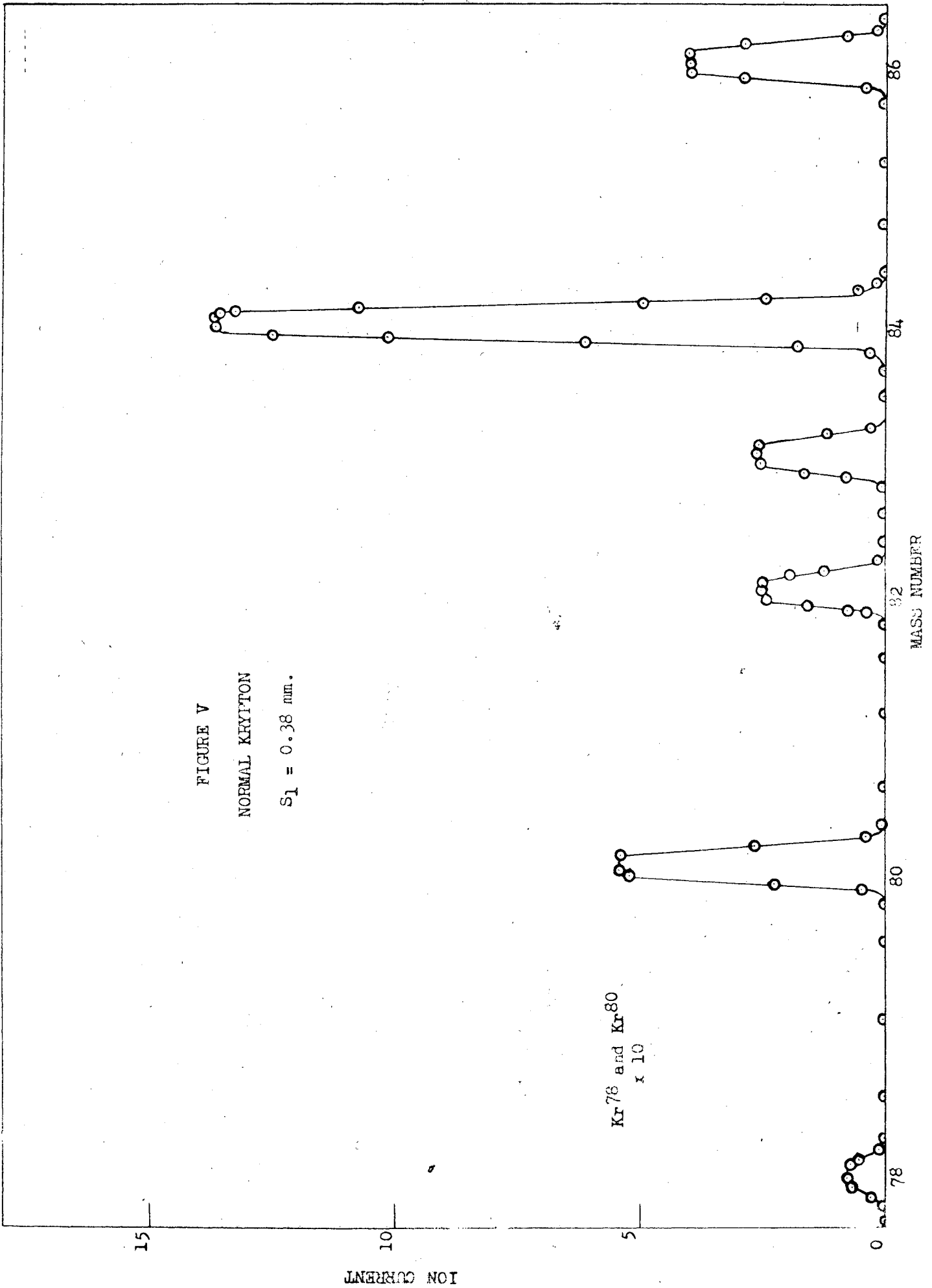
Purity of Sample: There were no residual gases in the mass spectrometer tube in the mass ranges involved in this investigation. The purity of the samples was indicated by the fact that purification of the gas, after passing through a liquid air trap, by fractionation from charcoal at liquid air temperature, and by passage through a calcium furnace (6) did not alter the measured isotopic abundances as compared with an untreated sample. This fact excluded the possibility of mass 80 contamination causing the observed discrepancy in the measured abundance of krypton 80.

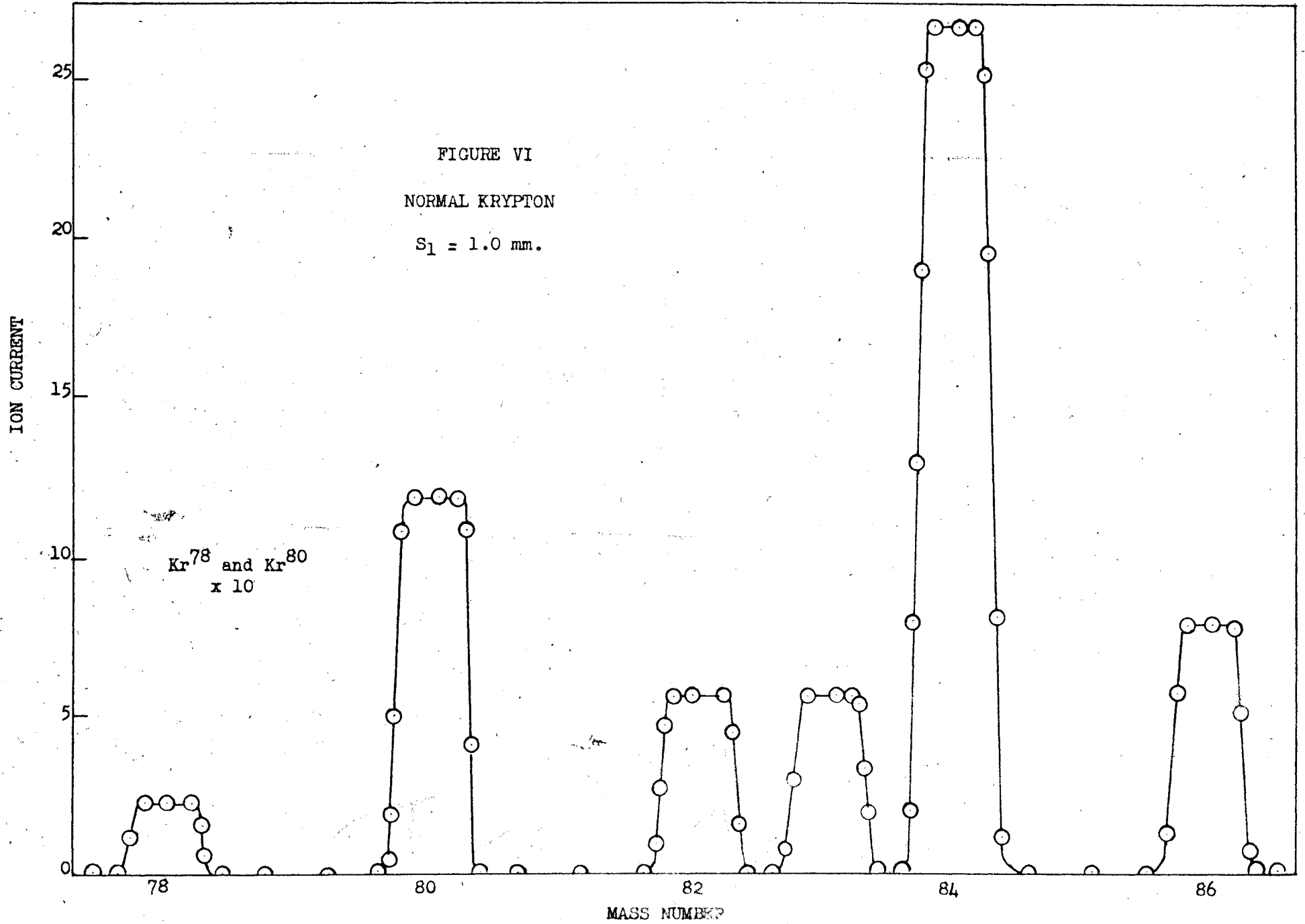
RESULTS FOR KRYPTON

As a matter of interest, a typical mass spectrogram, obtained by manual electrostatic scanning of the mass spectrum of normal krypton, is shown in Figure V. In this case, the width of the first exit slit (see Figure III) is 0.38 mm. A similar spectrogram obtained using an exit slit width of one mm. is shown in Figure VI. From these two spectrograms it will be noted that the narrower the first exit slit is, the greater is the resolution or separation of adjacent masses. However for the wide exit slit, the spectrogram shows a wide flat portion on the top of the peak, where ion current is constant for a considerable change in accelerating potential (or magnetic field), because the exit slit is wider than the ion beam. This condition is particularly desirable when precision measurements of the isotopic abundances are to be made, since the top of the ion current peak is then easily located. For this reason, the wide (1 mm.) exit slit was used in the present investigation.

After these preliminary investigations, a statistical study was made of the isotopic abundance of normal krypton, using automatic magnetic scanning of the mass spectrum, and automatic recording of ion currents. A

FIGURE V
NORMAL KRYPTON
 $S_1 = 0.38$ mm.





typical recorded spectrogram is shown in Figure VII; the experimental data of this study are presented in Table I. Each measurement of the ion current reported in Table I is the average of the measurements from a pair of spectrograms, one (A) obtained by scanning from low mass to high mass, the other (B) by scanning in the reverse direction. Thus the results given in the ten sets below are actually the result of measurements from twenty complete spectrograms of krypton. Ion current is given in this and in following tables in terms of recorder deflection in centimeters.

Table I

Mass Unit	78	80	82	83	84	86	Total
Spectrograms paired	Ion Current	Ion Current	Ion Current	Ion Current	Ion Current	Ion Current	Ion Current
1A - 1B	6.79	44.43	228.2	227.8	1138	345.8	1990.5
2A - 2B	6.61	43.29	223.5	224.0	1120	340.5	1957.9
3A - 3B	6.65	43.20	223.0	222.8	1105	337.2	1937.9
4A - 4B	6.62	43.20	222.8	222.6	1108	339.0	1942.2
5A - 5B	6.58	42.96	221.3	220.8	1095	336.0	1922.6
6A - 6B	6.60	42.90	221.3	221.0	1091	334.2	1917.0
7A - 7B	6.53	42.81	220.4	219.9	1090	332.7	1912.3
8A - 8B	6.61	42.87	221.0	220.3	1090	333.9	1914.7
9A - 9B	6.63	42.78	219.9	219.3	1083	331.8	1903.4
10A - 10B	6.64	42.57	220.0	219.7	1082	331.8	1902.7

In Table II are the percent abundances of the krypton isotopes calculated from the data of Table I.

FIGURE VII
NORMAL KRYPTON
MAGNETIC SCANNING

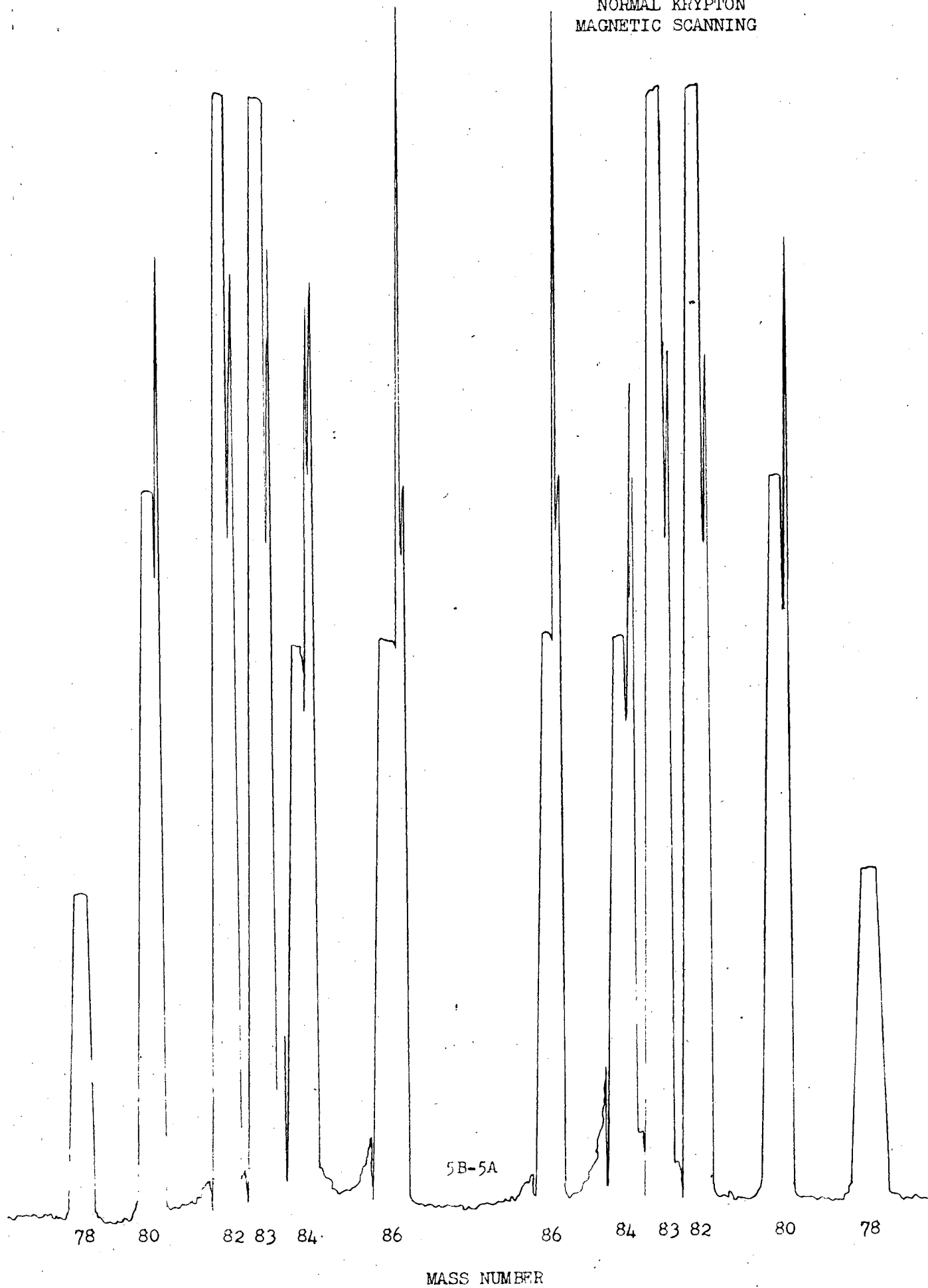


TABLE II

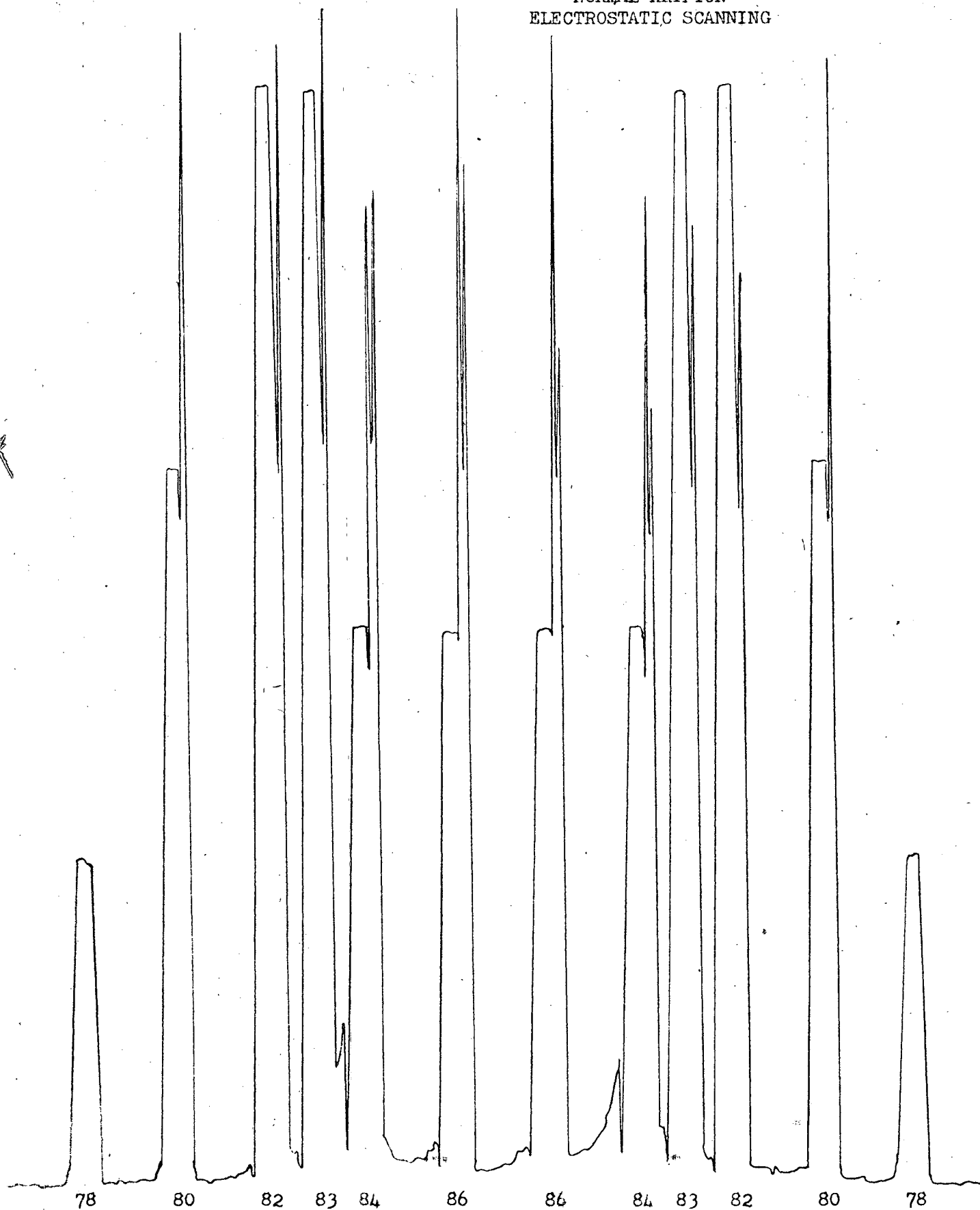
Mass Unit	78	80	82	83	84	86
Spectrograms paired	Atom %	Atom %	Atom %	Atom %	Atom %	Atom %
1A - 1B	0.340	2.232	11.46	11.44	57.15	17.37
2A - 2B	0.337	2.211	11.42	11.44	57.20	17.39
3A - 3B	0.343	2.229	11.51	11.50	57.02	17.40
4A - 4B	0.340	2.224	11.47	11.46	57.05	17.45
5A - 5B	0.342	2.234	11.51	11.48	56.95	17.48
6A - 6B	0.344	2.237	11.54	11.53	56.91	17.43
7A - 7B	0.341	2.238	11.53	11.50	57.00	17.40
8A - 8B	0.345	2.238	11.54	11.51	56.93	17.44
9A - 9B	0.348	2.247	11.55	11.52	56.90	17.43
10A - 10B	0.348	2.237	11.56	11.55	56.87	17.44
Average Atom % Ave.	0.343	2.233	11.51	11.49	57.00	17.42
Deviation	± 0.003	± 0.007	± 0.04	± 0.03	± 0.09	± 0.03
% Ave. Dev'n.	0.82	0.3	0.3	0.3	0.15	0.16

Another investigation of the isotopic abundances of normal krypton was made using automatic electrostatic (rather than magnetic as before) scanning and automatic recording. A typical spectrogram is shown in Figure VIII, and the experimental data obtained in this study are presented in Table III.

TABLE III

Mass Unit	78	80	82	83	84	86	Total
Spectrograms paired	Ion Current	Ion Current	Ion Current	Ion Current	Ion Current	Ion Current	Ion Current
4A - 4B	6.32	42.15	211.8	210.5	1049	318.6	1838.4
5A - 5B	6.34	41.82	211.7	210.9	1045	318.0	1833.8
6A - 6B	6.34	41.55	210.4	208.9	1046	314.4	1827.6
9A - 9B	6.24	40.65	207.3	206.0	1024	309.0	1793.2
10A - 10B	6.20	40.65	207.4	206.2	1024	309.9	1794.4
11A - 11B	6.23	41.16	208.0	206.5	1030	309.0	1800.9

FIGURE VIII
NORMAL KRYPTON
ELECTROSTATIC SCANNING



MASS NUMBER

In Table IV are the percent abundances of the krypton isotopes calculated from the data of Table III.

TABLE IV

Mass Unit	78	80	82	83	84	86
Spectrograms paired	Atom %	Atom %	Atom %	Atom %	Atom %	Atom %
4A - 4B	0.344	2.293	11.52	11.45	57.06	17.33
5A - 5B	0.346	2.280	11.54	11.50	56.99	17.34
6A - 6B	0.347	2.273	11.51	11.43	57.23	17.20
9A - 9B	0.348	2.267	11.56	11.49	57.10	17.23
10A - 10B	0.346	2.265	11.56	11.49	57.07	17.27
11A - 11B	0.346	2.276	11.55	11.47	57.19	17.26
Average Atom %	0.346	2.276	11.54	11.47	57.11	17.27
Ave. Deviation \pm	0.001	\pm 0.007	\pm 0.01	\pm 0.02	\pm 0.07	\pm 0.04
% Ave. Dev'n.	0.29	0.31	0.09	0.17	0.12	0.23

In Table V is a summary of the isotopic abundances of normal krypton obtained with the 90° mass spectrometer using automatic magnetic and electrostatic scanning and recording (data taken from Table II and Table IV). For purposes of comparison, similar data obtained (5) with the 180° mass spectrometer using automatic electrostatic scanning and recording is included, along with the early abundance measurements of Aston (7) and the later measurements of Nier (4).

TABLE V

Mass Unit	90° Electrostatic Atom %	90° Magnetic Atom %	180° Electrostatic Atom %	Nier Atom %	Aston Atom %
78	0.346 \pm 0.001	0.343 \pm 0.003	0.341 \pm 0.0003	0.35	0.42
80	2.276 \pm 0.007	2.233 \pm 0.009	2.223 \pm 0.002	2.01	2.45
82	11.54 \pm 0.01	11.51 \pm 0.04	11.49 \pm 0.01	11.53	11.79
83	11.47 \pm 0.02	11.49 \pm 0.03	11.47 \pm 0.02	11.53	11.79
84	57.11 \pm 0.07	57.00 \pm 0.09	57.04 \pm 0.04	57.10	56.85
86	17.27 \pm 0.04	17.42 \pm 0.03	17.44 \pm 0.03	17.47	16.70

In Table VI the data for krypton is summarized in a different manner in which the isotopic abundances are calculated as a percent relative to the most abundant isotope, krypton 84.

TABLE VI

Mass Unit	90° Electrostatic	90° Magnetic	180° Electrostatic	Nier	Aston
78	0.605	0.601	0.598	0.608	0.738
80	3.985	3.917	3.897	3.52	4.31
82	20.21	20.19	20.14	20.2	20.75
83	20.08	20.16	20.11	20.2	20.75
84	100.00	100.00	100.0	100.0	100.0
86	30.24	30.56	30.58	30.6	29.37

RESULTS FOR XENON

A similar examination of the isotopes of xenon was made by automatic scanning and recording of the mass spectrum. The determination of the xenon abundances was somewhat more difficult than that for krypton because for reasons outlined above, the isotopes of xenon are difficult to resolve using an exit slit (#1) which was 1 mm. wide. This difficulty was lessened by reducing the ion current (by reducing the pressure of xenon behind the capillary leak) so that the ion current peaks were recorded using the most sensitive shunt of the automatic shunt selector. The gas pressure was adjusted so that xenon 132, the most abundant isotope, gave full scale deflection on the most sensitive shunt. Under these conditions, the

least abundant isotopes, xenon 124 and 126 did not even appear in the recorded spectrogram. Twenty such spectrograms were recorded and the peak heights of xenon 128, 129, 130, 131, 132, 134 and 136 were measured. Then the gas pressure behind the leak was increased to the point where the ion currents for masses 124 and 126 gave a suitable deflection on the most sensitive shunt, and the xenon 136 ion current was measured on the fourth shunt. Ten such spectrograms were recorded and the peak heights for masses 124, 126 and 136 were measured. From these measurements, the average value of the peak heights for these three masses were calculated.

From the ratio of the peak height for mass 136 (obtained from each of the ten sets of paired spectrograms recorded at high sensitivity) to the average peak height of mass 136 obtained with high ion currents, a set of conversion factors was obtained. The average peak height of mass 124 multiplied by the appropriate conversion factor gave the peak height that mass 124 would have had if its height had been measurable when low ion currents were recorded (at high sensitivity). The same procedure gave corresponding values of the mass 126 ion current. The following is an example of the method of calculation:

Mass 136 ion current (from 3A - 3B of Table VIII) = 7.27 cms.

Average mass 136 ion current (from Table VII) = 312.8 cms.

Conversion Factor = $7.27/312.8 = 0.02323$

Mass 124 ion current to correspond with 3A - 3B (Table VIII) = $3.142 \times 0.02323 = 0.07307$ cms.

Mass 126 ion current to correspond with 3A - 3B (Table VIII) = $2.944 \times 0.02323 = 0.06851$ cms.

The corresponding conversion factor must be calculated for each of the ten sets of paired spectrograms of Table VIII.

A typical spectrogram for the ion currents (with high gas pressure) measured at different sensitivity levels is shown in Figure IX. The data on the ion currents of masses 124, 126, and 136 measured from five such sets of paired spectrograms are presented in Table VII.

TABLE VII

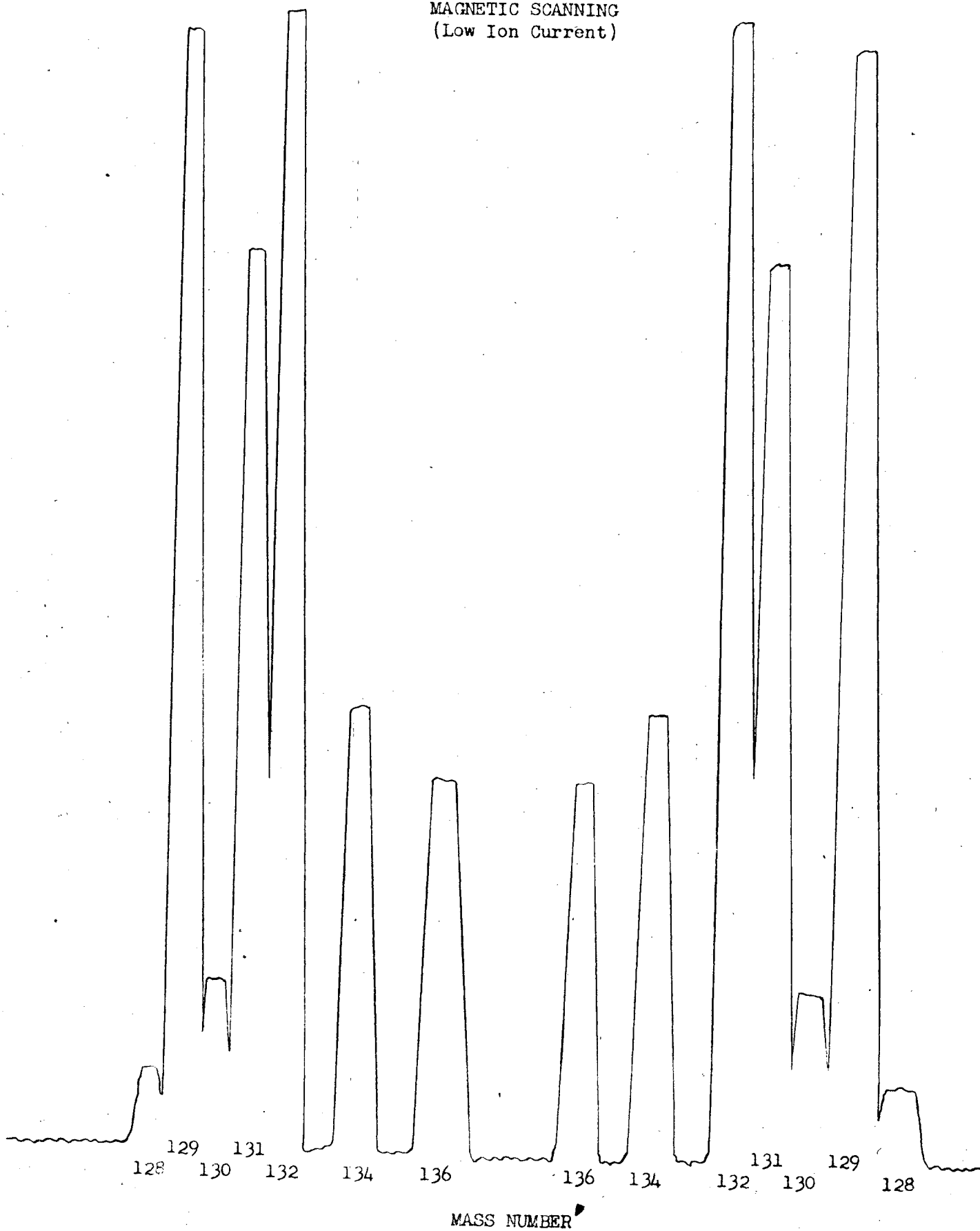
Mass Unit Spectrograms paired	124 Ion Current	126 Ion Current	136 Ion Current
30A - 30B	3.15	2.95	311.1
31A - 31B	3.14	2.89	310.8
32A - 32B	3.13	2.97	311.7
33A - 33B	3.16	3.01	316.2
34A - 34B	3.13	2.90	314.4
Average Ion Current	3.14	2.94	312.8
Average Deviation	± 0.01	± 0.04	± 1.96

In Figure X is a typical spectrogram in which all of the ion currents were recorded at the high sensitivity level. The experimental data for ion current measurements are recorded in Table VIII.

TABLE VIII

Mass Unit Spectrogram paired	124 Ion Cur.	126 Ion Cur.	128 Ion Cur.	129 Ion Cur.	130 Ion Cur.	131 Ion Cur.	132 Ion Cur.	134 Ion Cur.	136 Ion Cur.	Total Ion Cur.
3A - 3B	0.0731	0.0685	1.55	21.50	3.34	17.48	22.15	8.57	7.27	82.002
4A - 4B	0.0731	0.0685	1.56	21.56	3.30	17.33	22.03	8.54	7.29	81.752
5A - 5B	0.0737	0.0691	1.54	21.43	3.24	17.35	21.95	8.63	7.34	81.625
6A - 6B	0.0729	0.0683	1.51	21.40	3.24	17.25	21.84	8.52	7.26	81.161
7A - 7B	0.0727	0.0681	1.54	21.39	3.26	17.34	21.97	8.50	7.24	81.381
8A - 8B	0.0731	0.0685	1.51	21.40	3.20	17.19	21.83	8.54	7.27	81.082
9A - 9B	0.0731	0.0685	1.53	21.40	3.21	17.27	21.94	8.53	7.28	81.302
10A - 10B	0.0727	0.0681	1.55	21.50	3.27	17.37	21.99	8.60	7.24	81.661
11A - 11B	0.0733	0.0687	1.51	21.46	3.28	17.26	22.00	8.47	7.30	81.432
12A - 12B	0.0734	0.0688	1.50	21.44	3.28	17.25	21.98	8.49	7.31	81.392

FIGURE X
NORMAL XENON
MAGNETIC SCANNING
(Low Ion Current)



In Table IX are the calculated percent abundances of the xenon isotopes.

TABLE IX

Mass Unit	124	126	128	129	130	131	132	134	136
Spectrogram	Atom %	Atom %	Atom %	Atom %	Atom %	Atom %	Atom %	Atom %	Atom %
3	0.089	0.084	1.890	26.22	4.073	21.32	27.01	10.45	8.87
4	0.089	0.084	1.908	26.37	4.037	21.20	26.95	10.45	8.92
5	0.090	0.085	1.887	26.25	3.969	21.26	26.89	10.57	8.99
6	0.090	0.084	1.860	26.37	3.992	21.25	26.91	10.50	8.95
7	0.089	0.084	1.892	26.28	4.006	21.31	27.00	10.44	8.90
8	0.090	0.084	1.862	26.39	3.947	21.20	26.92	10.53	8.97
9	0.090	0.084	1.882	26.32	3.948	21.24	26.99	10.49	8.95
10	0.089	0.083	1.900	26.33	4.004	21.27	26.93	10.53	8.87
11	0.090	0.084	1.854	26.35	4.028	21.20	27.02	10.40	8.97
12	0.090	0.085	1.843	26.34	4.030	21.19	27.01	10.43	8.98
Ave. Atom %	0.090	0.084	1.878	26.32	4.003	21.24	26.96	10.48	8.94
Ave. Devn. ±	0.0003	±0.001	±0.018	±0.04	±0.032	±0.04	±0.04	±0.04	±0.04
% Ave. Dev.	0.32	1.35	0.95	0.15	0.79	0.18	0.15	0.42	0.43

In Table X is a summary of the isotopic abundances of normal xenon measured with the 90° mass spectrometer (using automatic magnetic scanning and recording) and with the 180° mass spectrometer (using automatic electrostatic scanning and recording). In the table are also included the earlier data of Aston (7) and Nier (4).

TABLE X

Mass Unit	90° MS.	180° MS.	Nier	Aston
124	0.090 ± 0.0003	0.095 ± 0.001	0.094	0.08
126	0.084 ± 0.001	0.088 ± 0.001	0.088	0.08
128	1.878 ± 0.018	1.917 ± 0.006	1.90	2.30
129	26.32 ± 0.04	26.24 ± 0.08	26.23	27.13
130	4.003 ± 0.032	4.053 ± 0.005	4.07	4.18
131	21.24 ± 0.04	21.24 ± 0.03	21.17	20.67
132	26.96 ± 0.04	26.93 ± 0.02	26.96	26.45
134	10.48 ± 0.04	10.52 ± 0.02	10.54	10.31
136	8.94 ± 0.04	8.93 ± 0.03	8.95	8.79

In Table XI, the data for xenon is summarized in the form of abundances relative to the most abundant isotope, xenon 132.

TABLE XI

Mass Unit	90° MS	180° MS	Nier	Aston
124	0.333	0.352	0.347	0.302
126	0.312	0.326	0.327	0.302
128	6.97	7.12	7.06	8.70
129	97.6	97.5	97.3	102.6
130	14.85	15.05	15.1	15.8
131	78.8	78.9	78.5	78.2
132	100.0	100.0	100.0	100.0
134	38.87	39.06	39.1	39.0
136	33.16	33.16	33.2	33.2

DISCUSSION OF RESULTS

Krypton: Krypton was the first element shown to have a highly complex isotopic constitution. Aston in 1930 first measured the relative isotopic abundances of krypton by photometry of its six-fold group of spectral lines obtained with his first mass spectrograph (8). More accurate data was obtained by Nier (4) in 1937 using his 180° mass spectrometer, and the absence of other masses was proved to a very high degree.

In the present investigation, the relative abundance data of Nier for krypton isotopes of masses 78, 82, 83, 84 and 86 was verified by the data obtained with our new 90° mass spectrometer (with magnetic scanning) and with our 180° mass spectrometer (with electrostatic scanning). However, the measured isotopic abundance of krypton 80 was greater by 10% than the value reported by Nier. On the other hand, the percent average

deviation from the average of the values measured with our 90° and 180° instruments is less than 0.3%. For this reason, and from all other considerations, great confidence is placed in the isotopic abundance measurements of the present investigation. Hence it would appear that the isotopic abundance of krypton 80 as reported by Nier must have been in error.

This fact was brought to the attention of Professor Nier. He returned to his original records of 1937 and found (10) that he had made an error in calculating the abundance of krypton 80. In computing the background correction under krypton 80, he had used the wrong shunt factor. The correction of this error by Professor Nier gives the relative abundance of krypton 80 as 3.97 rather than 3.52 as previously reported. His value of 3.97 compares more favorably with the value of 3.92 from the 90° instrument and 3.90 from the 180° instrument.

Xenon: Aston in 1920 investigated (11) the mass spectrum of xenon with his first mass spectrograph, and found five isotopes. The spectral lines were feeble and indistinct and their mass numbers were numbered a unit too low. Soon after, he corrected these numbers to masses 129, 130, 132, 134 and 136, and also found two more isotopes 128 and 131. He noticed faint effects at masses 124 and 126 and confirmed these in 1927 with his second mass spectrograph. He first measured the relative isotopic abundances of xenon by photometry in 1930 (12). Seven years later, more accurate mass spectrometer values for these nine isotopes were obtained by Nier (4) who also showed the absence of other mass numbers to a very high degree.

In the present investigation, the abundance measurements of xenon 129, 131, 132, 134, 136 agree with Nier's data to 0.3% or better. The data

for xenon 128 and 130 agree with Nier's data to 1% and 1.5% respectively. This agreement is to be expected due to the difficulty of measuring background corrections for portions of much larger peaks lying under these small peaks, because resolution of these peaks demanded more than the theoretical resolving power of the mass spectrometer. The data for xenon 124 and 126 agree with that of Nier to 4%. Nier claims an accuracy of only 3% for his data on these two isotopes. This agreement may be considered good remembering the difficulties with mass resolution and considering that these two isotopes are present in xenon only to the extent of approximately 9 parts in 10,000.

The abundance data for xenon isotopes obtained with our 180° mass spectrometer, where mass resolution is better, agrees remarkably well with the data obtained by Nier, as will be noted from Table X.

It should be possible to obtain very accurate data for the isotopic abundances of xenon by magnetic scanning with the 90° mass spectrometer if the width of the first exit slit of the spectrometer tube were reduced from its present width of 1.0 mm. to 0.75 mm. The resolving power would then be 1/150 and the xenon isotopes could be easily resolved.

SUMMARY

The performance of a new 90°-deflection sector-type mass spectrometer in measuring relative and absolute isotopic abundances has been demonstrated. The new instrument performs admirably in these determinations for krypton, but not so well for xenon isotopes, the resolution of which masses is beyond the theoretical resolving power of the mass spectrometer. It has been shown that the xenon isotopes could

be completely resolved if the width of the first exit slit of the mass spectrometer tube were reduced from 1.0 mm. to 0.75 mm., and very accurate absolute abundances obtained.

The usefulness of this mass spectrometer has been greatly extended by utilization of a unit which allows automatic scanning of the mass spectra and fast automatic recording of the ion currents. This unit makes it possible to scan and record a given mass spectrum a great number of times in a very short period of time. Thus its use with the mass spectrometer lends itself to the problem of making a statistical study of isotopic abundances with a higher degree of precision than that obtainable by manual scanning and recording of galvanometer deflections. To obtain isotopic abundances of xenon with its nine isotopes by the manual method requires a great deal of time, during which changes in the gas pressure, filament characteristics, source efficiency, and electronic circuit characteristics might occur. With automatic scanning and recording of the xenon spectrum possible in less than two minutes, the change in these factors is very small.

A discussion of the factors affecting absolute measurements of isotopic abundances has led to the conclusion that with magnetic scanning for the 90° sector-type mass spectrometer, the most accurate measurements are obtained. Similarly for absolute measurements with the 180° mass spectrometer, electrostatic scanning should be used.

It has been proven that the discrepancy discovered in the abundance of krypton 80 was not due to mass 80 contamination either in the mass spectrometer tube, or in the gas sample itself, but represented a real difference from the value reported by Nier in 1937. A careful

examination of the isotopes of krypton has been made and the measured isotopic abundances have been found to agree well with those of Nier except mass 80 as noted above. It was discovered that Nier had made an error in calculating the abundance of krypton 80 and that by correcting this error, the data of Nier and of the present investigation are in closer agreement. In Table XII is presented the average of the 90° and 180° mass spectrometer abundance data for normal krypton, along with the corrected data of Nier.

TABLE XII

Isotopic Composition of Normal Krypton.

Mass Unit	Present Data (Average) Atom %	Nier's Corrected Data Atom %
78	0.342	0.346
80	2.228	2.261
82	11.50	11.50
83	11.48	11.50
84	57.02	56.95
86	17.43	17.43

From this table, the good agreement between Nier's corrected value and our abundance data for krypton 82, 83, 84, and 86 is evident. However, in the case of krypton 78 and 80, a discrepancy of about one percent is noted.

A careful investigation of the isotopes of xenon has been made. It has been pointed out that the xenon isotopes cannot be completely resolved until the resolving power of the mass spectrometer is increased by reducing the width of the first exit slit of the tube. In spite of the resolution difficulty, the abundance measurements for xenon obtained

in the present investigation agreed remarkably well (except for the less abundant masses which are most affected by the resolution error) with the data obtained with out 180° mass spectrometer and by Nier. This is shown in the following table.

TABLE XIII
Isotopic Composition of Normal Xenon.

Mass Unit	90° Data Atom %	180° Data Atom %	Nier's Data Atom %
124	0.090	0.095	0.094
126	0.084	0.088	0.088
128	1.878	1.917	1.90
129	26.32	26.24	26.23
130	4.003	4.053	4.07
131	21.24	21.24	21.17
132	26.96	26.93	26.96
134	10.48	10.52	10.54
136	8.94	8.93	8.95

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