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Mass spectrometric study of "anomalous" water

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MASS SPECTROMETRIC STUDY OF
"ANOMALOUS WATER"

BY

BERNARD JEAN BOUY, 1946

A

THESIS

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_____

ABSTRACT

Considerable interest has developed recently in a material called "polywater" or "anomalous water". This material has properties quite different from those normally associated with liquid water.

The purpose of this study is to give some mass spectrometric observations of "polywater". The "polywater" samples were produced within silica capillaries. These capillaries were heated by means of a helical coil to vaporize the "polywater". The vapor was directed into the source of a mass spectrometer.

The results of this study show that a significant portion of the "anomalous water" samples is composed of a polymer of dimethyl-siloxane. To date, the observations are not complete enough to determine if this polymer is the main constituent of anomalous water. The question is still open as to whether the polymer of dimethylsiloxane is a contaminant or synthesized in the silica capillaries.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

I. INTRODUCTION

A. Problem Background

Recently, Deryagin and his coworkers[1] in the U.S.S.R. have

discovered that water, and possibly many other liquids, can literally

"remember" how they were formed, and behave differently from their

normal standards. In particular, Deryagin discovered that water,

when condensed in quartz capillaries, has properties completely

different from normal water. According to Deryagin, et al.,[2]

anomalous water, in addition to high viscosity and reduced vapor

pressure, can have a density ranging from 1.04 to 1.40 g/cm^3. It

hardens without freezing at -40 to $-50^{\circ}C$, and does not boil. It

appears to revert to normal water vapor at 650 to $700^{\circ}C$. Its index

of refraction is 1.48 compared with 1.33 for normal water.

This material has been called "polywater", "anomalous water",

"superwater", "orthowater", "water II" and most recently "cyclimetric

water". Because anomalous water is produced as columns of very

small mass (ususally 10^{-6} - 10^{-8} g), it has been difficult to determine

the true nature of this material. The object of this work is to

obtain the mass spectrum of anomalous water in order to form a basis

for understanding its molecular composition and structure.

B. The Research Program

The samples of "polywater" and deuterated "polywater" contained

within the silica capillaries were supplied by Dr. Barbara Howell

of the Graduate Center for Cloud Physics Research. These samples,
heated with a tungsten or platinum helical coil, were directed
toward the source of a General Electric Monopole Mass Filter
Model 22 PC 160. The products effusing from the capillary gave a
mass spectrum we had to identify. For this purpose we used "standard"
compounds which have known mass spectra. We also studied the
Arrhenius plots of ion currents of characteristic peaks to give
values of the activation energy for vaporization. These results
give new information about "anomalous water".

II. REVIEW OF LITERATURE ON "ANOMALOUS WATER"

Many papers have been published concerning the structure of "polywater". Deryagin and his coworkers[3][4], suggested that the molecules of the "anomalous component" have the formula $(H_2O)_n$. Bellamy, et al.,[5] suggested a tetramer in which the four water molecules form a square by strong hydrogen bonding. A tetrahedral cluster $(H_2O)_4$ was proposed by Bolander, Kassner, and Zung[6] and a rhombohedral structure similar to ice II was proposed by Erlander[7]. Some additional results have been presented recently[8]. Lippincott, Stromberg, Grant, and Cessac[9] have claimed to have found proof that anomalous water has a unique stable polymeric structure. This claim is based on their interpretation of the infrared spectrum obtained from microgram quantities of anomalous water.

Since Lippincott's publication of infrared data, other infrared data have been reported, as well as N.M.R., P.M.R. and Raman Spectra[5][9-13]. These data establish the existance of a material called polywater or anomalous water. Very few reports have been published on the mass spectrometric analysis of polywater.

The mass spectrometric measurements of Willis, et. al.,[11] yield a vapor molecular weight of 18 instead of 72, as reported by Burton[14]. Willis raised the temperature progressively up to $320^\circ C$; "again the only peaks in the spectrum were for 17 and 18" but "on removal of the probe some liquid still remained in the capillaries". Rabideau's analysis, reported by Thomsen[12], "came up with nitrogen, oxygen and carbon dioxide from air in the tube and

only ordinary water besides. This would tend to indicate that either the macromolecules of anomalous water do not exist or that they are too fragile to stand much handling". Rousseau and Porto[13] state, "we have determined that our samples consisted of approximately equivalent amounts of sodium, potassium, carbon, oxygen, and chlorine each present in the range of 5 to 35 percent of the total ion signal". Traces of calcium, boron, silicon, nitrogen and sulfur were found but no lines beyond m/e=44 could be detected from the sample. "The low concentration of oxygen and lack of intense bands at m/e=18 or at multiples of 18 indicated that nearly all the material in these samples consisted of the contaminants with relatively few H_2O molecules or H_2O polymers present". The presence of singly ionized CO_2 is shown.

Each of the published mass spectrometric studies concerning anomalous water give different results. The present study was designed to contribute more information on this subject.

III. EXPERIMENTAL SET-UP

A. Equipment Description (Figures 1 and 2)

1. The "Polywater" samples

The silica capillaries containing the "polywater" or the "deuterated polywater" were supplied by B. Howell. The material was grown from doubly distilled water by the Deryagin method.[1] Silicon grease was used to seal the pyrex vessels in which the anomalous water was made.

2. Set-up of the capillary inside the mass spectrometer (Figure 3)

The capillary with polywater was placed inside a stainless steel hypodermic needle in order to give a uniform temperature. A Pt/Pt-13%Rh thermocouple was spotwelded to this needle. The needle was fitted into a quartz tube. A tungsten (or platinum) helical coil was used to heat this assembly. The thermocouple temperature was measured by means of a millivolt potentiometer. Two essentially identical assemblies of this type were mounted on the same vacuum flange. The flange was fixed into the vacuum system in such a way that the ends of the capillaries faced the source of the mass spectrometer. With this set-up, the capillary was heated mostly by radiation. A plot of temperature versus the square root of the potential applied to the heating coil gave a straight line. This experimental result can be explained as follows: assume that the center of
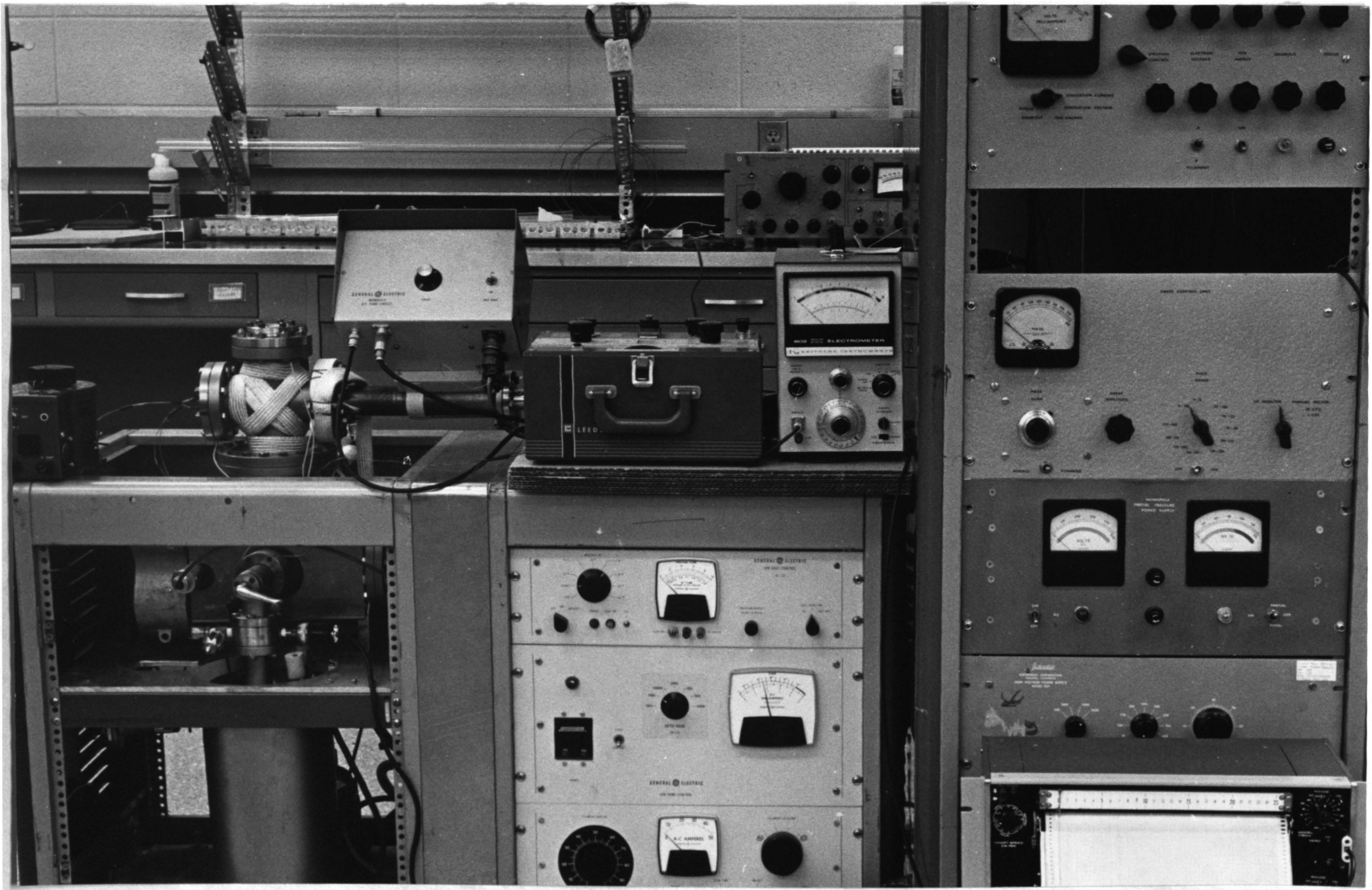
Figure 1. General Electric Monopole Mass Filter Model 22 PC 160
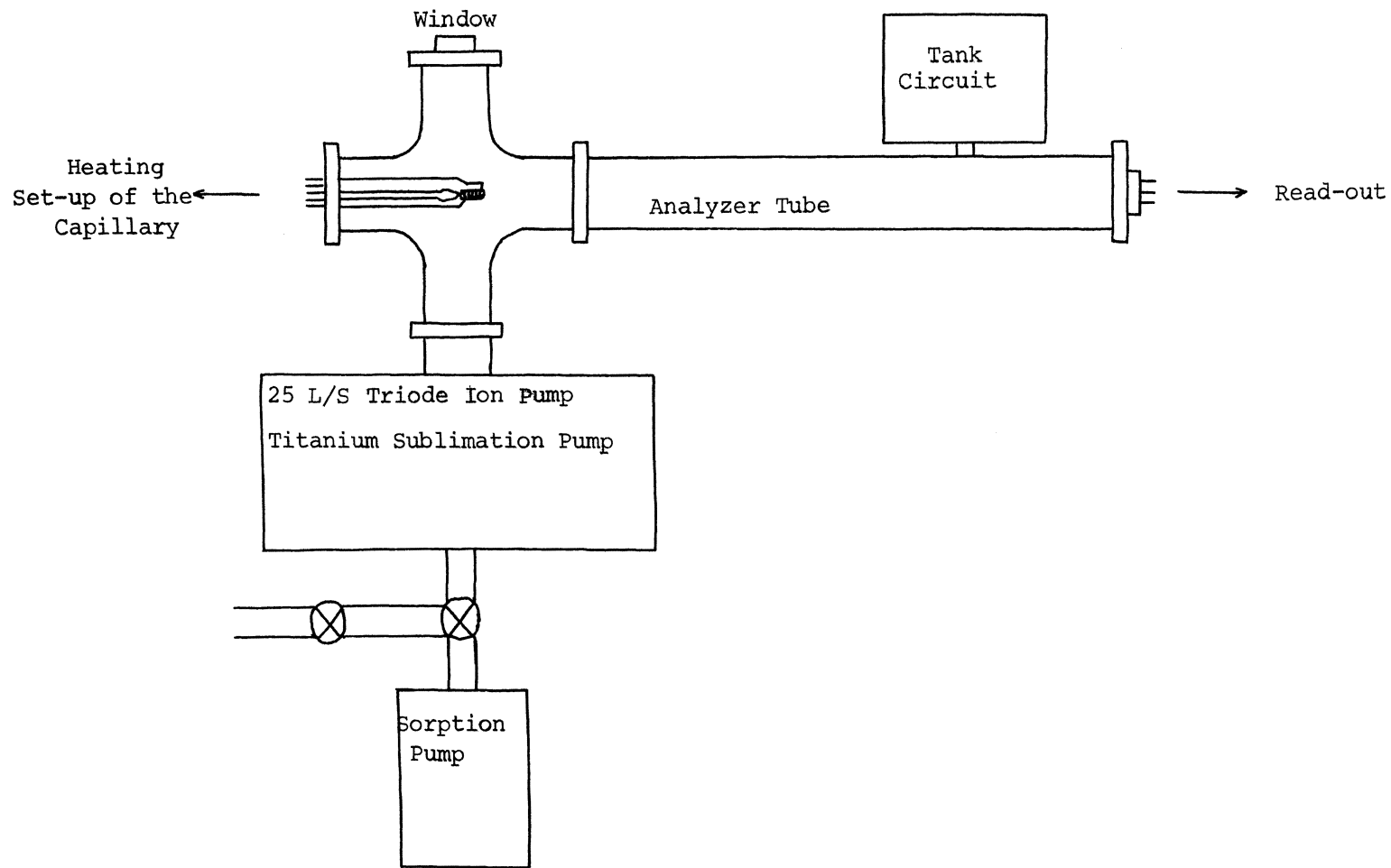
Figure 2. Schematic Diagram of General Electric Monopole Mass Filter Model 22 PC 160
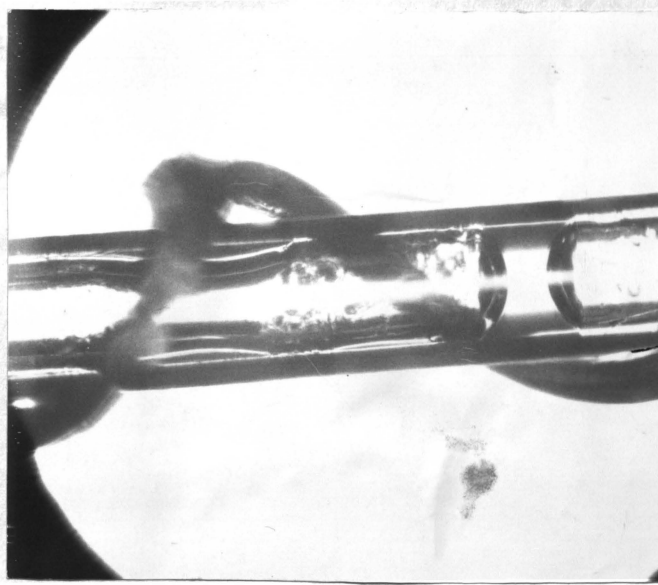
Polywater Capillary Surrounded by the Helical Coil
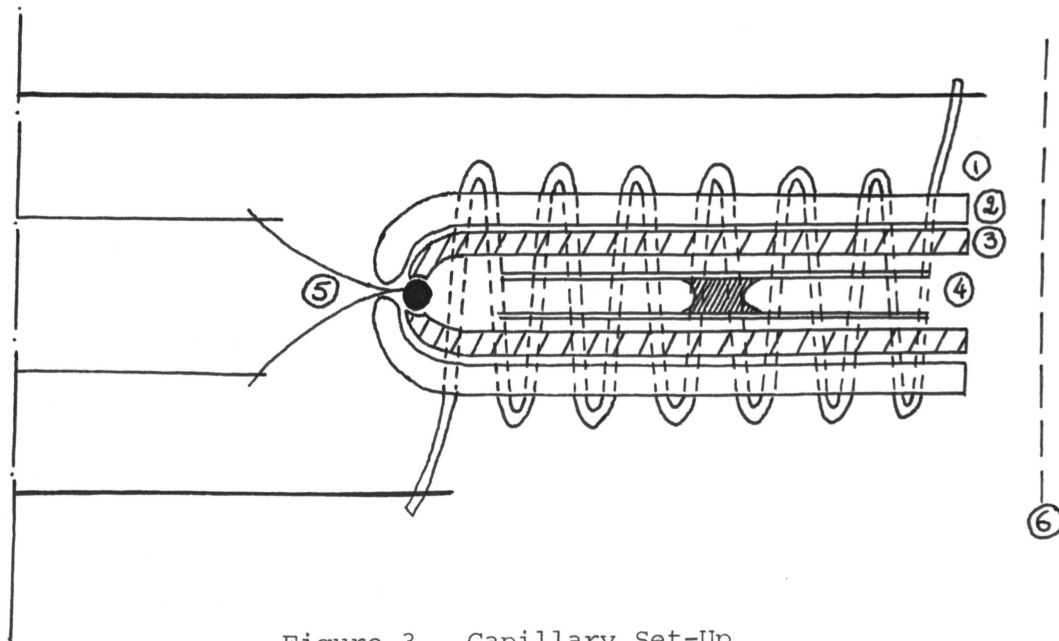
Figure 3. Capillary Set-Up

1. Helical Coil (Heater)
2. Quartz Tube
3. Hypodermic Needle
4. Capillary (sample)
5. Thermocouple
6. Mass Spectrometer Source

the wire is far from the ends and that we have a steady state for the coil. (The resistance R will not change drastically.) Assume further that the radiation heat for the hypodermic needle is equal to:

$$Q_r = A \varepsilon \sigma (T^4 - T_o^4)$$

A is the surface area of the hypodermic needle. ε and σ are constants. As T_o (equal to room temperature) is very small relative to T we can write:

$$Q_r \simeq A \varepsilon \sigma T^4$$

But this heat is furnished by Joule effect of the coil. So we must have the relation:

$$Q_r = A \varepsilon \sigma T^4 \alpha \frac{V^2}{R}$$

V and R are respectively the applied potential and the resistnace of the coil. As A, ε, σ and R are constants, we can write:

$$T^4 \alpha V^2$$

and $T \alpha (V)^{\frac{1}{2}}$.

Because the inside of the hypodermic needle was essentially a black body, it can be assumed that the enclosed sample was at the same temperature as the needle.

3. The vacuum device (Figure 2)

To obtain good mass spectra, a low residual pressure in the mass spectrometer system was required.

For the initial evacuation of the vacuum system, the Sorption Pump was filled with liquid nitrogen. When the pressure was about 10^{-4} torr the 25 liter per second Triod Ion Pump was started.

With this pump a pressure of about 10^{-6} torr was obtained. In order to get a better vacuum, the whole mass spectrometer was baked out to degas it. The bakeout temperature was held between 100°C and 200°C during 4 to 6 hours. After cooling the system to room temperature, the Titanium Sublimation Pump was run periodically. A pressure below 10^{-9} torr was usually obtained. The mass spectrometer was then turned on. The mass spectrometer instrument was a General Electric Monopole Mass Filter Model 22 PC 160 (Figure 1).

B. Monopole Mass Filter

The monopole mass spectrometer was first described by von Zahn[15]. It is related to the quadrupole mass filter but has a different method of operation and different properties. There has been an extensive theoretical analysis of the quadrupole filter, but little published work[16] on the monopole filter. Lever[17] has computed ion trajectories for a monopole filter and explored the properties of such an instrument.

In mass spectrometry some terms have to be defined: Transmission is defined as the ratio of the number of separated particles to the number of particles entering the mass spectrometer. It governs the instrument's sensitivity. Resolution is defined as the accuracy, i.e., the ability to separate adjacent mass peaks. Von Zahn[15] gives an expression for resolution in monopoles.

$$\text{Resolution} = m/\Delta m = (n/1.5)^2$$

where Δm is the width of the mass m peak at half maximum and n is the number of cycles the ion spends in the field. For a fixed energy in the z direction (Figures 5, 6) n^2 is proportional to the mass. To a first approximation, one thus expects a spectrum of equally spaced peaks of equal width.

Interpretation of the mass spectra produced by this study requires some understanding of the operation of the monopole mass filter. Therefore, a brief description of this instrument is given here. A more detailed outline of the theory of the monopole mass filter is given in the Appendix.

The heart of the Monopole Mass Filter is the analyzer tube (Figure 4). Gaseous molecules are ionized by electron bombardment and accelerated into the analyzer region. Here, an electrical field is maintained by impressing both RF (constant frequency) and DC voltage on the single pole (Figures 5 and 6). In this field, the ions undergo oscillations which are dependent upon mass-to-charge ratio and field parameters. For a given set of operating conditions, only those ions with one mass-to-charge ratio will follow a stable trajectory through the analyzer, i.e., the amplitude of the oscillations will not exceed the analyzer dimensions, and the ions will traverse the length of the analyzer region without striking the analyzer elements. All other ions follow unstable trajectories (wide-amplitude oscillations) and will be lost in the analyzer region. A separation of ions according to mass-to-charge is thus accomplished.

The separated beam of ions leaving the analyzer region impinges upon an electron multiplier. The electron multiplier amplifies
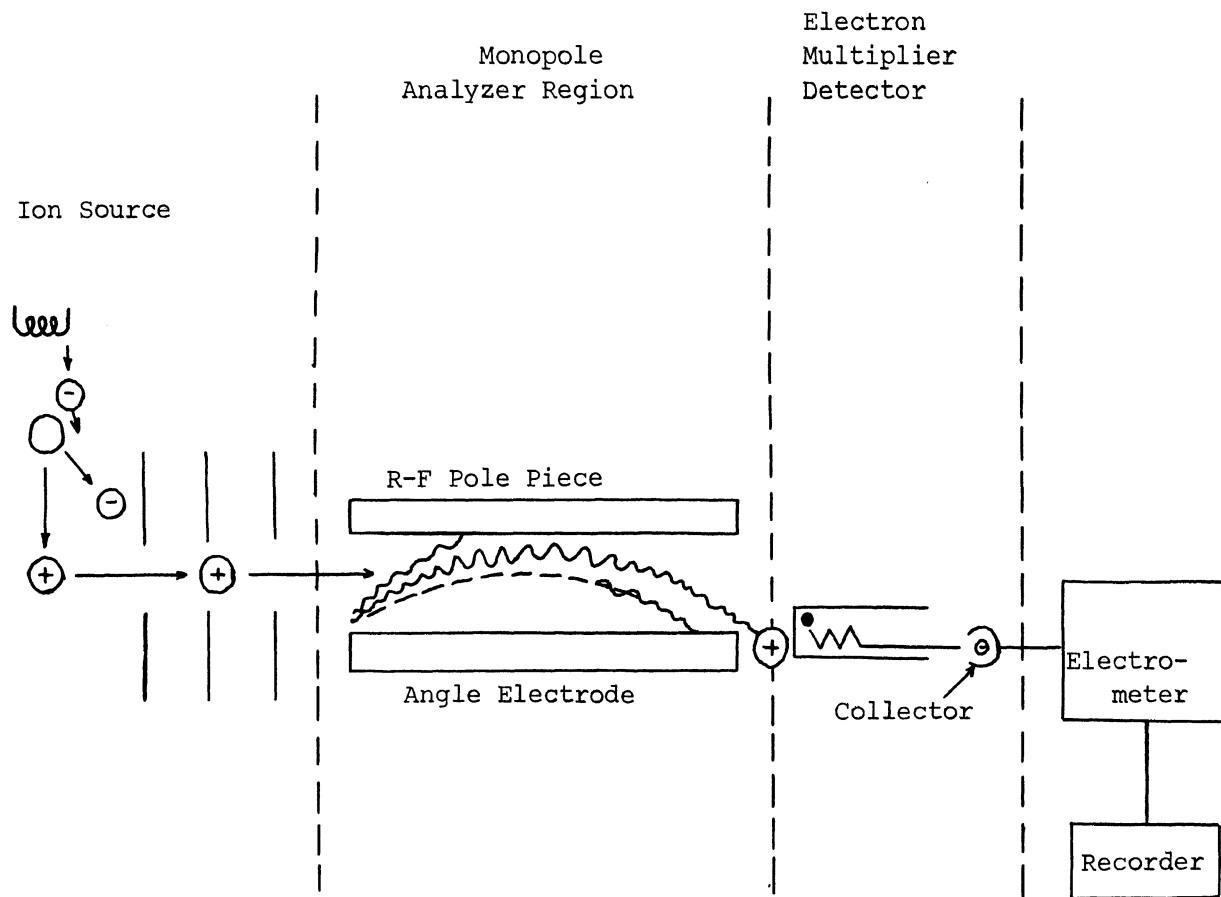
Figure 4. Diagram Monopole Mass Filter

13
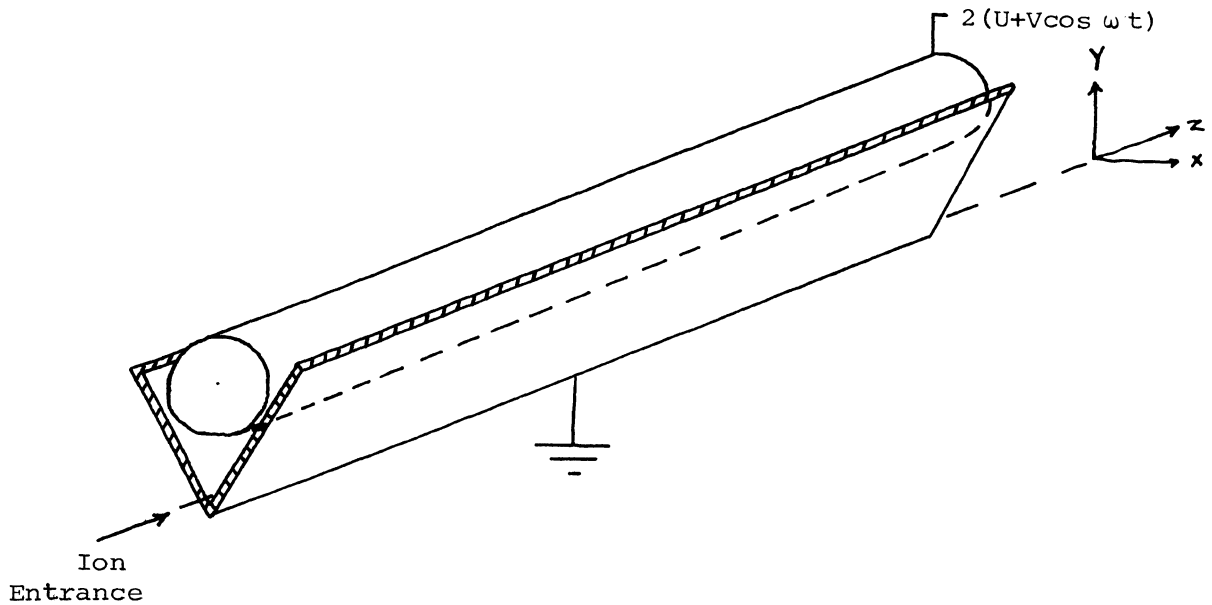
Figure 5. Schematic Diagram of the Monopole Mass Spectrometer.
Ions are injected into the device in the Z direction
with a small initial velocity in the y direction.
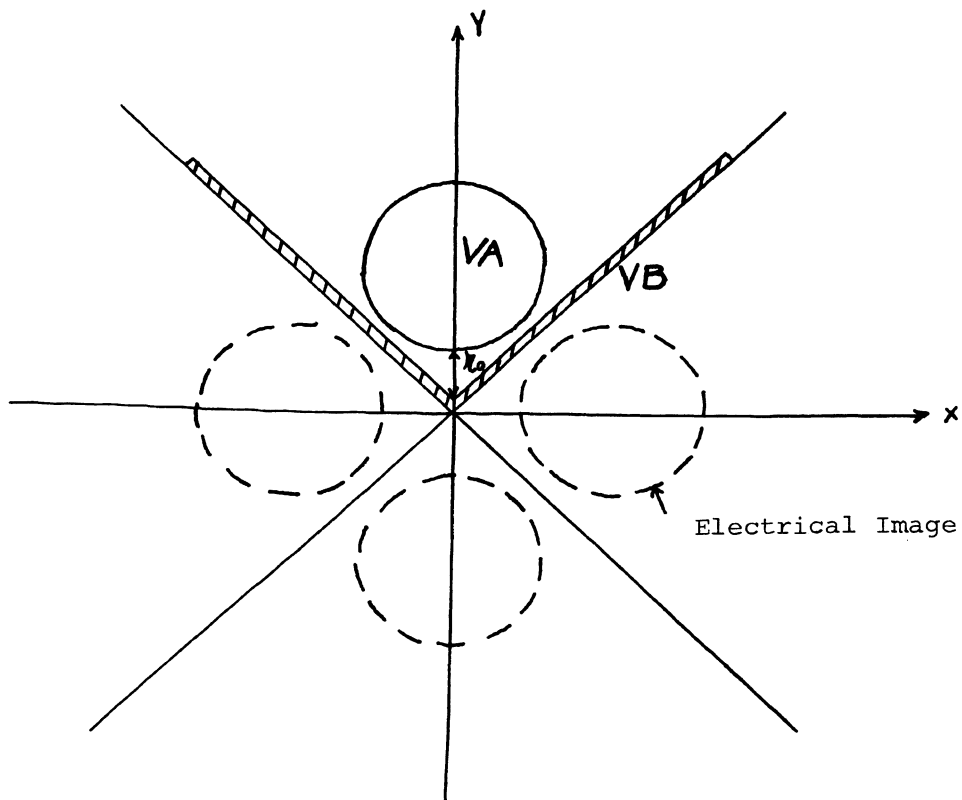
Figure 6. Monopole Mass Filter Schematic Diagram of the Analyser
Cross Section

the ion current by a factor of approximately one million. Thus, an output signal corresponding to the concentration of the separated gaseous species is obtained. By varying the RF and DC voltages, ions of each mass-to-charge ratio successively follow stable trajectories and a mass spectrum containing a peak for each species of the gas sample is obtained. The position of the peak in the spectrum identifies its mass to charge ratio and the height of the peak is a measure of its partial pressure or concentration.

An important aspect in sample-identification analysis is the ability of the instrument to operate over a wide mass spectrum. Then, a fragmentation pattern can serve as the basis for positive sample identification. It is helpful if the instrument is free of mass discrimination, i.e., changing sensitivity with mass. For operation at unit resolving power, the monopole analyzer tube exhibits less mass discrimination than the quadrupole type RF-DC mass filter.

IV.   EXPERIMENTAL RESULTS

A.   Mass Spectrum of "Normal Anomalous Water"

   1.   <u>Spectrum of "normal anomalous" water alone (Figure 7a and 8)</u>

   First, the mass spectrometer empty was run to get the background

spectrum.   Then a "normal polywater" capillary was put inside the mass

spectrometer.   At room temperature the presence of the sample did not

significantly change the residual gas mass spectrum.   The residual

gases were hydrogen, helium, methane, water, ethane, carbon monoxide,

oxygen, argon and carbon dioxide.   Usually, the total pressure of these

gases was lower than 10^{-9} torr and not higher than 5×10^{-9} torr.   A

small peak at m/e=23 indicated the presence of sodium in the mass

spectrometer ion source.   The main constituents of the residual gas

were hydrogen, methane, carbon monoxide and carbon dioxide in the

ratio of approximately 4:4:3:2.   No residual gas components having

values of m/e above 44 were found.

   When the background spectrum was established, the sample tempera-

ture was raised.   When the sample temperature reached ~200°C, new

mass peaks began to appear.   Of these, the largest peak appears at

m/e=73 with smaller peaks at 57, 96, 119, 131 and 147 A.M.U.   Associated

with the 73 peak are smaller ones at 74 and 75.   Typical values of peak

height ratios are given in Figure 12.

   The ion current I^+ of any mass peak associated with the sample is

directly proportional to the quasi-equilibrium vapor pressure P of

the sample, that is

   $$I^+ = kP$$
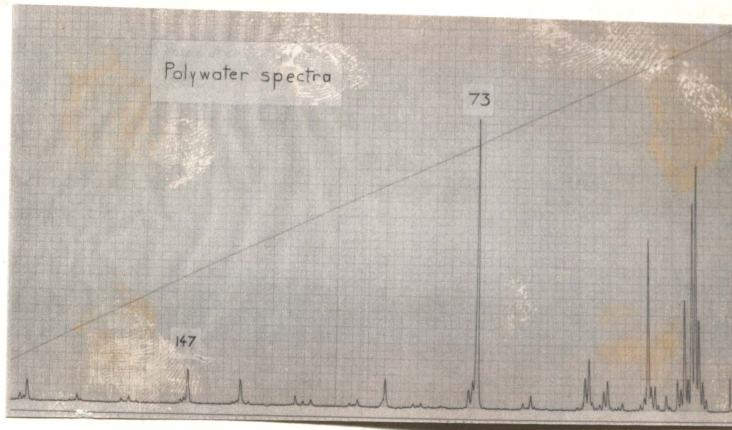
Figure 7a.   Spectrum of Normal Anomalous Water at 420°C.
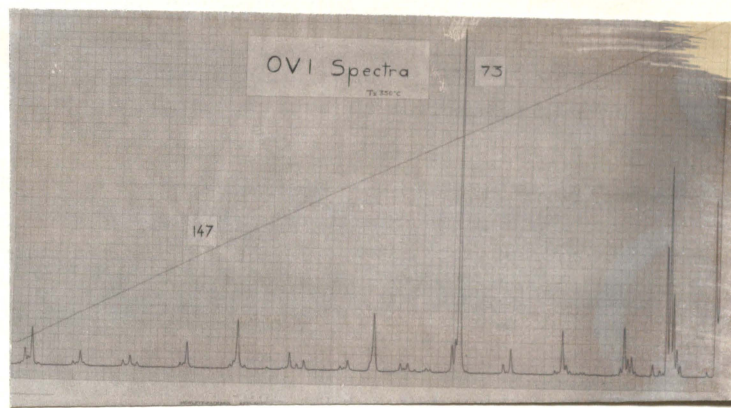
Figure 7b. Spectrum of OV-1 (Polydimethylsiloxane) at 350°C.
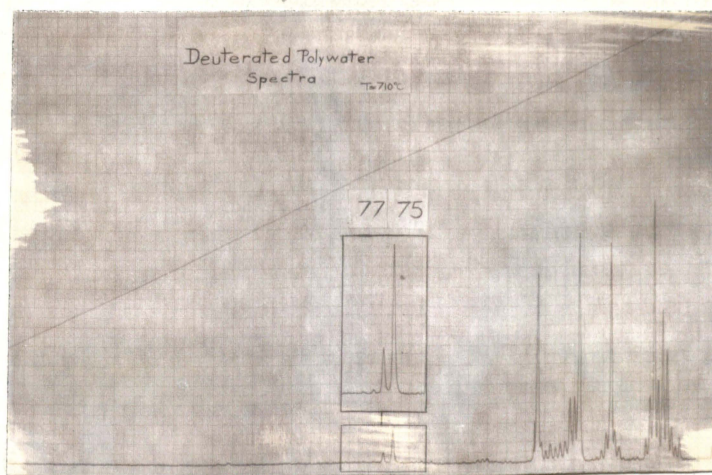
Figure 7c. Spectrum of Deuterated Anomalous Water at 710°C.

1x10^{-9} (ion current)

73

0   28   40   75   119   147

m/e
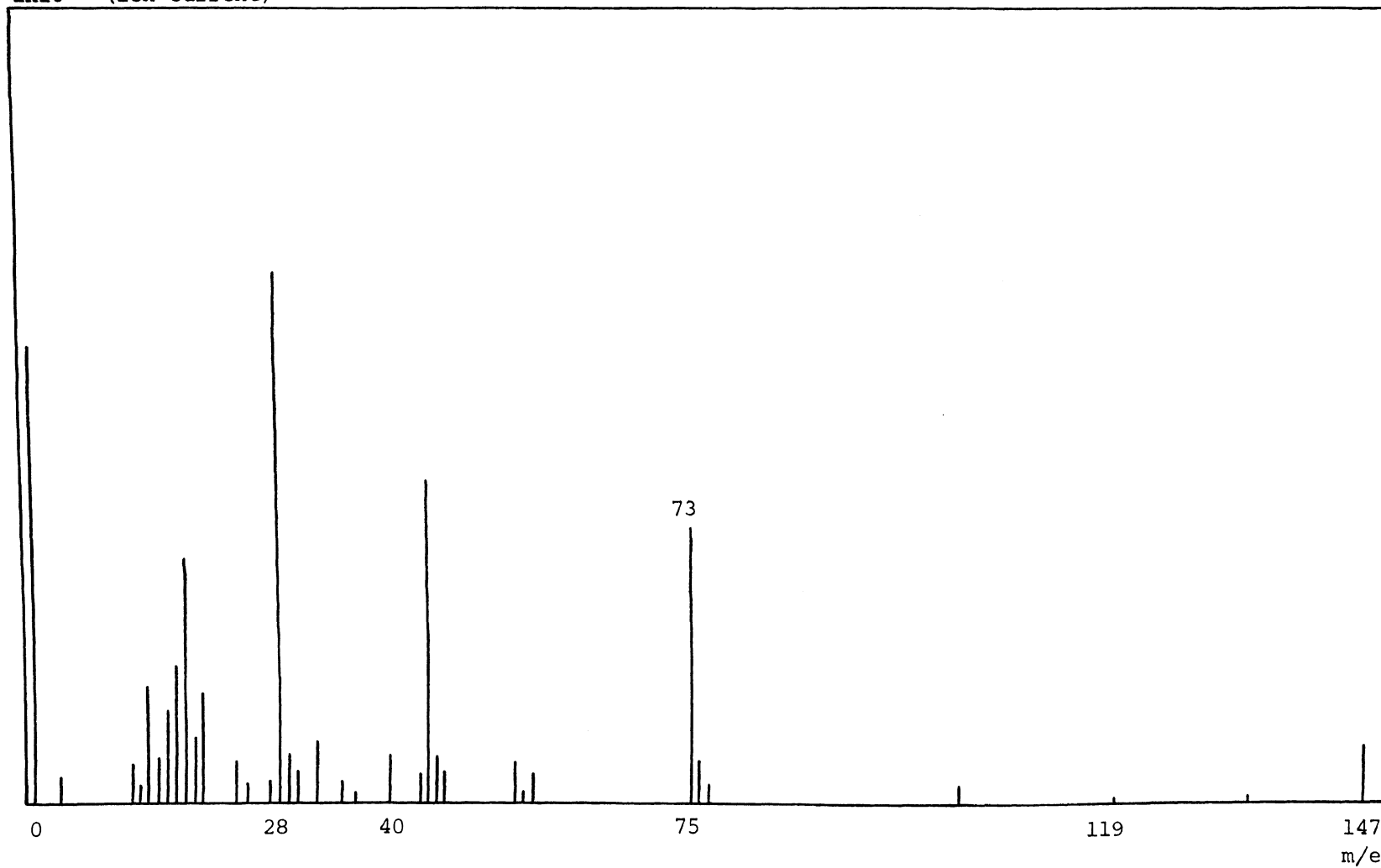
Figure 8. Mass Spectrum of "Anomalous Water" (T≅350°C)

where k is an instrument constant. Therefore the Clausius-Clapeyron equation

$$\frac{d(\ln\ P)}{d(\frac{1}{T})} = -\ \frac{\Delta H}{R} \quad \text{can be written} \quad \frac{d(\ln\ I^+)}{d(1/T)} = -\ \frac{\Delta H}{R}\ .$$

By plotting the natural logarithm of I^+ versus 1/T a straight line with slope $-\ \frac{\Delta H}{R}$ should be obtained, which gives a value of the activation energy of vaporization (Figure 9). The results of these plots for peaks 73 A.M.U. and 147 A.M.U. gave about the same activation energy, i.e., $\Delta H{\sim}44$ kcal/mole. This indicates that both peaks came from the same material.

At 600°C polywater evaporated rapidly from the capillary and the peaks soon vanished. The disappearance of the sample was checked by removing and examining it under a microscope. The capillary was empty.

Before it was possible to interpret the mass spectrum, it was necessary to determine the true values of the mass-to-charge ratios. To do this, the mass spectra of known compounds were obtained with the mass spectrometer.

2. Calibration of anomalous water spectrum with copper and silver (Figure 10)

To calibrate the "anomalous water" spectrum, anomalous water, copper and silver were simultaneously evaporated. This was done by fixing Cu and Ag beads to the sample heater. In this way, the 63 and 65 peaks of copper as well as the 107 and 109 peaks of silver were obtained. With these peaks it was possible to verify more accurately the values of the mass-to-charge ratios of the anomalous water mass spectrum.
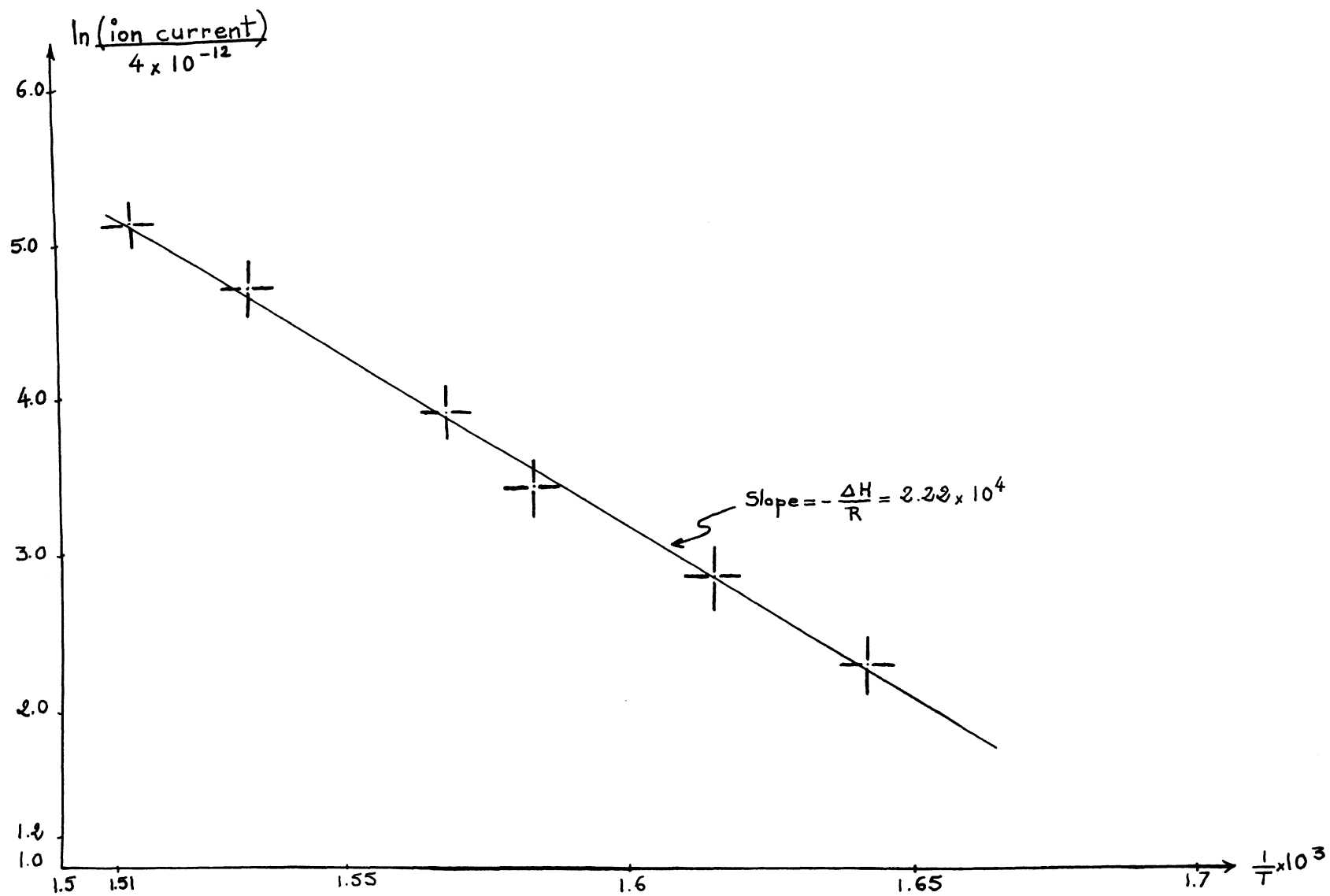
Figure 9. Arrhenius Plot of Ion Currents of "Anomalous Water" 73 A.M.U. Peak.
The activation energy of vaporization is equal to 44.1 kcal per mole.

$1x10^{-9}$ (ion current)

0   28   44   63   107   147
                                                             m/e
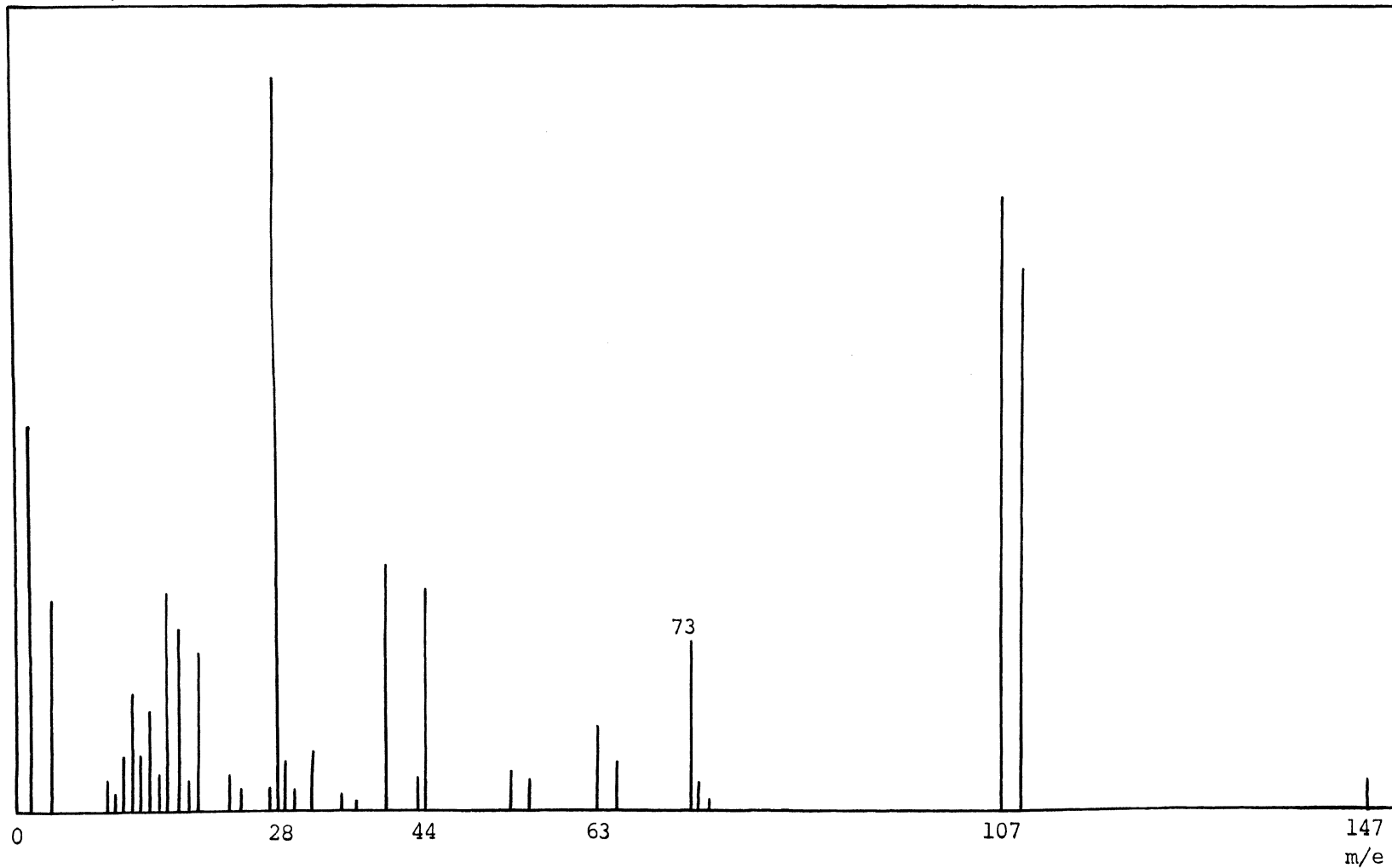
Figure 10.   Mass Spectrum of "Anomalous Water" With Copper and Silver (T≈320°C)

3. <u>Spectrum of polydimethylsiloxane (Figure 7b and 11)</u>

Polydimethylsiloxane is a material which has a mass spectrum very similar to that of polywater. The compound used was OV-1 polydimethylsiloxane purchased from Applied Science Laboratories, Inc. OV-1 is a polymer of dimethylsiloxane:

$$
CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - \left(O - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} \right)_n O - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - CH_3 \qquad \text{with } n > 30,000.
$$
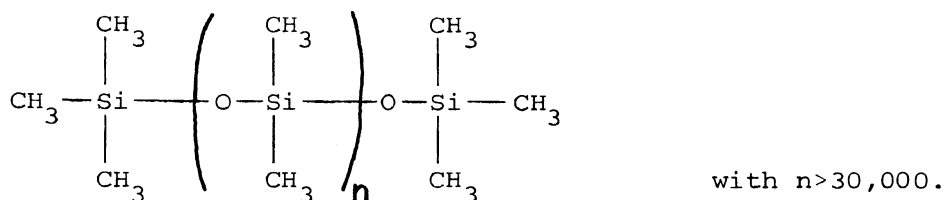
This material, soluble in chloroform and toluene, has a maximum temperature of 350°C. A complete mass spectrum of this compound was obtained from the organic mass spectrometry service of Finnigan Instruments, Inc. The spectrum was checked by Dr. G. Lewis in the Graduate Center for Materials Research with a Nuclide mass spectrometer. In the mass spectrometer used, OV-1 gives a mass spectrum which is practically identical to the mass spectrum of anomalous water. OV-1 gives main peaks at 73 and 147 A.M.U. as well as smaller peaks that match the anomalous water spectrum . All peaks found in OV-1 up to 200 A.M.U. were also found in the anomalous water samples studied. In comparison to OV-1 no extra peaks were present in the anomalous water sample.

Arrhenius plots of the 73 and 147 peaks gave an activation energy of vaporization of about 48 kcal/mole, which is close to the 44 kcal/ mole found for polywater.

1x10^{-9} (ion current)

73

0   18   44   75   147
m/e

22
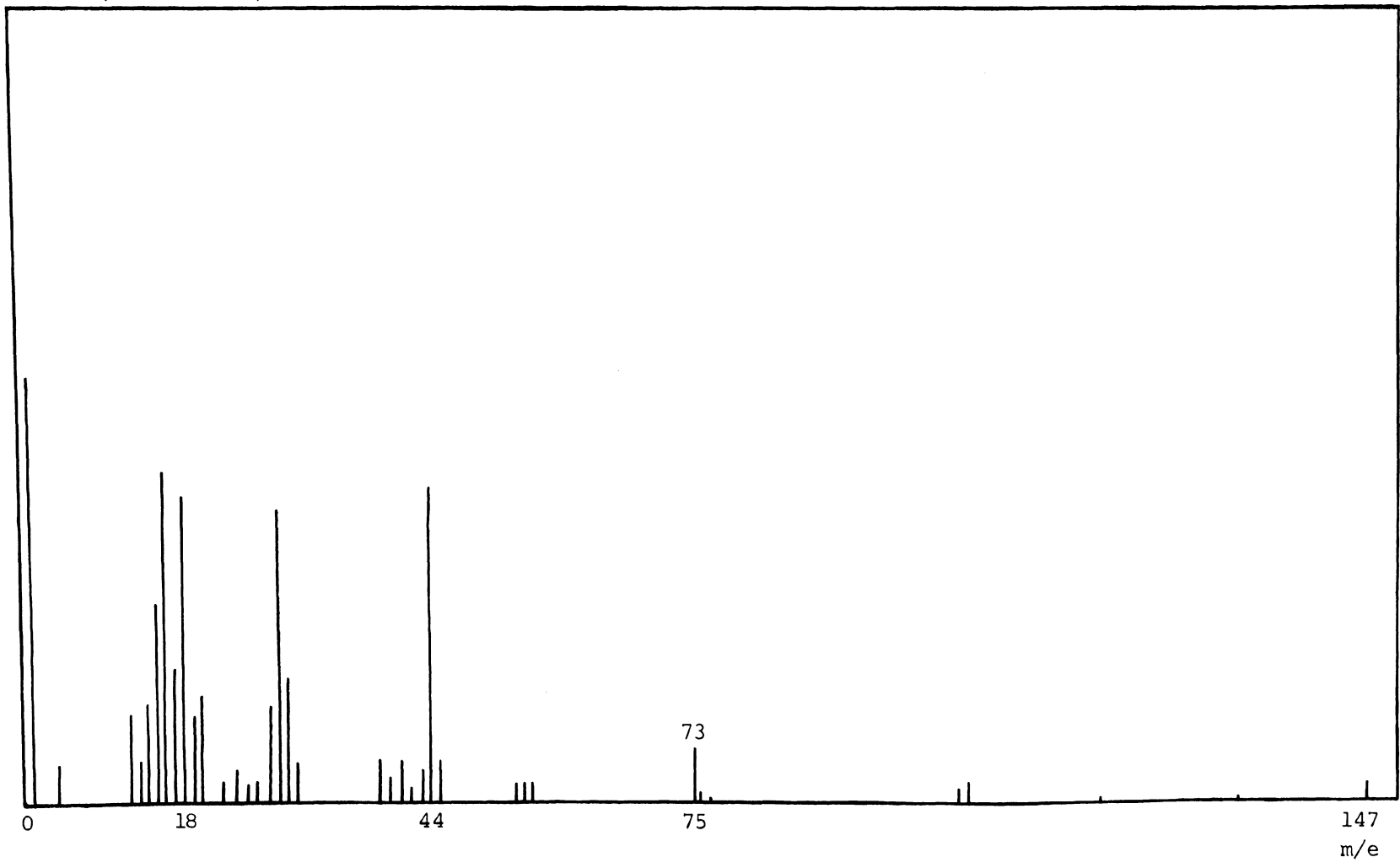
Figure 11.   Mass Spectrum of OV-1 (T=230°C)

4. <u>Spectrum of normal anomalous water and OV-1</u>

To better compare the mass spectra of anomalous water and OV-1 the sample heaters were arranged on the same flange, one for a "normal polywater" capillary, and another for an OV-1 filled capillary. These two capillaries could be heated separately or simultaneously. First, the OV-1 capillary was heated to about 200°C, and the mass spectrometer tuned to its 73 A.M.U. peak. Then the polywater capillary was heated. The peak height increased. If the OV-1 heater was turned off, the 73 A.M.U. ion current dropped to the value determined by the polywater sample alone. This proves, first that the mass to charge ratio is really 73 A.M.U. for polywater and second that the increase in the peak height is not due to the radiant heating of the OV-1 capillary by the polywater sample heater.

When the mass spectrum was scanned near 73 A.M.U., with both heaters turned on, it was recorded only a large 73 peak and small peaks at 74 and 75. It was speculated that perhaps some OV-1 vapor could condense on the polywater sample holder and that the polywater mass spectrum was really due to reevaporated OV-1 and not polywater. This possibility was eliminated by heating the polywater capillary until the whole 73 A.M.U. peak vanished. This sample heater was then cooled to room temperature. Then the OV-1 capillary was heated, and left for cooling. When the polywater capillary was reheated, no peaks due to OV-1 or polywater was seen. This proves that no OV-1 could have reevaporated from the polywater sample holder.

In this way it was verified that each large polywater peak corresponds to a large OV-1 peak.

B. Comparison of "Polywater" and OV-1 Spectra

Having shown the absence of cross-contamination between the OV-1 and polywater sample holders, their mass spectrum can be compared. The results show that, for peaks higher than 44 A.M.U., polywater and OV-1 spectra have exactly the same mass-to-charge ratios. The spectra can be superposed on (Figures 7a and 7b) and from Figure 12 it is possible to see that the relative peak heights agree fairly well. The activation energies of vaporization for "normal polywater" and OV-1 are similar. It appears, therefore, that OV-1, or polydimethylsiloxane, is a significant portion of the "anomalous water" composition.

C. Spectrum of Deuterated Anomalous Water (Figures 13 and 7c)

The deuterated anomalous water was prepared in the same way as anomalous water but from reagent grade heavy water (D_2O). Again, this material survived the normal bakeout procedures. Its presence in the vacuum chamber did not significantly change the residual gas mass spectrum. Indeed, it was necessary to heat the deuterated anomalous water samples to about $600°C$ before any significant mass peaks appeared beyond 44 A.M.U. Only three peaks, 75, 77 and 79 A.M.U. could be associated with the deuterated sample. The peak height ratios, taking the height of the 75 peak as unity were 1: 0.3: 0.03, (Figure 7c).

There was also a small increase of the 20 peak. For one sample, a large increase of peaks at 35 and 37, as well as 36 and 38 indicated the presence of chlorine and probably HCl. The chlorine peaks persisted after the 75 peak had vanished, so the source of this material is uncertain.

The values of these mass-to-charge ratios were verified with an OV-1 filled capillary. The same experimental set-up was used as the one for simultaneous use of OV-1 and normal polywater samples. Under nearly identical experimental conditions, peaks associated with "normal polywater" appeared at about 250°C and those associated with "deuterated anomalous water" appeared at 600°C. Therefore, it seems that "deuterated polywater" is considerably more stable than the "normal polywater". Furthermore its spectra are simpler than the polywater spectra.

PEAK	OV-1	POLYWATER
57	0.09	0.06
73	1.00	1.00
74	0.1	0.1
75	0.06	0.06
96	0.14	0.07
119	0.05	0.03
131	0.13	0.08
147	0.07	0.11

Figure 12. Relative Peak Heights for Anomalous Water and OV-1 Spectra

1x10⁻⁹ (ion current)

Figure 13. "Anomalous Heavy Water" Mass Spectrum (T≈700°C)

1×10^{-9} (ion current)

Figure 13. "Anomalous Heavy Water" Mass Spectrum (T≈700°C)

28
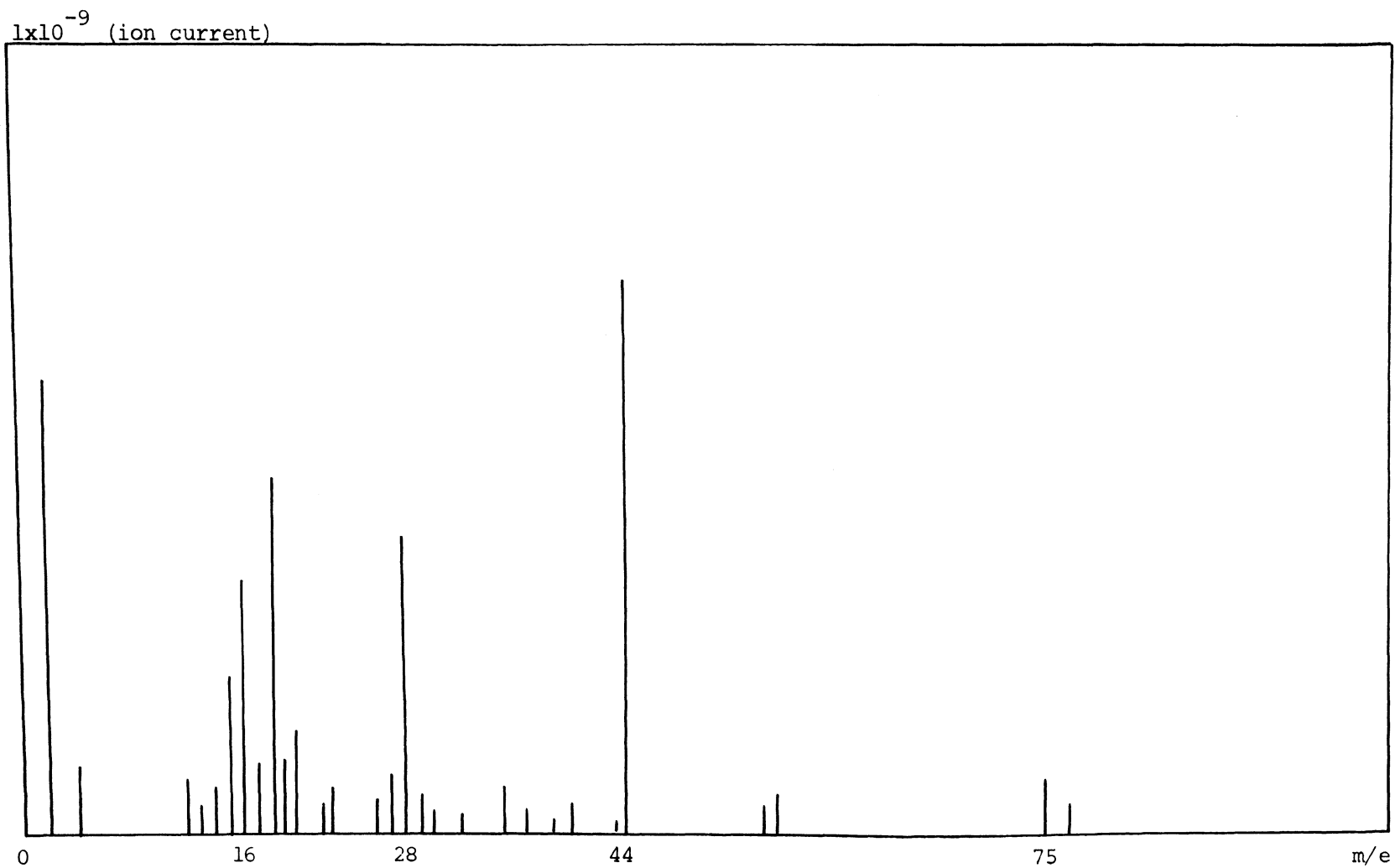
V. DISCUSSION AND CONCLUSIONS

A. Discussion

From the polywater samples, mass spectra were obtained almost identical to the spectrum of OV-1, which is a polymer of dimethylsiloxane. Major peaks at 73 and 147 A.M.U. were most probably:

$$CH_3 \text{---} Si \text{---} \quad 73 \text{ A.M.U.} \qquad \text{and} \qquad CH_3 \text{---} Si \text{---} O \text{---} Si \text{---} \quad 147 \text{ A.M.U.}$$

(with CH_3 groups above and below each Si)
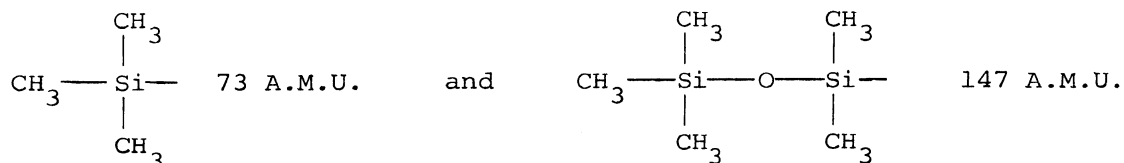
The small peaks appearing at 74 and 75 A.M.U. with peak height ratios $74/73 \simeq 0.1$ and $75/73 \simeq 0.06$ are perhaps due to the isotopes Si^{29} and Si^{30} in the $Si(CH_3)_3$ ions. The natural proportions of Si^{28}, Si^{29} and Si^{30} are 92.21%, 4.70% and 3.09% respectively[19]. The 75, 77, and 79 A.M.U. Peaks found at about $650°C$ for the "deuterated polywater" have no obvious explanation. It is not clear why there was such a difference between the relatively simple mass spectrum of "deuterated polywater" and the complex spectrum of "polywater". This is, in itself, a subject for further investigations.

Mass spectra, relative peak heights, activation energies of vaporization for polywater and OV-1 all correspond. This result is in accordance with the results of another study by Dechelette.[20]

He determined the radial distribution function of anomalous water by X-ray diffraction. A distance of 1.9Å was found which is likely to be the Si-C distance in the polydimethylsiloxane. Therefore a large constituent of our polywater is a polymer of dimethylsiloxane.

Having found polydimethylsiloxane in polywater, what can be the source of this product? There can be contamination from the silicone grease sealing the desiccator during the preparation. On the other hand, this material may be produced inside the capillaries. But if we try to synthetize the polydimethylsiloxane we need a source of methyl groups. The silicone grease is the only obvious source of methyl groups. However, even if the grease is a source of methyl groups, the synthesis of polydimethylsiloxane seems implausible.

It can be argued that the polydimethylsiloxane is only an impurity. However, the pure OV-1 evaporates rapidly at $250^{\circ}C$; it is a gum with a molecular weight of the order of a million. Our polywater sample, containing the polydimethylsiloxane, is liquid and does not evaporate rapidly below $500^{\circ}C$. Therefore, the polydimethylsiloxane in our samples has a much lower vapor pressure than OV-1. The reason for this is not yet certain. However, the answer to this problem is likely to appear when the true nature of polywater is understood.

The question we must ask is: if polywater is composed mainly of water and polydimethylsiloxane, what happens to the water constituent as the sample temperature increases? The mass spectra we obtained indicate that, in general, all peaks

from 2 to 44 A.M.U. increase initially with temperature. At a

fixed temperature these peaks decline with time. However, under

these conditions the peaks above 44 A.M.U. (associated with anomalous

water) remain constant in amplitude. Because we had no shutter

between the sample and mass spectrometer source, it was not easy

to distinguish between background gas (due to heating of the chamber

walls) and gas coming from the sample. Therefore, it was not

possible to distinguish directly between water molecules originating

from the sample and those desorbed from heated surfaces near the

sample. One attempt to detect water from an anomalous water

sample was made in the following way. While the mass spectrometer

was tuned to the m/e=18 peak, the sample temperature was increased

in steps from 400° to 500°C in a period of four minutes. A plot of

logarithm of the recorded 18 A.M.U. peak height as a function

of 1/T yielded 56 kcal/mole as an activation energy for vaporization.

If this is the energy required to liberate water molecules from

anomalous water, it means that the H_2O and polydimethylsiloxane

molecules are strongly bound.

How could H_2O be tightly held by polydimethylsiloxane?

We speculate that the important property of this polymer is the

Si-O-Si back bone which has dipoles

$$+\delta \qquad -\delta \qquad +\delta$$
$$Si\text{———}O\text{———}Si$$
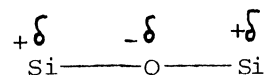
These dipoles can bind the molecules of water strongly.[21]

It can be suggested, for futher experiments, a mass spectrometric analysis of an "anomalous water" sample prepared from water with oxygen 18. If a significant change then occurs in the mass spectrum, we will have further clues as to the possible mechanisms for the formation of this material.

B. Conclusions

The polymer of dimethylsiloxane is a large constituent of polywater in our samples. Our samples of polywater have essentially the physical properties of "anomalous water" reported in the literature. The presence of this polydimethylsiloxane in large quantities makes it improbable that polywater is composed only of a polymeric water structure as postulated by Lippincott and coworkers.[9] However, this material is interesting in its own right and merits further study, both of its properties and origin.

APPENDIX

Theory of the Mass Filter

The monopole is related to the quadrupole mass filter.

The equations of the ion trajectories are very similar for these

two instruments. The theory of the quadrupole mass filter[22] first

will be analyzed.

1. Theory of the quadrupole mass filter

A quadrupole mass filter is made with four parallel metallic

cylinders. Ideally these cylinders would have a hyperbolic section,

(Figure 14). However, circular cylinders well approximate the

hyperbolic section, and are used in all instruments of this type.

In this geometry, the spatial repartition of the potential is:

$$V = \frac{x^2 - y^2}{2r_o^2}$$

The cylinders' surfaces are equipotential surfaces. If a constant

potential 2u is applied between the cylinders A and B (Figure 14)

as well as a time varying potential 2V cos ωt, the potential at

one point will be:

$$\Phi = 2(U + V \cos \omega t)$$

The dynamic equation for a charged particle is written:

$$\frac{d}{dt}(m\vec{v}) = -e\vec{V} \ \{[U + \cos \omega t] \ \frac{x^2 - y^2}{r_o^2}\}$$
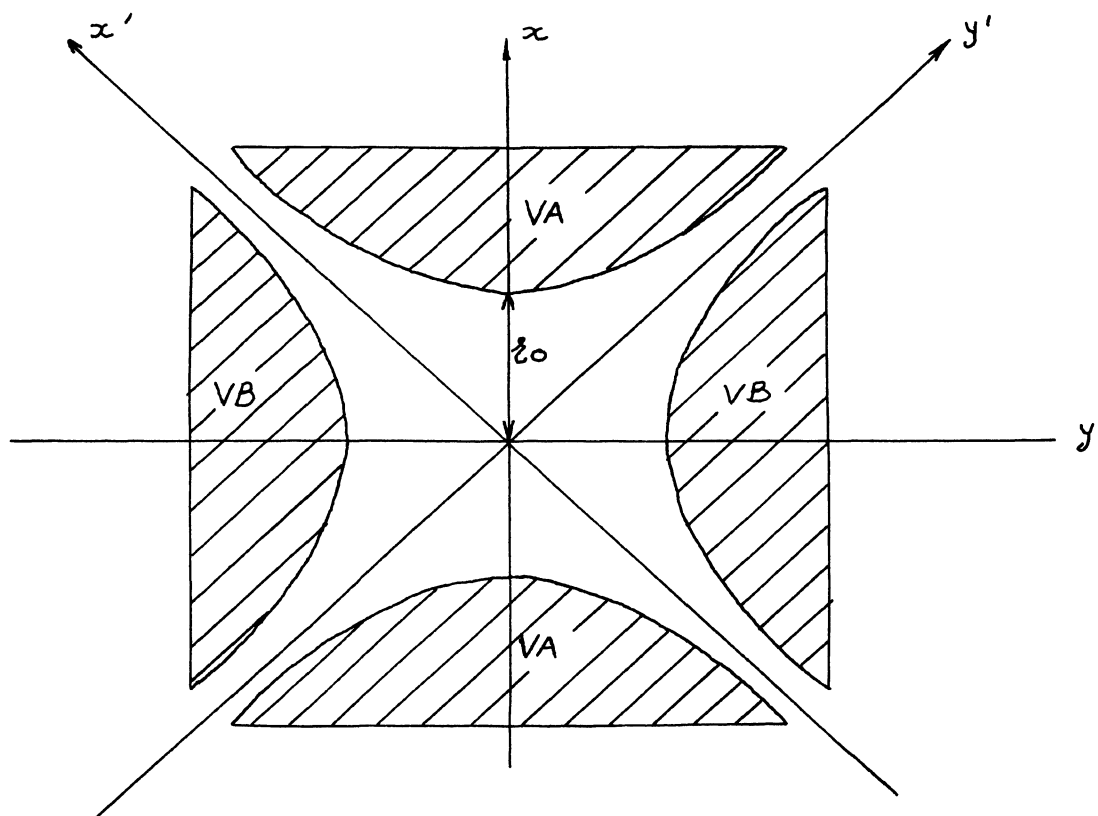
which gives by projection on the axis:

Figure 14. Quadrupole Mass Filter Schematic Diagram

$$m \ddot{x} + 2e(U + V \cos \omega t) \frac{x}{r_o^2} = 0$$

$$m \ddot{y} - 2e(U + V \cos \omega t) \frac{y}{r_o^2} = 0$$

$$m \ddot{z} = 0$$

The equations in x and y can be written in the particular form of the Hill's equations and also in the form of Mathieu's equations. These equations have stable roots only for particular values of the parameters.[16] We can see how ions of different masses are separated by considering the stability of these two equations.

We substitute now:

$$a = \frac{8eU}{mr_o^2 \omega^2}$$

$$q = \frac{4eV}{mr_o^2 \omega^2}$$

$$\xi = \frac{\omega t}{2}$$

to get:

$$\frac{d^2 x}{d\xi^2} + (a + 2q \cos 2\xi)x = 0$$

$$\frac{d^2 y}{d\xi^2} - (a + 2q \cos 2\xi)y = 0$$

For our purpose it is sufficient to notice that:

$$\frac{a}{q} = \frac{2U}{V}$$

and that if $m_1 = k \dfrac{V_1}{q_1}$, $m_2 = k \dfrac{V_1}{q_2}$

we will get

$$m = k V_1 \left(\frac{1}{q_2} - \frac{1}{q_1}\right) .$$

2. <u>Theory of the Monopole mass filter</u>

The theory of the monopole mass filter uses the same equations as above. The four electrodes of the quadrupole are replaced by one cylinder and one $90°$ vee-shaped electrode. This geometry gives the same electric field arrangement as found in one quarter of the quadrupole section (Figure 6). It is important to notice that the electric fields and the potentials Φ are the same and that the equations are similar.

But the monopole arrangement of the electrodes gives us another condition.

$$|y| > |x| .$$

This condition leads to the equations

$$\frac{d^2x}{d\xi^2} + (a + 2q \cos 2\xi)x=0$$

$$\frac{d^2y}{d\xi^2} - (a + 2q \cos 2\xi)y=0$$

As a result, the stability area of the diagram a, q for the monopole is smaller than the equivalent area for the quadrupole (Figure 15). One interesting property is worth noting: the ratio

$$\frac{a}{q} = \frac{2U}{V}$$

can vary over a larger range than for the quadrupole with a similar value of Δm. Von Zahn[15] has shown that the peak heights become independent of the ratio $\frac{a}{q}$ in this field.

Whether or not a given ion is stable for a given field configuration is uniquely specified by reference to the "stability diagram" (Figure 15). At constant ω, r_o, U, V (and consequently
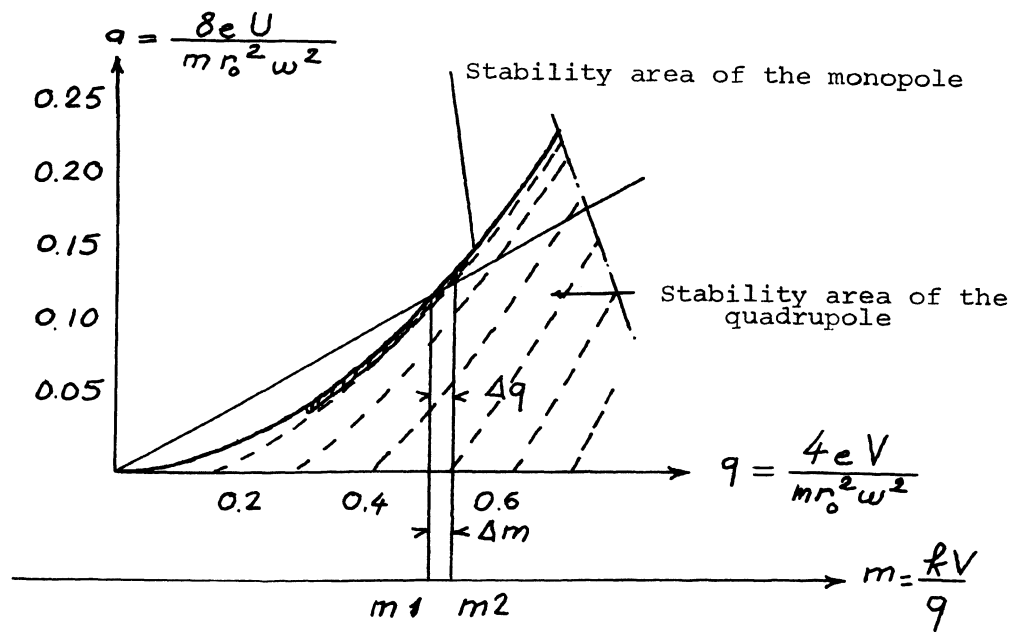
Figure 15. Stability Diagram for the Quadrupole Mass Filter and the Monopole Mass Spectrometer

U/V), all values of (a, q) lying on the portion of the line

through the origin of slope a/q = 2U/V and within the stable

(a, q) region define stable trajectories. Consequently all mass

values that satisfy the stable (a, q) conditions for this setting of

ω, r_o, U, V will follow stable trajectories through the analyzing

field and all others will follow unstable trajectories and be

filtered out before reaching the end of the field. Note that for

the quadrupole case, as the ratio a/q=2U/V is increased, (i.e., the

slope of the straignt line (Figure 15) is increased) the range of

stable (a,q) values decreases to the point (a_{lim}, q_{lim}) where

only one stable solution exists. Further increase in a/q results

in only unstable solutions being present. So this property

has the effect of increasing spectrometer resolution as a/q is

increased. When a/q is increased the stable mass range drops and

the number of stable operating points decrease.

There is a second condition which must be met in both

quadrupole and monopole instruments in order to insure that a

given ion will pass through the analyzing region. Not only must

the ion have a stable trajectory, but this trajectory must have

a maximum x (and y) amplitude less than the field radius. Ions

having stable trajectories with amplitudes larger than the field

radius will of course strike the pole pieces before reaching the end

of the analyzer. It has been shown[23] that the maximum amplitude

of a given ion's trajectory increases as the distance from the field

axis at which the ion is injected into the analyzer region increases

and that this maximum is also increased if the ion possesses suitable initial kinetic energy in the X or Y direction. Furthermore, even for ions injected on the field axis, the maximum amplitude increases for (a, q) points near the boundaries of the stable region.

In the monopole case, there is one additional condition which must be satisfied in order for an ion to reach the detector. This condition is contained in the Y-stable solutions to the equations of motion

$$y(t_o+t)=f \cdot y(t_o)\beta^{-1}\sin\tfrac{1}{2}\beta\omega t \sum_{s=o}^{\infty} sa_s \sin\omega t_o \sum_{s=o}^{\infty} a_s \cos\omega s(t_o+t)$$

which represents a beat of finite amplitude in the Y direction about the Z axis of the field.

Because of the construction of the monopole tube, an ion, although it has a stable trajectory, will still not reach the detector if one half of its beat length is shorter than the field region. In other words, an ion which, in a quadrupole, would follow a stable path through the field and be detected, will, if its beat length is too short, not be able to pass the monopole field. The relation between ion mass and beat length is such that ions of greater mass have longer beats. This means that at low resolution, i.e., very short analyzer sections, ions with almost any (a, q) in the triangular stable region will pass the field. As the analyzer section (in RF periods) is increased, the lower mass ions which have stable trajectories now have a 1/2 beat length

shorter than the field length and strike the V-shaped electrode, thus giving an apparent increase in resolving power and shifting the range of a, q values for which ions will pass the field into a bandary at the left side of the triangular diagram.

These specific properties of the monopole permit isotopic separations to be obtained, which are impossible with a quadrupole. Furthermore, the construction of the monopole is more simple and so there are less outgassing effect.

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