A STUDY OF THE ISOTOPIC ABUNDANCE OF BORON IN MINERALS

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SCOPE AND CONTENTS:

The B^{11}/B^{10} ratio has been determined with an accuracy of 0.3 per cent. and a reproducibility of 0.2 per cent. for minerals, Gabro and sea water to be in the range 4.129 to 3.987 with the corresponding atomic weights 10.815 to 10.810. These are in complete agreement with the currently accepted values. The absolute ratios are about 7 per cent. lower than those obtained by early researchers, but are in accord with the results of recent investigations. The results show freedom from fractionation in the evaporation of the samples in the mass spectrometer source, but it is observed that borax samples of the same mineral prepared by the chemical method yield higher ratios than those prepared by the resin method. Igneous rocks and boric acid are shown to have high isotopic ratios, whereas sea water possesses a value for B^{11}/B^{10} near the mean for minerals.

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CHAPTER I

INTRODUCTION

Historical

The study of the abundances of the stable isotopes of boron has been undertaken by a number of investigators since 1920, when Aston1) discovered the two stable isotopes of boron at masses 11 and 10, in a mass spectrographic study of boron trifluoride (BF_3). At the present time no general agreement has been reached on either the absolute value of the $\frac{B^{11}}{B^{10}}$ ratio or the variation of the ratio with the geological origin of the boron.

At the time of the discovery, Aston made an estimate of the boron isotopic abundance from the photographic intensities of the peaks, but the result did not agree with the then existing atomic weight of boron. In 1931, in a study of the isotopes of more elements, Aston2) made another photometric measurement of the isotopic ratio of boron, probably of European origin. Again he made the analysis on boron as boron trifluoride and obtained the value of 3.85 for the isotopic ratio, which is again too low. However, when this is corrected for photographic effects, the ratio comes to about 4.04 corresponding to an atomic weight of about 10.815 in good agreement with the then international value of 10.82.

It should also be mentioned that the abundance of boron isotopes was also measured by using band spectra at the early stages of the abundance measurements. Using photometry on the band spectra of BO (Chilian boron) Elliott3) gave an estimate of $\frac{B^{11}}{B^{10}}$ ratio as

3.63 ± 0.02 in 1930. In 1931 Paton and Almy 4), from study of BH bands reported $\frac{B^{11}}{B^{10}}$ ratio of 4.86 ± 0.15!

Long ago it was suggested that small variations in the isotopic abundances of boron, which had hitherto been considered to be constant in nature might be the cause of the controversies on neutron capture cross-sections as determined by British and American workers, using boron as a standard. In response to this bold suggestion nine samples of boron minerals were collected from different parts of the world for studies with a mass spectrometer as regards the variation of the isotopic ratio with origin of the sample. Interest in this problem, however, decreased in favour of more important work and the investigation came to a standstill for several years.

In 1946, on the basis of mass spectrometric analysis of boron trifluoride, Inghram 5) made a careful study of the isotopic composition of boron using the electron impact source and electrical collection, but gave no information on the source of his sample. He gave the values 81.17 ± 0.06 and 18.83 ± 0.06 (B^{11}/B^{10} = 4.31 ± 0.017) as the percentage concentrations of the two boron isotopes of masses 11 and 10 respectively.

Later, the problem of the isotopic ratio variation was taken up again and in 1948 H. G. Thode and his co-workers 6) detected small variations in the relative abundance of the boron isotopes B^{11} and B^{10} in terrestrial boron compounds. Values of B^{11}/B^{10} from 4.269 to 4.422 were obtained for the nine samples of the borates which were studied using ions characteristic of boron trifluoride. In 1950

O. Osberghaus⁷⁾ tackled the same problem, without knowledge of Thode's results, using a commerical product of six different compounds of boron. Within the limits of the number of the samples and experimental error he found no variation and reported the value $B^{11}/B^{10} = 4.11 \pm 0.04$. It should be noted that the number of samples all of which could probably have different origins from those of Thode, was smaller than the number Thode studied.

The results of Thode and Osberghaus differed in two respects, viz: while Thode's results showed variation, Osberghaus' did not, and the average value given by the latter fell outside the range of those given by the former. Since the publication of these results, a number of attempts to verify the abundance ratio with boron trifluoride and the electron impact source (Bentley, Parwell, et al.) with trimethylboroxine (Lehman and Shapiro); and by surface ionisation methods, Goris et al., McMullen et al., Finley et al. and Shima and many others) has resulted in a considerable range of values.

In 1955, Parwell et al.⁸⁾ performed a careful investigation on the boron isotopic ratio variation in order to study a greater variety of natural materials, because the previous investigations had not measured any boron containing silicates such as tourmaline or axinite. The 43 samples of boron minerals and sea water were analysed as boron trifluoride. Despite the fairly complete collection of boron minerals and their occurrences, no conclusive evidence was found that variations in the isotopic ratio do occur, except for sea water samples. Their results showed that if variations do occur at all they are less than a few parts per thousand. These results were in accord with those of Osberghaus, but contrary to those of Thode and co-workers who observed variations up to a few per cent. The cause of the discrepency seemed to lie partly in the chemical preparation because Parwell and co-workers themselves observed variations of the same magnitude as Thode, but when their techniques were supposedly improved these variations disappeared.

After an extensive study Lehman et al.$^{9)}$ concluded in 1959 that the "natural" B^{11}/B^{10} ratio is much closer to 4.00 than it is to the then accepted value of 4.31 (Inghram$^{5)}$) obtained from boron trifluoride measurements. With regard to the possible isotopic abundance variation, it is meaningless to talk about a natural B^{11}/B^{10} ratio and secondly there is no reason to expect the isotopic ratio to be a whole number. While attempts to check the abundance ratio from BF_3 by a number of workers resulted in a wide range of values, abundance ratios calculated by various investigators from mass spectra of boron hydrides yielded relatively consistent results of approximately 4.00. It is interesting to note that work in the laboratory of Lehman and Shapiro with other compounds like trimethylboroxine yielded the same ratio. Therefore, there must have been something peculiar about the analysis of boron trifluoride gas.

The inconsistency of the BF_3 results was attributed to the instrumental "memory effect" caused by the adsorption of BF_3 on the surface of the inlet system and also to the instrumental mass discrimination. In 1960 P. G. Bentley$^{10)}$ was able to reduce the boron trifluoride adsorption to a more workable level by carefully designing the inlet system. By calibrating the mass spectrometer with a prepared boron standard of known ratio he was able to correct for instrumental error obtaining the B^{10} atomic concentration in some naturally occuring boron to be 19.27 ± 0.13% ($\frac{B^{11}}{B^{10}}$ = 4.189).

Up until this time the reason for the extreme difficulties in measuring boron isotope ratios by gas samples can be attributed to "memory effect", fractionation in the source and a possible isotope fractionation in the sample processing10,11,12). These difficulties have been overcome in recent years by the application of surface ionisation techniques to mass spectrometry, based on the emission of $Na_2BO_2^+$ from boron and to methods of chemical analysis based on microamounts.

In 1961, McMullen et al.13) using a surface ionisation source for mass spectrometric determination of the isotopic composition in minerals gave a value of 4.040 for the B^{11}/B^{10} ratio in borax and 4.068 for the ratio in tincal of Searles Lake (California). These ratios are much less than those given by Thode and co-workers. They also found some variation in the B^{11}/B^{10} ratio depending on the layer which is sampled from the surface to the bottom of the Searles Lake. Their results relative to the value for California tincal (30ft.) agree with those of Macnamara14) obtained in 1949, but the absolute values do vary by about 7 per cent.

The B^{11}/B^{10} ratio for boric acid has been reported in 1959, by Semenov and Zonov15) as 4.18, in 1961 by Goris et al.16) as 4.00 and in 1961 by Finley and Leumang17) as 4.071. The chemical history of these products was not known and also isotopic fractionation in the chemical treatment could not be ruled out.

Using the same technique in 1962, Shima$^{18)}$ also obtained the isotopic ratios for a number of rock and sea water samples. These ratios are all around the value 4.05 ± 0.05 which is again much smaller than the results from gas samples.

Present Work

Because of the discrepencies connected with the values of the boron isotopic ratio, mentioned in the foregoing paragraphs, it is worthwhile to probe more in the isotopic abundance of boron. For this reason various boron mineral samples were collected for analysis in a solid source mass spectrometer suitably built for abundance measurements. Again considerable interest has been shown in the capture cross-section of many elements for neutrons of various energies which is not quite the same for all the isotopic species of a particular element. In the case of boron for example almost the whole neutron capture is dependent on the B^{10} content. In addition to these, past work was undertaken, partly because of the general drive to clearify nuclear properties. In fact, it was thought that a precise knowledge of the isotopic constitution would give a basis for testing some nuclear hypotheses.

The present work was undertaken with the following objectives in mind. To make use of the recent developments in mass spectrometry to:

(i) ascertain if there is really a variation in the boron isotopic constitution depending on the origin of the boron;

(ii) attempt an absolute determination of the B^{11}/B^{10} ratio;

(iii) calculate the atomic weight of boron for each boron sample;

(iv) compare the results with those of other investigations.

CHAPTER II

THEORETICAL CONSIDERATIONS

Isotopic Abundance and Atomic Weight

It is interesting to note that as far back as 1925, H. T. Briscoe19) reported variation in the atomic weight of boron, an effect which is most probably due to a variation in the isotopic abundance, but his results were not regarded with confidence at that time. He gave the atomic weight of boron from California to be 10.847, Tuscany 10.823 and Asia Minor 10.818.

Suppose the relative abundance of $B^{11} : B^{10}$ is $R : 1$ and the atomic masses of B^{11} and B^{10} are M_{11} and M_{10} respectively, then the atomic mass of the boron will be

$$M = \frac{R\,M_{11} + M_{10}}{R + 1} \qquad (1)$$

The values of M_{11} and M_{10} employed below are given, on the C^{12} scale by Everling and co-workers20)

$$M_{11} = 11.00931$$

$$M_{10} = 10.01294$$

$$\frac{\Delta M}{\Delta R} = \frac{M_{11} - M_{10}}{(1+R)^2} \qquad (2)$$

Assume R = 4 and that there is a variation in this by 3 per cent. (Thode et al.$^{6)}$). Then

$$\Delta R = \frac{3 \times 4}{100}$$

and

$$\Delta M = \frac{0.98637}{5 \times 5} \times \frac{12}{100} = 0.0047$$

a change in atomic weight which was too small to be detected by early chemical methods. The variation in atomic weight by 0.029 detected by Briscoe, mentioned above, would require a variation in boron isotopic ratio by about 18 per cent. Such a high boron isotopic variation has not been reported so far and this suggests that his result might have suffered from other effects.

Variation of Isotopic Abundance

After the discovery of deuterium in 1931 by H. C. Urey et al.$^{21)}$, H. T. Emeleus et al.$^{22)}$ made careful measurements of the densities of different water samples and detected variation of a few parts per million depending on the origin of the water. The possibility of small variation in the thermodynamic properties of other light elements is evidenced by this result, together with theoretical equilibrium constants of isotopic reactions, calculated by Urey and Rinterberg$^{23)}$ and also differences in the vapour pressures found by Washburn$^{24)}$.

In 1935 Urey and Greiff$^{25)}$ first showed from thermodynamic considerations that the isotopes of the light elements do, in fact, differ slightly in their chemical properties. These small differences in chemical properties very likely result in some fractionation of the isotopes in natural processes. The isotopic exchange constants involving the isotopes of lithium, carbon, nitrogen, oxygen and sulphur were calculated by methods of statistical mechanics and because these exchange constants were different from unity it would be expected that differences in the thermodynamic properties of isotopes might exist. The isotopic "equilibrium constant" of a chemical reaction involving the isotopes of an element may be expressed as the overall ratio of the isotopes of an element in one chemical compound as compared with a similar ratio in a second chemical compound. For instance the fractionation of the isotopes of oxygen when CO_2(gas) is in equilibrium with H_2O (liquid) is given by the ratio

$$\frac{2\left[C\,O^{18}_2\right] + \left[C\,O^{16}\,O^{18}\right]}{\left[C\,O^{16}\,O^{18}\right] + 2\left[C\,O^{16}{}_2\right]} \div \frac{\left[H_2\,O^{18}\right]}{\left[H_2\,{}^{16}O\right]} = \alpha \qquad (3)$$

α is a measure of the degree of isotopic fractionation. To a very good approximation Equation (3) has been shown to reduce to

$$\alpha = \frac{\left[C\,O^{18}_2/C\ \ O^{16}_2\right]^{1/2}}{\left[H_2\,O^{18}/H_2\,O^{16}\right]}$$ which is the

equilibrium constant for the reaction:

$$\tfrac{1}{2}\,C\,O^{16}_2\ (\text{gas}) + H_2\,O^{18}\ (\text{liquid}) \rightleftharpoons \tfrac{1}{2}\ C\,O^{18}_2\ (\text{gas}) + H_2\,O^{16}_2\ (\text{liquid})$$

(4)

α in this reaction has been calculated to be 1.046 at 0°C and the fact that this is greater than unity indicates that CO_2 is enriched in O^{18}. Immediately Weber, Mahl and Urey$^{26)}$ demonstrated that carbon dioxide in equilibrium with water at 25°C was in fact enriched in O^{18} in agreement with the theoretical results to within the experimental limit of error and also the probable error in the calculations of the theoretical value. At the same time Dole and co-workers$^{27,28,29)}$ observed variations up to about 3 per cent. in O^{18} content from air and minerals using precise density measurements. Nier and Gulbransen$^{30)}$ and Nier and Murphy$^{31)}$ found by mass spectrometric measurements that C^{13} content was high in limestone rock and other inorganic sources, but low in carbon of vegetable origin.

Later measurements by Thode and co-workers$^{32)}$ showed up to 5 per cent. variation in sulphur isotope abundances which were in good agreement with theoretical calculations where isotopic fractionation occurs due to differences in the thermodynamic properties of the isotopes of the elements involved in a reaction. Then the equilibrium exchange constants for the equations

$$NaHS^{32}O_3\ (\text{liquid}) + S^{34}O_2\ (\text{gas}) \rightleftharpoons NaHS^{34}O_3\ (\text{liquid}) + S^{32}O_2\ (\text{gas}) \qquad (5)$$

$$NaHS^{32}O_3(\text{liquid}) + S^{36}O_2(\text{gas}) \rightleftharpoons NaHS^{36}O_3\ (\text{liquid}) + S^{32}O_2(\text{gas}) \qquad (6)$$

were found experimentally by Thode and co-workers[33)] to be 1.019 and 1.043 respectively at 25°C. The fact that these results differ from unity again indicates the possibility of fractionation effect.

Much later in 1947 Urey[34)] again studied the thermodynamics of the isotopic substances and revised all the theoretical and experimental results obtained so far. The theoretical exchange constants of boron isotopes were confined to boron halides, however the predicted differences in the vapour pressures of the boron chlorides suggested the possibility of isotopic exchange process in nature which would result in some isotopic fractionation.

Apart from the chemical exchange reaction, there are other physical processes which could be used for isotope separation in practice. These processes may possibly exist in nature and affect the isotopic composition of compounds in the course of their formation:

(a) Diffusion - The rate of diffusion of a gas through a porous membrane is inversely proportional to the square root of its molecular weight (Graham's Law). In practice the isotope enrichment may be considerably increased by a repetition of the process.

(b) Evaporation - The rate of evaporation of lighter isotopes is greater than that of heavier ones and in fact a considerable isotopic separation may be effected if the reaction is slow enough and the vapour is prevented from condensing.

(c) Distillation - As mentioned earlier, the different isotopes will have different vapour pressures, which would cause the heavier isotopes to have higher boiling points, thus giving rise to fractional distillation.

(d) Centrifuging - The heavier isotopes of a molecules in a gravitation-like field will experience a greater force than the lighter isotopes, giving rise to fractionation, the degree of which depends on the mass difference between the isotopes.

(e) Thermal Diffusion - Subjected to a temperature gradient, the heavier isotopes tend to accumulate in either the hot or the cold region, according to the nature of the intermolecular forces[35)].
The principle was first successfully applied to isotopic separation by Clasius and Dickel[36)].

(f) Electrolysis - It is observed that in the electrolysis of water the residual solution is deuterium-rich.

Neutron irradiation could also cause a change in the isotopic ratio through the reaction,

$$B^{10} + n \rightarrow \left[B^{11}\right]^{*} \longrightarrow Li^{7} + \alpha \qquad (7)$$

since B^{10} has such a high neutron capture and cross-section, viz: 4010 barns for thermal neutrons. The cross-section for a mixture of B^{11} and B^{10} at the natural ratio is about 755 barns. However, the neutron intensities from cosmic rays and other sources appear to be too low to produce any significant changes, especially in the geological deposits below the surface of the earth. Work is also being done on the isotopic composition of boron in meteorites and it is interesting to note that Makoto Shima[37)] has determined the B^{11}/B^{10} isotopic ratio in a number of meteorites to be in the range 3.80 to 3.90. This is about 5 per cent. less than the ratio of terrestial boron. The results suggest that the meteoric boron is enriched in B^{10}

through synthesis by spallation or some other effect which cannot be neutron capture as one would expect this to decrease the B^{10} content and, therefore, give rise to a high B^{11}/B^{10} ratio. Since the neutron intensity would certainly be greater in the atmosphere than on the earth, and the results of meteoric isotopic ratio show that the effect of neutron capture on the ratio is negligible, the terrestrial boron isotopic ratios are a fortiori unaffected by neutron capture processes.

CHAPTER III

APPARATUS

Historical

For fast and accurate analysis of the absolute and relative abundance of stable isotopes, it is indisputable that the best tool is the conventional spectrometer with the exception of the wide use of infrared methods for D/H ratios.

Mass spectrometers have been used very extensively in physics and more recently in other branches of science, ever since J. J. Thomson carried on his pioneering experiments in the period of 1907-1913. The culmination of his work was the discovery, using the parabola method for positive ion analysis 38) that neon which had previously been considered as consisting of a single atomic species was actually made up of two different kinds of isotopes, one corresponding to a nuclide of atomic mass 20 and the other less abundant type to one of atomic mass 22. This was the first convincing evidence of the existence of stable isotopes. A third stable isotope was later found at mass 21.

The first isotopic abundance measurement was made by F. W. Aston with his first mass spectrograph in 1918, in which he used photographic detection 39). Despite the errors associated with this type of detection, he was able to give results for many elements with striking accuracy. Meanwhile, A. J. Dempster 40) built a different type of instrument based on the focusing properties of a semicircular homogeneous magnetic field, with which he also made measurements of the isotopic abundances of some light elements. In 1933 K. Bainbridge[41)] improved upon Dempster's apparatus by the incorporation of a Wien velocity filter, but he concentrated on isotopic mass determinations, and was able to give the first experimental demonstration of the Einstein mass-energy relation. Until A. O. Neir[42)] introduced some improvements to mass spectrometer design after 1935, the field of isotopic abundance measurements was not a very active one.

The investigation of the isotopic constitution of elements found in nature consists of the identification of the isotopes and the determination of the abundance. In the case of the former it seems that once the isotope is discovered nothing else can be done, but in case of the latter, the question arises as to the validity of the absolute ratios and their variations in nature. For closer investigations of these and for other applications, the conventional mass spectrometer has undergone such a considerable number of improvements that only radioactive-counting techniques surpass it in sensitivity for detection of isotopes. Now conventional mass spectrometers are available commerically for research and routine industrial use.

Although the magnetic field focusing theory had shown the feasibility of using sector magnetic fields, people continued using the Dempster[40)] semi-circular deflection principle until in 1940 Nier[43)] designed the first $\pi/3$-deflection instrument which he improved in 1947[44]. Hipple[45] was the first to make use of the $\pi/2$-sector field in 1942.

The majority of the modern mass spectrometers employ sector fields, the $\pi/3$ one being the most common. The advantages of the sector instrument as compared to the π-instrument is that it requires a smaller magnet and that the long object and image distances provide field-free spaces for the source and the detector. On the other hand, it has the disadvantage that the ions twice experience deflections due to the two fringing fields (see Figure 1) the effect of which is difficult to calculate. This gives rise to the need of provision, in construction, for experimental adjustment.

Focusing of ions in a uniform sector magnetic field

The focusing properties of the sector field was discovered independently by a number of people including Herzog[46] about 1934. Following the notation of Duckworth[47] the 1st-order theory as given by Herzog for the focusing properties of a sector homogeneous field for a symmetrical arrangement is as follows:

Suppose in Fig.1 ions of mass M_o charge q and velocity V_o emerge from the object slit O of the ion source, with a half-angular spread α in the plane of the paper ($\alpha \langle \langle 1$). A central ion ($\alpha = 0$), after travelling the distance ℓ_m, enters the uniform magnetic field B (which is assumed to have sharp boundaries) normally and follows a circular path of radius a_m given by

$$a_m = \frac{M_o V_o}{qB} \tag{8}$$

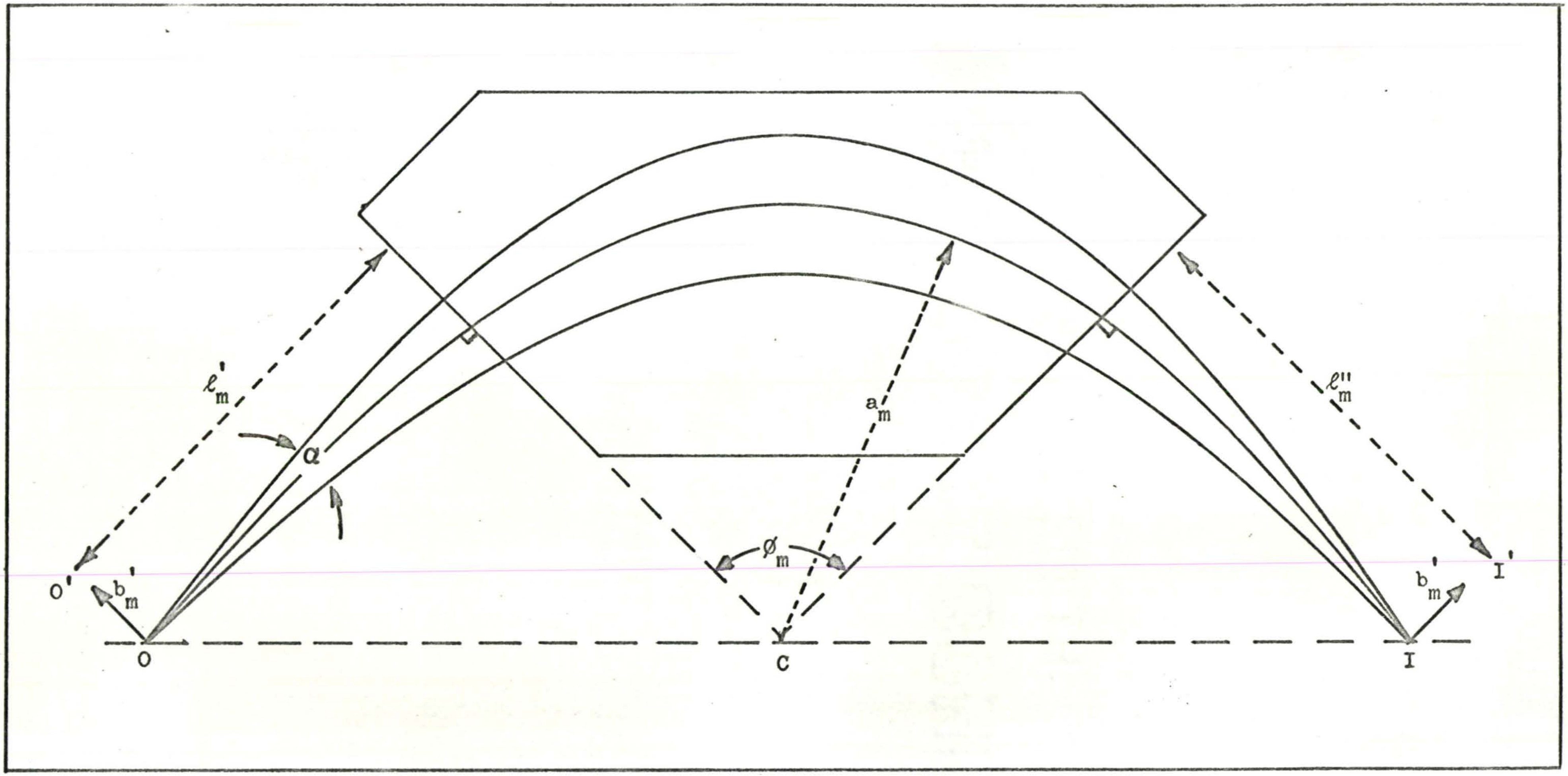


FIG. I FOCUSING PROPERTIES OF A HOMOGENEOUS MAGNETIC FIELD (H.E. DUCKWORTH [5])

The ion is deflected through an angle ϕ_m and then leaves the field normally, and continues to the point I where all the ions from O converge.

Herzog drew the analogy between the focusing properties of this arrangement and that of a thick lens in 'light' optics. He showed that its focal length, f_m is given by

$$f_m = a_m/\sin \phi_m \tag{9}$$

and that the relationship between object and image distances may be expressed in the form of the equations used in geometrical optics

$$f_m/(\ell_m' - h_m) + f_m/(\ell_m'' - h_m) = 1 \tag{10}$$

Since it can be shown that

$$f_m = g_m - h_m \tag{11}$$

Therefore,

$$(\ell_m' - g_m)\ (\ell_m'' - g_m) = f_m^2 \tag{12}$$

where ℓ_m' and ℓ_m'' are the image and object distances and

$$g_m = f_m/\cos \phi_m \tag{13}$$

where g_m is the distance from the lens surface to the principal focus, and h_m the distance from the principal planes to the lens surfaces. The relation (12) is equivalent to Barber's rule which states that the object, the centre of curvature and the image lies on a straight line as shown in the Fig.1. Suppose an ion of mass $M = M_o (1 + \gamma)$ and of velocity $V = V_o(1 + \beta)$, where γ and β are small quantities, originates from a point O' displaced b_m' from O and gives rise to an image at I' displaced b_m'' from I, the displacements b_m'' and b_m' are related by the equation

$$b_m'' = a_m (\beta + \gamma) \left[1 + \frac{f_m}{\ell_m' - g_m} \right] - b_m' \frac{f_m}{\ell_m' - g_m} \tag{14}$$

From Equation (14), considering the original ion group $(M_o V_o)$ the magnification m is given by

$$m = \left| \frac{b_m''}{b_m'} \right| = \frac{f_m}{\ell_m' - g_m} \tag{15}$$

For a symmetrical arrangement, $\ell_m' = \ell_m''$. Therefore, from Equation(11)

$$(\ell_m' - g_m) = (\ell_m'' - g_m) = f_m \tag{16}$$

thence $m = 1$.

If $S_o = 2b_m'$ is the width of the object slit at O, the images corresponding to two mass groups M and $M_o (1 + \gamma)$ are just resolved when their centres are $2b_m'' = \dfrac{S_o f_m}{\ell_m' - g_m}$ apart.

For a monoenergetic ion beam

$$\frac{1}{2} M_o V_o^2 = \frac{1}{2} MV^2 \tag{17}$$

Since $\frac{1}{2} MV^2 = \frac{1}{2} M_o (1 + \gamma) (V_o (1 + \beta))^2$, to the first approximation then,

$$2\beta + \gamma = 0 \tag{18}$$

and from Equation (14) the resolution for photographic detection will be given by

$$\frac{\Delta M}{M_o} = \frac{2S_o}{a_m} \times \frac{f_m}{(\ell'_m - g_m)\left(1 + \frac{f_m}{\ell'_m - g_m}\right)} \qquad (19)$$

Thus for a symmetrical arrangement

$$\frac{\Delta M}{M_o} = \frac{S_o}{a_m} \qquad (20)$$

For electrical detection where a slit of width S_i followed by a sensitive electrical detector is placed at I, the resolution for a symmetrical arrangement becomes

$$\frac{\Delta M}{M_o} = \frac{S_o + S_i}{a_m} \qquad (21)$$

For maximum sensitivity the image slit S_i should not be narrower than the actual width of the image. In the case of unit magnification referred to above this means S_i should be equal to or greater than S_o. In the machine used for this work, $S_o = 0.3\text{mm} = S_i$; $a_m = 254$ mm. Therefore the resolving power (R.P.) $= \frac{M_o}{\Delta M} \approx 420$.

In practice because of fringing fields and other effects the geometrically symmetrical arrangement may not correspond to the case of unit magnification. However, it gives an idea of where to start from, in looking for the position of unit magnification. This involves moving the magnet slightly about this geometrically symmetrical position.

From Equation (14) the displacement of the image corresponding to 1 per cent. mass change gives the dispersion, which is equal to $\frac{a_m}{100}$ cm, in the case of a monoenergetic ion beam in a symmetrical spectrometer.

The general theory of focusing in a sector magnetic field has also been given by Herzog and others. This and higher order theory of ion optics in other forms of both magnetic and electrostatic fields are described in detail in many text books on mass spectrometry 48, 49, 50).

Description of the apparatus

The mass spectrometer used for the work described in this thesis was suitably built for isotopic abundance studies of solid samples. It is a first order direction focusing, single stage instrument with a homogeneous magnetic field of $\pi/2$-sector shape and radius of magnetic deflection of 10 inches. The source of positive ions ($Na_2BO_2^+$) employed was a triple filament type to be described later. The detection was made by means of a fourteen-stage electron multiplier of gain, 6×10^4, and a vibrating reed electrometer coupled to a recorder. The scanning of the peaks was done by varying the magnetic field.

One of the most important aspects in the operation of a mass spectrometer is the ion production and a great variety of ion sources for mass spectrometers have been developed. Not one of these sources is by any means ideal for all applications and, in fact, the choice of source for a particular problem is dictated by the nature of the sample and the type of information being sought.

Every source should have the following fundamental qualities in order to give satisfactory results:-

(i) The resulting ion beam should be sufficiently intense for reliable measurement.

(ii) The ion beam should be stable, but this is not possible for certain sources like vacuum-spark source.

(iii) For a high resolving power, when using a single focusing instrument as the one employed in this work, the ions produced should have a low energy spread.

(iv) The background ions must be minimum.

(v) There should be no memory effects. This and (iv) require provision for outgassing the source (and the entire spectrometer tube) at high temperatures.

(vi) The probability that the ions produced enter the analyser tube should not be dependent on their masses (mass discrimination).

(vii) Fractionation of isotopes should be a minimum, especially in application to abundance measurements.

(viii) The ideal source material used in the construction should be non-magnetic, resistant to corrosion, non catalytic, a non adsorber of gases. Common source materials are Nichrome V, Monel and stainless steel. The surface finish and alignment of the plates are important factors which control secondary electron production from and polarization of the source plates.

As mentioned in Chapter I there were a number of difficulties associated with the use of gas source instruments, employing the electron impact source, where a stream of gas sample is bombarded with energetic electrons to produce ions. As an attempt to minimize these difficulties and because certain samples cannot be obtained in gaseous form at room temperature, the process of surface ionisation in which positive ions are produced directly from a solid when it is heated on a metal surface was developed. This phenomenom discovered by Gercke and Reichenheim[51,52)] was first used by Dempster[40)].

In the case of a solid in a thermal equilibrium with a hot surface an approximate expression for the number of positive ions is given by S. Datz and E. H. Taylor[53)] as

$$\frac{n_+}{n_o} \propto \exp\left(\frac{e(\emptyset - I)}{kT}\right) \qquad (22)$$

n_+ = number of positive ions

n_o = number of neutral particles

$\emptyset$ = work function of the surface

I = ionisation potential of the element

T = absolute temperature of surface

e = electronic charge

k = Boltzmann's constant

(a) With elements having a high ionisation potential ($I > \emptyset$), the sample evaporates from the surface before the atoms are ionised, and a low ionisation efficiency results.

(b) The molecular form of the ionized fragments cannot be controlled since it depends only on the temperature fixed by the required evaporation rate.

(c) In the case of samples that evaporate at low temperatures, the background ions from hydrocarbons is troublesome.

The source used in the present apparatus is a triple filament surface ionisation source, which was designed on the basis of the original one constructed by Inghram and Chupka in 1952[54). This type of source in which the sample is coated carefully on one of two side filaments which is close to a high temperature ionising filament was developed to eliminate the difficulties mentioned in the previous paragraph. The molecules that evaporate from the side filament are ionised when they impinge on the hot central filament. In this way the evaporation and ionization could be controlled independently by adjusting the two filament currents.

They give the relative efficiencies for ionisation of the multiple and single filament source as:

$$\frac{n^{+}_{T_1}}{n_{T_2}} = \exp \frac{e\,(\emptyset - I)}{k} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (23)$$

where T_1, T_2 are the temperatures of the ionisation filaments, the sample evaporates only in the atomic form and where the work function is the same for both ionisation filaments.

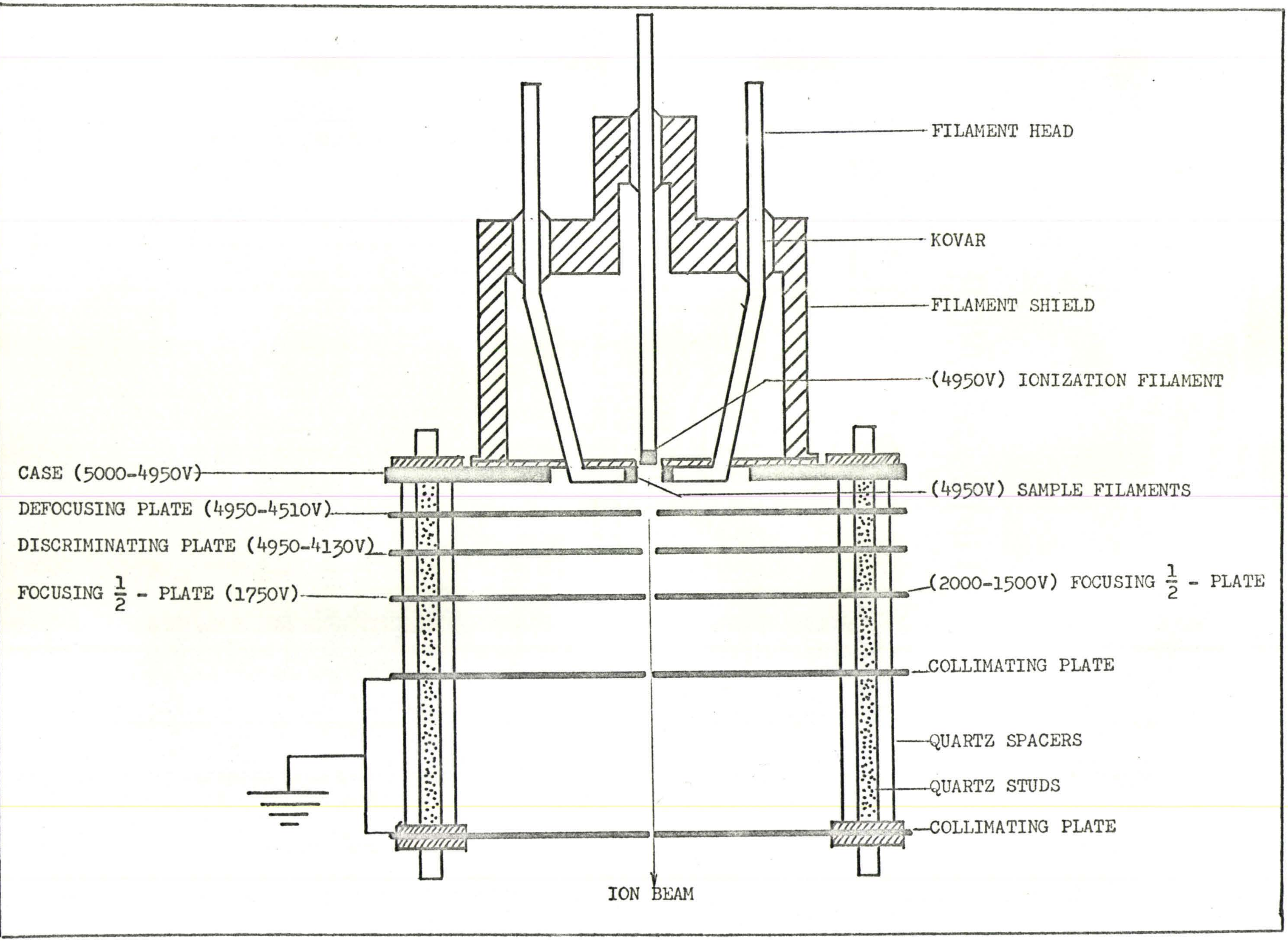
From what has been noted above it can be said that in a carefully designed triple filament source memory effects can be made negligible and for many elements a few micrograms of sample are sufficient for a successful analysis especially with the help of an electron multiplier detector. Since the ions possess only thermal energies on formation, the energy spread is sufficiently low that the use of a single-focusing magnetic analyser is possible.

However, only a limited number of the elements can be successfully analysed using this source and boron, which is the subject of this experimental work, is one of them. Also for each sample introduction the vacuum must be broken or a vacuum lock employed. There is also an isotopic fractionation effect, especially in the case of light atomic mass ions, since the evaporation and also other processes are dependent on the mass.

The mass discrimination effect should decrease with increase in mass number of the ions investigated, e.g. the effect of mass difference between masses 10 and 11 corresponding to B^{10} and B^{11} should be a lot greater than that due to the difference between 88, 89 corresponding to $Na_2B^{10}O_2$ and $Na_2B^{11}O_2$.

There is a tendency of the ion current to drift, especially at the start of an experiment. If the drifting is steady the isotopic ratio obtained from a number of peaks obtained by switching from one peak to the other many times should, as shown in Fig.7, give quite reliable results.

Figure 2 shows a schematic diagram of the triple filament source, including the ion gun. All plates and the filament shield are made of Nichrome V, and filaments are of tungsten ribbon 0.03 inches wide, 0.001 inches thick and 0.4 inches in length. The approximate voltage ranges, as supplied by a voltage divider are also indicated (for 5KV across the divider).


FILAMENT HEAD
KOVAR
FILAMENT SHIELD
(4950V) IONIZATION FILAMENT
CASE (5000-4950V)
(4950V) SAMPLE FILAMENTS
DEFOCUSING PLATE (4950-4510V)
DISCRIMINATING PLATE (4950-4130V)
FOCUSING $\frac{1}{2}$ - PLATE (1750V)
(2000-1500V) FOCUSING $\frac{1}{2}$ - PLATE
COLLIMATING PLATE
QUARTZ SPACERS
QUARTZ STUDS
COLLIMATING PLATE
ION BEAM

IG.2(a) SOURCE

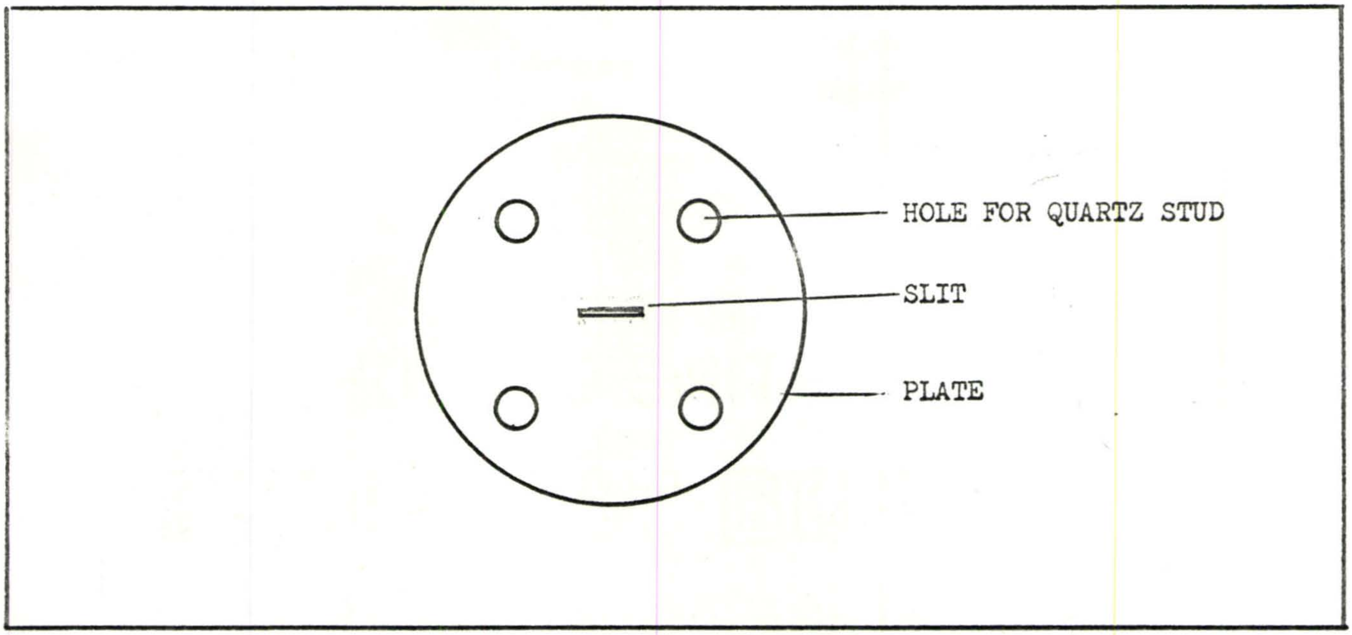


FIG.2(b) TOP VIEW OF COLLIMATOR

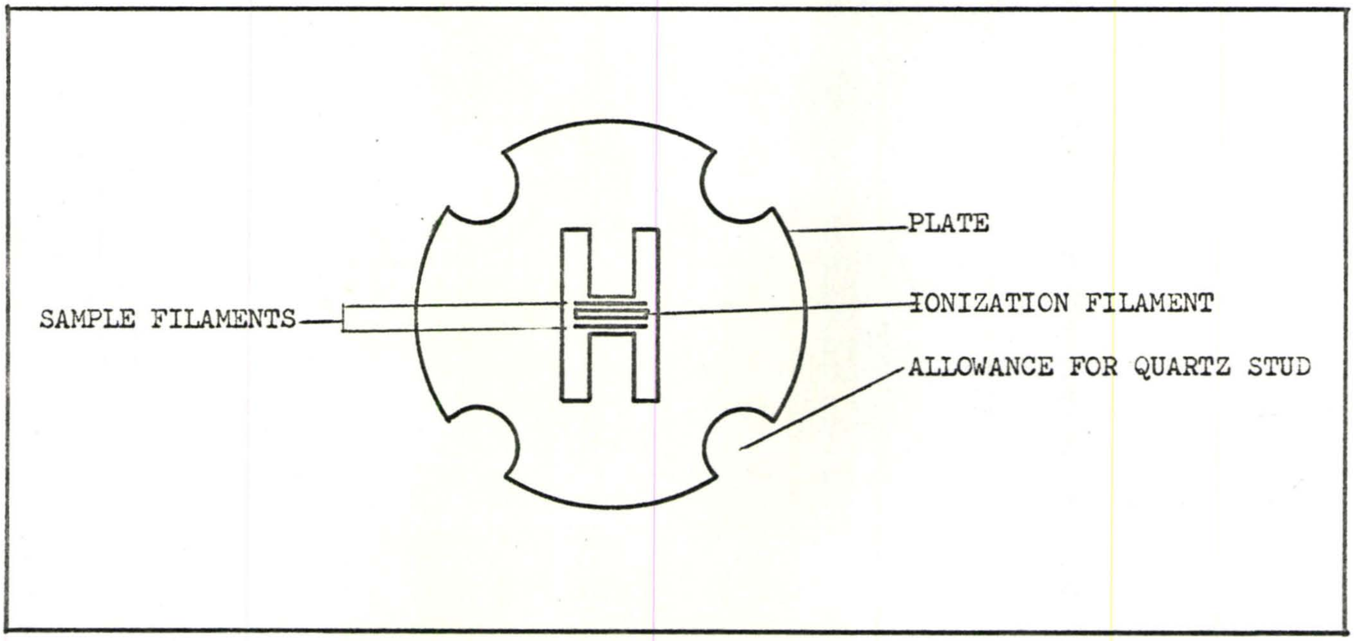


FIG.2(c) END ON VIEW OF SOURCE

The mass spectrometer tube which has a 10 inch mean radius of curvature is made of stainless steel. There is an electrical heating provision for baking out the tube to reduce background interference. The tube itself is rigidly fixed, but the magnet coils plus pole pieces could be oriented in all directions by adjusting screws provided for this purpose. There are two vacuum systems, one at each end, for producing the vacuum in the tube. Each vacuum system consists of a conventional oil backing pump and a mercury diffusion pump. There are ionisation guages at both the source and the collector ends of the spectrometer for measuring the pressure.

Figure 3 is a full size diagram of the single collection electrical collector used in this apparatus. It consists of a system of slit plates, insulated from each other by means of quartz spacers. The plates are made of Nichrome V. On top of the collector itself is a conventional 14-stage electron multiplier which extends the lower limit of ion detection to about 10^{-18} amps. It also makes the use of a fairly rapid response time possible by the use of a low grid leak resistor in the case of large ion currents. When the multiplier is used, the voltages on the plates are as shown in the figure. The positive ions are caused to impinge on a cathode surface (first dynode) to liberate electrons. These electrons are in turn caused to strike a succession of fourteen dynodes, each producing one or more secondary electrons which are directed to the next dynode by means of a potential difference between the dynodes. The multiplier is insulated from the plates by means of steatite supports. In the acceleration region between the plates and the

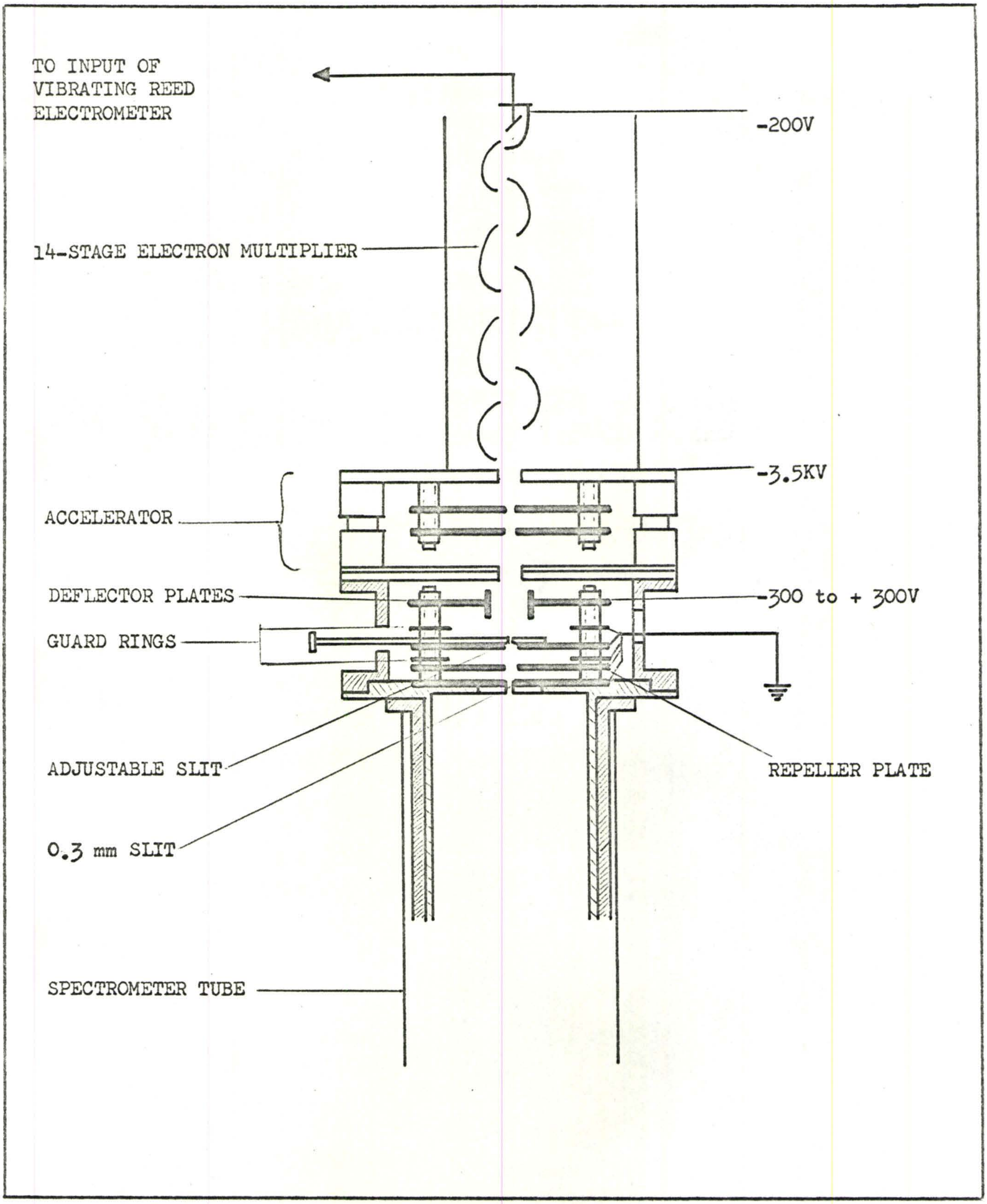


FIG. 3 COLLECTOR

multiplier is a cone system for preventing the return of secondary electrons into the machine. The multiplier response is dependent on time, vacuum, surface conditions and the nature of the positive ions. The efficiency for electron production on the first dynode increases with energy of the positive ions. It varies as the inverse square root of the mass of the ion, causing some mass discrimination. It also decreases with the ionisation potential of the incoming ion and increases with the angle of incidence, which is controlled by the deflector plates. The secondary electrons from the last dynode are detected by means of a vibrating reed electrometer and a recorder to be described below.

When the multiplier is not used, i.e. for direct positive ion detection, required for the multiplier gain measurement, the adjustable slit is closed and acts as the collector plate. The repeller plates are biased in such a way as to prevent the return of secondary electrons to the collector. The guard rings provided, prevent charge leakage.

The d.c. voltage developed across a grid-leak resistor by the secondary electrons from the last dynode of the multiplier is fed into a vibrating reed electrometer (Model 30) manufactured by the Applied Physics Corporation. The principle of operation is as follows: a metal reed is made to vibrate close to a static anvil at 400 c.p.s. and the d.c. signal applied across them is converted to an a.c. as a result of their varying capacity. The signal is then fed into a narrow-band width a.c. amplifier before being rectified and applied to the imput of a negative feed-back circuit.

The output of the amplifier is fed into a $\frac{1}{2}$ second Honeywell recorder (Model Y153X(19)(X)-X-118(V)). There is a resistor shunt arrangement across the recorder to divide its input signal by known factors.

In Appendix A are given the circuit diagrams for the electronic supplies used in this instrument. The electron multiplier voltage supply could deliver a maximum of -10KV, but the multiplier was run at -3.5KV all the time. The positive accelerating voltage supply could give up to about 5 KV and the machine was operated at near maximum output. The two low voltage current filaments supplies are identical in circuitry, but different from the magnet current supply. All these supplies were stable to about a part in ten thousand when in good operating conditions.

A number of circuit designs can be found in the literature and many of these can, in fact, be obtained commercially.

Fig.4 shows a schematic diagram of the complete mass spectrometer

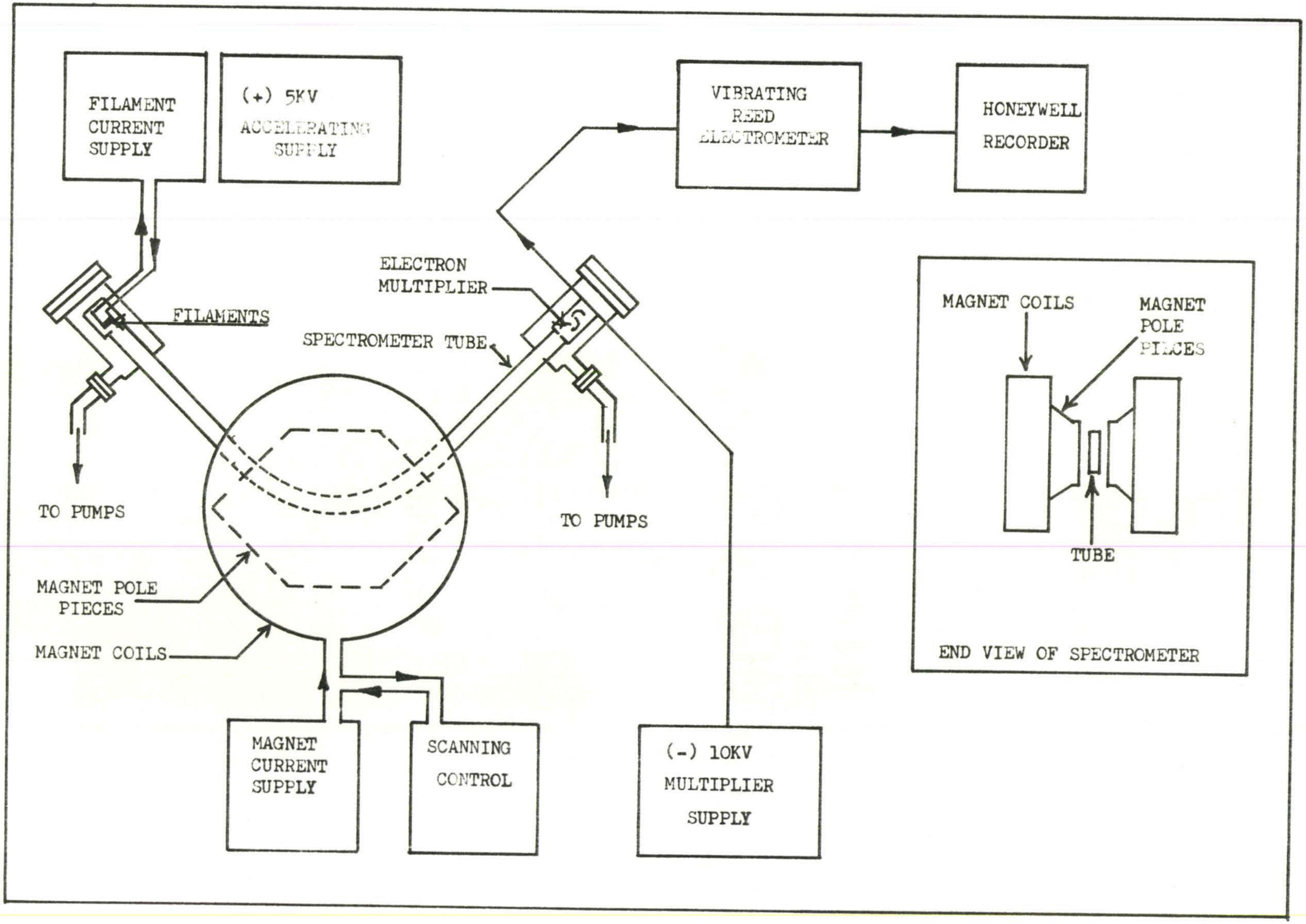


FIG. 4 SCHEMATIC DIAGRAM OF SPECTROMETER

Fig. 5 and Fig. 6 are pictures of the entire mass spectrometer, employed in this research, taken from different angles.

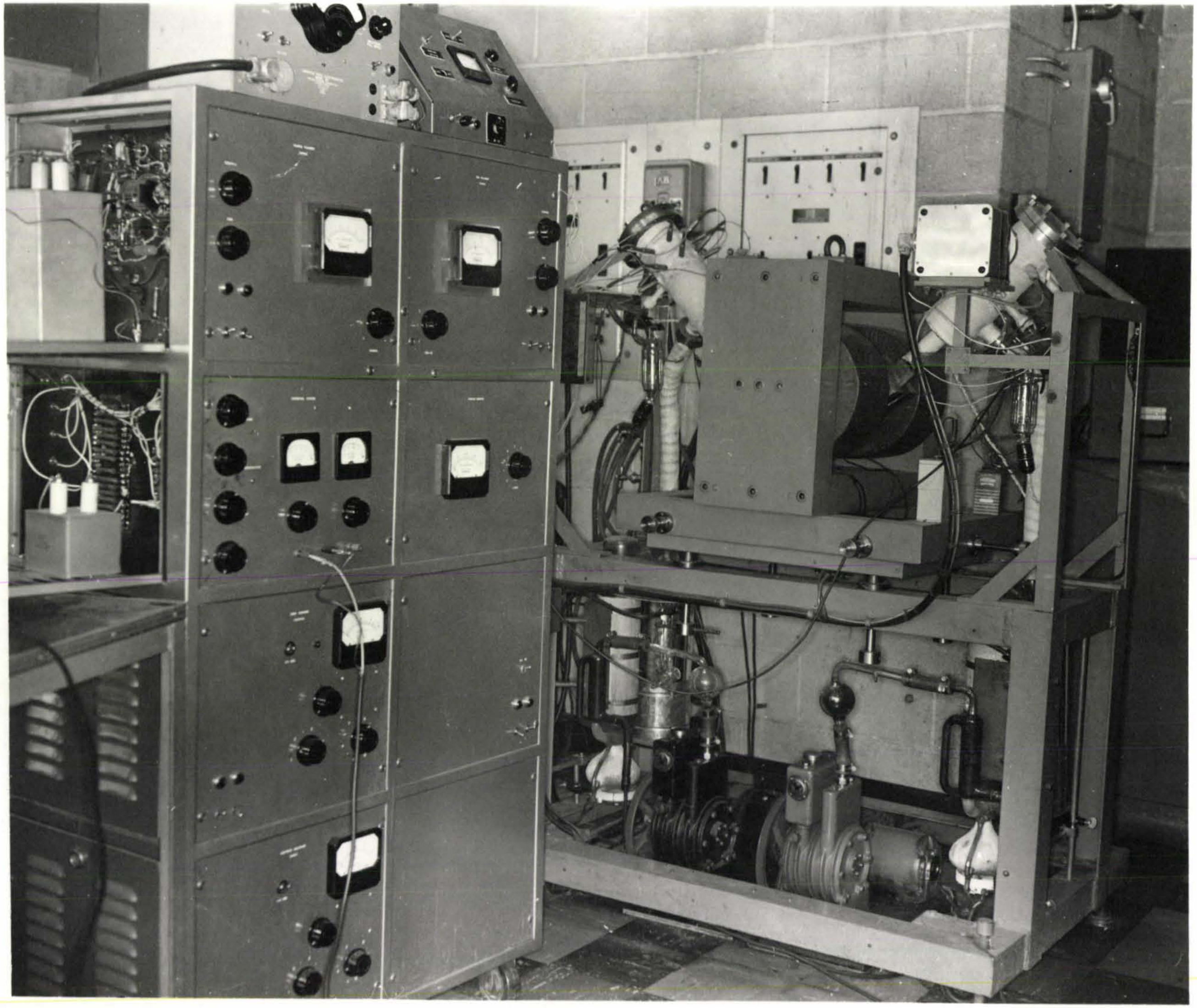


FIG. 5 SPECTROMETER (without recorder)

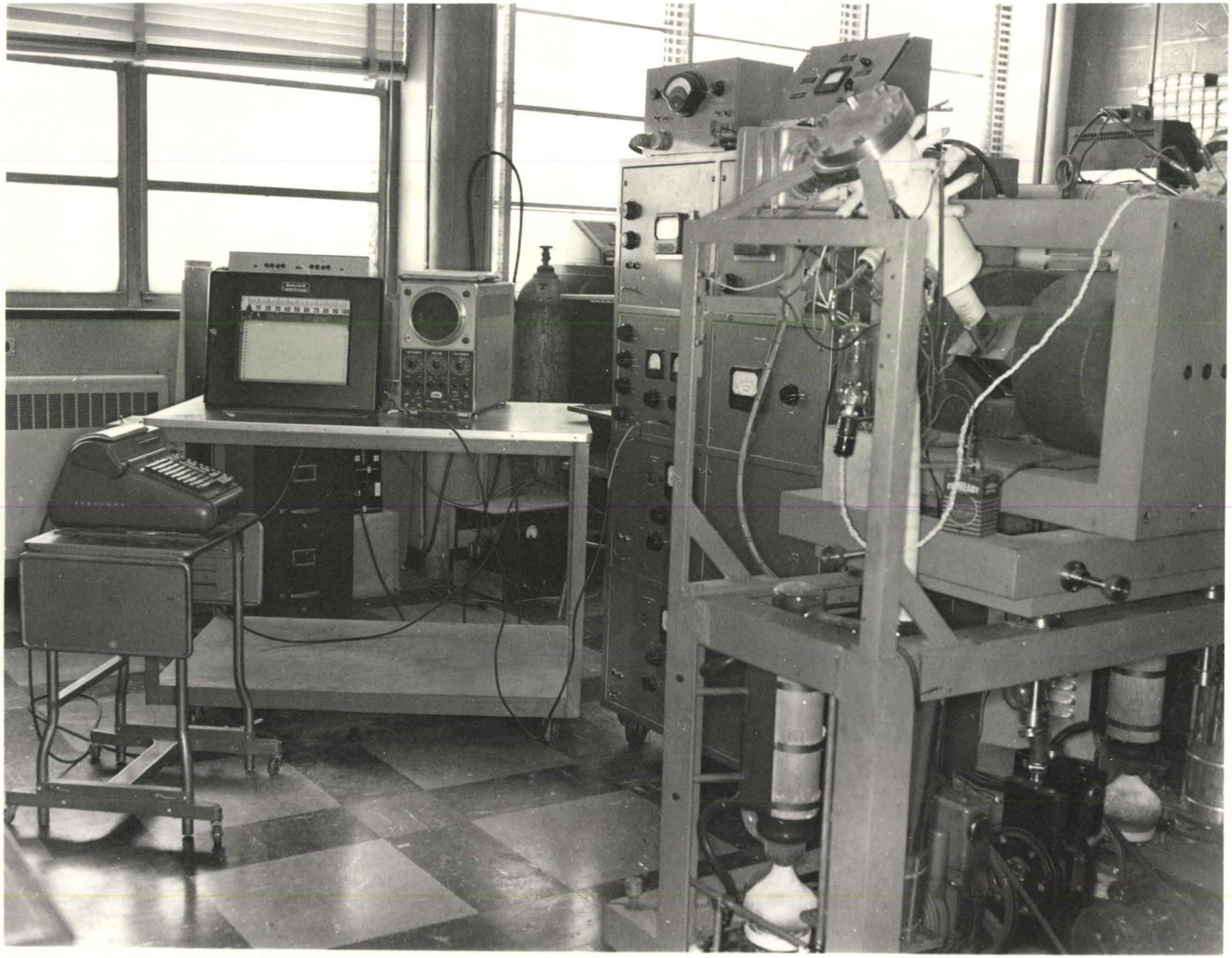


FIG. 6 SPECTROMETER

CHAPTER IV

BORON STANDARDS AND SAMPLES

Two boron standards of known isotopic composition boron - A ($\frac{B^{11}}{B^{10}} = 4.270$) and boron - B ($\frac{B^{11}}{B^{10}} = 3.956$) were used to calibrate the instrument from time to time in the course of analysis of the samples.

The preparation of the synthetic mixtures provided by McMullen et al.[13)] was done in this laboratory by a method which could be divided into the following three steps:

(a) determination of the isotopic content of the enriched samples in the form of boric acid;

(b) preparation of the enriched samples in a form suitable for quantitative combination and

(c) combination of portions of B^{10} and B^{11} enriched samples in accurately known amounts to obtain the synthetic mixtures.

Theory of Preparation of Standards

Using the notation of Bentley[55)] the B^{10} concentration say, of the mixture will be given by

$$C_m = fCd + (1-f) Ce \qquad (24)$$

where C_m is the B10 concentration of the mixture

C_d is the B10 concentration of the B10 depleted (or B^{11} enriched) blending material;

C_e is the B^{10} concentration of the B^{10} enriched (or B^{11} depleted) blending material;

f is the molar fraction of the depleted material used in the mixture.

The quantities C_d and C_e are approximately determined on the mass spectrometer to be calibrated. The calculated B^{10} concentration in the prepared standard will be in error depending on the errors associated with the measurement of C_d and C_e.

From Equation (24), the error ΔC_m is given by

$$\Delta C_m = f \, \Delta C_d + (1 - f) \Delta C_e \qquad (25)$$

It should be noted that usually in mass spectrometric measurements the quantity that is determined directly is the isotopic abundance ratio. Errors arising from instrumental mass discrimination will affect this ratio which will be assumed to be related to the absolute ratio by the expression

$$R = kR'$$

where R is the absolute $\frac{B^{11}}{B^{10}}$ ratio

R' is the observed ratio

k is a constant for all values of R.

The instrumental discrimination error $\frac{\Delta R}{R'}$ is given by

$$\frac{\Delta R}{R'} = \frac{(R' - R)}{R'} = 1 - k \qquad (26)$$

The concentration of an isotope can be written as

$$C = \frac{1}{1 + R'}, \qquad (27)$$

The error in C arising from the use of R' in place of the true value R will be

$$\Delta C = - \frac{\Delta R}{(1+R')^2} \qquad (28)$$

and from Equation (26)

$$\Delta C = - \frac{(1 - k) R'}{(1 + R')^2} \qquad (29)$$

From Equations (25) and (29) the error ΔC_m can be computed. This corresponds to an error ΔR_m in the calculated isotope ratio R_m. As can be shown readily, the error in the calculated value of the constituents of the standard mixture, $\frac{\Delta R_m}{R_m}$ is always smaller than the corresponding error $\frac{\Delta R}{R'}$ (= (1-k)) which arises from mass discrimination in a direct measurement on the constituent materials. That is to say the isotope ratio of the standard is calculated to a greater accuracy than that of the blending materials. This is shown in Appendix B1 for the mixtures used in this work.

The discrimination factor between the calculated and measured values of the synthetic mixture can be used to recalculate the isotopic ratios of the enriched samples. With the use of successive approximations in this way, errors introduced into the calculated isotopic ratios from instrumental discriminations can be made negligible.

Since the best way of mixing the enriched samples is by weighing with an analytical balance it is desirable to prepare the enriched samples in a gravimetrically pure form. The enriched samples of the boron isotopes which were obtained as boric acid were converted to pure borax since borax has been used as a gravimetric standard in acidimetry56). Also it can be analysed in the solid-source like the spectrometer in the present work, without further processing.

Preparation of Standards

Preparation of pure borax from the boric acid was done as follows: The boric acid sample was converted to methyl borate57) by heating the boric acid with synthetic methanol and taking off the methyl borate-methanol azeotrope through a glass-helix-packed fractionating column. The azeotrope boils at 55°C and the reaction was considered complete when the temperature at the top of the column reached 64°C. Titrations of the distillate in test runs with standard sodium hydroxide solution indicated that the yield of this step is greater than 95 per cent.

The methyl borate-methanol solution was then mixed with a stoichiometric amount of 1N sodium, hydroxide solution. When this solution was seeded with a small crystal of borax and stirred, crystals of borax were precipitated. The sodium hydroxide solution, prepared from Analar sodium hydroxide and distilled was found free of other metal ions on analysis with a "spectoral" optical spectroscope.

The methanol was expelled with the minimum loss of boron as methyl borate by allowing the solution to evaporate to dryness at room temperature. The borax was further purified by two recrystallization from distilled water, after which the borax crystals were washed with ethanol and ether and stored in a dessicator over a saturated aqueous solution of sucrose and sodium chloride.

A sample of pure borax produced from the B-10 enriched boric acid and a sample from the B-11 enriched boric acid were weighed on an analytic balance and combined to form the synthetic standards A and B. A small amount of the pure borax from the enriched samples was set aside for mass spectrometric analysis. To ensure uniform isotopic mixing in the synthetic standard, the borax was dissolved in a minimum of hot water, held in solution and stirred for about half a hour, then chilled and allowed to evaporate to dryness at room temperature.

Since in the first approximation the calculated difference in the isotopic content between the two samples should agree with the difference measured with the mass spectrometer, this proceedure provided a test of the preparation and weighing. This point is clarified in Appendix B2.

Preparation of borax from boron mineral samples

The samples which were obtained from C. C. McMullen in the form of borax were prepared in this laboratory by M. Shima using the method outlined below.

Each mineral was dissolved in water, acid or by fusion (with sodium bicarbonate), e.g. Tincal was dissolved in water, Inyoite by hydrochloric acid and Datolite by the fusion method. The borax was prepared from the resulting solutions by one or both of the following two methods:

(a) Chemical Proceedure: The boron in the solution was concentrated to methyl borate, by heating with methanol. The methyl borate methanol distillate was then mixed with a stoichiometric amount of 1N NaOH13).

(b) Ion Exchange Proceedure: The solution was passed through a cation exchange resin column and the anion portion was separated58). After that it was passed through an anion exchange resin and most of the chloride ion was separated. All the boron in the solution was mixed with a stoichiometric amount of 1N NaOH.

The solution was then evaporated to dryness at room temperature and the borax which remained was purified by two recrystallizations from distilled water. After washing with ethanol and ether, the crystals were stored in a dessicator, over a saturated aqueous solution of sucrose and sodium chloride.

A list of the samples, together with their particulars is given in Appendix D.

CHAPTER V

EXPERIMENTAL

Adjustment of Spectrometer:

Since among other things a good resolution between adjacent peaks and well-focused peaks with flat tops are essential for reliable results, before the analysis proper was started, the mass spectrometer was adjusted to approach these conditions as near as possible. The adjustments were made by moving the magnet pole pieces with respect to the spectrometer tube about the theoretical symmetrical arrangement till the best obtainable W^+ peaks were obtained. A resolution of about 390 as compared to the theoretical value of 420 (see page 21) was easily obtained. This is quite sufficient for most abundance measurements. The reason for using the tungsten peaks is because they correspond to heavier masses (180-186) than the masses of interest in this analysis (see below) and correspond to ions produced on the hot ion filament. The dispersion of these ions was smaller hence it was easier to tell any improvement on the resolution in the adjustment of the spectrometer.

On heating borax, the positively charged ions which are produced in greatest quantities are $Na_2B^{11}O_2^{16+}$ and $Na_2B^{10}O_2^{16+}$. Hence for the sake of sensitivity, these are the ions employed in the analysis of the borax samples. They are also suitable because their atomic masses of 88 and 89 are fairly high so that mass discrimination effects are reduced considerably. Considering that oxygen has three stable isotopes, O^{16}, O^{17}, O^{18}, it is seen that while the mass 88 corresponding to B^{10} is completely free from any effect of the other isotopes of oxygen, there is a contribution due to $Na_2B^{10}O^{17+}_2$ to the mass 89. This contribution, however, is negligible since the isotopic content of O^{17} is about 0.037% (compare with the accuracy of the experimental results in Chapter VI).

The Rb^+ peaks at masses 85 and 87 serve as a guide, in searching for the $Na_2BO_2^+$ peaks. Apart from the Rb^+ peaks, at the sensitivity at which the mass spectrometer was usually operated, no ions were observed several mass units on either side of masses 88 and 89.

Sampling:

Following the preliminary adjustments, one of the prepared boron standards was introduced into the machine as follows. A few micrograms of the standard were placed in a thoroughly cleaned and dried teflon crucible. The specimen was then dissolved in a small drop of water and concentrated by evaporation under an infrared lamp. The small droplet of concentrate was then pipetted onto the centre of one of the side filaments and all three filaments simultaneously heated cautiously in the atmosphere, to expel any residual water. Then the filament head was put back on to the source which had previously been cleaned and installed in its place, in the mass spectrometer. The instrument was then sealed and pumps turned on. Practically all of the samples were analysed on the same side filament, but from a preliminary study it was found that, provided the beams were properly focused it made little or no difference in the isotopic ratios determined on this instrument, which of the side filaments was used.

When the pressure dropped to about 5×10^{-6} torr, the filament currents could be turned on and increased gradually. Normally the pressure increased at this time and also at the temperature at which the borax starts to decompose. This is due to the evaporation of any residual water used in dissolving the sample, hydrocarbons from the filament and walls of the source if it is dirty, and other fragments from the dissociation of borax. The rest of the electronics were turned on when the pressure reached about 10^{-6} torr.

The instrument was operated on a grid-leak resistor of 10^{8} ohms, and on the 1000 mV range of the vibrating reed electrometer. The ion and sample filament currents were normally about 4.9 and 1.2 amps respectively which correspond to temperatures of about 2000°C and 120°C respectively. At the steady state condition the intensity of the ions formed was very sensitive to either of the filament currents, a point that calls for the use of very stable current supplies. The supplies employed in this research were as mentioned earlier, stable to about one part in ten thousand.

Shunt Ratio:

The more abundant boron isotope was measured with a sensitivity one-fourth of that used for the less abundant isotope by the use of the shunt system across the recorder so that both peaks were almost of equal height. This is a step taken to eliminate any non-linearity which might exist in the recorder. Shown in Fig.7 is a specimen of the mass spectrogram of the $Na_2BO_2^+$ ions. Since the instrument was

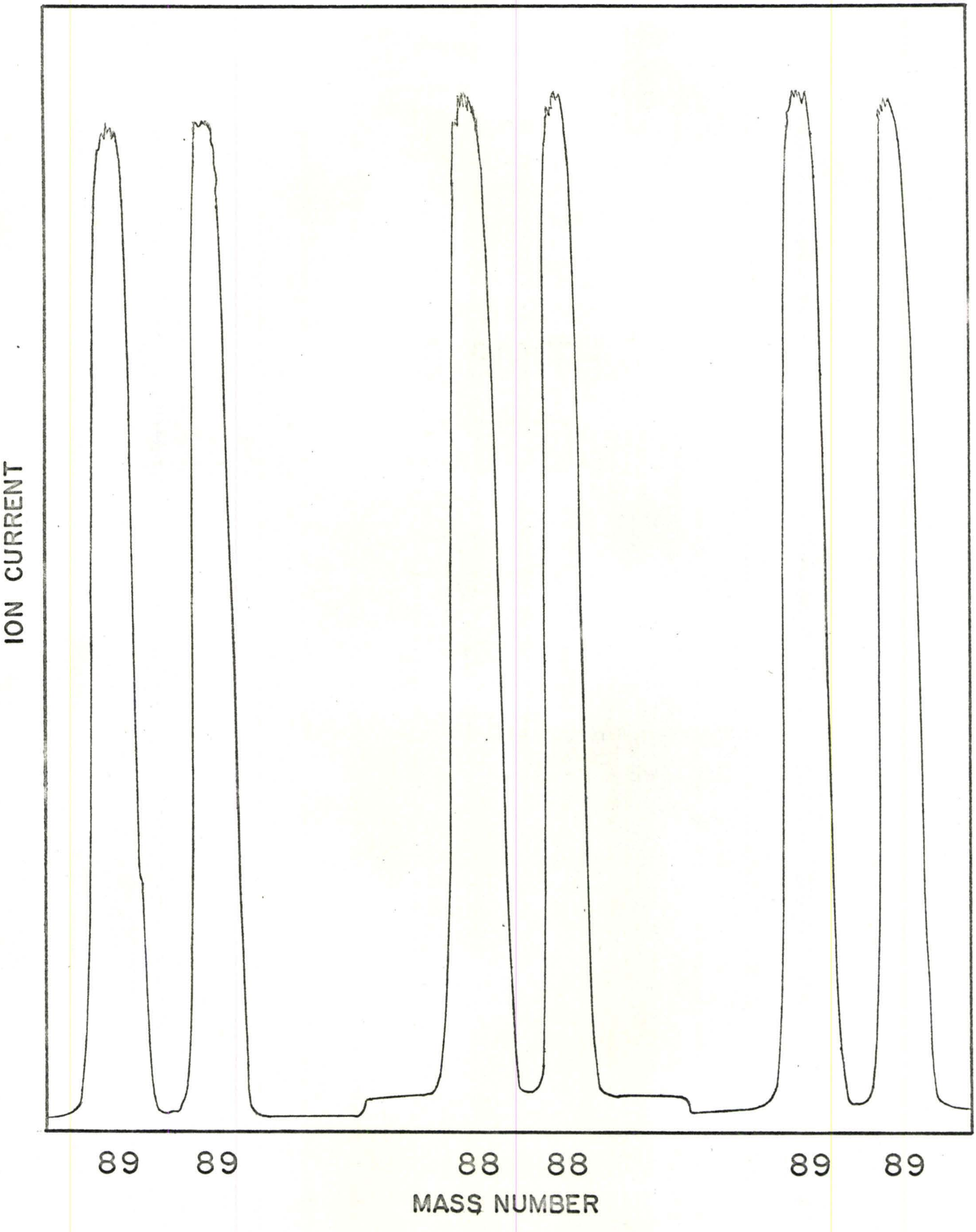


FIG.7 MASS SPECTROGRAM OF $Na_2BO_2^+$

calibrated from time to time it may seem superfluous at first sight to take this precaution, but it should be noted that the non-linear effects might not be constant and this could give erroneous results. The actual ratio of the sensitivities (shunt ratio) mentioned above was determined by applying constant d.c. voltages in the ratio of exactly one-quarter, from a potentiometer to the linear feedback vibrating reed amplifier, the output of which was fed to the recorder through the shunt selector.

The shunt ratio was measured several times in between the analyses of the samples and the average value was found to be 4.020 with a deviation less than 0.1 per cent. The occasional analysis of the boron standards also provided another check on the shunt ratio and the mass spectrometer in general.

Analysis:

In order to employ statistics in the calculation of the results for each sample analysis, as many as two hundred peaks of either isotope were measured with a metric scale which could be read to 0.5 mm. These comprise ten sets of ten ratios of the measured peak heights obtained by scanning over and back across the mass region. The scanning was done at a slow rate in order to be certain that each peak top was completely reached, but not so slow that all of the sample would evaporate before a sufficient number of peaks were measured. The focusing conditions were usually checked and peaks brought back to workable size before each set.

The measurement of the peaks (ion currents) took on the average three hours, after which time all three filaments were vigorously heated to drive off any unused sample. To ensure complete burn-off this was usually done for periods of six hours or more. Before a new sample was introduced, the filaments were allowed to cool down to the operating temperature for borax samples and the region of mass 88 and 89 scanned slowly. The temperature was raised gradually again while the scanning was continued at an increase in sensitivity of a factor of ten to one hundred. Having made certain that no traces of the previous sample (which might cause memory effects) were detectable, the pumping was stopped, and the spectrometer tube was filled with nitrogen before it was opened to the atmosphere for the introduction of another sample. The latter procedure prevents adsorption of atmospheric gases and water vapour which might be troublesome during operation of the instrument.

It was observed that in the operation of this apparatus the maximum peak did not always correspond to the best peak shape. This effect probably was caused by ions formed on the side filaments, giving rise to a larger energy spread in the ions. It was, therefore, deemed advisable to use the best shaped peaks.

Cleaning and Baking:

Occasionally, hydrocarbons did show up in the measurement, when the instrument was first turned on, but usually they quickly disappeared from the mass range of interest because they decompose to form lighter mass ions which are removed by the pumps. However, when such an effect was observed the source was cleaned before the next sample was analysed and on several occasions, when the results obtained were in doubt in part, because of such an effect, the same sample or one of the standards was reanalysed under more normal operating conditions.

After analysis of four or five samples it was usually necessary to dismantle the entire source and clean it thoroughly in an ultrasonic cleaner. This procedure was made necessary by instability in the peaks, high voltage break down, voltage drift due to polarisation and inconsistent results with large errors. A few of the samples were analysed twice with time intervals ranging from a day to several months. These, together with the results of the boron standards which were taken at several weeks interval provided an estimate of the reproducibility of the experimental results.

To outgas the mass spectrometer tube in order to reduce background ions and memory effects, it was baked at about 300°C for a period of twenty-four hours or more. The source filament currents were also turned on during the bake-out period. Before the baking was stopped, measurements were taken to see if the background was negligible.

CHAPTER V1

RESULTS

Table I shows the results of the measured $\left[\frac{89}{88}\right]$ ratio for a complete run of three of the samples, viz: Argentine Inderite, Standard A, Kashmir Tincal. The errors indicated are standard deviations. Each run was taken over a period of several hours and consists of about ten ratios, each of which is the mean of ten sets of ratio measurements. These runs are quite representative of the distribution of the experimental results. It is evident that each ratio is independent of the length of time required for each sample to be run, signifying that if there is any isotopic fractionation at all in the sample evaporation process, its effect on the isotopic ratio may be well within the experimental error. These can be compared to the results obtained by T. Matsuura59) where a considerable amount of fractionation effect was observed for BF_3 in the decomposition of boron trifluoride-calcium fluoride compound.

Looking at the specimen of experimental measurements it appears that the distribution of the ratios is random and therefore the results can be treated by statistical analysis.

TABLE I

Check for fractionation effects during analysis

Measured $\left[\frac{89}{88}\right]$ ratio

Argentine Inderite	Standard A	Kashmir Tincal
1.008 ± 0.007	1.059 ± 0.005	0.991 ± 0.003
1.005 ± 0.006	1.053 ± 0.012	0.983 ± 0.007
1.008 ± 0.006	1.055 ± 0.013	0.990 ± 0.007
1.003 ± 0.007	1.053 ± 0.004	0.985 ± 0.009
1.004 ± 0.006	1.053 ± 0.012	0.982 ± 0.010
1.004 ± 0.008	1.053 ± 0.007	0.986 ± 0.007
1.010 ± 0.007	1.056 ± 0.006	0.990 ± 0.003
1.008 ± 0.008	1.005 ± 0.005	0.988 ± 0.005
1.004 ± 0.008	1.057 ± 0.009	0.987 ± 0.008
1.010 ± 0.013	1.058 ± 0.012	0.984 ± 0.013
1.005 ± 0.012	1.053 ± 0.007	
1.006 ± 0.002	1.055 ± 0.002	0.987 ± 0.003

Table II gives an indication of the reproducibility of the measured isotopic ratio of boron. The measured ratios are obtained from the observed ratios by multiplying the latter by the 'shunt factor 4.020' mentioned earlier. As has been mentioned elsewhere in this work, apart from the statistical fluctuation of the ratios, the ratios are liable to be affected by a number of instrumental errors. These errors may not be constant from day to day, hence the more reproducible the results of the isotopic ratios, the less effective the instrumental errors are or the more constant the errors must be. In the table an average of the index of reproducibility obtained from measurement of seven of the samples is given. This is about 0.21%.

TABLE II

Reproducibility

(i) Standards:	Observed $\frac{B^{11}}{B^{10}}$	Reproducibility (% deviation)
A	4.237 ± 0.044	
	4.229 ± 0.020	
	4.265 ± 0.020	
	4.241 ± 0.024	
	4.241 ± 0.008	
	4.243 ± 0.013	0.306
B		
	3.923 ± 0.004	
	3.952 ± 0.004	
	3.932 ± 0.008	
	3.920 ± 0.016	
	3.932 ± 0.014	0.356
(ii) Samples:		
Argentine Hydroboracite	4.036 ± 0.012	
	4.040 ± 0.008	
	4.038 ± 0.003	0.074

TABLE II (continued)

(ii) Samples	Observed $\frac{B^{11}}{B^{10}}$	Reproducibility (% deviation)
Larderello Soffionis	4.096 ± 0.034	
Acid Vapour	4.068 ± 0.012	
	4.082 ± 0.020	0.490
Turkey Datolite	4.036 ± 0.012	
	4.040 ± 0.008	
	4.038 ± 0.003	0.074
Argentine Ulexite	4.044 ± 0.020	
	4.044 ± 0.012	
	4.044 ± 0	0
Kashmir Tincal	3.956 ± 0.012	
	3.968 ± 0.012	
	3.962 ± 0.006	0.151
	AVERAGE REPRODUCIBILITY:	0.21%

Table III is an estimate of the instrumental discrimination computed from the calculated and measured isotopic ratios of the two standards of boron. The mass discrimination in per cent. per mass unit is 0.63 hence the observed isotopic ratios must be multiplied by 1.0063 in order to obtain the absolute ratios (see Table IV).

As mentioned in the theory for the preparation of the standards, the difference between the isotopic content in Standard A and Standard B as given by calculation and as given by measurement should be equal in the first approximation. Substituting the results in equations (27 - 30) we find for B^{10}

$$\Delta C_{\text{calculated}} = \left(\frac{1}{5.270} - \frac{1}{4.956}\right) = -0.0120_3$$

$$\Delta C_{\text{measured}} = \left(\frac{1}{5.243} - \frac{1}{4.941}\right) = -0.0120_3$$

which shows that $\Delta C_{\text{calculated}} \approx \Delta C_{\text{measured}}$.

TABLE III

Instrumental Discrimination

B^{11}/B^{10} ratio

Sample	Calculated	Measured	Instrumental Discrimination % per mass unit
Standard A	4.270	4.243 ± 0.013	0.64
Standard B	3.956	3.932 + 0.014	0.61
AVERAGE			0.63

Table IV gives the final results of the absolute isotopic ratios of eighteen of the samples analysed, all of which are minerals except the last one which comes from a boric acid vapour. The errors indicated are the standard deviations.

The results marked with asterisks are those which were repeated for the reproducibility check (see Table II). They are the averages of two analyses of the same samples, the members of each pair taken independently on different days, the time intervals ranging from a few days to several months.

The chemical formula of each mineral is given in column 2 against the name of the mineral. Columns 3 and 4 are the measured and absolute ratios $\frac{B^{11}}{B^{10}}$ respectively, the latter obtained from the former by applying the correction factor from Table III. The last column gives the atomic weight corresponding to each determined isotopic ratio calculated by using equation (1). Because the C^{12} physical scale is almost equal to the chemical scale, the figures in the last column representing the atomic weights of boron from the minerals are obtained from Equation (1).

In Appendix C are given more details about the minerals which were obtained from Borax Consolidated Limited. A summary of the chemical treatment for each sample can be found in Appendix D.

For the purpose of comparison the boron isotopic ratios of certain minerals obtained by Thode 6), Shiuttse 12), McMullen 13), Finley 17) and Shima 18) are quoted in Appendix E.

TABLE IV

Isotopic Abundance Ratios and Atomic Weights of Boron

	SAMPLE			Measured $\frac{B^{11}}{B^{10}}$ ratio	Absolute $\frac{B^{11}}{B^{10}}$ ratio	Atomic weight[‡]
	Location	Mineral				
1.	Argentina	Tincal (chemical)[†]	$Na_2B_4O_7.10H_2O$	4.008 ± 0.008	4.033 ± 0.008	10.811
2.	Argentina	Tincal (resin)[†]	$Na_2B_4O_7.10H_2O$	3.972 ± 0.016	3.997 ± 0.016	10.810
3.	Argentina	Ulexite	$NaCaB_5O_9.8H_2O$ or $NaCaB_5O_9.5H_2O$	4.044	4.070*	10.813
4.	Argentina	Colemanite (with Inyoite)	$CaB_6O_{11}.5H_2O$	4.020 ± 0.012	4.045 ± 0.012	10.812
5.	Argentina	Hydroboracite	$CaMgB_6O_{11}.6H_2O$	4.039 ± 0.002	4.063 ± 0.002*	10.813
6.	Argentina	Inderite	$Mg_2B_6O_{11}.H_2O$	4.044 ± 0.008	4.070 ± 0.008	10.813
7.	Turkey	Inyoite	$Ca_2B_6O_{11}.13H_2O$ or $Ca_2B_6O_{11}.9H_2O$	4.012 ± 0.012	4.037 ± 0.012	10.812
8.	Turkey	Colemanite	$CaB_6O_{11}.5H_2O$	3.968 ± 0.008	3.993 ± 0.008	10.810
9.	Turkey	Pandermite	$Ca_4B_{10}O_{19}.7H_2O$	4.044 ± 0.016	4.070 ± 0.016	10.813
10.	Turkey	Datolite	$H_2O.2CaO.B_2O_3.$ $2S_iO_2$	4.039 ± 0.008	4.063 ± 0.003*	10.813
11.	Turkey	Ulexite	$NaCaB_5O_9.8H_2O$ or $NaCaB_5O_9.5H_2O$	4.048 ± 0.012	4.074 ± 0.012	10.813

TABLE IV (continued)

Isotopic Abundance Ratios and Atomic Weights of Boron

SAMPLE				Measured $\frac{B^{11}}{B^{10}}$ ratio	Absolute $\frac{B^{11}}{B^{10}}$ ratio	Atomic weight‡
	Location	Mineral				
12	Japan	Sassolite (chemical)$^{+}$	$B(OH)_3$	4.072 ± 0.016	4.098 ± 0.016	10.814
13	Japan	Sassolite (resin)$^{+}$	$B(OH)_3$	4.048 ± 0.012	4.074 ± 0.016	10.813
14	Kashmir	Tincal (chemical)$^{+}$	$Na_2B_4O_7.10H_2O$	3.980 ± 0.012	4.005 ± 0.012	10.810
15	Kashmir	Tincal (resin)$^{+}$	$Na_2B_4O_7.10H_2O$	3.962 ± 0.006	3.987 ± 0.006*	10.810
16	New Caledonia	Datolite	$H_2O.2CaO.B_2O_3.$ $2SiO_2$	4.032 ± 0.012	4.057 ± 0.012	10.812
17	Korea	Kotoite	$Mg_3B_2O_6$	4.020 ± 0.012	4.045 ± 0.012	10.812
18	Larderello, Italy	Soffionis boric acid vapour	$B(OH)_3$	4.082 ± 0.020	4.108 ± 0.020*	10.814

+ see Appendix D

* These are the results used for the reproducibility estimate (see Table II)

‡ The corresponding standard deviations in the atomic weights can be computed using equation (2)

Table V shows the results of the boron isotopic composition of Gabro from Insizwa (Africa) and sea water from Tokyo Bay

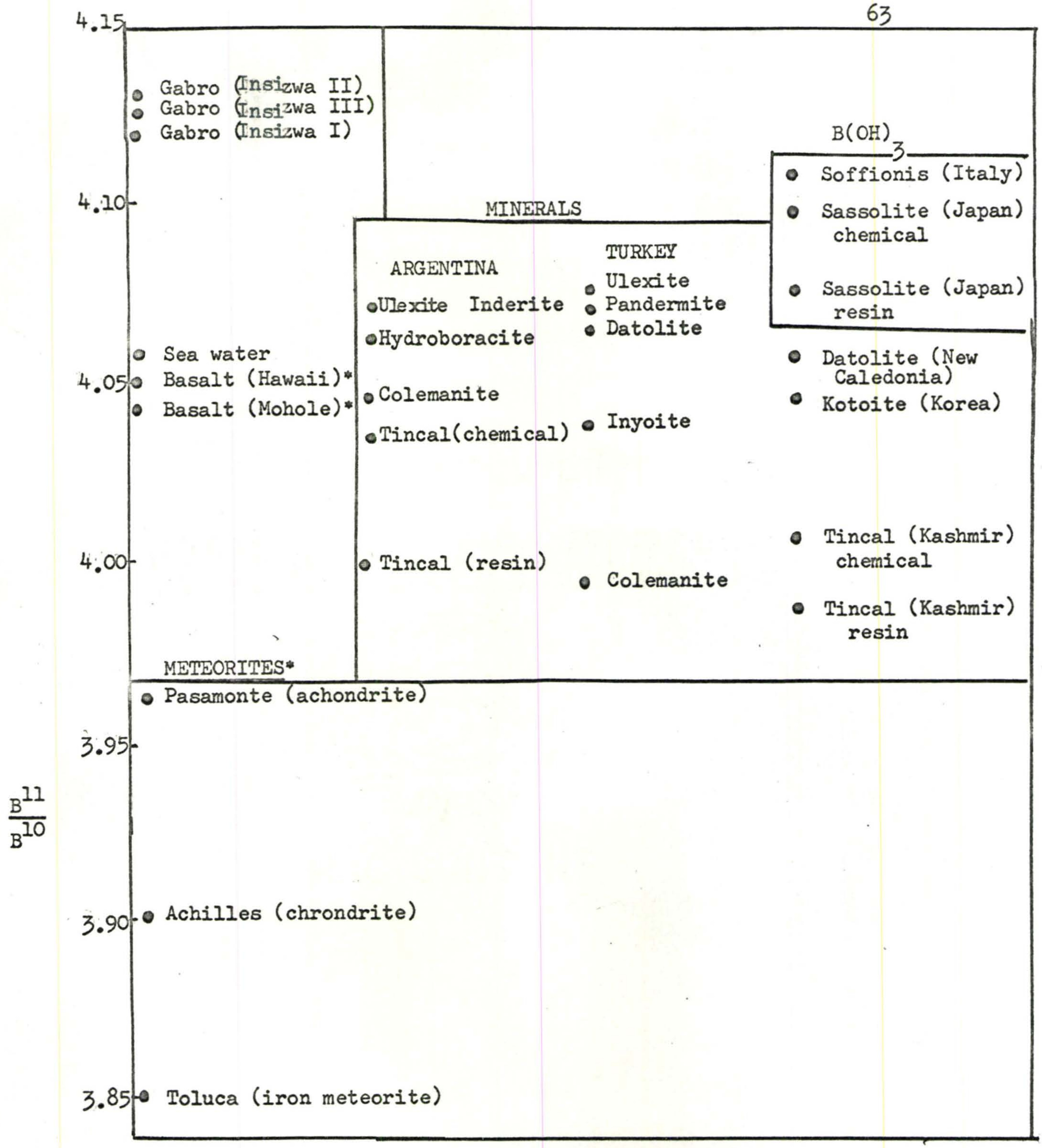
TABLE V

Boron in Insizwa Gabro and Sea Water

SAMPLE	Boron Content	Measured B^{11}/B^{10}	Absolute B^{11}/B^{10}	Atomic Weight ‡
Insizwa Gabro I (700-1400 ft.)	5 ppm	4.093 ± 0.04	4.118 ± 0.04	10.815
Insizwa Gabro II (1500-1800 ft.)	6 ppm	4.104 ± 0.012	4.129 ± 0.012	10.815
Insizwa Gabro III (1900-2100 ft.)	10 ppm	4.100 ± 0.008	4.125 ± 0.008	10.815
Tokyo Bay (sea water)	--	4.032 ± 0.012	4.056 ± 0.012	10.812

‡ The standard deviations in the atomic weights can be computed using Equation (2).

In Fig.8, B^{11}/B^{10} ratios obtained for the samples studied in this research are displayed graphically, together with $\frac{B^{11}}{B^{10}}$ for meteorites and Basalt obtained by Shima[37].



* Results taken from Reference37).

FIG. 8 BORON ISOTOPE RATIOS

CHAPTER VII

DISCUSSION

The isotopic abundances of boron from several sources were determined with an average accuracy of 0.3 per cent. and a reproducibility of 0.2 per cent.

In agreement with the results of practically all the previous investigations, the isotopic ratio was found to vary with the source of the boron compound by up to about 3.5 per cent. Because of this agreement and the fact that the variations are much larger than the experimental deviations, the variations in the isotopic ratios cannot be fortuitous.

Again, in accordance with recent determinations by researchers, using the solid source mass spectrometer, the absolute $\frac{B^{11}}{B^{10}}$ ratios are about 7 per cent. lower than those obtained by early workers using gas source. The isotopic ratio obtained for Turkey Colemanite is in striking agreement with that determined by Finley17). It is interesting to note that the Ulexite from both Argentina and Turkey also have practically the same isotopic constitutions. It is not surprising that the Colemanite from Argentina has a higher $\frac{B^{11}}{B^{10}}$ ratio than that from Turkey, because the former is mixed with Inyoite which is known to have a higher ratio than Turkey Colemanite. The ratios for Datolite from Turkey and New Caledonia are not too different. Again the samples prepared from Kashmir Tincal and Argentine Tincal, using resin method, have essentially the same ratio.

In making such deductions one should be a little cautious and take into account the method employed in preparing the borax samples from the minerals. In this work for instance, it is observed that isotopic ratios of borax from the same minerals prepared by resin method are always lower than those by chemical procedure. Such an observation indicates that either the B^{10} is depleted (B^{11} enriched) in the chemical method or the B^{10} is enriched (B^{11} depleted) in the resin method due to some fractionation effects. In this experiment in particular the yields of the chemical method always seem to be less than that of the resin method (see Appendix D). If these results are correct, then preparations with very low yields, say less than 50% should exhibit what has been noticed here much more clearly. In order to correct for such errors, it is suggested that a method be deviced whereby the boron standards could be prepared by methods involving the same reactions used for the samples, trying as much as possible to obtain the same yields. If one cannot claim with absolute certainty that the prepared samples are representative of the minerals it is difficult to obtain an absolute determination of $\frac{B^{11}}{B^{10}}$ ratio.

Though more must be done in this regard a lot of interesting points evolve from the results obtained so far when they are shown on a graph as in Fig.8, together with the results obtained by M. Shima37) for Basalt and meteorites. Considering the samples grouped on the left column of Fig.8, which are of primary origin, we observe that the Insizwa Gabro has the highest $\frac{B^{11}}{B^{10}}$ ratio among the entire suite of samples and that there is a tendency for the ratio to increase with depth. One may explain this by gravitational differentiation of the isotopes during the initial solidification of the molten rock. Hawaii and Mohole Basalt which is also of primary origin, however, have isotopic ratios much lower than that of Gabro. This is presumably because, as has been demonstrated experimentally, Basalt shows a minimum of gravity differentiation.

The very low isotopic ratio for boron in meteorites could only be explained by spallation as mentioned briefly in Chapter II. The possibility of B^{10} (n, α) L^7 effect was ruled out. In fact, according to nucleo-synthetic theories B^{10} and B^{11} are produced in the ratio of about three and a half to one in the spallation process caused by the bombardment of relativistic cosmic rays on medium mass nuclei. It is estimated that a spallation of about three parts in hundred million of the meteorite is sufficient to decrease the $\frac{B^{11}}{B^{10}}$ ratio from the value of that of sea water to what is observed by Shima37).

The group of samples under the heading 'Minerals' in the centre of Fig.8 appear to have a B^{11}/B^{10} ratio between those of Gabro and meteorites. These minerals are from secondary deposits. It may be postulated that at one time they had $\frac{B^{11}}{B^{10}}$ ratio near that of sea water but due to different geological conditions in the process of their formation the ratios changed and became distributed around the value for sea water.

Boric acid which originates in hot springs can be considered as a mineral form and it exhibits an interesting feature. The three samples (soffionis boric acid vapour and Sassolite) indicated in Fig.8

show high isotopic ratios. If the boric acid is produced by distillation from a reservoir of boric acid beneath the earths surface, one might expect that B^{10} would be enriched in the vapour phase and hence give a low $\frac{B^{11}}{B^{10}}$ ratio when the boric acid is completely recovered by condensation. Either the source material from which the boric acid originates is enriched in B^{11} and no significant fractionation effects are occuring in the vapourization process or some unknown mechanism which favours the enrichment of B^{11} is operating in the evolution of boric acid from the earths crust. Since the concentration in the Insizwa Gabro is only a few parts per million it may be mere coincidence that the isotopic ratios in Gabro and in boric acid are the same.

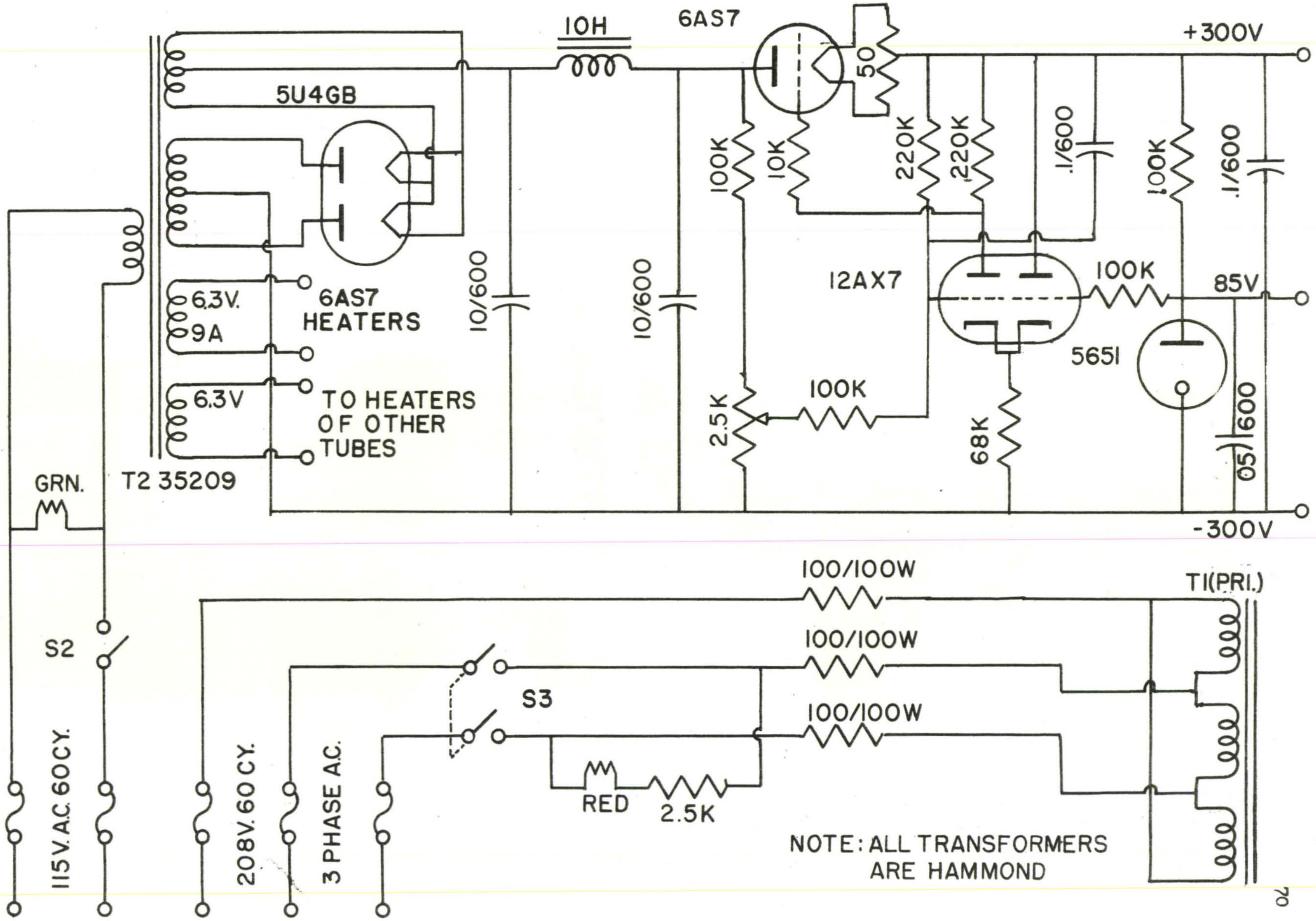
The range of values determined for atomic weight of boron in this investigation is in perfect agreement with the range of values currently accepted for the atomic weights of boron.

The results of this work indicate a number of further experiments which can be performed. Laboratory experiments to study fractionation in the steam distillation of boric acid should be carried out. Further work should be initiated to determine whether fractionation effects exist in the procedures for the production of borax for mass spectrometric analysis.

It would be worthwhile to carry out further studies on intrusives to ascertain whether the boron ratio in sills is characteristic of that found in the Insizwa sill by Shima37). The boron ratios in the Leitch sill (Canada) which has shown no significant fractionation of sulphur through its entire depth may provide useful information concerning gravity differentiation of boron in igneous rocks. Further studies of the boron ratios in meteorites should be carried out to confirm the observations made by Shima37). Finally further work should be done to determine $\frac{B^{11}}{B^{10}}$ ratio of a wider variety of boron containing minerals.

APPENDIX A

Circuit Diagrams



FIG, A1 POWER SUPPLY FOR EMISSION CONTROL

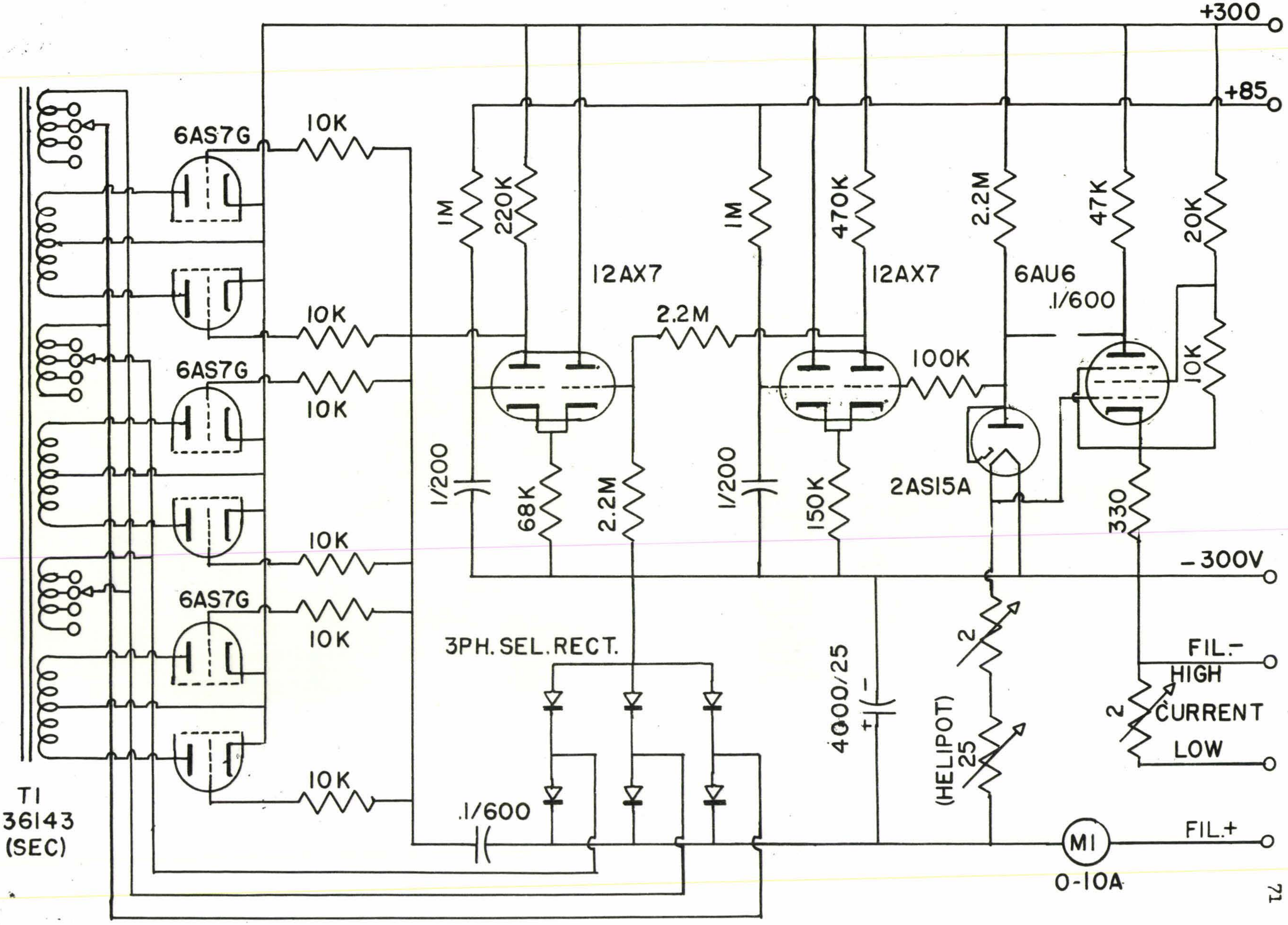
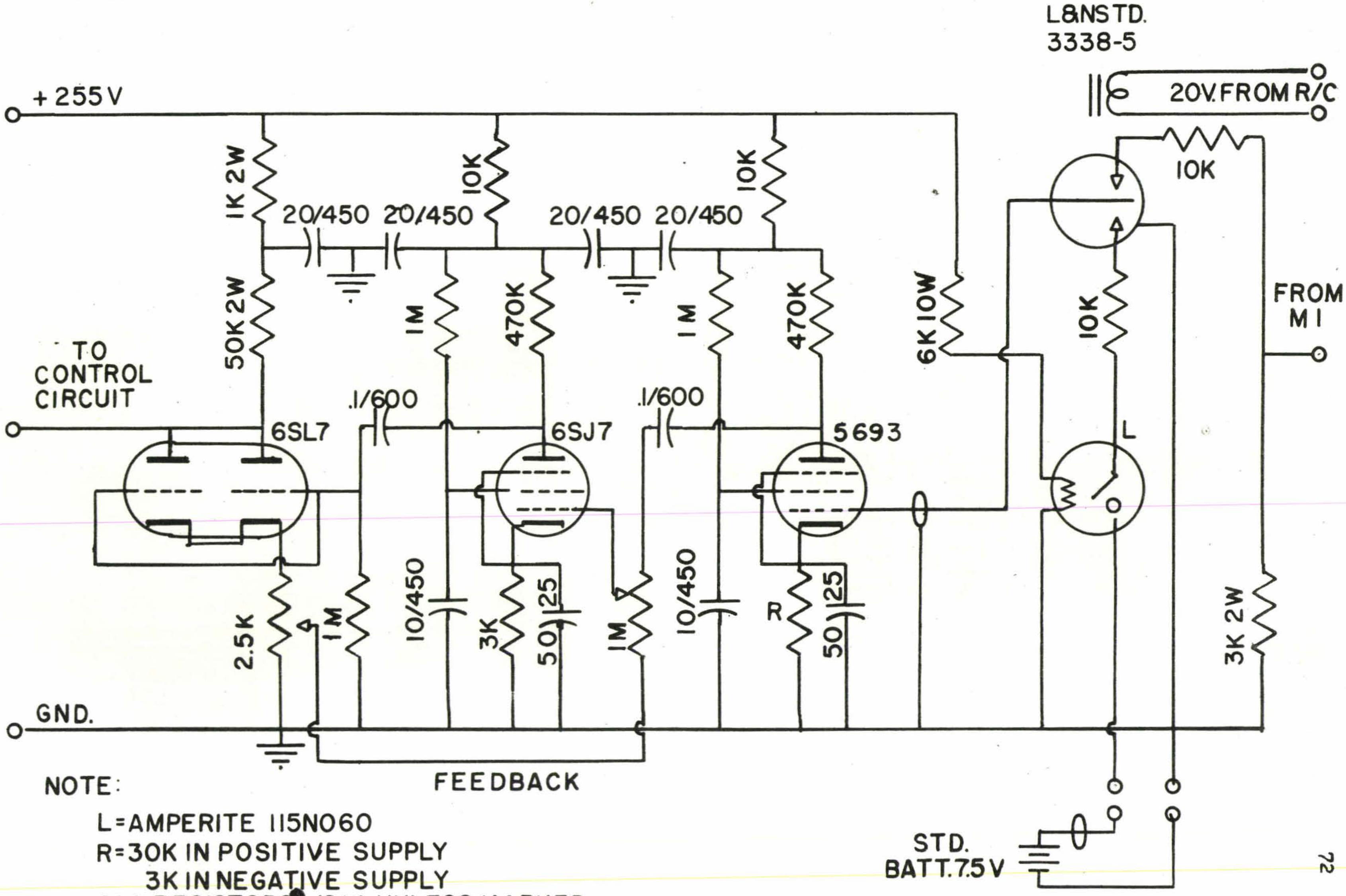


FIG. A2

THREE PHASE EMISSION CONTROL



NOTE:

L=AMPERITE 115N060
R=30K IN POSITIVE SUPPLY
3K IN NEGATIVE SUPPLY
ALL RESISTORS 1/2 W. UNLESS MARKED

FIG. A3 60 CYCLE AMPLIFIER FOR 10KV. AND 5KV. STABILIZED SUPPLIES

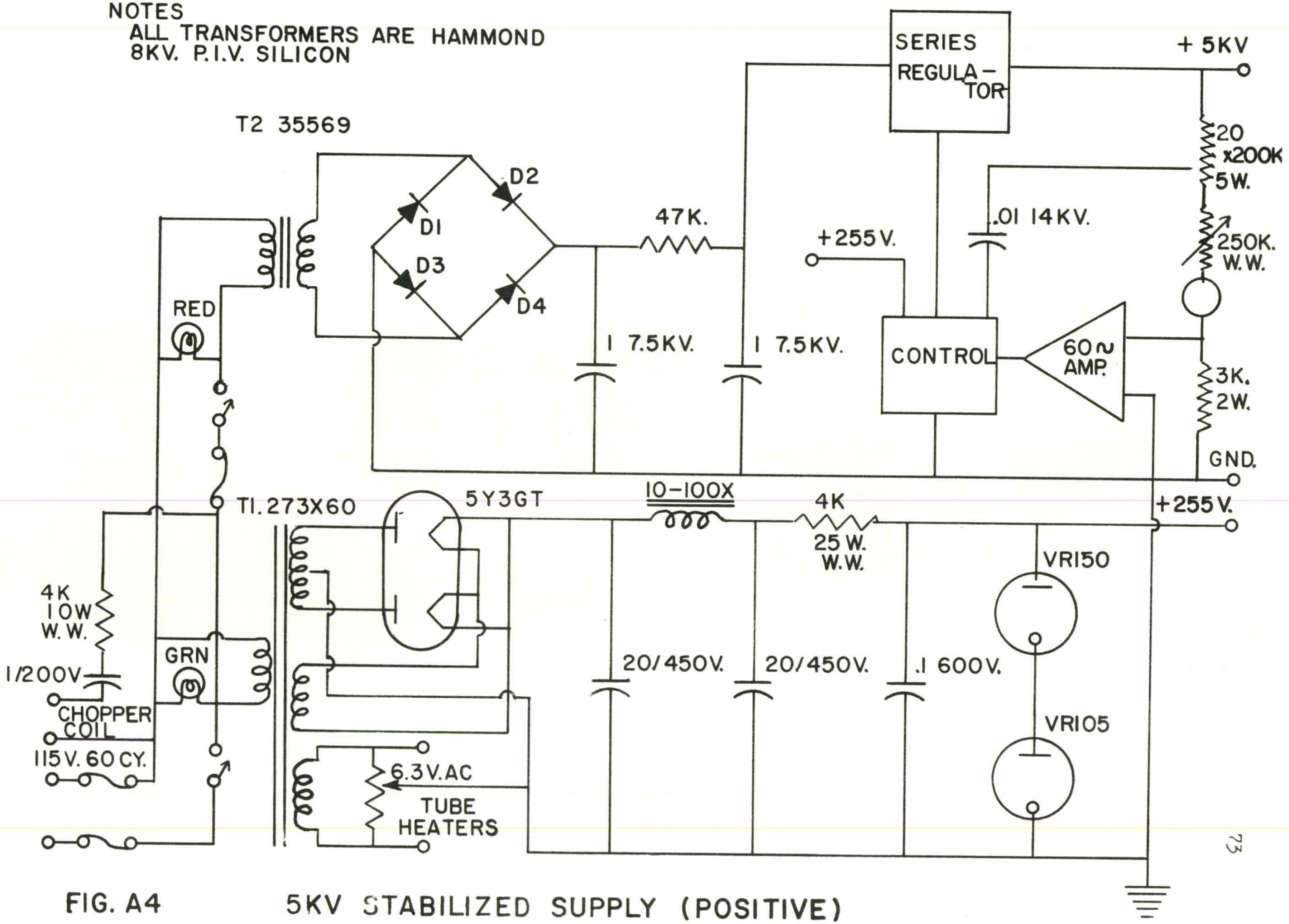

NOTES
ALL TRANSFORMERS ARE HAMMOND
8KV. P.I.V. SILICON

FIG. A4 5KV STABILIZED SUPPLY (POSITIVE)

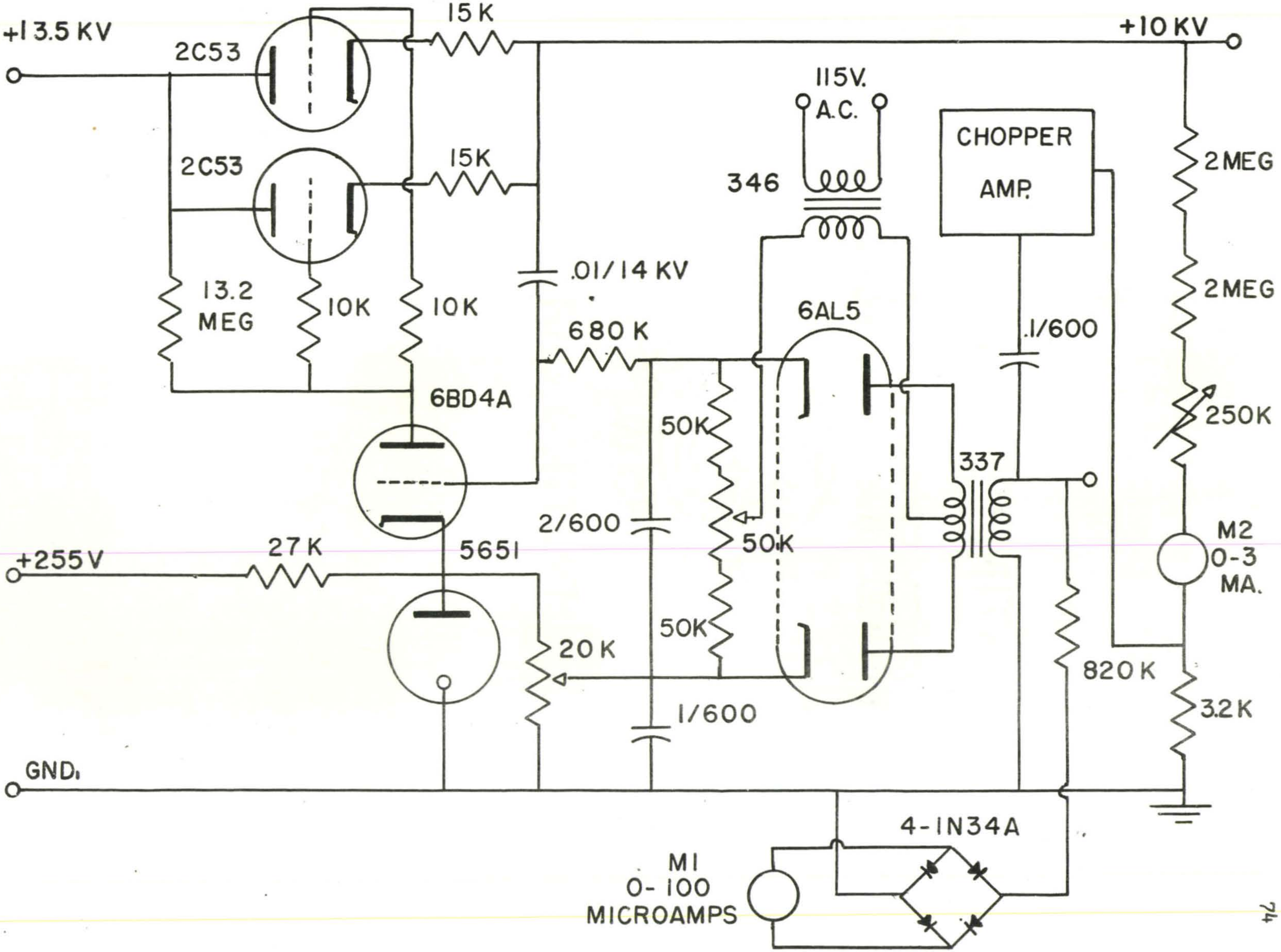


FIG. A5 CONTROL CIRCUIT FOR 5KV. POSITIVE SUPPLY

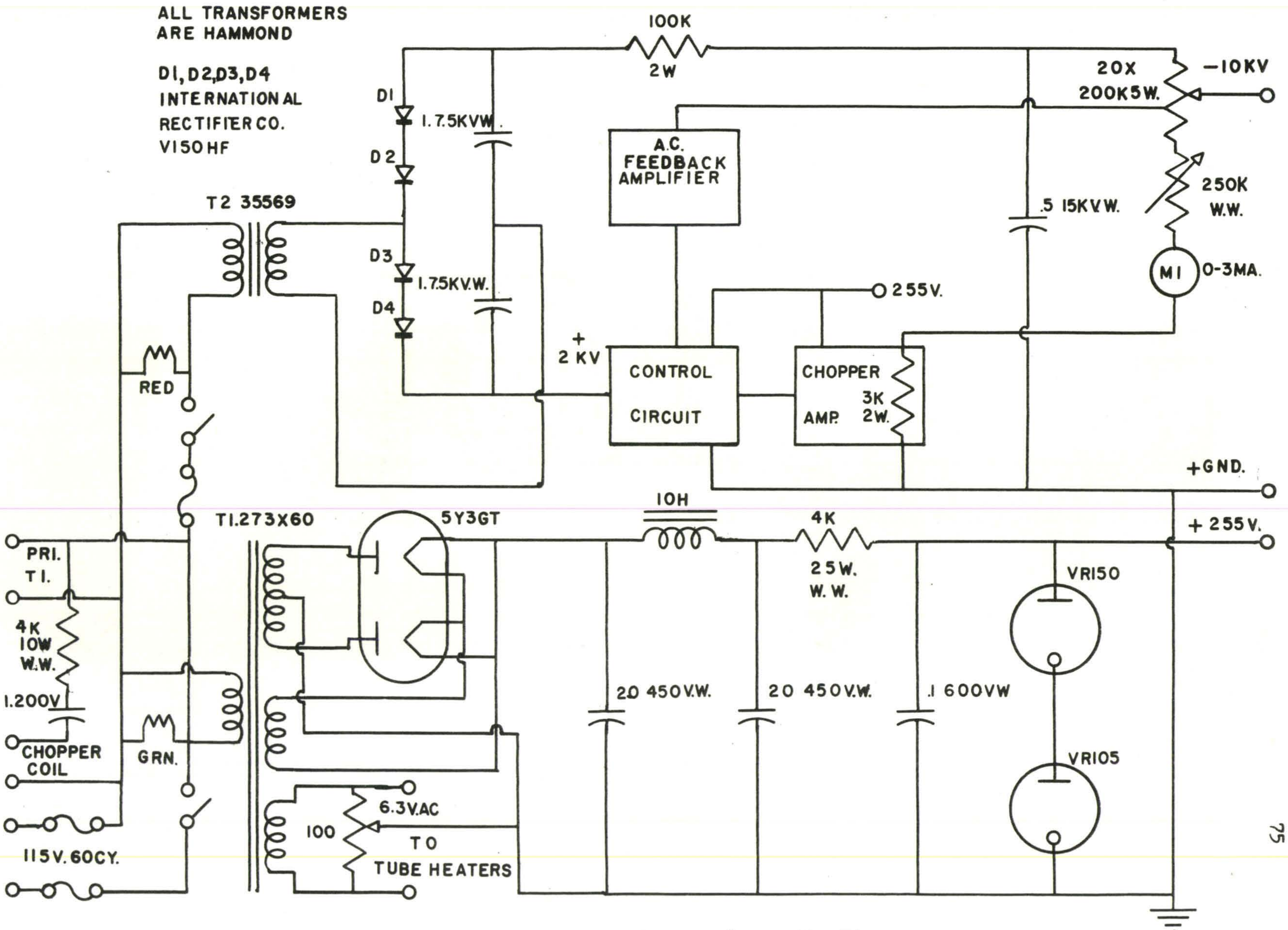


FIG. A6

10KV. STABILIZED SUPPLY (NEGATIVE)

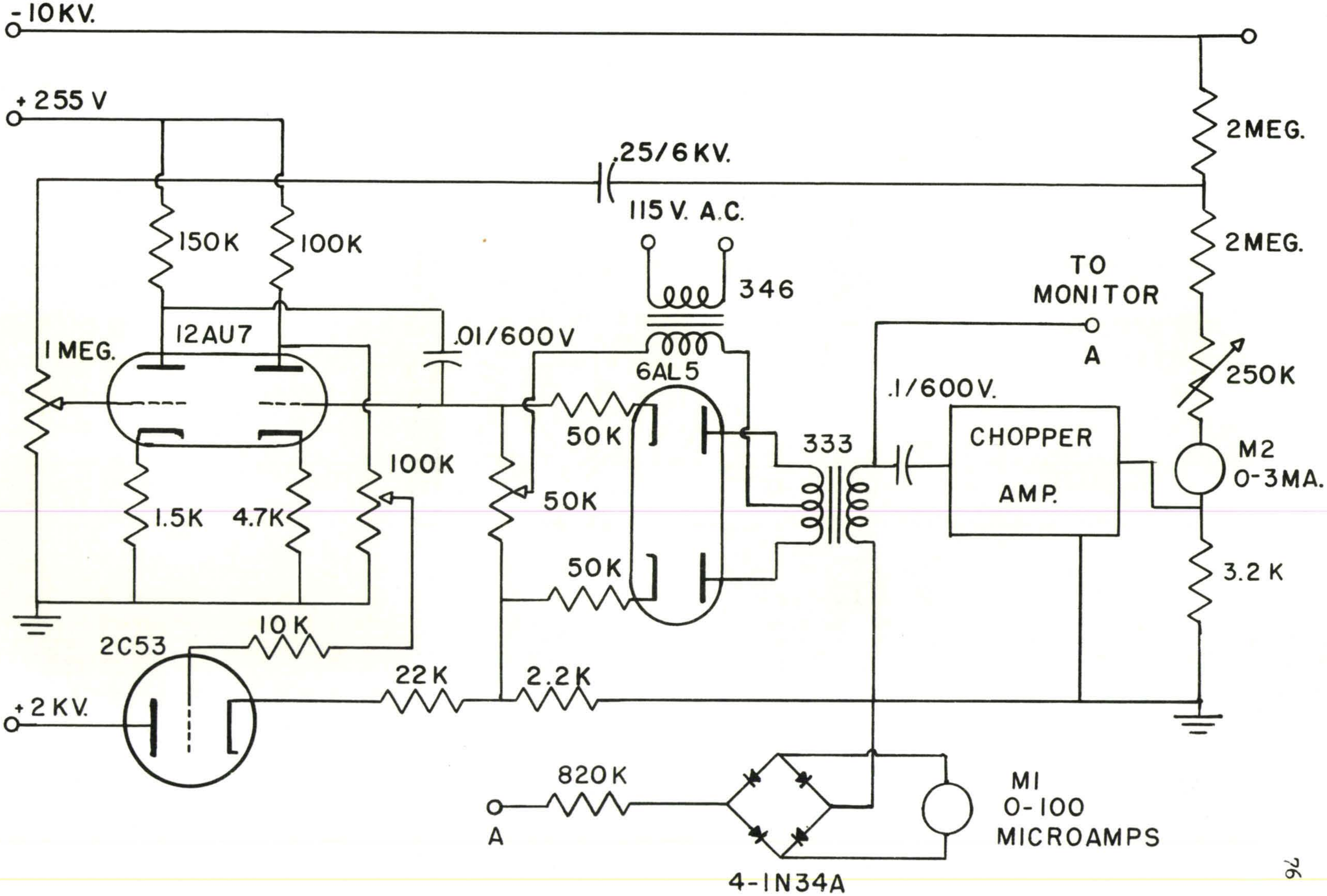


FIG. A7 CONTROL CIRCUIT FOR 10KV. NEGATIVE SUPPLY

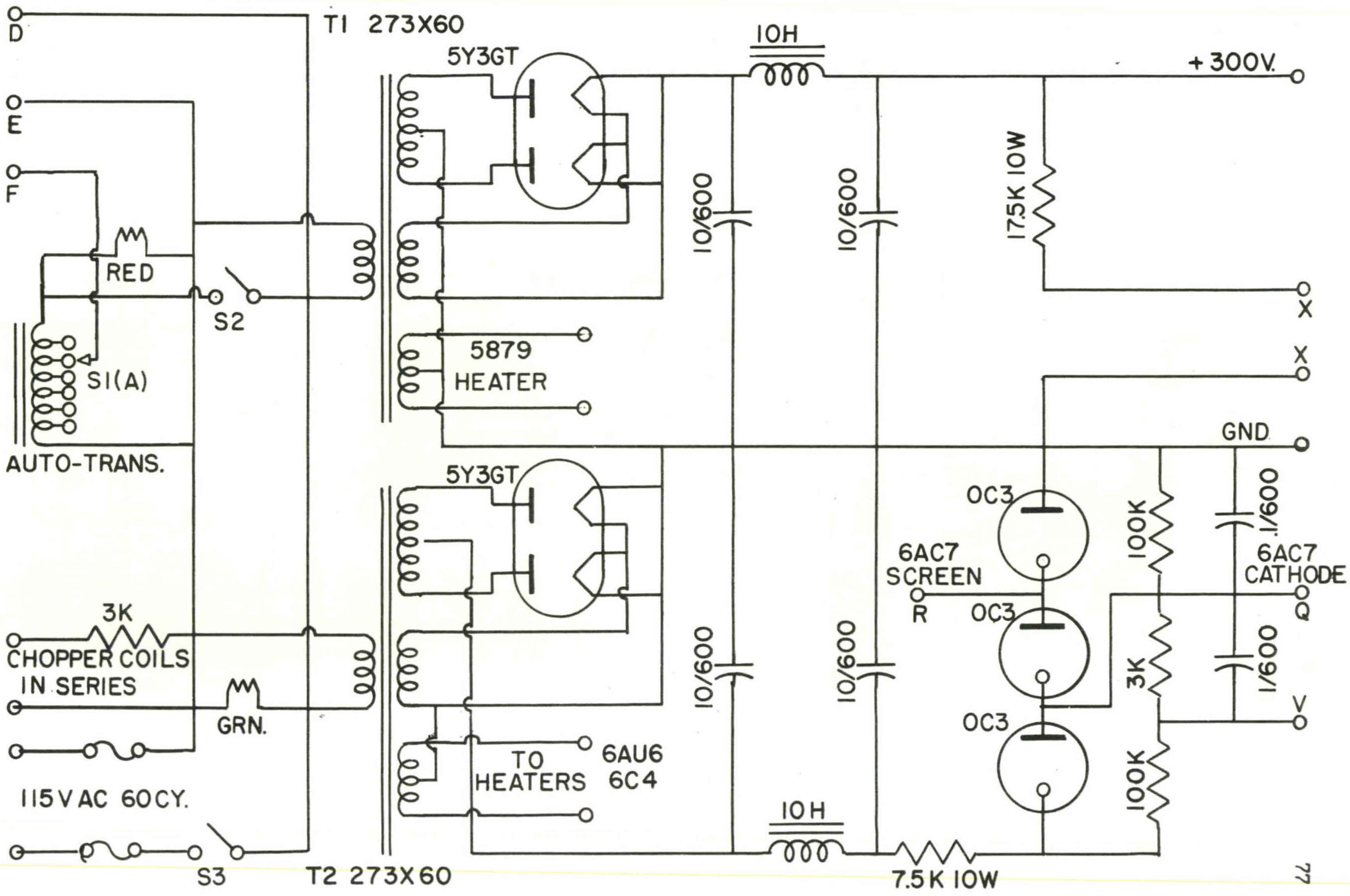


FIG. A8 "B" SUPPLY FOR AMPLIFIER & CONTROL CIRCUIT (MAGNET SUPPLY)

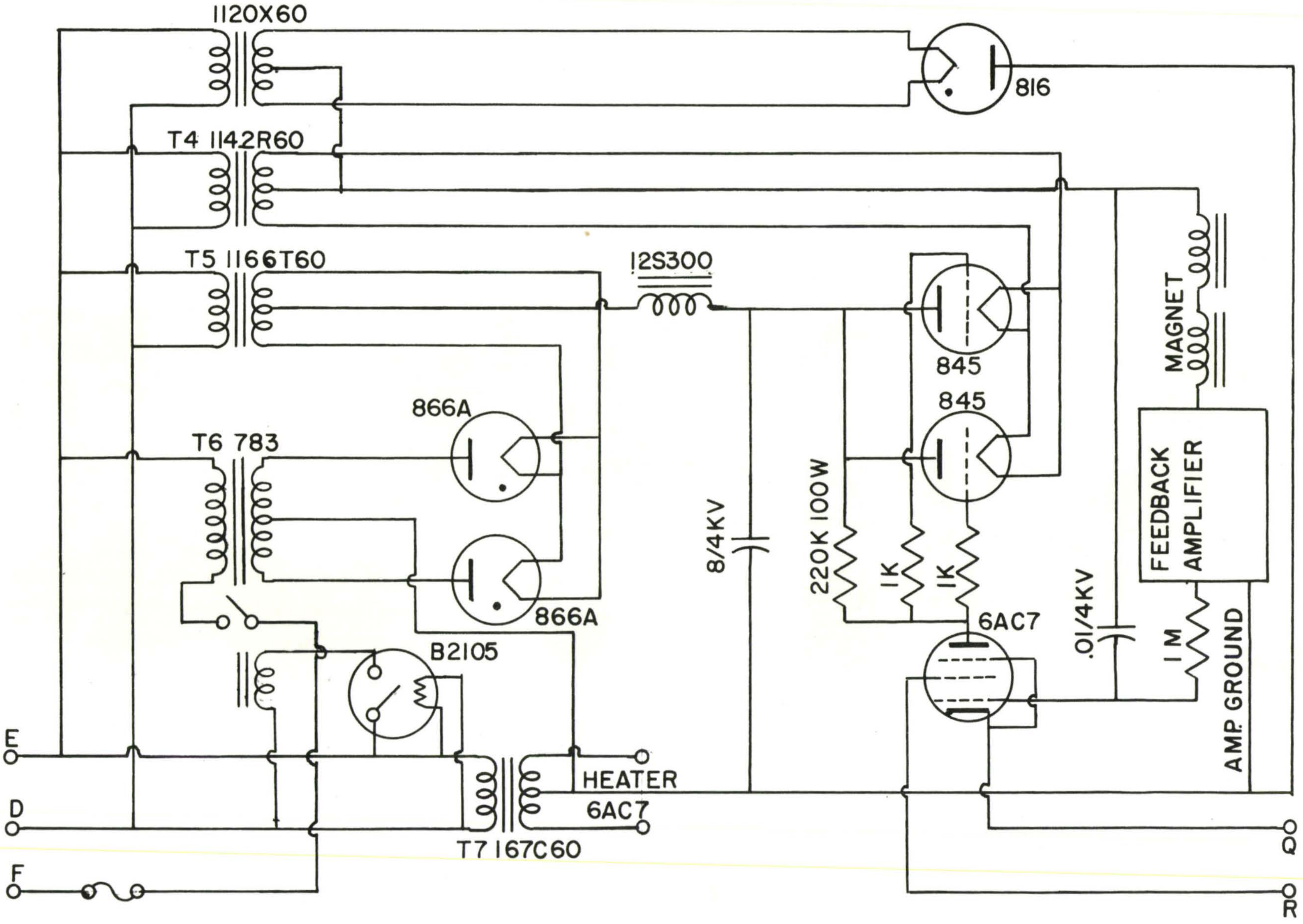
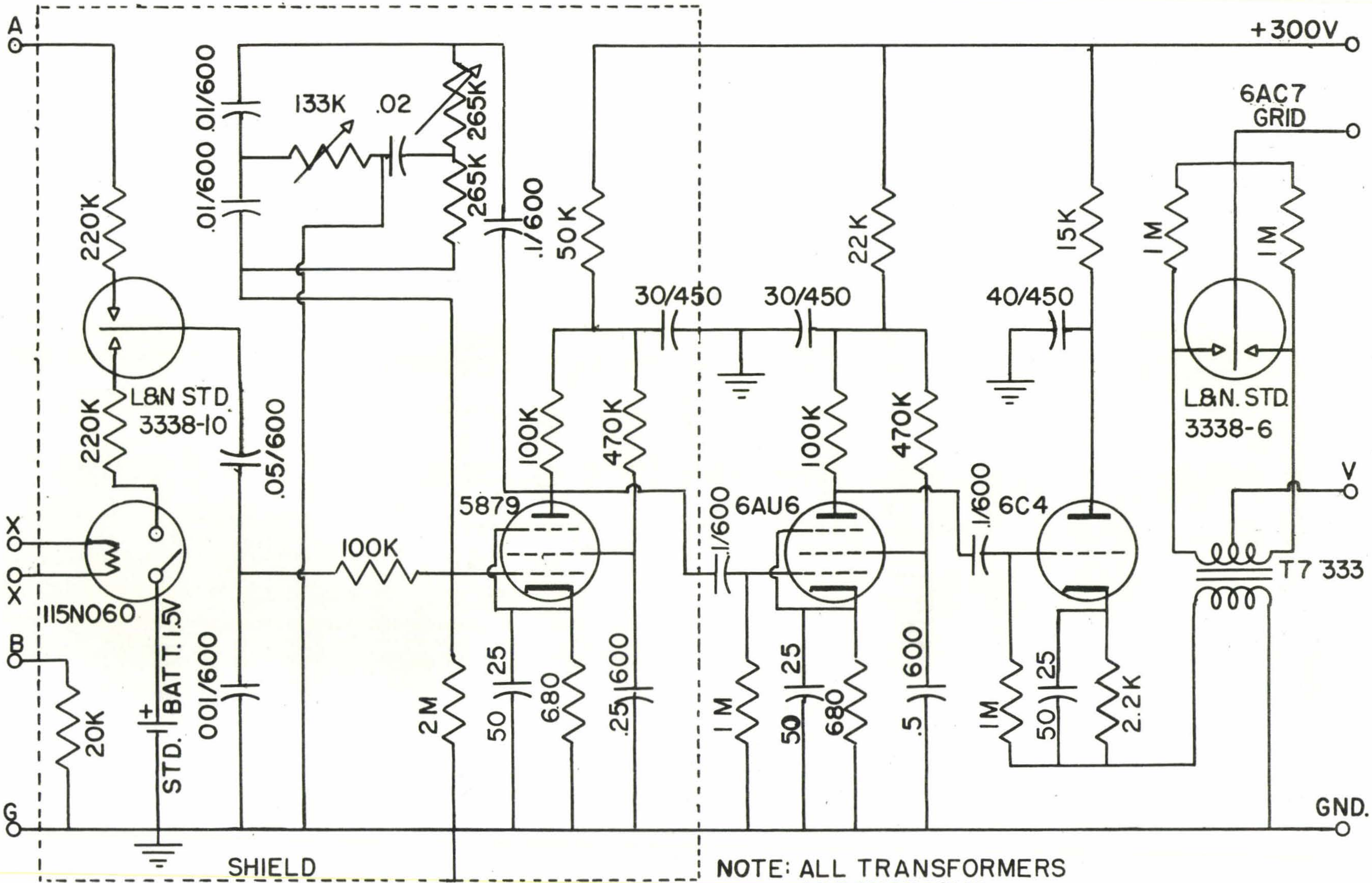


FIG. A9 MAGNET CURRENT SUPPLY



NOTE: ALL TRANSFORMERS ARE HAMMOND

FIG.A10 60 CYCLE FEEDBACK AMPLIFIER FOR MAGNET CURRENT SUPPLY

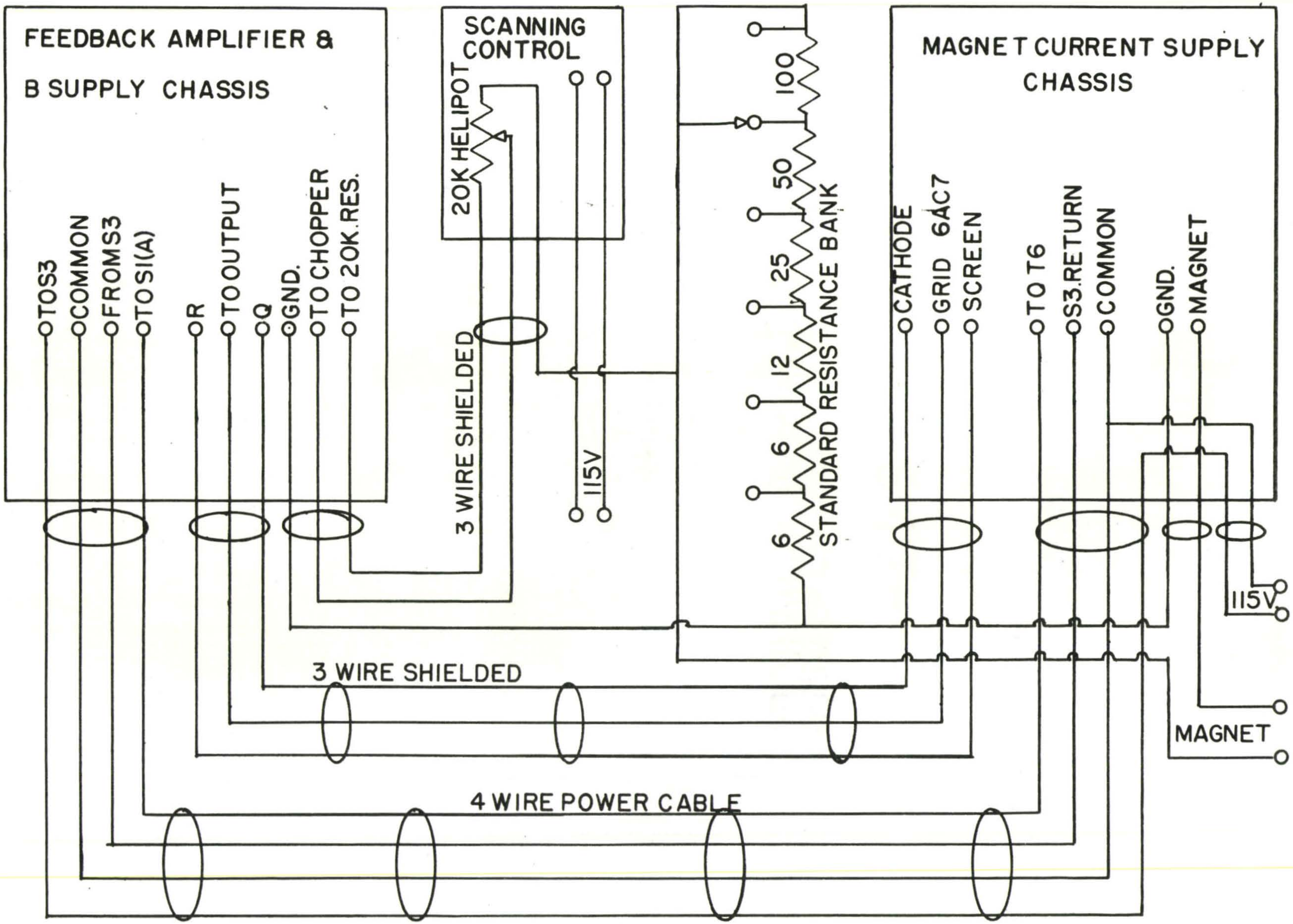


FIG. A11 CABLE CONNECTIONS OF MAGNET CURRENT SUPPLY

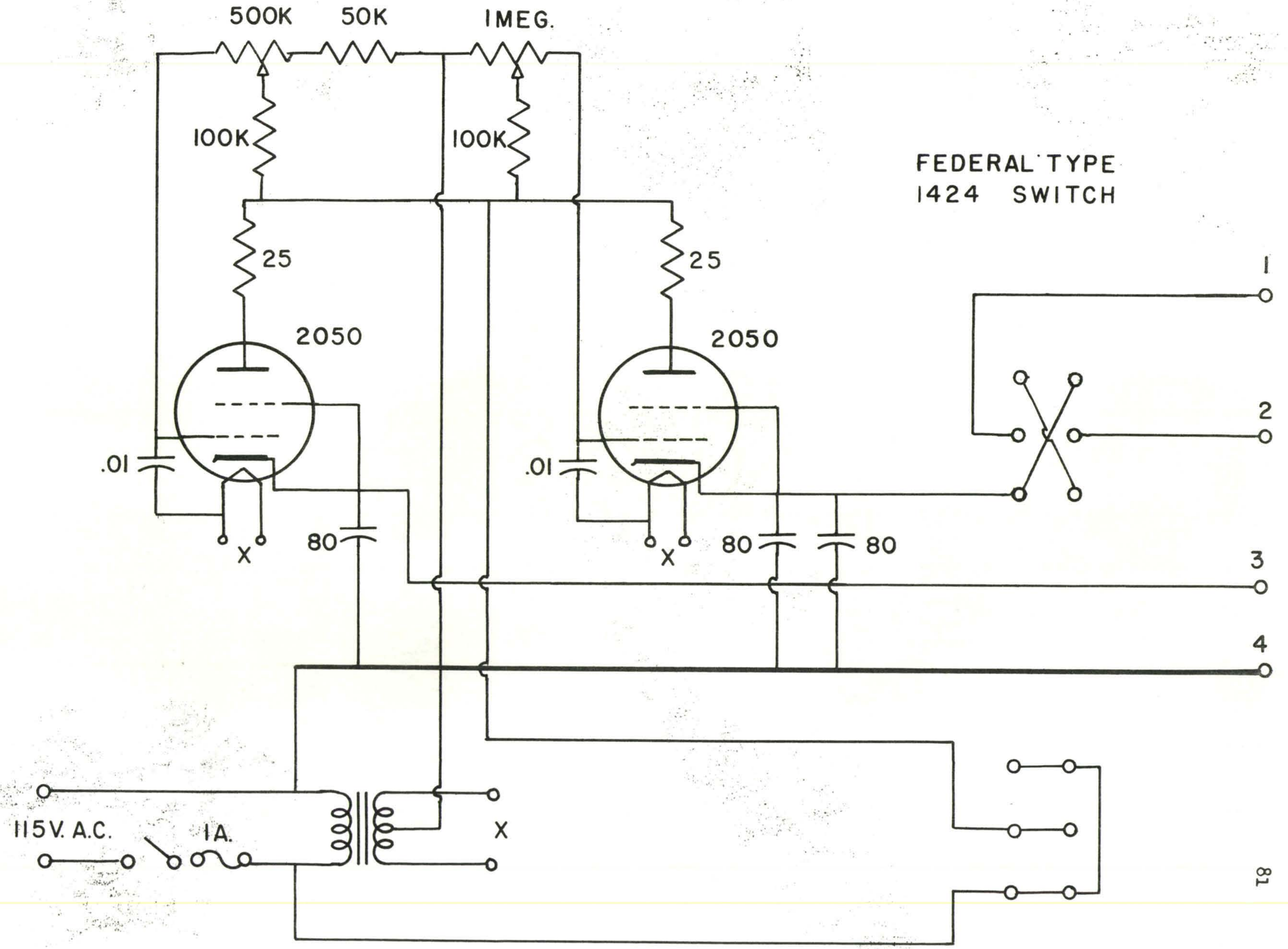


FIG. A12

SCANNER MOTOR CONTROL

APPENDIX B1

Accuracy of Preparation of Boron Standards

In the preparation of the boron standards used in this work, for example $R'_d \approx 28$ for the depleted blending material

$$\Delta c_d = -(1-k)\ R'_d/(1+R'_d) \qquad \text{(see Chapter IV).}$$

$$\approx -0.033\,(1-k)$$

and $R'_e \approx 0.01$ for the enriched blending material

$$\Delta c_e \approx -0.01\,(1-k)$$

From Equation (25)

$$\Delta c_m = -f \times 0.033\,(1-k) + (1-f) \times 0.01\,(1-k)$$

$$= -0.028f\,(1-k) + 0.01\,(1-k)$$

$$= -(1-k)\,(0.023\,f + 0.01)$$

From Equation (28), the associated error R_m is given by

$$\Delta R_m = -\ \Delta c_m\,(1+R_m)^2$$

$$= (1+R_m)^2\,(1-k)\,(0.023\,f + 0.01)$$

$$\frac{\Delta R_m}{R_m} = \frac{(1+R_m)^2}{R_m}\,(1-k)\,(0.023\,f + 0.01)$$

For the depleted blend where f is chosen to be ≈ 0.2 to give $R_m \approx 4$ we can write

$$\frac{\Delta R_m}{R_m} = \frac{25}{4} \times 0.0146 \, (1 - k)$$

$$= 0.091 \, (1 - k)$$

Comparison of this value with Equation (26) indicates that the error in the calculated isotopic ratio of the standard mixture is about ten per cent. of the instrumental discrimination error in the approximate determination of the quantities C_d and C_e. The next step is to analyse the standards thus prepared on the mass spectrometer to be calibrated and from the measured isotopic ratios R_m', an estimate of the constant k is made. This is used to adjust the values of R_d' and R_e' needed in the calculation of C_d and C_e so that C_m is determined with greater accuracy. This procedure could be repeated as many times as required by the accuracy needed for the experiment.

APPENDIX B2

Boron Standards

From the theory given in the text,

$$R = kR'$$

$$C = \frac{1}{1 + R'},$$

where the parameters are as defined earlier.

Consider the two boron standards A and B used in this work. The B^{10} concentrations given in the two standards A and B by calculation, and measurement are respectively,

$$C_A = \frac{1}{1 + R_A} \tag{30}$$

$$C_B = \frac{1}{1 + R_B} \tag{31}$$

$$C'_A = \frac{1}{1 + R'_B} \tag{32}$$

$$C'_B = \frac{1}{1 + R'_B} \tag{33}$$

Equations (27) and (28) can be written as

$$C_A = \frac{1}{1 + kR'_A}, \tag{30a}$$

$$C_B = \frac{1}{1 + kR'_B} \tag{31a}$$

The difference in the measured B^{10} concentration in the two standards is given by the difference between (32) and (33)

$$C_A' - C_B' = \Delta C_{measured}$$

$$\Delta C_{measured} = \frac{1}{1 + R_A'} - \frac{1}{1 + R_B'} \qquad (34)$$

and in the calculated B^{10} concentration it is the difference between (30a) and (31a). Therefore

$$\Delta C_{calculated} = \frac{1}{1 + kR_A'} - \frac{1}{1 + kR_B'} \qquad (35)$$

Now, k is generally ≈ 1

Therefore, put $k = 1 + \epsilon$ where $\epsilon << 1$ and in this work, particularly

$$R_A' \approx R_B' \approx 4 \quad \text{(see results Chapter VI)}$$

Equation (35) can be written as

$$\Delta C_{calculated} = \frac{1}{1 + (1 + \epsilon)\, R_A'} - \frac{1}{1 + (1 + \epsilon)\, R_B'}$$

$$\approx \frac{1}{1+R_A'}\left(1 - \frac{\epsilon R_A'}{1+R_A'}\right) - \frac{1}{1+R_B'}\left(1 - \frac{\epsilon R_B'}{1 + R_B'}\right)$$

$$\approx \frac{1}{1 + R_A'} - \frac{1}{1 + R_B'}$$

Therefore $\Delta C_{calculated} \approx \Delta C_{measured}$.

APPENDIX C

Minerals from Borax Consolidated Limited

Country of Origin	Mineral	Location
Argentina	Ulexite-cotton ball	Sijes, Salar Pastos Grandes Area, Salta Province.
Argentina	Hydroboracite	Sijes, Salar Pastos Grandes Area, Salta Province.
Argentina	Colemanite with Inyoite	Sijes, Salar Paston Grandes Area, Salta Province.
Argentina	Tincal (diamond drill core)	Tincalayu Mine, Salar Hombre Muerto, Salta Province.
Argentina	Inderite	------------
Turkey	Inyoite	Acep Mine, Bigardic District, Balikesir Vilayet.
Turkey	Pandermite	Borax Mine, Sultan Cayir, Susurluk District, Balikesir Vilayet.
Turkey	Colemanite	Guveni Mine, Bigadic District, Balikesir Vilayet.
Turkey	Ulexite	Salmanli Mine, Bigardic District, Balikesir Vilayet.
Turkey	Datolite	Canakkale.
New Caledonia	Datolite	-------------
Kashmir	Tincal	-------------

APPENDIX D

Preparation of Samples

Minerals	Solvent	Preparation Method	Yield %
1. Argentine Tincal	Water	Chemical	80
2. Argentine Tincal	Water	Resin	90
3. Argentine Ulexite	Hydrochloric acid	Resin	93
4. Argentine Colemanite	Hydrochloric acid	Resin	90
5. Argentine Hydroborate	Hydrochloric acid	Resin	90
6. Argentine Inderite	Hydrochloric acid	Resin	88
7. Turkey Inyoite	Hydrochloric acid	Resin	82
8. Turkey Colemanite	Hydrochloric acid	Resin	91
9. Turkey Pandermite	Hydrochloric acid	Chemical	90
10. Turkey Datolite	Fusion	Resin	72
11. Turkey Ulexite	Hydrochloric acid	Resin	88
12. Japan Sassolite	Water	Chemical	88
13. Japan Sassolite	Water	Resin	95
14. Kashmir Tincal	Water	Chemical	80
15. Kashmir Tincal	Water	Resin	91
16. New Caledonia Datolite	Fusion	Resin	81
17. Korea Kotoite	Hydrochloric acid	Resin	85

APPENDIX E - $\frac{B^{11}}{B^{10}}$ ratio.

Sample	Thode et al.	Shiuttse	McMullen et al.	Finley et al.	Shima
Borax, Searles Lake, U.S.A.	4.370 ± 0.005				
Borax, Searles Lake (lower part)			4.020 ± 0.008		
Borax, Searles Lake (upper part)			4.020 ± 0.008		
Borax, Searles Lake					(4.248 ± 0.022 (4.240 ± 0.008
Tincal, Searles Lake (75 ft.)			4.048 ± 0.012		
Tincal, Searles Lake (30 ft.)			4.052 ± 0.012		
Tincal, Tibet	4.326 ± 0.004				4.010 ± 0.010
Colemanite, Death Valley U.S.A.				3.995 ± 0.008	
Colemanite, Turkey				3.995 ± 0.008	
Ulexite, Argentina	4.270 ± 0.001			3.922 ± 0.008	4.002 ± 0.009
Howlite, Sun Valley, U.S.A.				3.962 ± 0.008	
Inyoite, Russia				4.141 ± 0.008	
Szaibelyite, Douglas, Canada				4.064 ± 0.008	
Hambergite, Imalo, Madagascar				4.026 ± 0.008	
Stassfurtite, Germany	4.422 ± 0.004				
Boric Acid, Italy	(4.416 ± 0.004 (4.411 ± 0.003				

APPENDIX E - $\frac{B^{11}}{B^{10}}$ ratio (continued).

Sample	Thode et al.	Shiuttse	McMullen et al.	Finley et al.	Shima
Pandermite, Turkey	4.297 ± 0.01				
Sultantchair, Turkey	4.291 ± 0.004				
Rasorite, California, U.S.A.	4.322 ± 0.008				
Amorphous, boron Kal'baum, Italy		4.106			
Crystalline, boron Shering-Kal'taum		4.100			
Boric oxide, Shering-Kal'taum		4.112			
Boron carbide, ?		4.238			
Borax, Glavkhimreaktiv SSR		4.232			
Boric Oxide, Glavkhimreaktiv SSR		4.240			
Boric Oxide, Glavkhimreaktiv SSR		4.308			
Boric Oxide, Glavkhimreaktiv SSR		4.241			
Boric Oxide, Glavkhimreaktiv SSR		4.461			

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