

CHEMICAL ANALYSIS OF SOLID STATE MATERIALS BY MASS SPECTROMETRY

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Introduction

The mass spectrometer is a relatively old and established tool of analytical chemistry. Normally one thinks of the mass spectrometer only in terms of the analysis of gaseous species. However, recently the usefulness of the mass spectrometer has been extended to analysis of any materials regardless of their physical state. Therefore, in the very near future, advances will be seen in mass spectrometric analysis in at least three areas of work: (1) Qualitative and quantitative analysis of ultra pure materials such as conductors, semiconductors and insulators; (2) Structural studies on high molecular weight materials; and (3) Reliable identification of unknown materials by accurate measurement of molecular weight. Investigations in these areas had been severely limited because of inadequate commercial instrumentation, but instrumentation is now available to investigate the areas mentioned due to support by the Directorate of Materials and Processes of the development of a solid source, Mattauch type mass spectrometer by Consolidated Electrodynamics Corporation. This instrument and its uses will be discussed in this paper.

The Mattauch Mass Spectrometer

Mass Resolving System and Ion Path

The overall plan of the mass resolving system is seen in figure 1. Here we have an object slit behind which is situated the rf spark source; then a radial electric field which produces no mass dispersion, but which introduces velocity dispersion that closely compensates the velocity dispersion of the magnetic field that follows. The electric and magnetic fields act together to produce a mass spectrum in which the displacement of the ions is proportional to the square root of the mass. The radius of curvature in the electric sector is 25.188 inches, and in the magnetic sector the radius of curvature varies between 2 and 12 inches depending on the mass of the ion. The mass range of 36 to 1 on the photographic plate then allows coverage of all the solids in the periodic table in a single exposure. Much higher masses may be detected by changing the electrical and magnetic fields.

The next several figures are shown to acquaint the reader with the general appearance of the instrument and differences between this prototype instrument and the commercial model that is now being produced by Consolidated Electrodynamics Corporation.*

Figure 2 shows an end view of the instrument with the source housing in the foreground, the electric field sector further back, and the magnetic field and photographic plate holder in the background. Figure 3 shows the mass resolution system without gage and electronic panels, and figure 4, a close-up of the spark source. The knurled knobs on the source

* Consolidated Electrodynamics Corporation, 360 North Sierra Madre Villa, Pasadena, California

permit movement of either one or both electrodes during the sparking process. One degree of freedom that is not available in our instrument is movement of both electrodes back and forth in addition to the degrees of freedom, up and down and side to side. This would be very desirable since the ionization efficiency is dependent on the position of the electrodes in front of the slit system. Another near necessity which should be built into the source housing but is not in our instrument, is a high intensity light source for positioning electrodes preparatory to sparking. Figure 5 shows the spark source sample holder. Visible are the pin vise-type holders in which two pieces of the material to be analyzed are placed. These holders best accommodate flat samples about 1/16-inch thick and 1/4 to 1/2-inch long. A very desirable addition would be a set of claw-type holders which would allow the use of more irregular samples. Many facts of the instrument itself could be discussed further, but this short review will have to suffice.

Applications

Varied types of analyses have been made on this instrument, principally of the refractory metals, niobium, and tungsten. Although quantitative and semi-quantitative analyses have been accomplished with this instrument, it has been used mostly in qualitative analysis, where it is possible to identify on one spectrum all of the stable elements in the periodic chart. Further, every element has, within an order of magnitude, the same sensitivity, which makes comparison of one element with another more meaningful than in emission spectroscopy.

Such a survey spectrum of tungsten is shown in figure 6. Here, the photographic plate was shot in three sections, the top portion covering mass 7 through 41, the center portion covering mass 42 through 114, and the bottom portion covering mass 115 through 202. The tungsten is very impure even though prepared carefully from supposedly ultra pure tungsten hexachloride. Notable in the spectrum are lines due to multiply ionized tungsten.

To give an idea of the number of impurities to be seen in one tungsten spectrum, figure 7 was prepared with some thirty-two elements and compounds present in a sample of commercial tungsten rod. Lines due to compounds such as thorium dioxide and monoxide are seen, in addition to lines due to elemental species present in the sample. The appearance of ionized masses due to compounds is considered a distinct advantage, both in the analysis of purposely added dispersed second phases and in the detection of trace and minor impurities. In another tungsten sample containing 2.0 percent thoria, the mass spectrometric analysis gave the following amounts of thorium containing materials: Thorium, 1.90 percent, ThO, 0.10 percent, giving a total of 2.01 percent of elemental thorium and thorium compounds. Other analyses of dispersed second phases in tungsten which were investigated were B_4C , TaC, and ZrO_2 . Analytical results from these compounds were satisfactory, but in general not exceptionally accurate. However, it must be pointed out that these samples were not standards, but only wet chemically analyzed tungsten. More interesting perhaps, were inter-element effects occurring between the matrix, and additives with other elements, such as the formation of thorium carbides, tungsten oxides, and tungsten carbides. Figure 8 is a densitometer trace of a section of tungsten spectrum between mass 218 and 180 and shows the presence of WC, WC_2 , WO, and WO_2 . Note that oxides and carbides are seen for each major isotope of tungsten. Also the very broad lines between mass 180 and 186 which are the parent (plus one charged) tungsten ions. Even though this is a very strong exposure, minor components can be detected one mass unit from the parent tungsten masses. Also no trace is seen of any

mercury isotopes in this spectrum. We feel that since this is a mercury pumped system, it shows the effectiveness of the trapping design in the instrument.

One question that arises from data such as this is: did the tungsten originally contain oxides and carbides, or were these compounds formed in the vapor state between the electrodes? From the data taken thus far it appears that the answer to both questions is "yes" but, that most compounds seen are formed in the spark. To show the extent to which vapor state reactions do occur, electrodes of two different materials were sparked together. One such experiment used tungsten in one electrode and graphite in the other. Products which were identified were WC, WC₂, WC₃, WC₄, WC₅, WC₆, and WC₇. No tungsten oxides heavier than WO₂ have yet been identified, x-ray diffraction patterns taken of material sputtered in the source from the tungsten-carbon run showed the formation of one or more compounds which could not be identified.

Many such reactions are seen also when the same metal or compound is in both electrodes. Figure 9, for instance, shows some of the many compounds and associated elements formed in the spark of silicon carbide. Mass numbers are shown with the products to point out the formation of mixed dimers, trimers, etc. of isotopes of silicon. Many other mass numbers would be visible if mixed compounds of C¹³ containing products were visible in the spectrum. Abundances of some compounds were very small, so that every isotopic combination was not observed.

From the earlier tungsten spectrum and from the many products shown in figure 9, it becomes evident that high resolution is an absolute necessity in this sort of an instrument. Figure 10 shows a slow densitometer trace of a doublet at mass sixty due to Nickel 60 and Tungsten 180 having a plus three charge. The mass difference in this case is rather large, but it does serve to illustrate the sort of resolution possible using this instrument. The resolution of course could be made even better if a loss of sensitivity could be tolerated.

One set of elements in which resolution is not good enough to do isotope abundance measurements is the rare earth series. Figure 11 shows a densitometer scan of a run of Spex Industries' rare earth mix, which contains each of the rare earths. From this data we found that there are a number of rare earth doublets which are not resolved; this trace was run much too fast to detect resolution, if it were possible. Except for isotope abundance measurements, the mass spectrometer gave good results of rare earth analysis, and as can easily be seen from this trace which shows all rare earth lines, the spectrum is much simpler than that seen in emission spectroscopy. Just to show a comparison, figure 12 of an emission plate was prepared showing the emission spectrum of the same rare earth mix used in the earlier figure. The spectrum immediately below the rare earth mix is Yttrium.

The graphite matrix which is frequently used in our Laboratory to contain inorganic compounds for solid source mass spectrometric work has provided interesting data all its own. An interesting phenomenon observed in graphite mass spectra is "clumping" or the association of more than one carbon atom in ionized states. When a heavy exposure is made using only graphite electrodes as a source, a series of doublets is seen across the plate beginning at C₁ (which is one C¹² atom; or on C¹³ atom) and continuing to C₂₈ or twenty-eight carbon atoms. Probably more associations in graphite are possible, but

C_{28} is the largest mass seen thus far. It is interesting to note that the literature shows C_{28} as the top figure, also in work done by Dornenburg and Hintenberger.* The exact structure of these associated ions is not clear, but it appears that they are clumps, fragments, or chains of C_{12} atoms bound together. The doublet of "mass plus one" seen with the C^{12} atoms is about 1/100 as strong as the other peak and is ascribed to one C^{13} atom occurring in the carbon polymer, chain, or fragment. A plot of the intensity of these associated groupings agrees fairly well with data of Dornenburg and Hintenberger. Figure 13 shows both sets of data. Although both curves follow the same general pattern, several differences are evident. The most important difference in data is at C_3 where Dornenburg and Hintenberger show C_3 to be stronger than C_2 . Our data indicates that C_2 is much stronger than C_3 , so strong in fact that reversal occurred on the spectrum at this point and the intensity could not be measured. Also there is a slight difference at C_{18} which we measure as the high point in that region while the referenced authors show C_{19} to be stronger than C_{18} . Other types of carbon and carbon containing compounds are currently being studied to see if abundances are different in carbons and carbon compounds other than graphite. Interesting work of this sort is being done on the analysis of coal in the spark source in cooperation with the U.S. Bureau of Mines. Results of this work will be reported at a later time by A.G. Sharkey, Jr. of the Bureau of Mines, Pittsburgh, Pennsylvania.

In addition to investigations of association in graphite and hydrocarbons in coal, many different kinds of organics have been ionized in the spark source.

The technique used most for running organic materials in the spark source is as follows: graphite rods 1/8-inch diameter, spectrographic purity are drilled to a depth of about 1/2-inch with a No. 60 to No. 70 twist drill. The organic is then packed into the depression. Sometimes both electrodes contain samples and are pointed at the sparking rod. Usually only one electrode contains a sample and is left flat with a pointed counter electrode, just as in emission spectroscopy.

Another technique that is used and is more reproducible is mixing the sample with a good conductor such as silver, pressing it into a pellet, and using the pellet slivers as electrodes. Agreement between these two techniques is fairly good; but with the pelleting technique, frequently the organic compound and metal react in the spark to form a salt which adds a degree of complexity.

Various organic compounds have been run using one or the other of the techniques mentioned. In no system run thus far have we seen complete fractionation of the compound into only its elemental constituents. Many more relatively high mass fragments are formed than were originally predicted. Masses as high as 228 have been observed in organics, this particular one occurring in Ribose Nucleic acid. Other types of compounds which were ionized in the spark source are steriods, metallic salts, and urea adducts. Specific data will not be given on these compounds, but could be made available later upon request.

* Von E. Dornenburg and H. Hintenberger, Z. Naturforschg. 14a, 765-767 (1959)

The specific family of organics that will be described is the amino acid. Figure 14 shows most of the spectrum of an amino acid salt, L-lysine hydrochloride. As can be seen, many masses are present beginning at mass twelve and continuing well into the mass eighty region. Many doublets are present which probably cannot be seen in this figure. The total number of lines seen on the complete plate of L-lysine HCl was 101.

Figure 15 shows a plot of mass lines present in glycine, valine, phenyl, alanine, and L-lysine HCl along with masses from the matrix material, graphite. Since so many lines were present, including doublets and triplets, individual lines are not shown in this figure and intensities are not indicated. Many lines are present in each of the amino acids with only two similar gaps occurring in the spectra at about mass 19 to 23 and mass 31 to 35. Also it is interesting to note that glycine spectra shows many masses well above its molecular weight of 75, indicating many molecular recombinations, while valine and phenyl alanine show only one mass unit higher than the parent molecular weight, and no masses are seen in the lysine salt that even approach the parent molecular weight.

One of the most interesting results of these cracking patterns is the occurrence of the parent mass of the molecule and in addition, a line appears that is one mass unit heavier which apparently is due to the addition of a hydrogen to the amino group on the molecule. Usually the parent mass plus one is somewhat stronger than the line due to the parent mass, and in some spectra, only the parent plus one is seen. In all salts of amino acids investigated thus far, such as copper valine and L-lysine HCl, no parent masses of the salt are seen, and no parent-plus-one masses are seen. A more complete study on degradation of organic solids will be carried out upon the installation of a crucible source on the double focusing mass spectrometer. In this study we plan to compare thermal degradation of amino acids with effects seen in the spark source.

Within the next several months, the mass spectrometer will be equipped to analyze materials regardless of their physical state. The spark source, Knudsen cell capable of 2000°C, and the conventional gas source will be available. In addition, a Z-axis lens will be installed for focusing the ion beam which should increase the sensitivity by at least a factor of five.

This has been a quick survey of the various uses to which our instrument has been put. Other results on materials such as semiconductors have been obtained. Noted have been many advantages and some disadvantages of the system; generally, the advantages far outweigh the disadvantages.

Research Expectation in Mass Spectroscopy

At the beginning of this paper, it was mentioned that there appear to be several important areas of research in which mass spectroscopy should in the near future contribute heavily. Instrumentation such as that described, along with experimental models and commercial equipment* manufactured in other countries, will be used increasingly in analytical applications, structural studies, and measurement of molecular weights. Specifically, it is felt that a great deal will be done in the area of thermodynamics by use of the mass spectrometer equipped with crucible sources capable of temperatures up to 3000°K. This is an area in which both the Time-of-Flight Mass Spectrometer and the

* Associated Electrical Industries, Manchester 17, Great Britain

Contrails

conventional mass spectrometer should make significant contributions in the thermodynamics of both inorganic and organic systems. Studies of ion-molecule reactions and electron-molecule collisions by the mass spectrometer should provide large advances in the theory of these processes. Of course, the greatest contribution of mass spectral analysis should be in the area of solids analysis in the parts-per billion range of any material of a complete insulator. Work in this area will undoubtedly flourish, and although the solid source mass spectrometer probably will never supplant the emission spectrograph, it may eventually be the only technique sensitive enough to analyze ultra pure research materials for the space age.

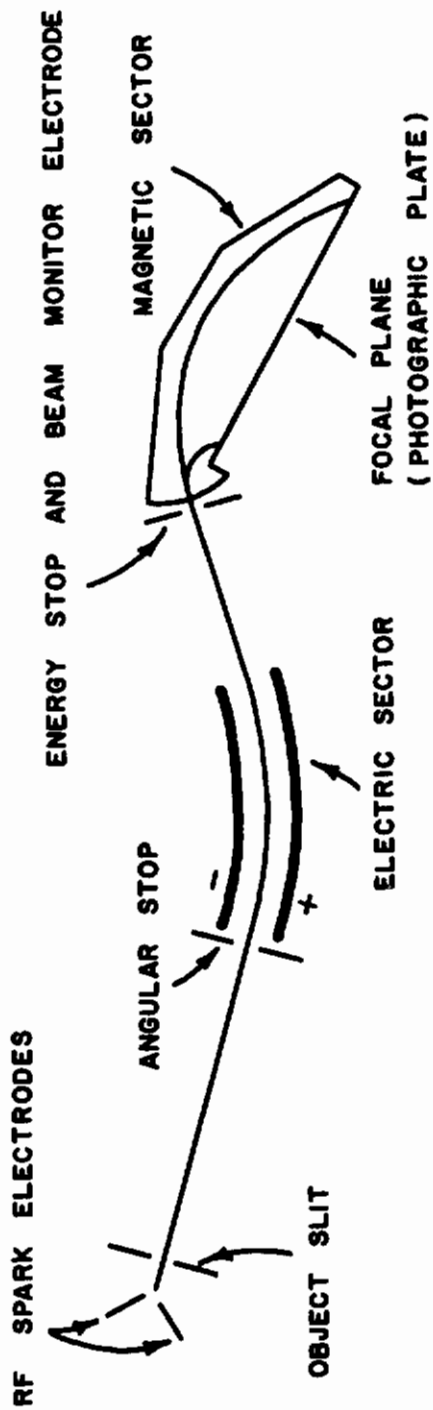


Figure 1. Schematic of Mass Resolving System

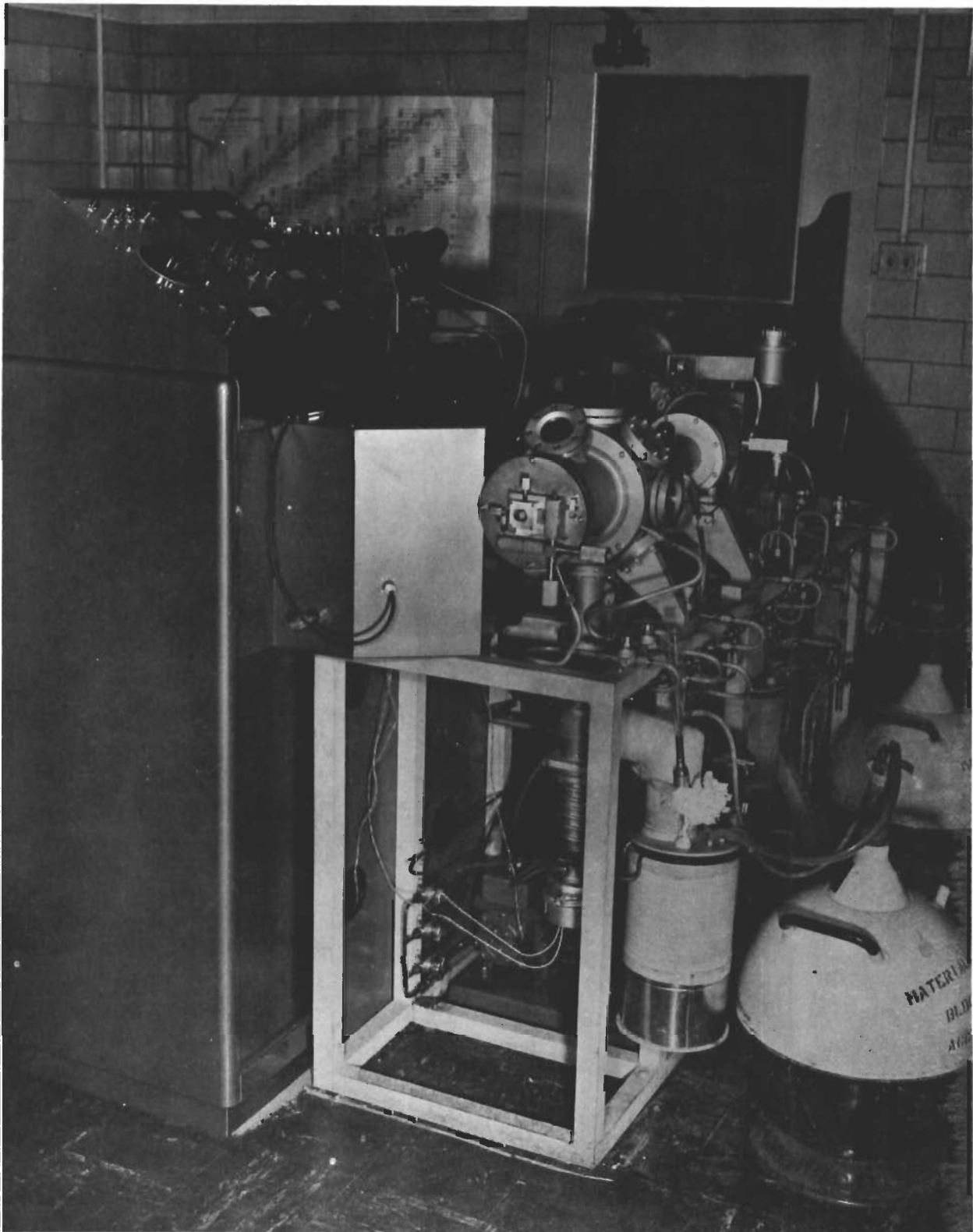


Figure 2. End View of Mass Spectrograph

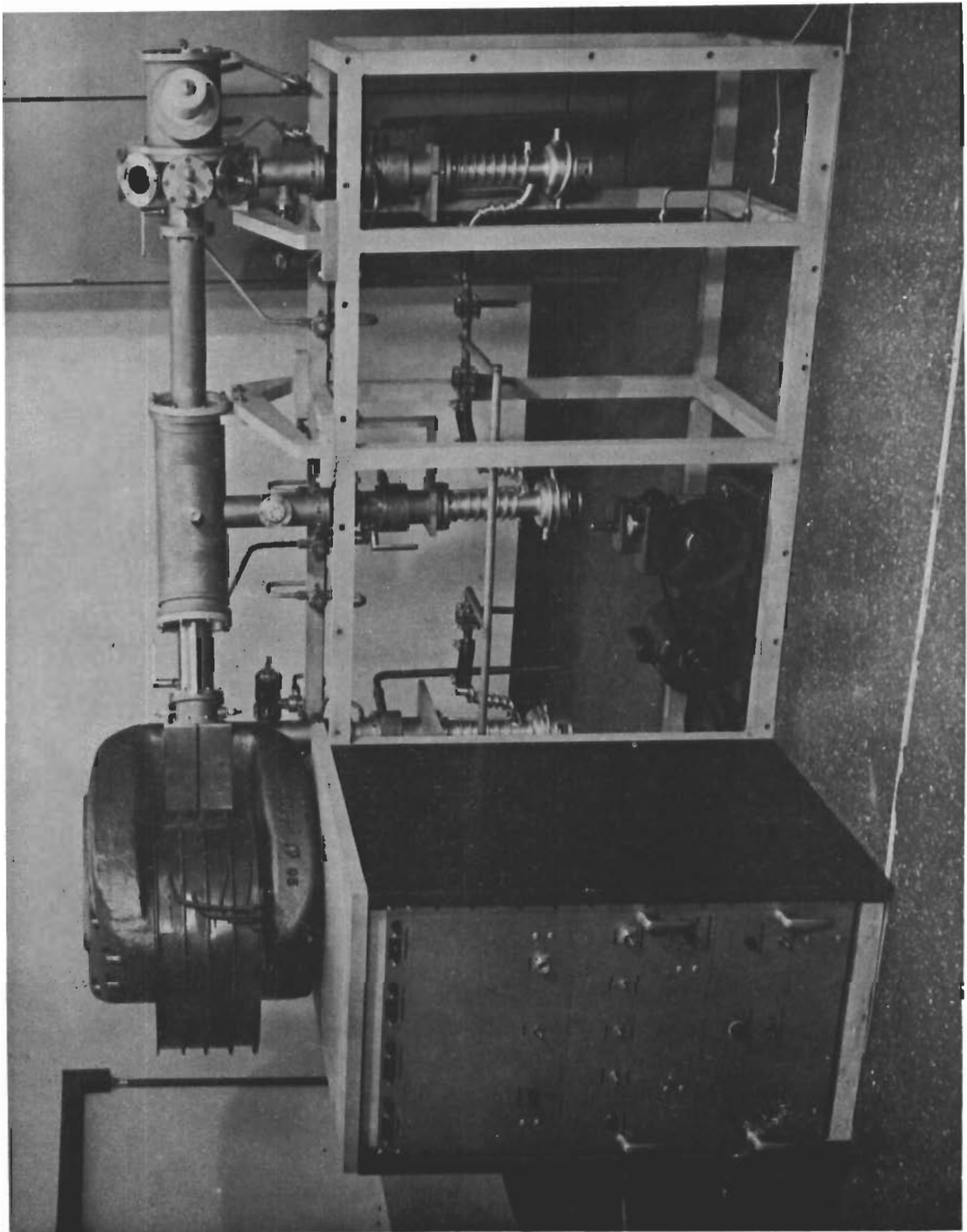


Figure 3. Mass Resolution System

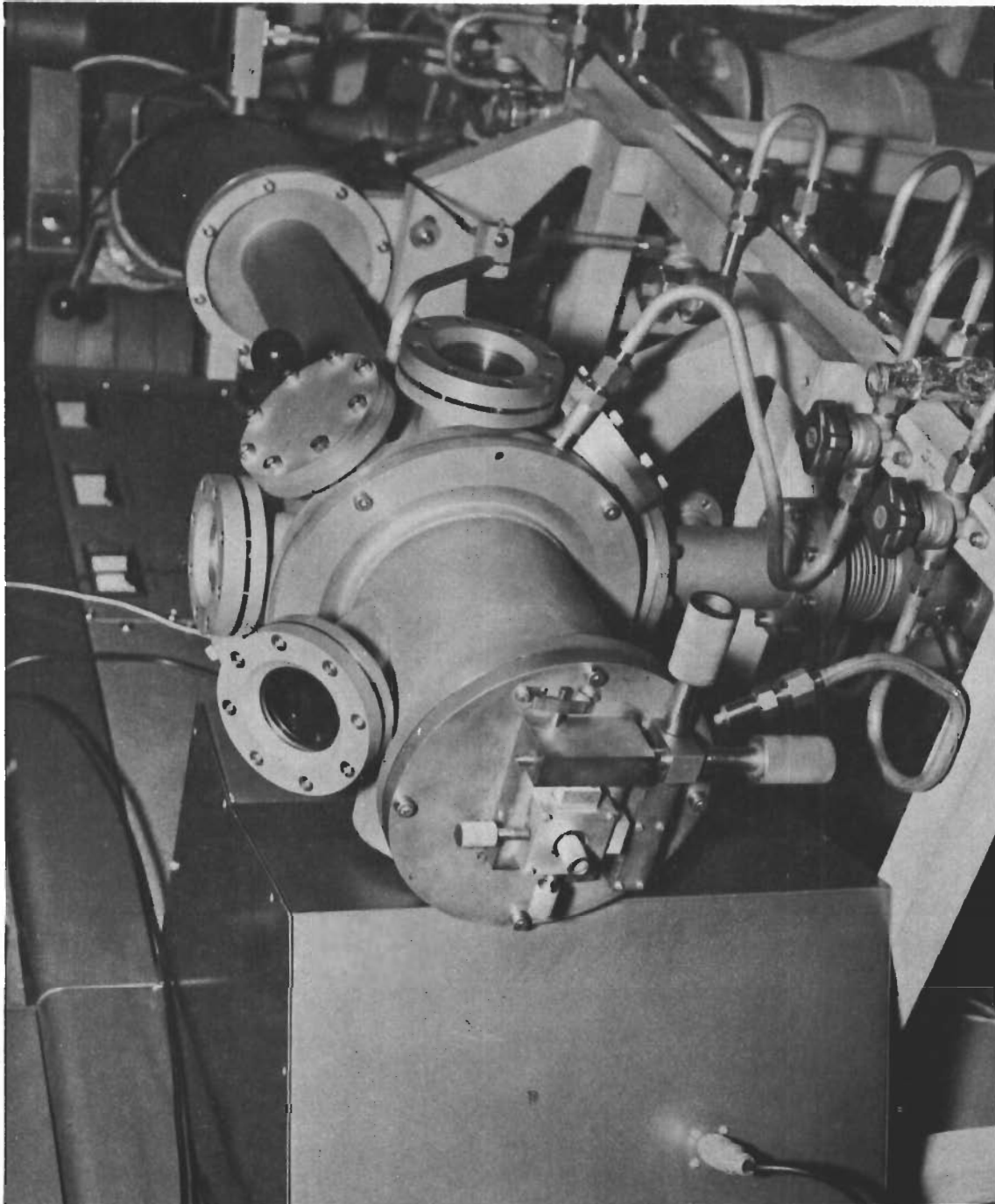


Figure 4. Closeup of Spark Source

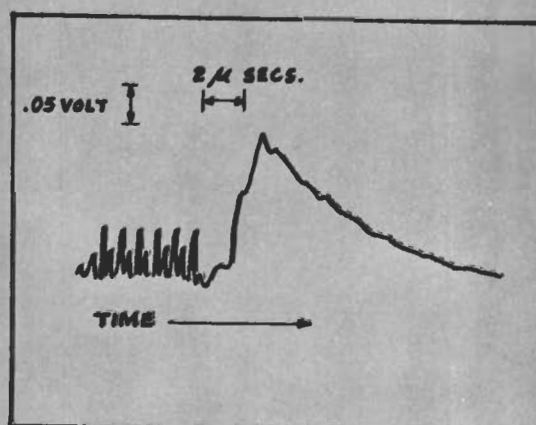
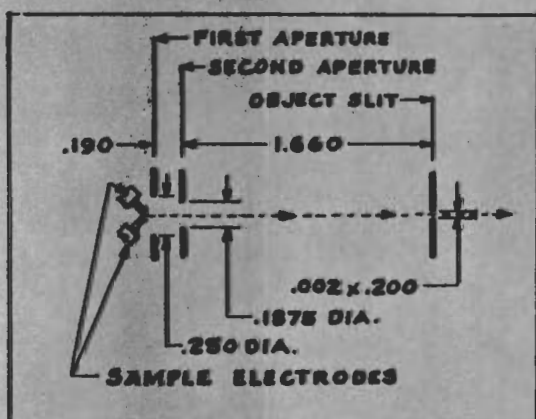
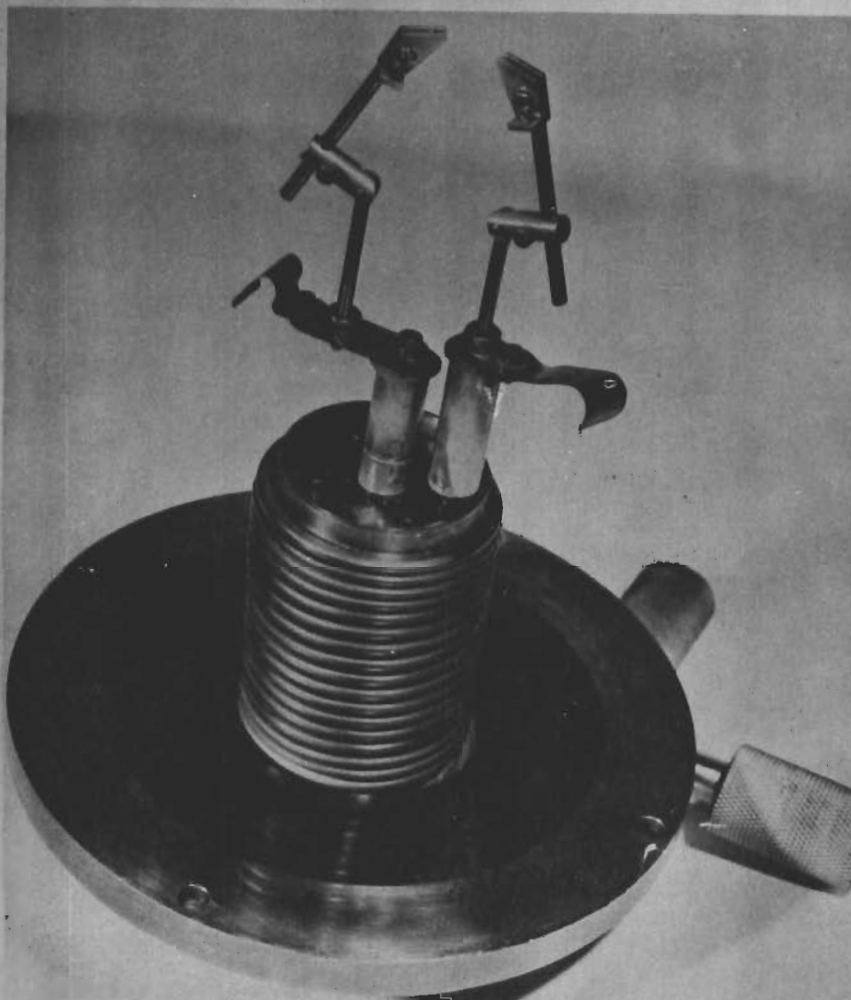


Figure 5. Spark Source Sample Holder

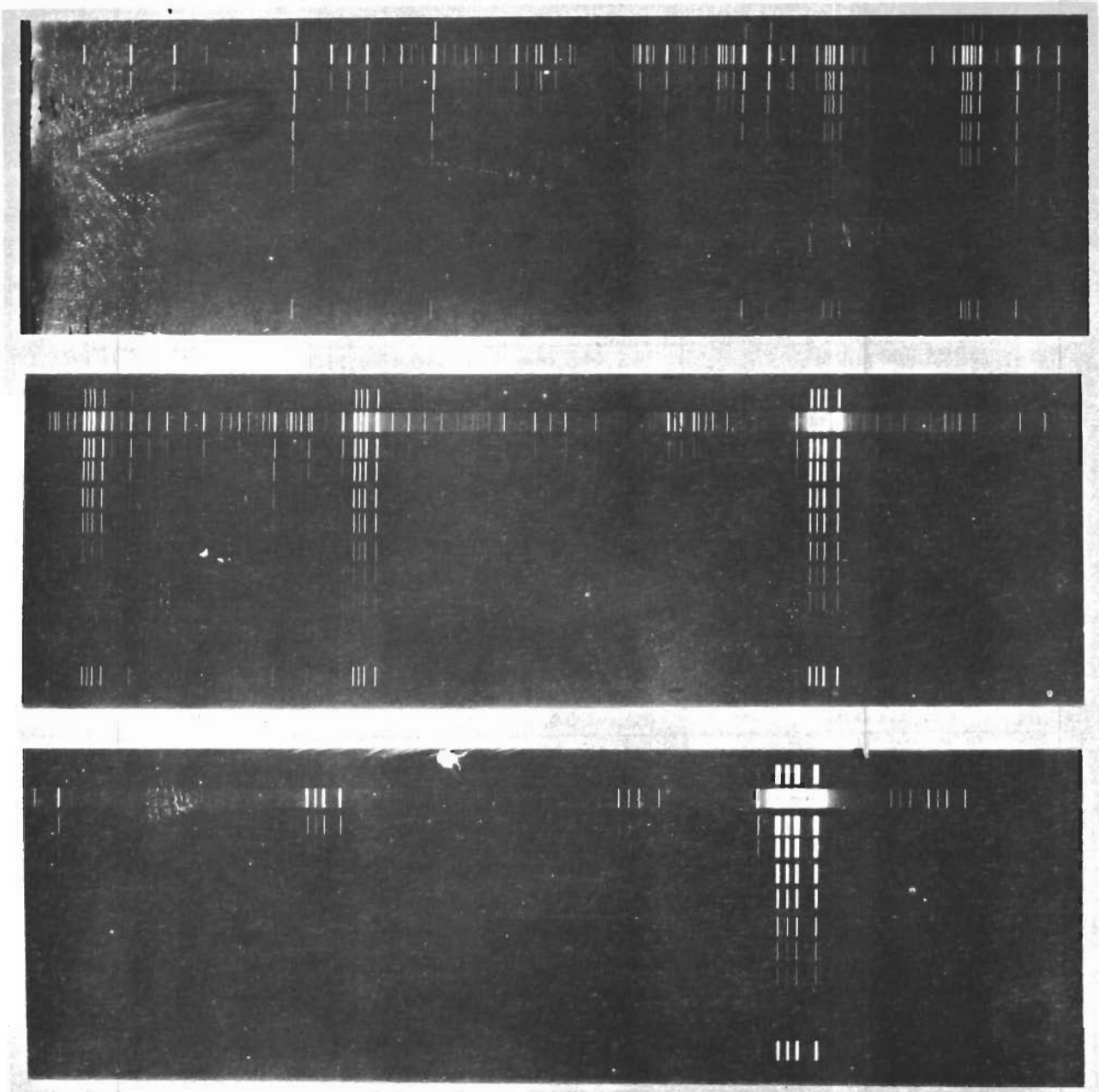


Figure 6. Survey Spectrum of Tungsten

ELEMENTS AND COMPOUNDS DETECTED IN COMMERCIAL TUNGSTEN ROD	
ELEMENT	CHARACTERISTIC LINES
THORIUM DIOXIDE	264
THORIUM MONOXIDE	248
THORIUM	232
LEAD	204,206,207,208
TUNGSTEN OXIDE	196,198,199,200,202
GOLD	197
TUNGSTEN CARBIDE	192,194,195,196,198
NEODYMIUM	142,143,144,145,146,148,150
CERIUM	136,138,140,142
TIN	112,114,115,116,117,118,119,120,122,124
INDIUM	113,115
SILVER	107,109
MOLYBDENUM	92,94,95,96,97,98,100
YTTRIUM	89
COPPER	63,65
NICKEL	58,60,61,62,64
IRON	54,56,57,58
MANGANESE	55
CHROMIUM	50,52,53,54
CALCIUM	40,42,43,44,46,48
ARGON	36,38,40
POTASSIUM	39,40,41
CHLORINE	35,37
PHOSPHORUS	31
SILICON	28,29,30
ALUMINUM	27
MAGNESIUM	24,25,26
SODIUM	23
OXYGEN	16,17,18
NITROGEN	14,15
CARBON	12,13
LITHIUM	6,7

Figure 7. Impurities in Commercial Tungsten Rod

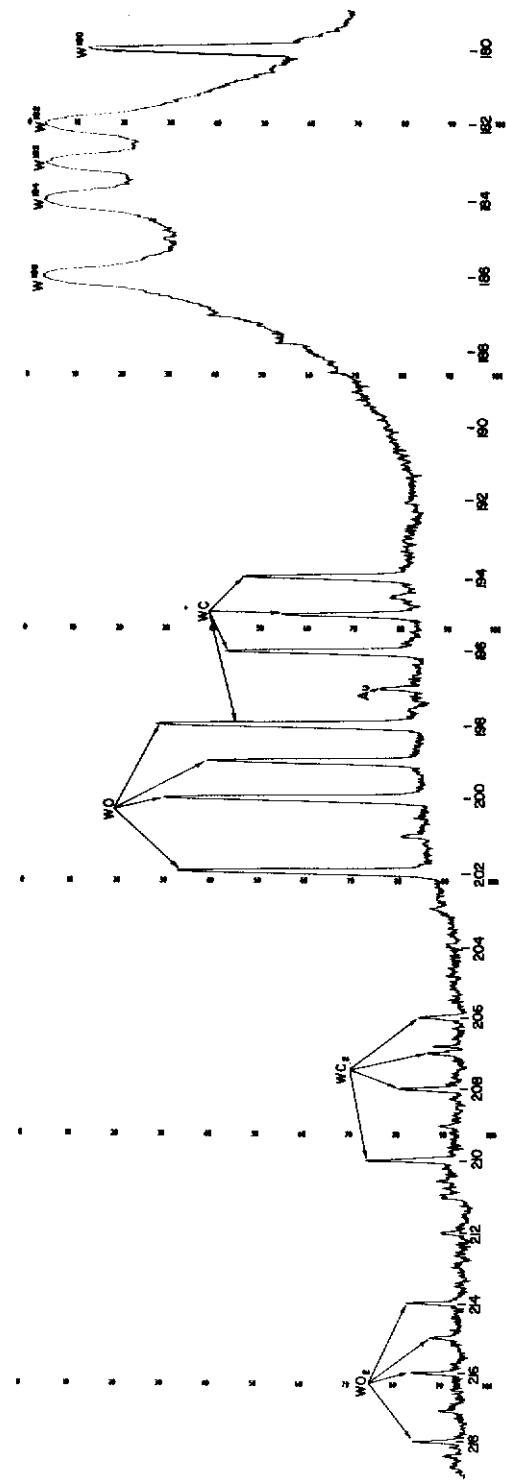


Figure 8. Densitometer Trace of Portion of Tungsten Spectrum

COMPOUND	MASS LINES VISIBLE
C	12, 13
Si	28, 29, 30
SiC	40, 41, 42
SiC ₂	52, 53, 54
Si ₂	56, 57, 58, 59, 60
SiC ₃	64, 65, 66
SiC ₄	76, 77, 78
Si ₂ C	68, 69, 70, 71, 72
Si ₂ C ₂	80, 81, 82, 83, 84
Si ₃	84, 85, 86, 87, 88, 89, 90
Si ₂ C ₃	92, 93, 94, 95, 96
Si ₃ C	96, 97, 98, 99
Si ₃ C ₂	108, 109, 110
Si ₄	112, 113, 114
Si ₄ C	124



Figure 9. Compounds Formed in SiC Spark

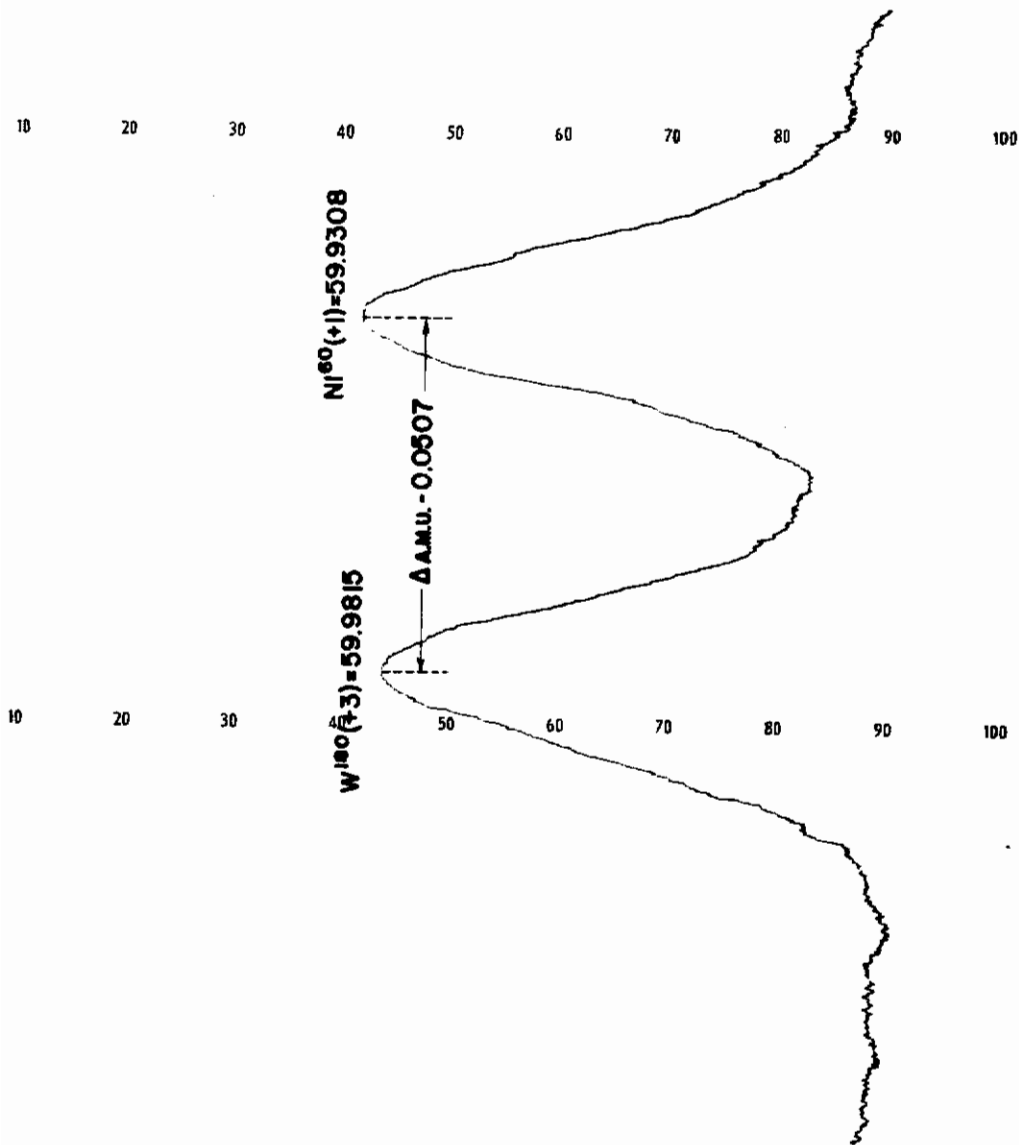


Figure 10. Densitometer Trace at Mass 60 ($W^{180} 3$ and $Ni^{60} 1$)

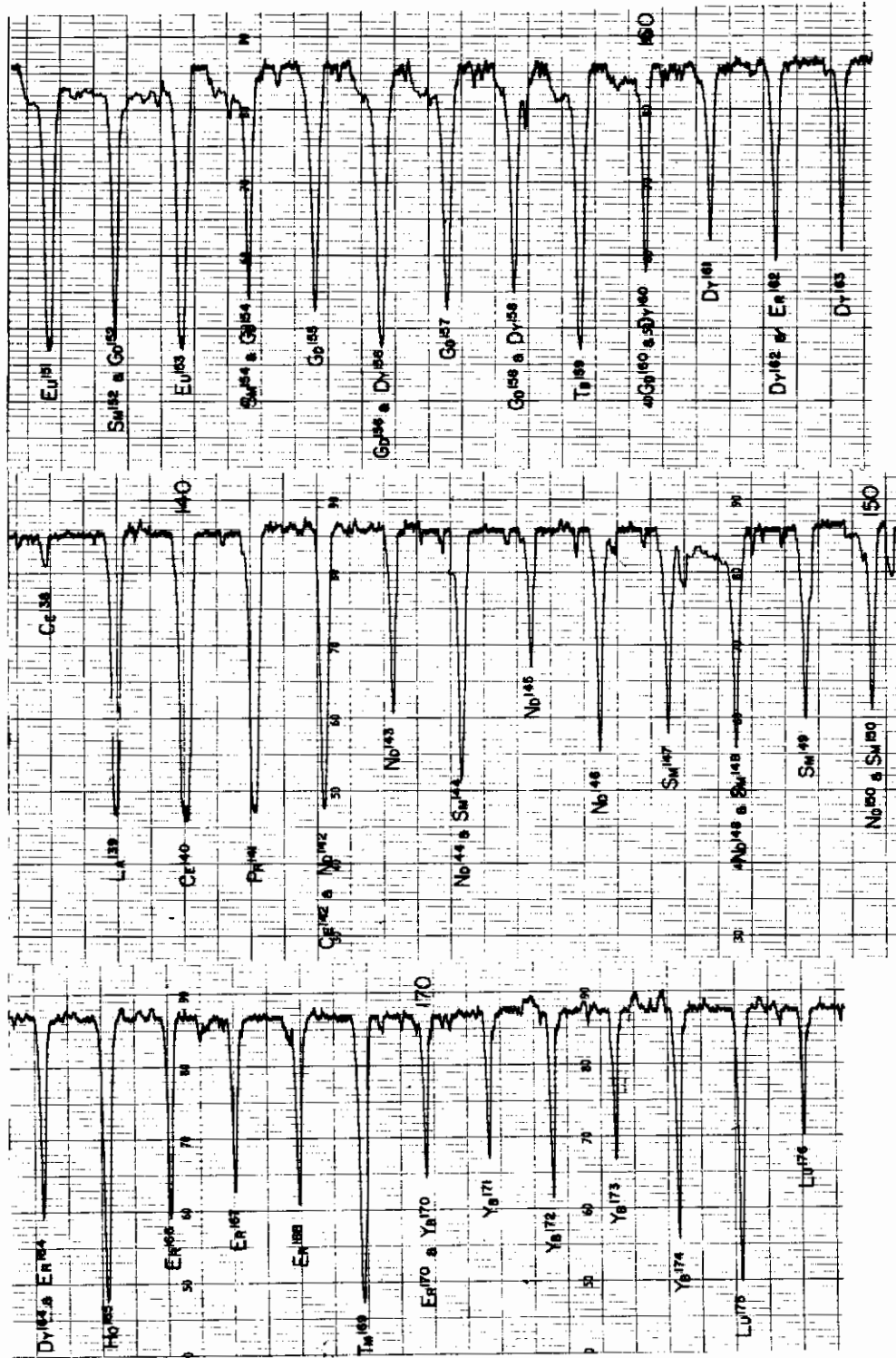


Figure 11. Densitometer Scan of Rare Earth Mix

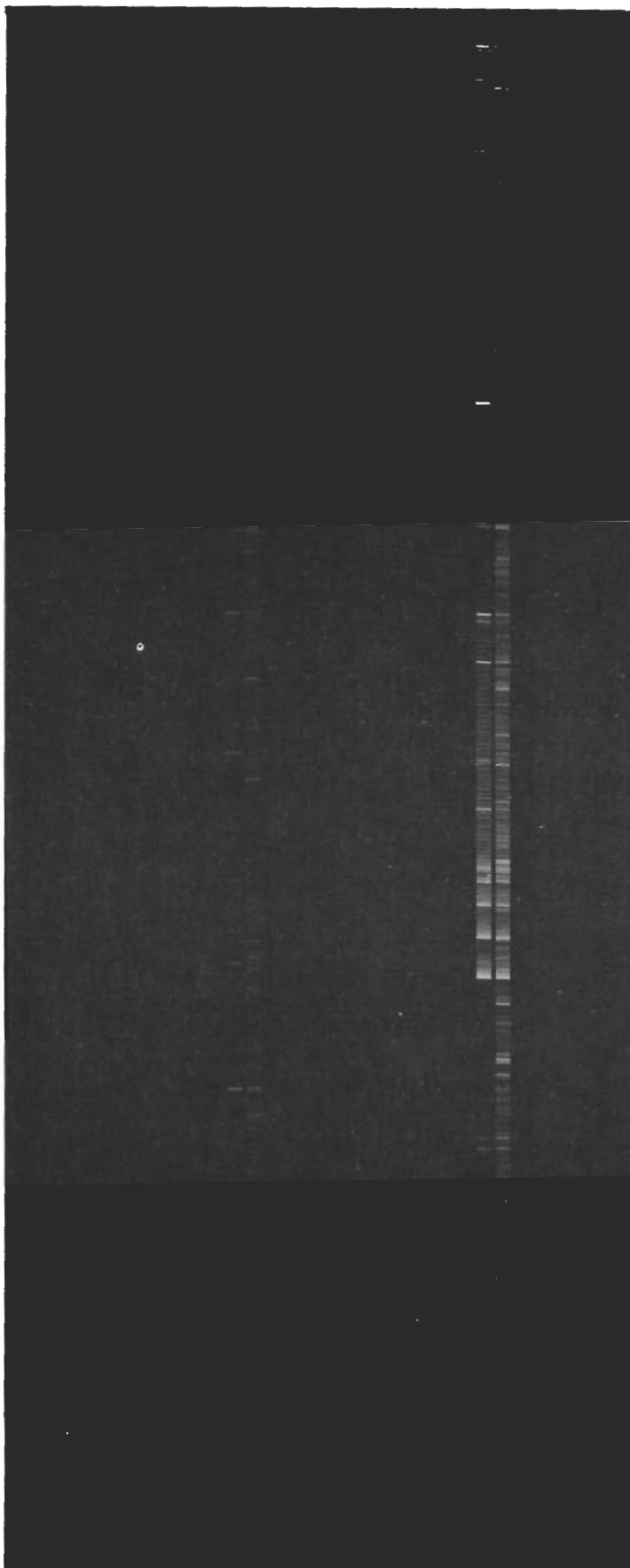


Figure 12. Emission Spectroscopic Plate of Rare Earth Mix

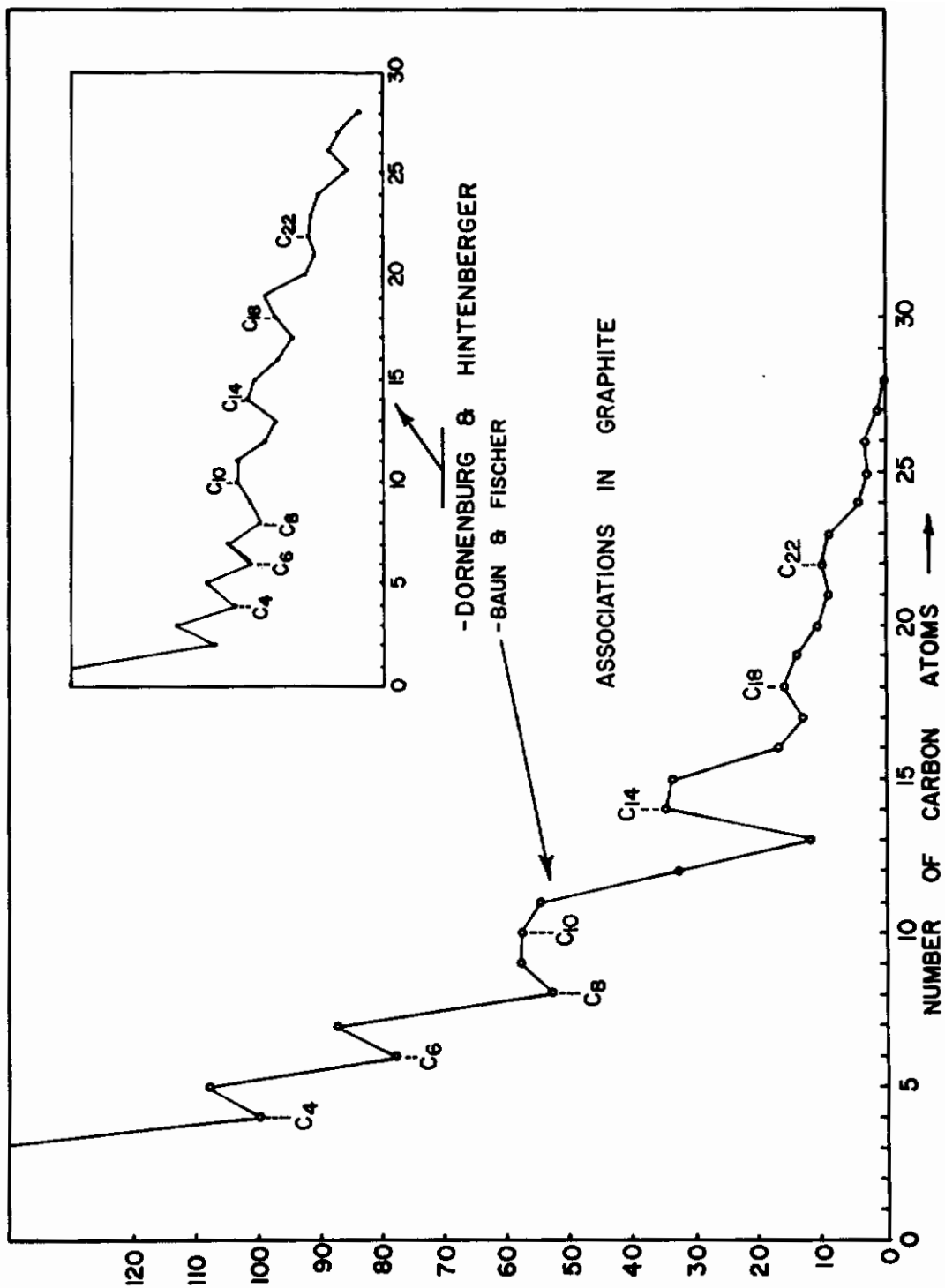


Figure 13. Association of Carbon in Graphite

L-LYSINE HCL IN GRAPHITE ELECTRODES

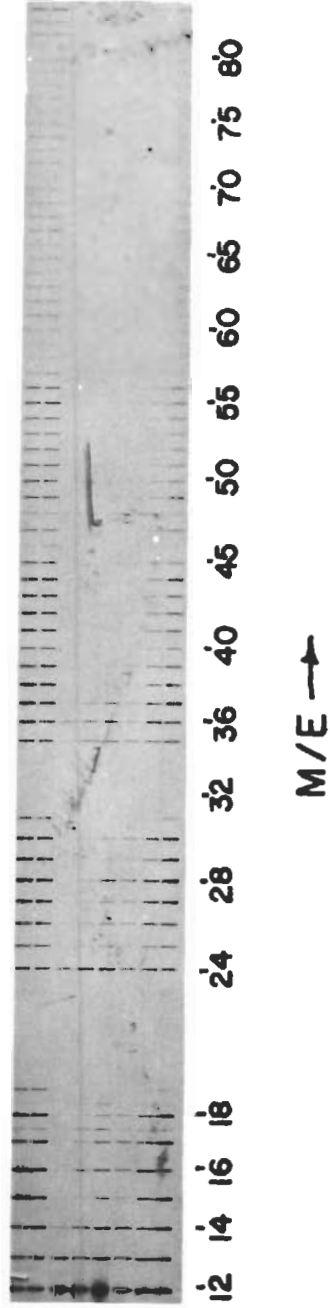


Figure 14. Mass Spectrum of L-lysine Hydrochloride

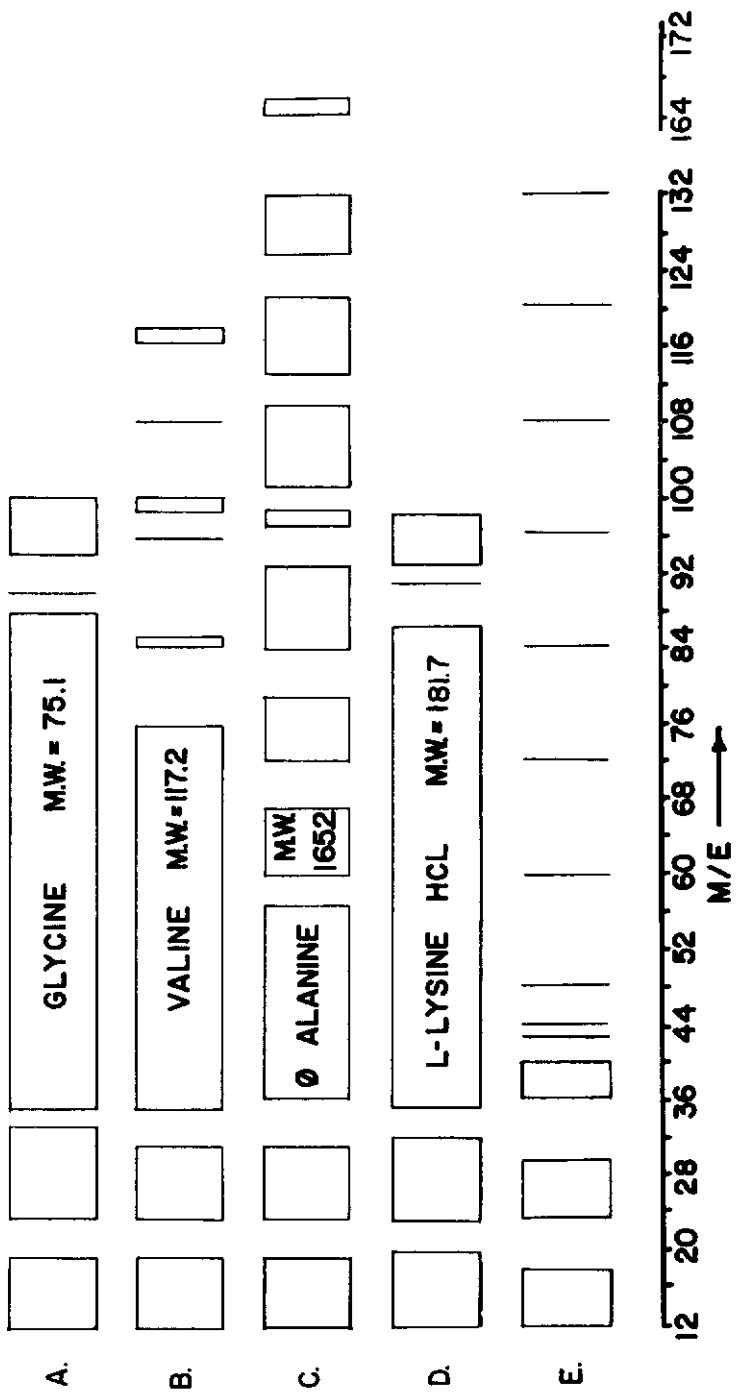


Figure 15. Masses Present in Amino Acids