MASS SPECTROMETRIC MEASUREMENTS OF ISOTOPIC MASSES AND ABUNDANCES

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1. Introduction to Mass Spectrometry

(1) Historical development

A. Earlier stage: In England, F. W. Aston invented the first mass spectrograph in 1911 using photographic plate for the ion detection. The mass resolution of that instrument was only about 130. Second mass spectrograph developed by Aston for the nuclear mass measurement had achieved mass resolution about five times of the first one. With this instrument, Aston had plotted the first packing fraction curve and found the variation of packing fraction related to the stability of nuclei. In the same time, A. J. Dempster in the United States had designed a mass spectrometer for the isotopic abundance measurement using gold leaf electroscope to detect ion current down to 10^{-13} A.

B. Industrial application of mass spectrometer had introduced mass spectrometry into chemistry field: Before 40's, mass spectrographs were mostly used by physics departments of universities and colleges, until petroleum industries adopted the mass spectrometry for the analysis of complex hydro-carbon compounds, it began entering the chemistry field. About the same period, in the United States the Consolidated Engineering Corporation first produced the commercial mass spectrometer for chemical analysis, and from then on mass spectrometer became one of the most important analytical instruments in many chemistry laboratories all over the world. In recent years, the success of mass spectrometer coupling with gas chromatograph or liquid chromatograph made the applications of mass spectrometer in chemistry even popular. These made people to consider that mass spectrometer is a chemical instrument.

C. Nuclear mass and isotopic abundance measurement had decided the important role of mass spectrometer in the scientific developments: During the Second World War, the development of nuclear weapon required the precision measurement of nuclear masses and isotopic abundances, which related directly and indirectly to the atomic and nuclear physics and nuclear engineering as well. The techniques of measuring the trace quantity and determining the abundance ratio by mass spectrometer had lead mass spectrometry into wide-spread fields. Today, mass spectrometer is no longer a professional instrument of physists or chemists, it became the basic instrument that must be equipped with by a modern laboratory for either nature or applied science.

(2) Types of mass spectrometers

There are so many types of mass spectrometers that we can not decribe them all in this text, we will restrict our discussion to those frequently used for the nuclear mass and isotopic abundance measurements.

A. Single magnet single focusing mass spectrometer: The Aston's first mass spectrograph belongs to this type. Ions passing through a magnetic field subject to direct focusing at different radii for different masses. There are several kinds of single magnet single focusing mass spectrometers, they are usually designated by the angle of the magnet sector, e.g. the 60°, 90°, and 180° magnet sector mass spectrometer. Schematic diagrams of the Aston's mass spectrograph, the 60° magnet sector, and the 90° magnet sector mass spectrometers are shown in Figures 1, 2, and 3 respectively.

B. Double-focusing mass spectrometer: A double-focusing mass spectrometer consists of a magnetic mass analyzer and an electrostatic energy analyzer. The magnetic field which works as a mass analyzer can be a permanent magnet or an electromagnet. The electrostatic field which works as an energy filter for ions is usually a cylindrical condenser plates. As the electrostatic field has also the focusing property for ions, the combination of it with the magnetic analyzer forms a double-focusing instrument and consequently the mass resolution is much increased. Some famous double-focusing mass spectrometers such as the Mattauch and Herzog type 1) and the Nier type 2) are shown in schematic diagrams Figures 4 and 5 respectively.

C. Multiple magnet mass spectrometer: The abundance sensitivity for a single magnet mass spectrometer is limited even it is a double-focusing one. For the measurement of high isotopic abundance ratio two or multiple magnets system is always necessary. Two 90^{o} magnets arranged in a C-type configuration, so that the deflection of the ion beam in the same direction was built by White and Collins 3) as shown in Figure 6. This tandem magnet system has achieved very high isotopic ratio measurements for many natural abundance determinations. Another two types of multiple magnets system developed by White et al 4,5) are shown schematically in Figures 7 and 8 respectively. The three-stage mass spectrometer of S-type configuration as shown in Figure 7 consists of two magnets and an electrostatic energy analyzer, it has high mass resolution and also better abundance sensitivity. The four-stage tandem magnet mass spectrometer shown in figure 8 is essentially two double-focusing mass spectrometers connected in tandem. Due to its unique configuration, the author has used it to separate super-pure isotopes and to determine reaction products of neutron reaction by the isotopic ratio measurements 6).

(3) Isotopes and mass spectrometry

One of the most important features of the mass spectrometer is its unique ability to determine isotopic abundance. Although isotope was first found from radioactive decay of uranium, but most measurements of isotopic abundances and the idenfications of natural isotopes have been done by mass spectrometers. There are more than three hundred natural isotopes in the 92 exsisting natural elements, except few monoisotopic elements, each element has at least two or more isotopes. Due to the fact that natural isotopic abundance of the element remains constant disregard the form or state of the element, and due to the development of the techniques of the isotopes separation, the mass spectrometry becomes the most powerful instrument in scientific works.

Major Characteritics of Mass Spectrometer

) Mass resolution

The mass resolution of a mass spectrometer can be determined by following two definitions:

$$R = \frac{M}{\Delta M} \cdot \frac{S}{W_{\frac{1}{2}}}$$

As shown in Figure 9, S represents the distance between two mass peaks where the major peak has nuclear mass M and the minor peak has nuclear mass $M \pm \Delta M$, and $W_{\frac{1}{2}}$ represents the full width at half maximum of the major peak.

$$R = \frac{M}{\Delta M} \cdot \frac{y}{y - x}$$

As shown in Figure 10, x and y are the near and far distances respectively from the tangent lines drown from both sides of the two mass peaks.
From these two definitions of the resolution it is evident that high resolution gives better separation of two adjacent mass peaks.

In the measurement of nuclear mass, the resolution is the major consideration of the mass spectrometer.

(2) Abundance sensitivity

The abundance sensitivity is the ability of measuring isotopic ratio by mass spectrometer which may be defined as the ratio of ion current measured at mass position M to the ion current measured at mass position M ± 1 due to the scattered ions of mass M.

Obviously if the scattered ion current of mass M at the M ± 1 position is larger than the ion current of mass M ± 1 itself, it is impossible to measure the abundance ratio of isotope M to isotope M ± 1. Hence, for the determination of abundance ratio, high abundance sensitivity is required.

(3) Sentivity

The sensitivity of a mass spectrometer usually means the least amount of sample that can give measurable signal in a mass spectrometer. This characteristic may not be important in some cases, as there are plenty of sample available for the measurement. But, in cases of determination of rare gases from rocks, analyses of moon sample or meteorite, and measurement of reaction products of nuclear reaction etc., the amount of sample is a critical problem and the sensitivity of the mass spectrometer becomes very important.

3. Measurements of Nuclear Masses by Mass Doublet or Multiplet Methods

(1) Mass Doublet Method

Nuclear masses compiled in Nuclear Mass Table or Nuclear Mass Chart have been determined mostly by mass spectrometrical method using mass doublet or multiplet methods. Two species having the same mass number but different in accurate masses are called mass doublet. When a mass spectrometer of low mass resolution is used, these two mass peaks can not be resolved and they appear as one mass peak. If the mass spectrometer has rather high mass resolution, these two peaks can be well separated and by adding or subtracting the mass difference between these two peaks from the known mass (one of the doublet), the mass of the unknown species is thus determined. Figure 11 shows an example of one multiplet. $^{14}N_2$, $^{12}C^{16}O$, and $^{12}C_2{}^1H_4$ are species of mass number 28, the doublet N_2 - CO has mass difference of 0.01 mass unit, knowing the masses of C and O, the mass of N can be determined. To determine nuclear masses by comparing the mass of a known hydro-carbon compound ion in a mass doublet may subject to interference by the satellite mass peak accompanying with the hydro-carbon ion peak due to the isotope ^{13}C. Although the isotopic abundance of ^{13}C is only 1.108%, because it is so close to the major mass peak, e.g. the satellite peak $^{13}C^{12}C_{m-1}{}^1H_{n-1}$ and the major peak $^{12}C_m{}^1H_n$ has mass difference 0.0044693 mass unit, to separate these two peaks requires a mass resolution of 60,000. Mass doublet is not restricted to the species of the same mass number, species of neighbor isotopes different in one or two mass number may also be used. Such doublet is often called isotopic doublet. Some examples of mass doublets and their mass differences are shown in Table 1.

(2) ^{12}C = 12.0000 Mass Unit

Except those determined by nuclear reactions, most nuclear masses have been determined by mass spectrometer using hydro-carbon compounds as reference standard masses, it is more convenient if the most occurring carbon can be used as standard. In 1960, IUPAP decided to adopt the mass of ^{12}C isotope as 12.0000 mass unit and abbreviated as u.

4. Direct and Indirect Measurements of Isotopic Abundance Ratios

Isotopic abundance ratio of most natural occurring elements have been measured by mass spectrometer. No matter whether the direct or indirect method has been adopted, mass spectrometer of high abundance sensitivity is usually required.

(1) Direct measurement of isotopic abundance ratio by mass spectrum determination

Usually, a mass spectrum is used to determine the isotopic abundance ratios of an element, however, in case of determination of very less abundance isotope, the accuracy is very hard to obtain unless a mass spectrometer of very high abundance sensitivity is used. Figure 12 shows an example of a lead mass spectrum, the isotopic abundance ratios can be directly determined from the spectrum.

(2) Isotope Dilution Method for indirect measurement of isotopic abundance ratio.

If the quantity of the sample element is known, by adding a known quantity of enriched isotope to the sample and mixing them together, then the isotopic abundance ratio of the mixture is measured by a mass spectrometer, the isotopic abundance ratios of the sample element can be caculated.

For simplicity, take an example of an element of two isotopes, as shown in Figure 13, a nature lithium of 2,680 μg is used as the sample. The Li has two isotopes, one is the major isotope ^{7}Li and the other is the ^{6}Li to be determined. If 1.8 ug enriched ^{6}Li with known ^{7}Li to ^{6}Li isotopic ratio (R_2 = 0.004) is mixed to the sample, and the ^{7}Li to ^{6}Li isotopic ratio of the mixture is measured by a mass spectrometer to be R_3 = 1.13, the natural isotopic abundance ratio of ^{7}Li to ^{6}Li, R_1, can be calculated from the formula:

$$M_n = M_s \frac{(R_2 - R_3)(1 + R_1)}{(R_3 - R_1)(1 + R_2)}$$

where M_n is the number of natural lithium atoms, and M_s is the number of enriched ^{6}Li atoms.

From this formula, the isotopic abundance ratio of ^{7}Li to ^{6}Li is calculated to be 12.4. For the elements of isotopes more than two, more complicated formulae are needed, one can always use a computer to do the calculations.

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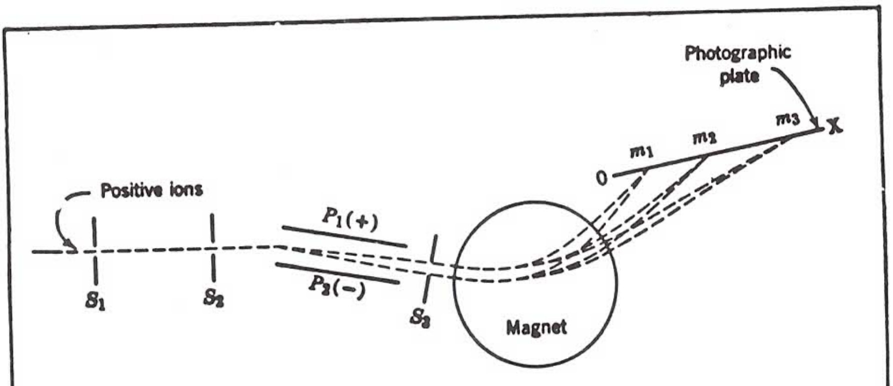
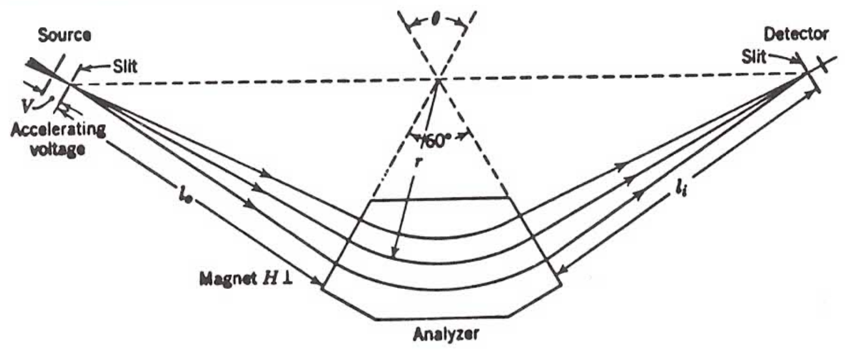


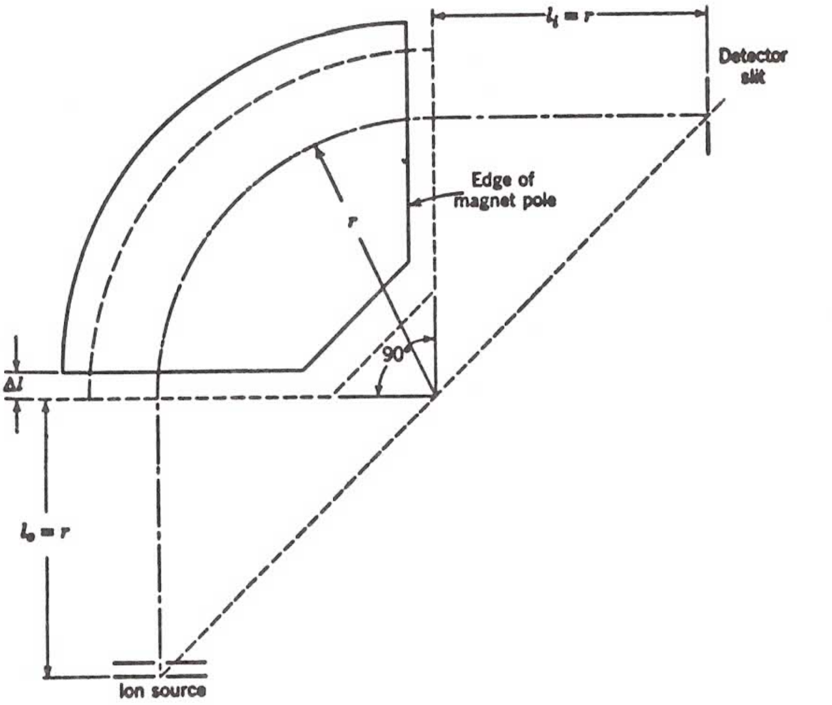
Aston's mass spectrograph.

Figure 1



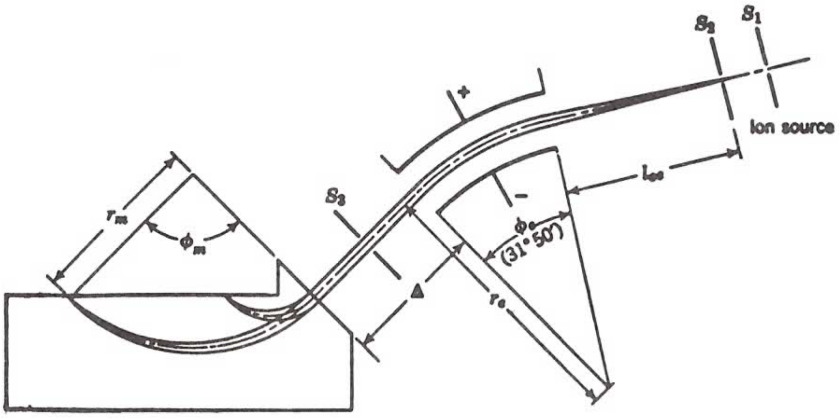
The 60° magnetic analyzer.

Figure 2



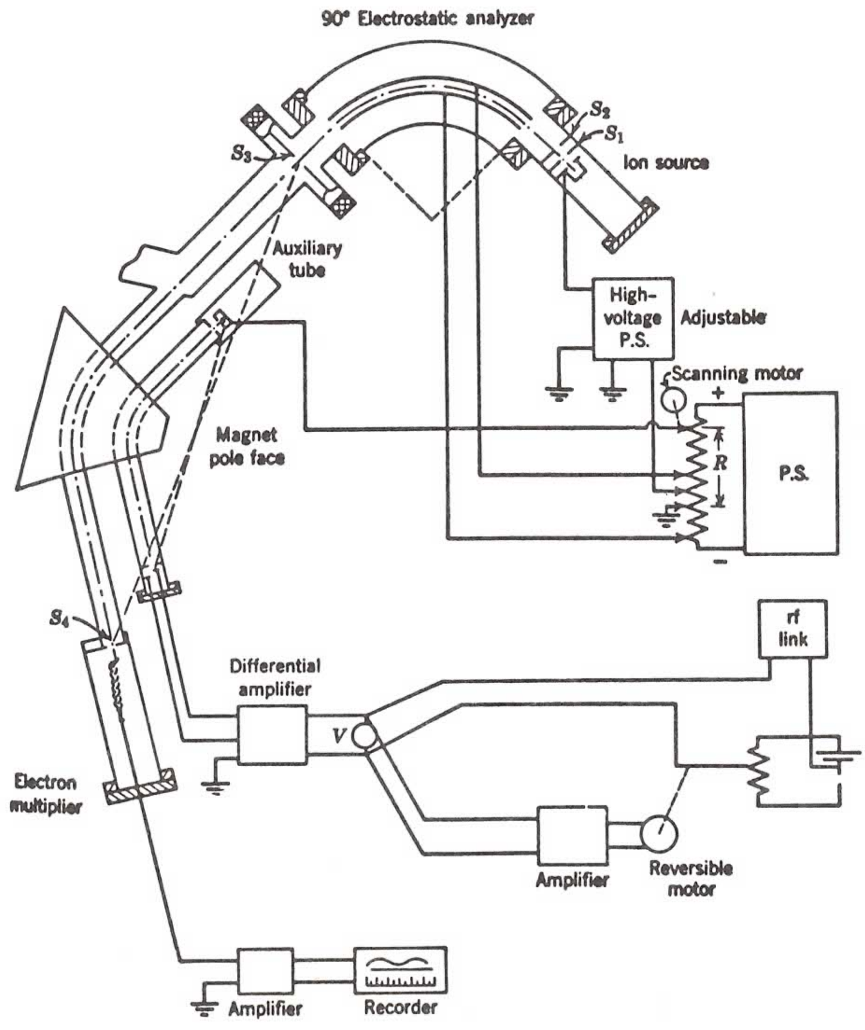
A 90° magnetic sector displaced from its theoretical position to correct for the fringing field.

Figure 3



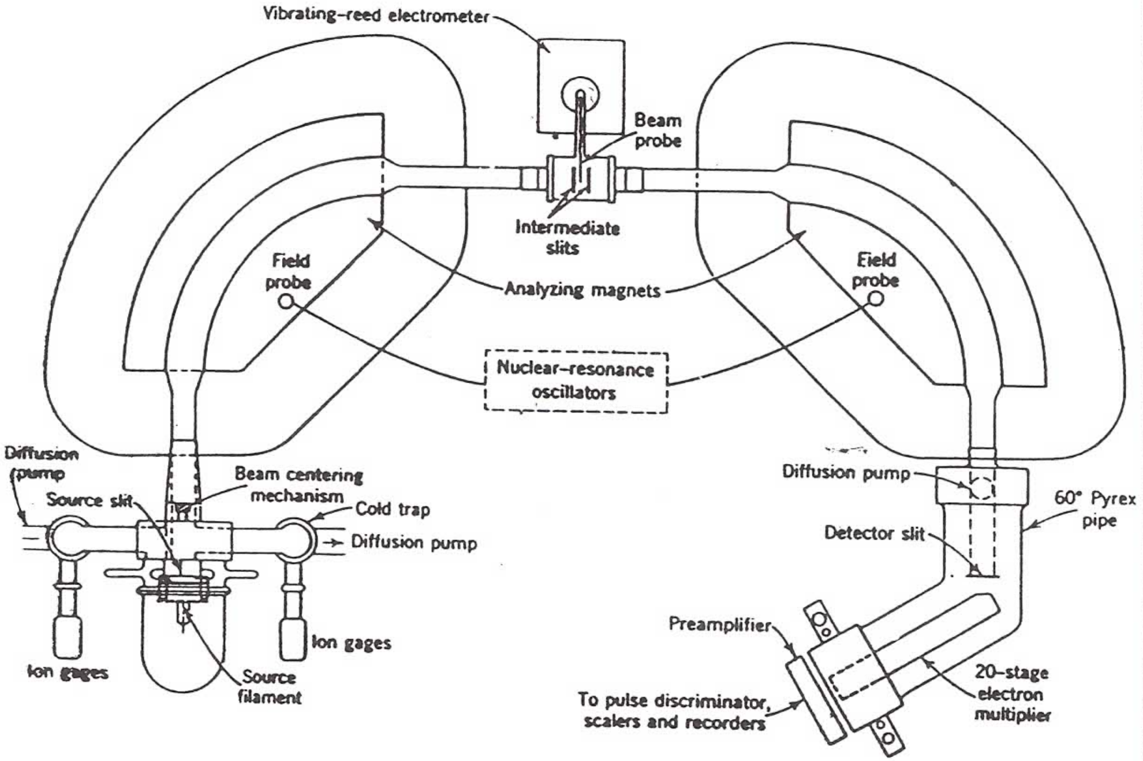
Double-focusing system of Mattauch and Herzog.

Figure 4



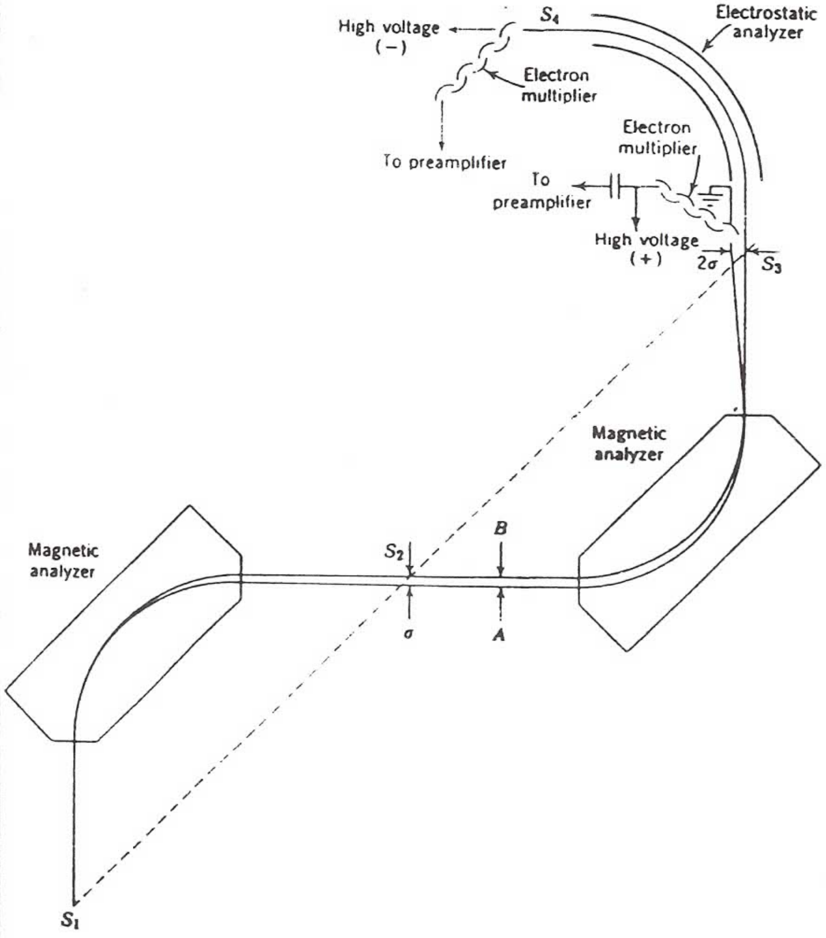
Double-focusing spectrometer designed by Nier.

Figure 5



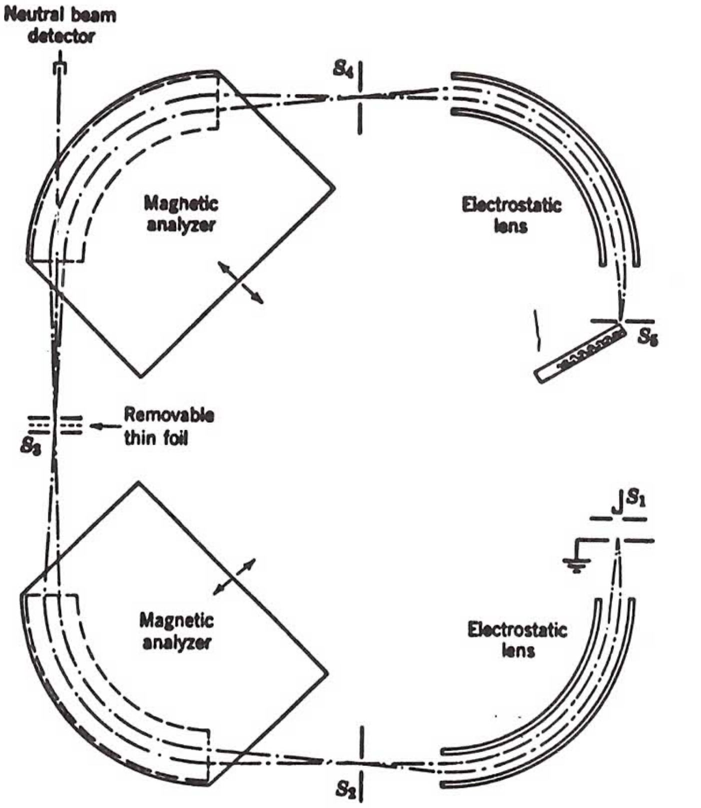
Two-stage spectrometer with "C"-shaped geometry.

Figure 6



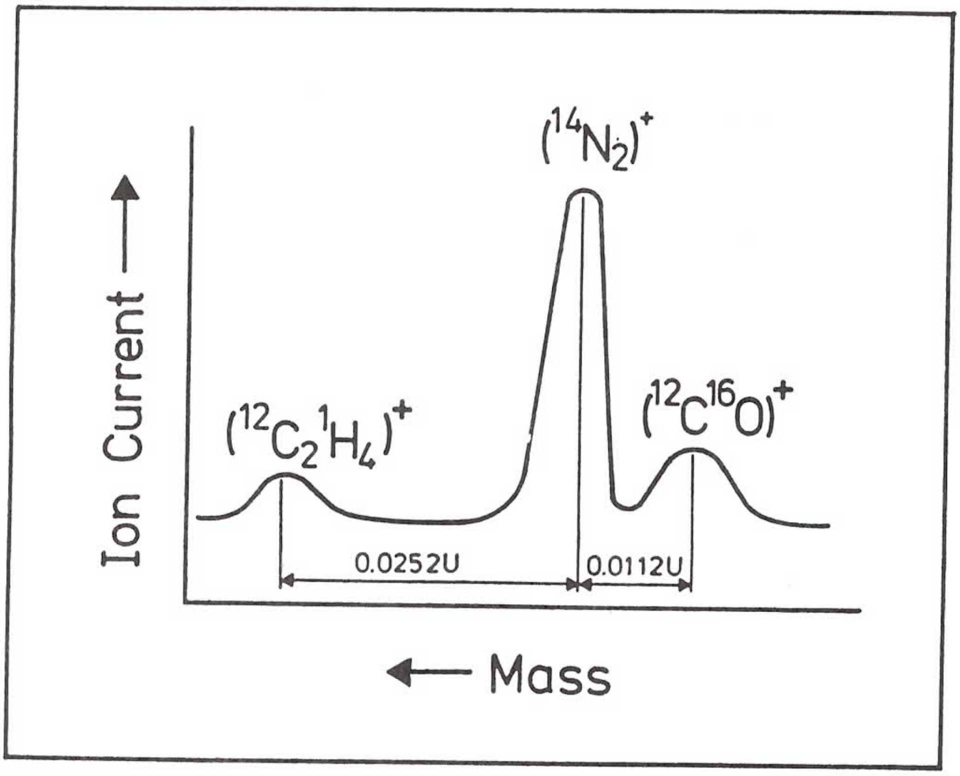
Three-stage spectrometer with "S"-shaped trajectory

Figure 7



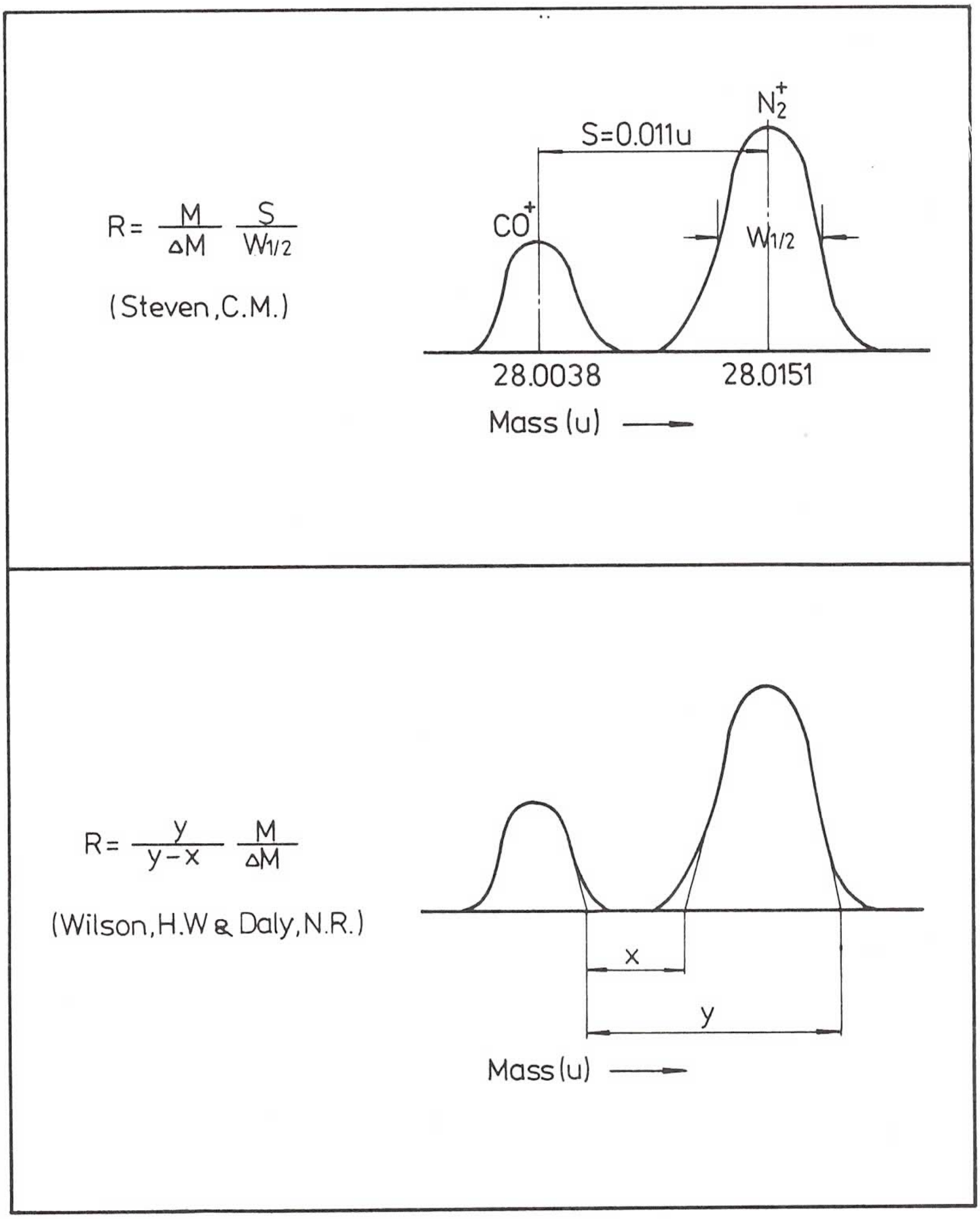
Four-stage mass spectrometer schematic of "C"-shaped geometry of magnets and electrostatic lenses.

Figure 8



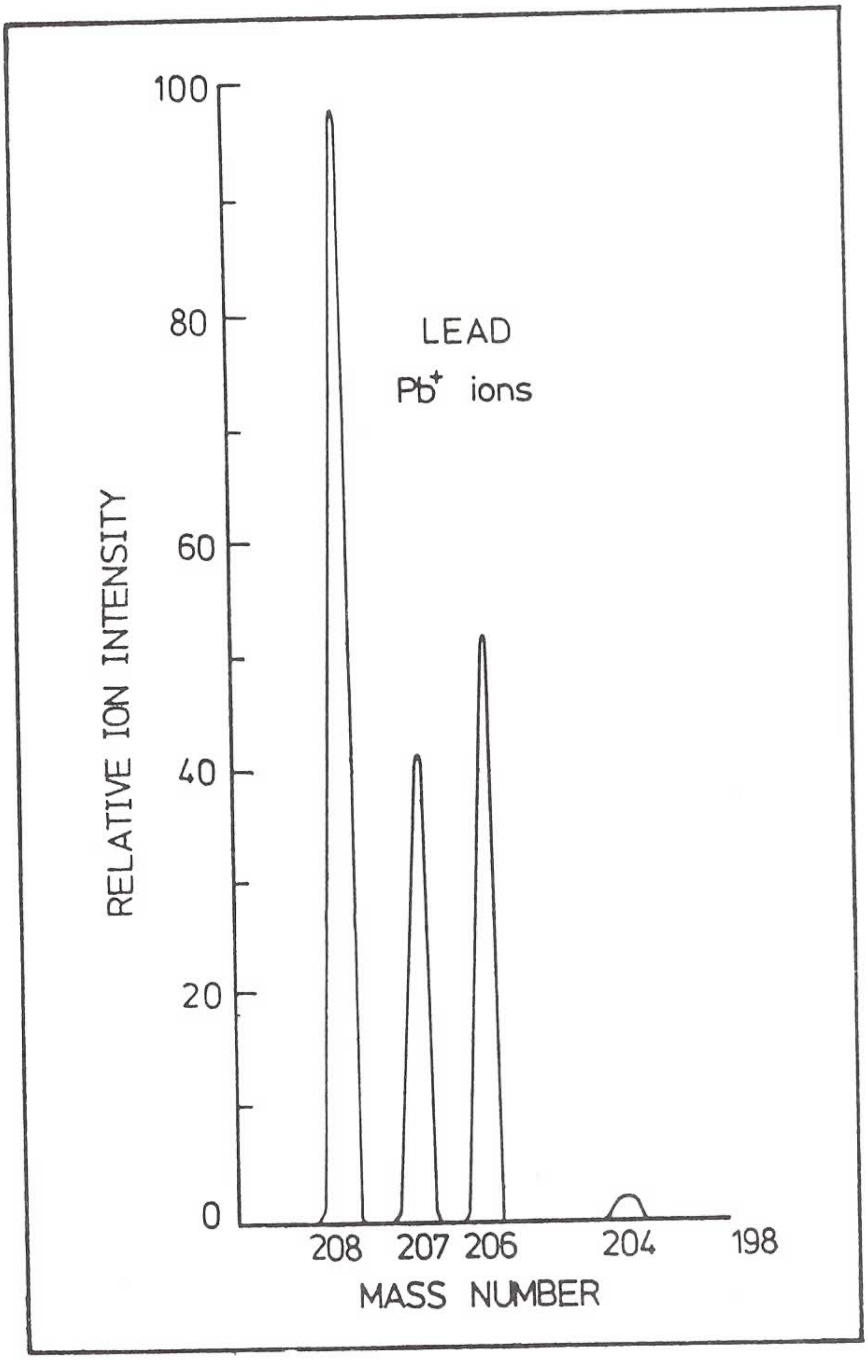
Mass Doublet and Triplet

Figure 9



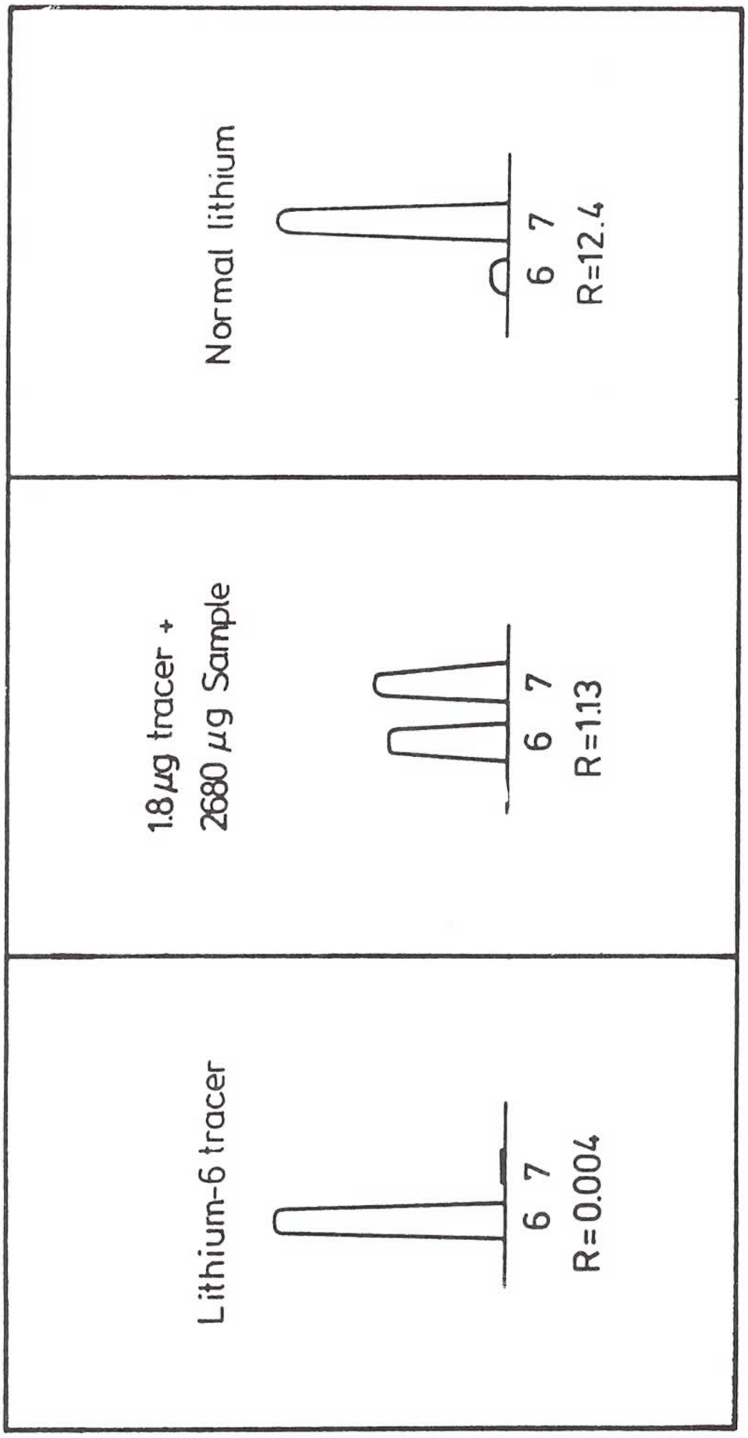
Resolution

Figure 10



Mass spectrum of lead

Figure 11



Isotope Dilution Method

Figure 12

Mass doublets

Doublet	Mass difference (mu)	Error
$C_6H_2-{}^{74}Se$	93.173 8	38
$C_6H_4-{}^{76}Se$	112.009 9	81
$C_6H_5-{}^{77}Se$	119.211 9	42
$C_6H_6-{}^{78}Se$	129.642 6	22
$C_6H_8-{}^{80}Se$	146.068 5	29
$C_6H_{10}-{}^{82}Se$	161.545 0	46
$C_6H_6-{}^{78}Kr$	126.584 3	36
$C_6H_8-{}^{80}Kr$	146.225 7	46
$C_6H_{10}-{}^{82}Kr$	164.769 8	34
$C_6H_{11}-{}^{83}Kr$	171.946 8	34
$C_6H_{12}-{}^{84}Kr$	182.399 4	25
$C_6H_{14}-{}^{86}Kr$	198.936 7	27
${}^{83}Kr-{}^{82}Kr$	1000.647 9	120
${}^{84}Kr-{}^{83}Kr$	997.371 6	120
$C_4H_{10}O_2-{}^{90}Zr$	163.377 1	55
$C_7H_7-{}^{91}Zr$	149.143 1	44
$C_7H_8-{}^{92}Zr$	157.569 4	38
$C_7H_{10}-{}^{94}Zr$	171.929 4	39
$C_7H_{12}-{}^{96}Zr$	185.628 0	57
${}^{91}Zr-{}^{90}Zr$	1000.942 0	116
${}^{92}Zr-{}^{91}Zr$	999.397 2	117

C, H and O refer to ${}^{12}C$, ${}^{1}H$ and ${}^{16}O$ respectively. Mass difference are given in milliunits. Nuclear mass of ${}^{12}C$ is exactly equal to 12 units (symbol u).

Table 1