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A Mass Spectrometer for Isotope Ratio Determinations

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Research workers in the fields of chemistry and biochemistry have today an attractive opportunity to use the stable isotopes of a number of common elements for tracer experiments, largely as a result of two recent developments. First, compounds enriched in the stable rare isotopes have become generally available at reasonable cost. Second, a mass spectrometer designed specifically for isotope ratio measurements now can be purchased as a complete unit.

The advantages of using stable rare isotopes for tracer experiments, as compared to using radioisotopes, are that nitrogen and oxygen have suitable stable but no suitable radioactive isotopes, and that deuterium, the stable isotope of hydrogen, may be obtained in nearly pure form. The main disadvantages are that the assay equipment is much more complex and expensive, and that the rare stable isotopes occur in nature in relatively large abundances, thus limiting their ultimate dilution when they are used as tracers. Their occurrence in nature makes possible, however, the interesting work in the field of geology reported by H. C. Urey, A. O. Nier, and others.

Following the work of J. J. Thompson, demonstrating the isotopic nature of neon, A. J. Dempster, F. W. Aston, and others designed and used mass spectrographs for the accurate determination of the masses of the isotopes of many elements. Several years ago A. O. Nier published a fairly complete description of a mass spectrometer in use at the University of Minnesota for the precise determination of the relative abundances of the stable isotopes (*1*). The basic design of this instrument has been employed in the isotope ratio mass spectrometer described here.

The fundamental principles of the mass spectrometer are illustrated in Fig. 1. The sample of gas, at an absolute pressure of about 30 mm Hg, is continuously bled through a capillary restriction into an "ion source." In the ion source, which is maintained at greatly reduced pressure, the gas molecules are bombarded by a stream of electrons emitted by a tungsten filament. The electrons have sufficient energy so that on the collision of an electron and a molecule there is a high probability that the molecule will be ionized. A certain portion of the collisions result in dissociation and the ionization of one or more fragments of the molecule. The ions are projected into the analyzer tube at high velocity by means of an electrostatic field in the source. In the analyzer tube the ions pass through the field of a 60° sector magnet, which causes the ions of different masses to follow different paths. The intensities of the accelerating and magnetic fields are adjusted to focus all ions of one particular mass on a collector, and the current to this collector is amplified and measured.

Most mass spectrometers have only a single ion collector. A comparison of the intensities of the two different ion beams requires the focusing and measuring of each beam in turn. In the isotope ratio instrument, however, there are two collectors, arranged so that all ions of one specific mass strike one collector at the same time that all ions of another specific mass strike the other collector. The currents to each of the two are amplified and the ratio of their magnitudes read directly.

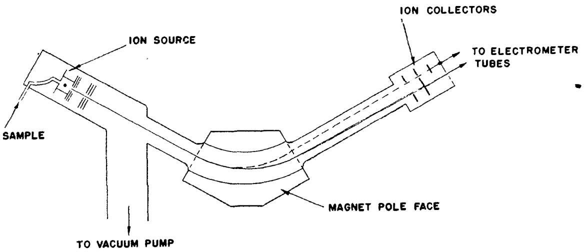

FIG. 1.

The ion source, analyzer tube, and dual collector assembly of the Consolidated-Nier isotope ratio mass spectrometer (*2*) follow closely the construction described by Nier. Except for small glass insulators, these parts are all metal, principally nichrome, inconel, and nonmagnetic stainless steel. The analyzer tube is covered by a heater winding and may be baked out at a controlled temperature to reduce background gases after exposure to the atmosphere.

A permanent magnet is used in place of the usual electromagnet and associated power supply. The magnetic field strength can be changed over a range of four to one by means of movable shunts which divert the flux from the main gap. The position of the shunts is adjusted by rotating a small hand wheel.

The high vacuum system for the analyzer tube consists of a cold trap, a water-cooled mercury diffusion pump, a ballast volume, a mechanical backing pump, and a vacuum gage. Dry ice or liquid nitrogen is used as the coolant in the trap.

The electronic circuits consist of a high voltage power supply for the ion-accelerating potentials, an electron emission regulator, and the ion current amplifiers and their power supply. The high voltage power supply provides a voltage of 2000 v, regulated to about 0.1%. The emission regulator maintains the electron ionizing current at a constant value by controlling the temperature of the tungsten filament. Two identical ion current amplifiers are used, each amplifying the current to one of the two collectors. The amplifiers employ a unity gain circuit in order to meet the severe requirements with respect to dynamic range, sensitivity, and stability. The first stage, or preamplifier, of each amplifier is mounted close to the collector assembly and its components are carefully matched to the other to reduce the drift of the amplifiers with respect to each other.

The few controls and switches are mounted within easy reach of the operator. The most important of these are the decade dials and null indicating meter used in measuring the isotope ratio.

The resolution of the isotope ratio mass spectrometer is adequate for precise ratio measurements up to about mass 70. In the case of CO_2 the contribution of mass-44 ions to the mass-45 ion beam is less than 0.04% of the mass-44 ion beam intensity.

The dual collectors cannot be used for the simultaneous collection of hydrogen and deuterium ions because of the greater spatial separation of the two ion beams at the points of focus. Provision is made, however, for conveniently comparing their intensities by using a reference voltage as a standard.

TABLE 1

REPRODUCIBILITY OF SUCCESSIVE ISOTOPE-RATIO DETERMINATIONS

Reading No.	N_2 $\frac{\text{Mass 29}}{\text{Mass 28}}$	CO_2 $\frac{\text{Mass 45}}{\text{Mass 44}}$	H_2 $\frac{\text{Mass 3}}{\text{Mass 2}}$
1	.007569	.011596	.000395
2	.007563	.011598	.000393
3	.007570	.011594	.000396
4	.007564	.011599	.000398
5	.007567	.011593	.000395
6	.007564	.011594	.000397
7	.007565	.011596	.000396
8	.007567	.011597	.000399
Mean	.007566	.011594	.000396
S. D.	.0000025	.000003	.000002

Only gas samples can be introduced into the instrument, so the products of an experiment must be converted to CO_2, N_2, O_2, or H_2-D_2, depending on the tracer used. The sample is bled into the evacuated introduction system from a suitable container through a system of stopcocks, and a Toeppler pump is provided for adjusting the sample pressure. Gas samples as small as 0.1 ml S.T.P. can be handled. To achieve maximum precision all related samples are compared to a standard sample, and this standard is run frequently in order to overcome the effects of long term drifts. The excess of rare isotope is computed with reference to the standard.

It is of great practical interest to know the maximum dilution which an enriched material can undergo and still be detected. This ultimate dilution can be computed from the enrichment of the tracer material and the minimum detectable excess of the rare isotope over its natural abundance in the dilutant. While the minimum detectable excess may be affected by natural variations of the normal material, it is the precision in measuring a change of isotope ratio at the normal abundance level which is considered here. With the mass spectrometer described, the ratio is read to six figures and is significant to about .000005, as illustrated in Table 1. Each column of this table represents eight successive measurements made within a short period of time on a single sample of the gas indicated.

With precision comparable to that shown in Table 1, 30 atom % enriched hydrogen, nitrogen, or carbon may be diluted to 1 part in 100,000 in normal material. For the great majority of applications, this precision is highly satisfactory; thus the isotope ratio mass spectrometer is a tool of outstanding value in the numerous scientific investigations involving stable isotopes.

References

1. NIER, A. O. *Rev. sci. Instr.*, 1947, **18**, 398.
2. WASHBURN, H. W. *U. S. Naval Medical Bulletin*, Supplement, March–April, 1948.

The Photographic Plate as an Instrument in Nuclear Research Autoradiography and Radiation Monitoring

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The photographic plate has become in recent years a very valuable tool for measurement of radiation from radioactive materials. Such radiations include charged particles of all types—electrons, protons, alpha particles, and ionized atoms, as well as electromagnetic radiation such as X-rays and gamma rays. Extensive applications of the photographic plate have been made in the fields of nuclear physics, autoradiography, and in radiation monitoring.

Nuclear physics. In 1945, following the tremendous expansion in nuclear physics during the war period, and the development of higher energy accelerators, physicists began to look seriously to the photographic plate as a means of registering the paths of high energy charged particles. For this purpose, the photographic plate resembles closely in action that of the Wilson cloud chamber. However, the silver bromide emulsion with its high stopping power (about 2,000 that of air), continuous sensitivity, and simplicity, gives it distinct advantages not possessed by the cloud chamber.

The Ilford Company in England pioneered in the field of producing the modern type nuclear emulsion and in 1945 produced a series of plates that far surpassed in sensitivity plates previously made. Subsequently, the Eastman Kodak Company in America, together with their British affiliate, Kodak Limited, started a program of