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A mass spectrometer system, operating in the static mode, is being used to measure helium concentrations as low as 10^{-11} atom fraction in solid and water-based liquid samples ranging in mass from < 1 mg to ~ 1 g. This system is being used extensively for the determination of helium in neutron-irradiated pure elements, isotopes, compounds, and alloys and in α- and proton-injected samples. Other applications have included measurements of helium in the atmosphere, helium in stratospheric particles subjected to solar wind, and tritium concentrations in water samples.

Several developments have resulted in increased sensitivity in mass spectrometer systems. Hoffman and Nier[1] used a double-focusing mass spectrometer to determine helium from meteorites by allowing the whole gas sample to go into the mass spectrometer source region. This method was later modified by others (e.g., Schaeffer and Zähringer[2]) by isolating the mass spectrometer tube from the vacuum system before allowing the helium sample to enter. This "static mode" operation improved the sensitivity by several orders of magnitude over the more conventional "leak" method.

The static mode of operation is used in the mass spectrometer system described here. The principal features of the system are shown in Figs. 1 and 2. The mass spectrometer itself is a 2-in. (5.1-cm)-radius, 60°, permanent magnet instrument (modified Veeco GA-4 residual gas analyzer) with a single electron-multiplier collector. The mass spectrometer is connected to sample gas handling lines through a series of physical and chemical getters, including liquid-nitrogen-cooled activated charcoal and ambient-temperature Zr–Al alloy. The getters purify the helium gas sample and ensure that reactive and other potentially interfering gases are not admitted.

The analysis of the ^{4}He or ^{3}He content of a solid or liquid sample is accomplished by using an isotope-dilution method, which involves adding a precisely known quantity of either ^{3}He or ^{4}He "spike" to the helium released from the sample. This method has the advantage of being independent of the absolute sensitivity of the mass spectrometer. For samples that are known from previous experience to contain only one of the two helium isotopes, the added spike is the helium isotope not present in the sample. For samples that contain a mixture of both isotopes, preliminary isotopic ratio measurements are made using similar samples, but without adding a spike, to obtain the relative isotopic abundances. The added spike is then of the isotope in the smaller abundance. The measured isotopic ratio of the helium gas mixture, together with the precise knowledge of the amount of helium in the spike, allows a determination of the helium released from the sample. Altogether, seven separate storage volumes dispense ^{3}He and ^{4}He spikes in aliquots ranging from

$\sim 10^{13}$ to $\sim 10^{16}$ atoms. This range, and the practice of allowing only a very small fraction of the larger gas mixtures to enter the mass spectrometer for the ratio measurement, allows absolute helium measurements in the range of 10^8–10^{18} atoms.

Figure 2 shows schematically one of the spike systems and the mercury U-tube manometer, which is used for accurate pressure measurements during spike filling. The spikes are obtained by expanding and partitioning a known quantity of gas through a succession of calibrated volumes. Glass stopcocks are used throughout the spike system, because they provide a positive and reliable barrier, and the volumes between stopcocks can be measured readily. Most of the spike system, including the stopcocks, is made of borosilicate glass. The containers used for long-term helium storage, however, are constructed from Corning Type 1720 aluminosilicate glass and stainless steel to reduce atmospheric helium permeation. The volumes of the small glass sections of the system were determined by filling them with mercury and then weighing the mercury. The larger volumes (> 100 cm^3) were determined by weighing before and after filling the sections with vacuum-degassed distilled water. Determinations of the helium permeation into and out of the spike systems are made by periodically measuring the increase of atmospheric ^{4}He into the ^{3}He spike storage volumes. Small corrections for atmospheric ^{4}He permeation into the sample furnaces, for "memory" effects from previous samples, or for desorption of helium from the glass, stopcock lubricants, or furnace parts are usually negligible compared with the helium released from the sample. These corrections are nevertheless determined accurately by performing "blank" runs (no sample, no spike), and by vaporizing "blank samples" consisting of similar amounts of the same material but not containing helium.
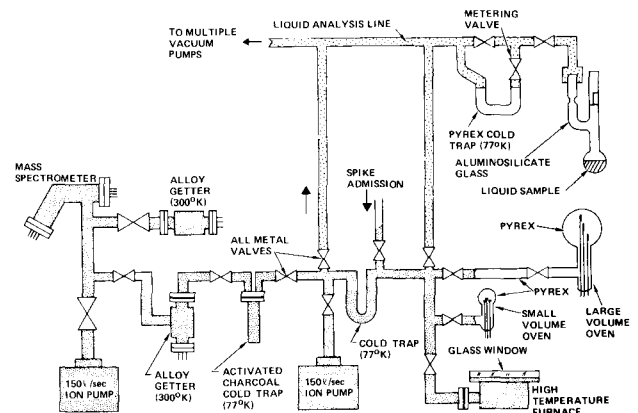

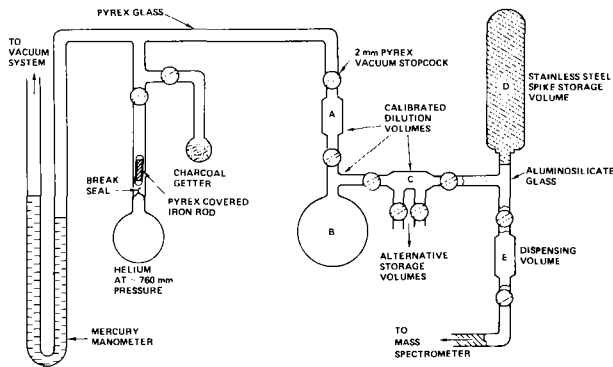FIG. 1. Schematic diagram of mass spectrometer system.

FIG. 2. Partial diagram of mass spectrometer spiking system.

The mass sensitivity for ^{3}He relative to ^{4}He (discrimination factor) for the mass spectrometer is ~ 1.53. This ratio is determined daily by analyses of various combinations of the helium spikes and of a separate spike containing a known mixture of ^{3}He and ^{4}He. The discrimination factor is essentially constant from day to day. Linearity of the mass spectrometer detection system is occasionally verified by measuring mixtures of the various large and small helium spike aliquots.

Measurement uncertainty in the mass spectrometer system comes from three sources: (1) systematic uncertainty in the absolute number of helium atoms in the spikes, (2) systematic uncertainty in the determination of the discrimination factor, and (3) random uncertainty (reproducibility) in the measurement of the helium isotopic ratio. Extensive analyses of the system, described in detail elsewere,[3] have indicated potential uncertainties from sources 1 and 2 of $\sim 0.2\%$ each. Uncertainty from source 3 is determined largely by the stability of the system electronics and by background helium release in the system during the helium extraction process. Generally, for samples with $> 10^{11}$ atoms of helium, this uncertainty is $\lesssim 0.5\%$.

The mass spectrometer system is capable of analyzing essentially any solid or liquid sample that can be readily vaporized or degassed. For solid materials, the helium is extracted by vaporization. In this case, an appropriate helium spike (^{3}He or ^{4}He) is admitted to the vacuum system, and the sample is then vaporized under vacuum in either a resis-

tance-heated tungsten wire or graphite crucible in one of the system's high-temperature vacuum furnaces. Several types of furnaces are available, varying in volume from ~ 20 cm^3 to several liters. The choice of furnace is determined by several factors, including the sample melting temperature and its expected helium content.

For water-based samples, the helium is released by a method similar to that used by Clarke et al.[4] A schematic diagram of the water analysis line is shown in the upper right section of Fig. 1, and it should be easily adaptable to other liquids with suitable vapor pressures. In general, a liquid sample for helium analysis must be collected and kept isolated from air and from other gases that could affect the helium content by exchange. At present, the system has been used only to measure tritium in water samples through the tritium's decay to ^{3}He. For this application, the tritiated water sample is first degassed to remove dissolved ^{4}He and previously generated ^{3}He, and then sealed in an aluminosilicate vial with a break seal, to allow generation of new ^{3}He. The rate of evaporation during degassing is controlled by an adjustable orifice, which also serves as a "diffusion pump" to transfer the helium from the water toward the mass spectrometer volume. Approximately 2% of the water is transferred to a cold trap during this degassing step. A small correction to account for a $\sim 0.1\%$ enrichment of the tritium in the remaining water is easily made. After a suitable decay time, the vial is reattached to the system, the seal is broken, and the sample is degassed again, spiked with ^{4}He, and transferred into the mass spectrometer volume for helium analysis.

[1]J. H. Hoffman and A. O. Nier, Phys. Rev. 112, 2112 (1958).
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[3]B. M. Oliver, J. G. Bradley, and H. Farrar IV, Geochim. Cosmochim. Acta 48, 1759 (1984).
[4]W. B. Clarke, W. J. Jenkins, and Z. Top, Int. J. Appl. Radiat. and Isot. 27, 515 (1976).