which had been modified to permit the exact setting and measurement of ionizing voltages. Instrumentation was the same as previously described (*1*), except that ionizing potentials were obtained from, and read on, a Shallcross No. 835 decade potentiometer connected across a calibrated 20-volt source.

The compounds to be studied were introduced into the gas-handling system in the regular manner, at reservoir pressures usually between 40 and 200 microns. Measurements were made on each sample by changing the ionizing voltage in 0.1-volt steps over the critical range (larger steps elsewhere) and scanning electrically the mass range of interest.

Care was taken to run samples containing trace impurities always before the impurity calibrations, so as to avoid instrumental background effects.

RESULTS AND DISCUSSION

The method described above was applied to the analysis of synthesized methane-*d*, propane-1*d*, and propene-2*d*, as well as several samples of 2-methylpropane. In order to test it, synthetic mixtures of these compounds with known amounts of impurities were prepared and analyzed. All the results have been collected in Table II. The errors quoted represent the standard deviation within each individual run. Agreement between duplicate runs is satisfactory.

The synthetic and measured values generally agree well to within the stated errors. It is noticed that the results are more accurate for methane-*d* than for the two substituted propanes. This is readily explained by the fact that the propane potentials involved [$A(C_3H_6D^+) = 11.6$ volts; $I(C_3H_8^+) = 11.2$ volts] lie much closer together than the corresponding values for methane [$A(CH_2D^+) = 14.3$ volts; $I(CH_4^+) = 13.0$ volts].

The considerable discrepancy between synthetic and measured values for the 2-methyl butane plus 0.1% 2-methylbutene mixture is not readily explained, as it lies outside the estimated error. Conceivably, difficulties experienced in admixing a 0.1% impurity may be partially responsible.

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Determination of Heavy Water by Mass Spectrometer

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A procedure employing the mass spectrometer has been developed for the rapid analysis of aqueous samples containing low concentrations of heavy water in water. The aqueous liquid mixtures are introduced directly into the mass spectrometer vacuum system and the analysis is based on the relative abundances of mass 19 from DOH and mass 18 from HOH. Calibration data are obtained from known mixtures covering the desired range of heavy water in water. The method appears to be accurate to ±0.2% in the range of 0.2% to 1% and to ±0.3% in the range of 1 to 10% D_2O. Instrument and calculation time requirements are 15 to 20 minutes per analysis.

DEUTERIUM, the mass 2 isotope of hydrogen, has been used extensively in such fields as atomic energy research (*8*), hydrocarbon reaction and ionization studies (*1, 2, 6, 13*), and biological tracer techniques (*9*). These applications invariably depend largely upon suitable means for detection and measurement of the deuterium isotope. Use of the mass spectrometer in conjunction with various chemical reaction procedures has been found satisfactory for the analysis of mixtures resulting from these studies (*2, 3, 6, 7, 13*). The present paper is concerned with a simple procedure in which the mass spectrometer alone is used for the rapid analysis of heavy water in concentrations of 0 to 10% in normal water.

Although this procedure was developed primarily for the analysis of low concentrations of heavy water in aqueous samples resulting from studies on drowning being conducted by Swann (*10*) of The University of Texas, Medical School, other studies of this type (unpublished) have indicated that the mass spectrometer method may be employed for higher concentrations of heavy water in water.

APPARATUS AND EXPERIMENTAL TECHNIQUE

The Westinghouse mass spectrometer employed in this investigation and the elevated temperature conditions under which it was operated have been described (*12*). The liquid mixtures of heavy water and water were introduced directly into the heated inlet system of the mass spectrometer by means of a sintered-glass disk submerged in mercury (*11*). Approximately equal amounts of liquid were introduced for both known and unknown samples based on the delivery of liquid from a microburet used in admitting the sample to the sintered disk. Adsorption difficulties encountered earlier by Fischer, Potter, and Voskuyl (*3*) upon the introduction of water vapor to the mass spectrometer appear to have been reduced sufficiently for the present analysis by the use of heated glass lines and the replacement of grease-containing stopcocks with heated metal valves. Pumpout times of approximately 12 minutes were employed throughout this program in which some sixty runs were made during one week.

DEVELOPMENT AND EVALUATION OF METHOD

In order to investigate the possibility of determining low concentrations of heavy water in normal water on the mass spectrometer, a study was made of the mass spectra obtained from eleven samples of distilled water to which had been added known concentrations of heavy water covering the range of 0 to 10 liquid volume %. (The heavy water was obtained through the Atomic Energy Commission from Stuart Oxygen Company, San Francisco, Calif. Its purity was said to be 99.8%.) Data for masses 17, 18, 19, and 20 on these blends are shown in Table I. In theory, mass 17 is produced by fragmentation and ionization of water and HDO molecules into OH^+ ions; mass 18 results from parent ionization of water molecules into HOH^+ ions and from fragmentation and ionization of heavy water molecules into OD^+ ions; and masses 19 and 20 are produced from ionization alone of molecules of HDO and heavy water, respectively.

It is readily observed that the use of mass 20 from heavy water would be unsatisfactory for measuring the heavy water

Table I. Mass Spectral Data on Heavy Water Calibration Samples

Run No.	Peak Heights, Recorder Divisions				Peak Height Ratios × 10^2			Heavy Water Added to Distilled H_2O, Liquid Vol. %[a]
	Mass 17	Mass 18	Mass 19	Mass 20	Mass 17/ Mass 18	Mass 19/ Mass 18	Mass 20/ Mass 18	
17	235.8	1044	7.3	1.7	226	0.70[b]	0.16[b]	0.00
18	258.6	1122	5.0	1.7	225	0.45[b]	0.15[b]	0.05
19	246.3	1080	4.6	1.8	228	0.43	0.17	0.10
0	264.9	1159	8.0	1.6	229	0.69	0.14	0.30
21	293.0	1317	13.6	1.9	223	1.04	0.14	0.50
25	383.0	1719	24.6	3.3	223	1.43	0.19	0.70
26	291.0	1273	24.7	2.0	229	1.94	0.16	1.00
39	268.8	1155	62.8	2.0	233	5.44	0.17	3.00
40	252.9	1076	93.9	2.9	235	8.73	0.27	5.00
47	243.0	1071	89.6	3.4	227	8.36	0.32	5.00
55	257.1	1111	135.0	6.5	232	12.15	0.59	7.00
67	234.0	1004	178.0	10.1	233	17.73	1.01	10.00

[a] Normal abundance of D_2O in pure H_2O is assumed to be zero in these values; although present procedure may be applicable with certain modifications, it is not designed for measurement of normal abundance of D_2O and H_2O.

[b] Irregularities of these values, probably caused by anomalous adsorption on vacuum system walls, place lower limit of about 0.2% D_2O on present method of analysis.

concentration in this range. Instead, however, it appears that the abundance of mass 19 bears a nearly linear relationship to the amount of heavy water that had been added to the distilled water. Hence, the abundances ratios of masses 19 and 18 were plotted against the liquid volume per cent of heavy water. Use of this ratio instead of mass 19 peak height (abundance) eliminates the need for measurement of a sensitivity coefficient for mass 19 and adjustment of data variations caused by changes in instrument sensitivity or by differences in the quantity of sample introduced. The nearly straight line resulting from a plot of the ratios of masses 19 to 18 versus per cent heavy water, shown in Figure 1, was used as a calibration curve from which heavy water concentrations were read for the unknown samples.

The increasing abundance of mass 19 with increasing concentrations of heavy water indicates that an exchange of deuterium occurs between heavy water and water. Because all three types of water molecules ionize, a net equilibrium according to $H_2O + D_2O \rightleftharpoons 2HDO$ is to be expected. In the concentration range of 0 to 5% heavy water, however, the mass spectrometer data do not indicate a correlation between mass 20 and the per cent heavy water added to the calibration samples. This discrepancy, which does not appear to offset the present procedure adversely to an amount greater than ±0.2% may be caused by anomalous adsorption of heavy water on the vacuum system walls. It is possible that more extensive degassing between sample runs may permit the extension of the procedure to the measurement of lower concentrations of heavy water. The increase in mass 20 abundance for the mixtures containing 5 to 10% heavy water is in accordance with the equilibrium equation. Previous unpublished data in this laboratory indicated that the maximum abundance of mass 19 results from a 50:50 mixture of heavy water and water and that shifting the concentration ratios in either direction causes a reduction in the abundance of mass 19 with corresponding changes in the abundances of masses 18, 19, and 20. Hence, for the analysis of samples containing more than 10% heavy water it may be necessary to employ measurements of masses 18, 19, and 20.

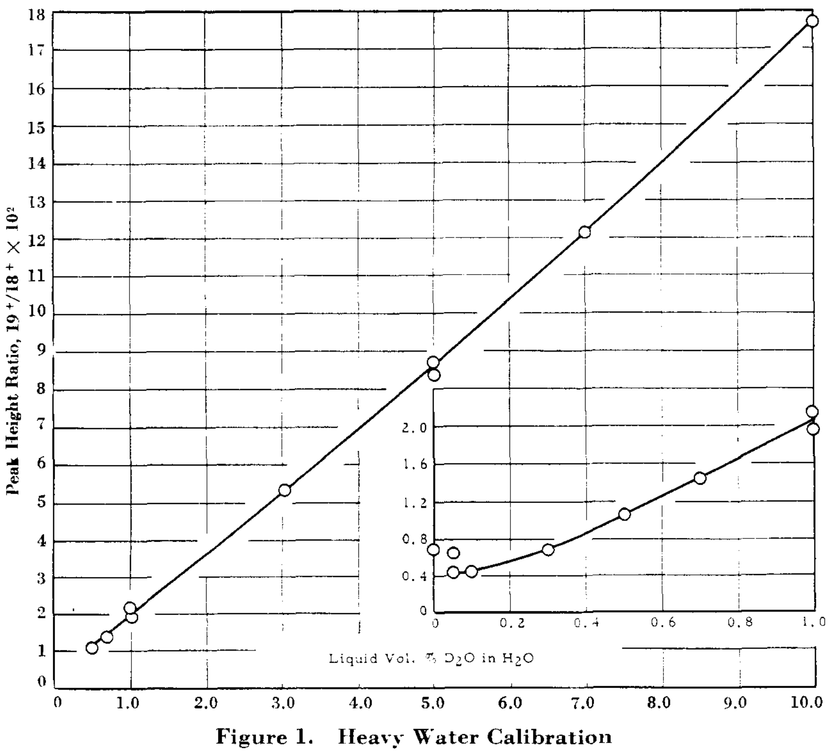

Figure 1. Heavy Water Calibration

Table II. Mass Spectral Data on Unknown Heavy Water Samples

Run Order No.	Peak Height, Recorder Division			Peak Height Ratios × 10^2, Mass 19/ Mass 18	Computed Liq. Vol. % D_2O
	Mass 18	Mass 19	Mass 20		
1	730	1.7	1.0	0.23	<0.1
6	927	0.9	1.3	0.10	<0.1
11	1093	24.9	2.1	2.28	1.2
38	1070	46.7	2.0	4.37	2.4
57	1030	59.6	3.0	5.79	3.3
60	1113	137.3	7.1	12.34	7.1
66	1196	197.5	11.4	16.51	9.3

In view of the nearly linear relationship indicated in Figure 1 between the abundance ratios of masses 19 and 18 and the known amounts of heavy water added to the samples of distilled water, it appears that this ratio furnishes a satisfactory means for the determination of heavy water in the unknown samples studied. Typical determinations of heavy water and related mass spectral data obtained by this procedure on aqueous samples resulting from studies on drowning being conducted by Swann (*9*) are shown in Table II. The excellent agreement of these analyses with previous studies on water metabolism in animals has been discussed in a separate paper (*9*). It was found that intravenously injected heavy water was rapidly distributed through space equivalent to 63 to 65% of the weight of dogs, confirming the studies of Hevesy and Jacobsen (*5*) and Flexner, Gellhorn, and Merrell (*4*).

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Infrared Absorption Spectra of Minerals and Other Inorganic Compounds

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A method is described for utilizing the infrared spectrophotometer in the analyses of minerals and other inorganic compounds. Mineral samples are ground to a powder having an average particle diameter smaller than 5 microns. The powder is deposited as a film on a conventional rock salt window. The spectra of 64 minerals, rocks, and inorganic chemicals are shown for the wave-length region from 2 to 16 microns. Spectral positions of the principal absorption bands of these compounds are tabulated. The technique is used in the study of fine-grained rocks. Analytical chemists in other fields such as catalysis, soils, and ceramics may find the same methods applicable to their problems.

INFRARED spectroscopy is used extensively for the identification of organic molecules (*2, 4*), but its application to the field of inorganic analysis has been rather limited. Inorganic solids cannot be analyzed in polar solvents such as water because such solvents generally have strong absorption bands of their own in the infrared range. Spectra have been obtained from thin sheets, but many substances cannot be sliced thin enough to prevent them from being opaque to infrared radiation. Conventional methods of mulling the sample in Nujol (*8*) produce spectra which are poorly defined because of reflection and refraction of the incident radiation by crystal particles. In addition, the absorption bands of Nujol must be distinguished from those of the substance being analyzed.

The infrared technique described herein was developed as a means of analyzing rocks, but the same methods are applicable to analytical problems in other fields such as catalysis and ceramics. The technique involves grinding the sample to a powder having an average particle diameter of less than 5 microns. This powder is spread as a thin film over the sodium chloride window through which the infrared radiation passes. Qualitative determinations of the major constituents of rocks can be obtained rapidly by this technique. Semiquantitative data may be obtained if all of a sample is ground to the desired particle size.

The infrared absorption of very small particles was first studied extensively by Pfund and associates (*9, 10*). They found that when a crystalline material is ground to a size finer than the wave length of the infrared radiation, its spectrum is sharpened considerably.

Pfund also found that films made from particles larger than the wave length tended to scatter the infrared radiation at all but a few wave lengths. At these few positions most of the radiation was transmitted through the film, giving rise to transmission bands.

Barnes and Bonner (*1*) demonstrated that the scattering of radiation by large particles was due mainly to refraction. They established that the transmission peaks observed by Pfund were due to a lack of refraction at wave lengths where the refractive index of the particles is 1.0. Such abnormally low refractive indexes occur on the short wave-length side of absorption bands as a result of the phenomenon of anomalous dispersion.

Henry (*6*) studied the effect of particle size and layer thickness on the infrared transmission of dry films of quartz powder. True absorption spectra were obtained from thin films of quartz particles 1 micron in average diameter. Scattering by refraction occurred only at the very short (less than 3-micron) wave lengths. With large particles none of the light was transmitted in the 2- to 16-micron range except at the few wave lengths where refraction was at a minimum.

The authors separated fine particles into uniform sizes by sedimentation. Transmission spectra were obtained from powder films made up of only large particles ($>$20 microns), whereas absorption spectra were obtained from powder films of only small particles ($<$5 microns).

Transmission spectra of four minerals are shown in Figure 1. The major transmission bands on these spectra occur at the following wave lengths: 7.3, 12.2, and 14.2 microns for quartz; 7.9 microns for montmorillonite; 6.1, 11.2, and 13.9 microns for

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