The Determination of Water by Gas Chromatography

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In the determination of water, the introduction of a sample directly into a gas chromatograph has been reported by many workers, who have used a wide variety of column packings.[1-5] However, the retention time of water was very long and the peak of water in gas chromatograms was very broad, both of which features interfered with the analysis of the other gases in the sample. In analysing gas samples containing water, Desty et al.[6] decomposed the water to hydrogen, using calcium hydride, before introducing it into gas chromatography they thus obtained satisfactory results for the gases other than water vapor in the sample.

Recently, Arnett[7] ascertaind the amount of heavy water in light water by decomposing the heavy water to DH and by analysing the DH using a charcoal column. Green[8] has reported results obtained by decomposing water to hydrogen, using an iron powder bed heated electrically to heat.

However, detailed experimental conditions have not been examined for the adsorption of water on calcium hydride, for the complete decomposition of water by calcium hydride, for the limitation of detection, for the reaction between calcium hydride and other gases, or for the reproducibility of the experiments.

The present authors used a lithium aluminum hydride, which is widely used in organic chemistry, to reduce water to hydrogen, and developed a method for determining the amount of water by gas chromatography. By this method they could determine water in amounts as small as 0.1 μg. in 10 ml. of a gas sample with a high degree of accuracy. The reaction between lithium aluminum hydride and water follows this chemical equation :[9]

$$LiAlH_4 + 4H_2O = LiOH + Al(OH)_3 + 4H_2$$

To determine such small amounts of water, the following experiments were carried out. By using water of crystallization in hydrated copper sulfate as a standard, it was first confirmed that lithium aluminum hydride could decompose water completely to hydrogen at room temperature. Second, the reactions between lithium aluminum hydride and oxygen, nitrogen, carbon dioxide, carbon monoxide, methane and C_2–C_4 hydrocarbons were studied. Third, the adsorption of water vapor on the lithium hydride surface was studied. Fourth, in order to the limitations of the detection of

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[1] P. W. Darby and C. Kemball, *Trans. Faraday Soc.*, **55**, **833** (1959).

[2] K. G. Woolmington, *J. Appl. Chem.*, **11**, 114 (1961).

[3] C. E. Benett, S. D. Nogare and L. W. Sabranski, "Treatise on Analytical Chemistry," Part I, Vol. 3, Interscience Publishers, New York and London (1961), p. 1703.

[4] L. Brealey, S. A. Elvidge and K. A. Proctor, *Analyst*, **84**, 221 (1959).

[5] D. A. Elvidge, and K. A. Proctor, ibid., **84**, 461 (1959).

[6] D. H. Desty, T. J. Warhan and B. H. F. Whyman, "Vapor Phase Chromatography," Butterworths Scientific Publications, London (1957), p. 346.

[7] E. M. Arnett, M. Strem, N. Hepfinger, J. Lipowits and D. McGuire, *Science*, **131**, 1680 (1961).

[8] G. W. Green, *Nature*, **180**, 295 (1957).

[9] A. E. Finhort, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

water, a molecular sieve-5A column and completely-purified argon carrier gas were used for determining the hydrogen; thereby 10 p.p.m. of hydrogen could be determined in 10 ml. of a gas sample. Last, by applying the above method, the gas content of uranium dioxide was studied; satisfactory results were obtained. One example of the results is reported on in this paper.

Experimental

Apparatus.— A flow diagram of the experimental apparatus is shown in Fig. 1. The apparatus consists of an electric furnace, a U-tube packed with lithium aluminum hydride powder, and an automatic Toepler pump. The sample was heated by the electric furnace, the temperature of which was controlled by an automatic temperature regulator.

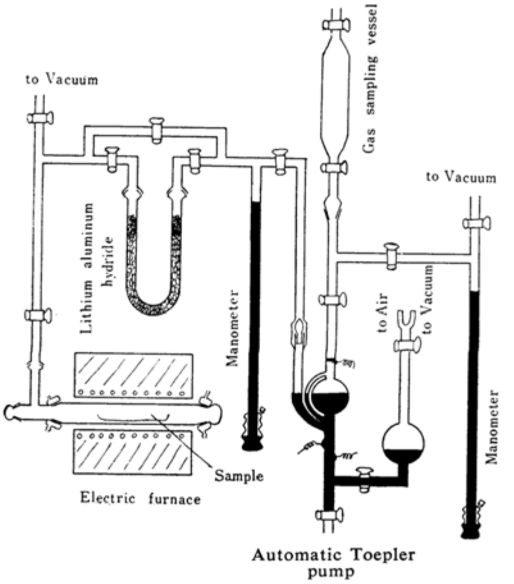

Fig. 1. Apparatus.

The automatic Toepler pump took one minute for one cycle, and its effective volume was about 100 ml., that is, if the pump was operated at S. T. P., it could draw out 100 ml. of gas per minute. The pump could bring the apparatus up to a pressure of 10^{-2} mmHg.

To Pack Lithium Aluminum Hydride into the U-Tube and to Degas the Impurity Gases Adsorbed on It.—The lithium aluminum hydride commercially available is a white powder with particle sizes of less than one micron and with various impurity gases adsorbed on its surfaces.

When lithium aluminum hydride is used as it is sold, these impurity gases are released slowly during the experiment and make the accuracy of the analysis poor. To remove these impurity gases, lithium aluminum hydride was heated for two hours at 100°C in a vacuum. The release rate of the impurity gases was reduced to 0.001 μl. per minute for the degassed lithium aluminum hydride; this release rate was negligible within the range of experimental error. To increase the passage of sample gases through the U-tube, lithium aluminum hydride was mixed with glass wool, which was then packed into the U-tube.

The amount of lithium aluminum hydride packed in the U-tube was about 0.5 g. The U-tube used was 1 cm. in diameter and 20 cm. long.

Procedure.—The sample was placed in the center of an electric furnace, and the whole apparatus was evacuated by a rotary pump to less than 10^{-3} mmHg. Then the automatic Toepler pump was operated, and the temperature in the electric furnace was raised to a given temperature.

The water vapor and the other gases released from the sample were passed through the U-tube packed with lithium aluminum hydride, where the water vapor was decomposed to hydrogen; the hydrogen was collected in the gas-sampling vessel by the automatic Toepler pump, along with other gases. The collected gases were then analysed by means of a gas chromatograph.

Gas Analysis. — A GC-IA type Shimazu gas chromatograph was used in all the experiments. Sample of gas were introduced by an attached apparatus, which is used to make the calibration curve. This apparatus is shown in Fig. 2; it is so designed that the current of the carrier gas is not interrupted during the sampling. The gas-sampling vessel containing the gas sample was attached to this calibration apparatus. Then the gas sample was transferred into a gas pipet by replacing it with mercury in the gas-sampling vessel, and a definite volume of gas was transferred from the pipet to vessel A (cf. Fig. 2).

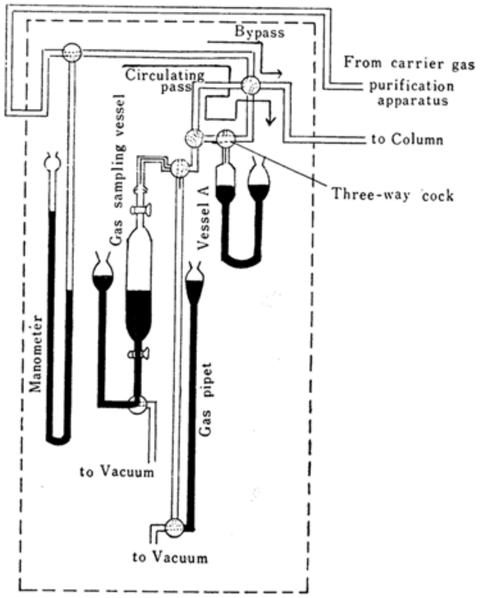

Fig. 2. Apparatus for making calibration curve.

The flow of the carrier gas was changed from the bypass to the circulating path in which the gas sample in vessel A was pushed by mercury; the sample gas was then sent to the gas chromato-

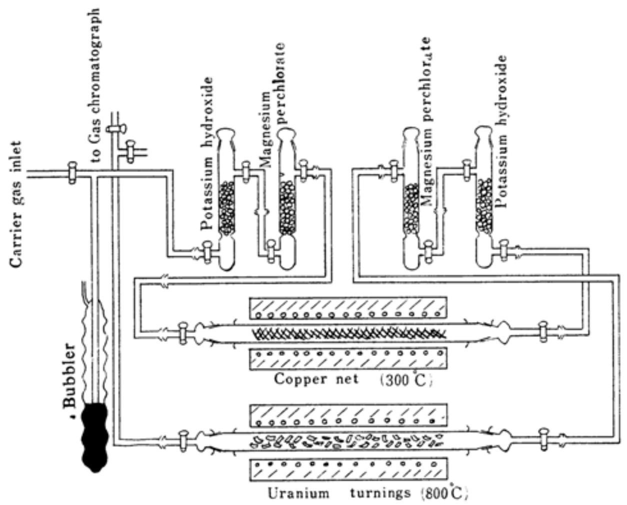

Fig. 3. Carrier gas purification apparatus.

TABLE I. DETERMINATION OF WATER OF CRYSTALLIZATION IN HYDRATED COPPER SULFATE

Weight of $CuSO_4\cdot5H_2O$ g.	Volume of H_2 released from $CuSO_4\cdot5H_2O$ (Experimental value) ml.	Weight of water in $CuSO_4\cdot5H_2O$ (Experimental value) g.	Weight of water in $CuSO_4\cdot5H_2O$ (Calculated value) g.	The ratio of the third and fourth columns
0.0358	15.85	0.0127	0.0129	1.0157
0.0779	34.17	0.0274	0.0273	0.9963
0.0883	39.87	0.0320	0.0318	0.9937
0.1503	68.47	0.0550	0.0542	0.9854
				1±0.0022*

* Standard deviation

graph, along with the carrier gas. The determination was carried out with a ball-disc-type automatic integrator fixed on the SAP-type recorder. A molecular sieve-5A column was used for the separation of the components (0.6 cm. in diameter and 75 cm. long). The flow rate of the carrier gas was 40 ml. per minute. For the determination of hydrogen, argon gas was used as the carrier, while for oxygen, nitrogen, methane and carbon monoxide, helium gas was used. Both the carrier gases were completely purified by the gas purification apparatus shown in Fig. 3. A constant flow rate of the carrier gas was obtained by maintaining a constant pressure at the inlet of the chromatograph by using the mercury bubbler set in the gas purification apparatus. The sensitivity of the recorder was increased to 30 μV. per full scale by using an electronic galvanometer, model AD-6, made by the Toa Dempa Kogyo Co.

Results and Discussion

The Determination of the Water of Crystallization in Hydrated Copper Sulfate.—To confirm the complete decomposition of water to hydrogen by lithium aluminum hydride at room temperature, hydrated copper sulfate was used as standard material and the water of crystallization in it was determined. The copper sulfate weighed was heated in the furnace at 250°C, and the water vapor released was passed through the U-tube with lithium aluminum hydride powder packing, in which the vapor was decomposed to hydrogen. The hydrogen was then drawn into and collected in the gas sampling vessel by the automatic Toepler pump, and analysed by the gas chromatograph. The results obtained are shown in Table I.

As the table shows, the water completely decomposed to hydrogen by lithium aluminum hydride under the experimental conditions.

The Reaction of Lithium Aluminum Hydride with Gases Other than Water Vapor.—It was confirmed that lithium aluminum hydride quantitatively reduced water to hydrogen at room temperature. Then the reactions between lithium aluminum hydride and other gases were examined. The results of the reaction between lithium aluminum hydride and oxygen are shown in Fig. 4, where the small circles indicate the oxygen calibration points which were obtained by passing it through the U-tube packed with lithium aluminum hydride, and the small triangles show the calibration points which were obtained by not passing it through it. The points obtained for both cases

TABLE II. DETERMINATION OF WATER IN STANDARD SAMPLE

Volume of standard sample introduced to gas chromatograph ml.	Volume of water in standard sample (Experimental value) ml.	Concentration of water in standard sample (Experimental value) %	Concentration of water in standard sample (Calculated value) %	The ratio of the third and fourth columns
7.90	0.018	0.228	0.230	0.9913
7.33	0.017	0.232	0.230	1.0097
5.45	0.001	0.020	0.019	1.0536
				1±0.0311*

* Standard deviation

TABLE III. VOLUME AND COMPOSITION OF GASES EVOLVED BY 50 g. OF URANIUM DIOXIDE

Temp. °C	Heated time hr.	Volume ml.	Gas constituents, %				
			H_2O	O_2	N_2	CH_4	CO
300	6.0	13.1	94.3	0.0	3.0	2.8	0.0
300	18.0	2.7	100.0	0.0	0.0	0.0	0.0
600	6.0	3.7	39.8	4.5	42.7	13.0	0.0
600	18.0	3.4	0.0	0.0	100.0	0.0	0.0
1000	6.0	15.9	0.0	0.0	100.0	0.0	0.0
1000	18.0	6.7	0.0	0.0	100.0	0.0	0.0
Total	72.0	45.5					

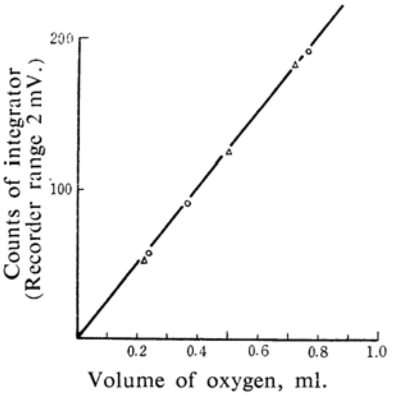

Fig. 4. Calibration curve of oxygen.

Carrier gas; Helium
Flow rate; 70 ml./min.
Column; Molecular sieve-5A, 1.5 m.

lie on the same line.

From the results, it is clear that the reaction between lithium aluminum hydride and oxygen does not occur. Following the same procedure, the reactions between lithium aluminum hydride and nitrogen, carbon monoxide, carbon dioxide methane and C_2–C_4 hydrocarbons were examined; no reactions could be detected.

The Adsorption of Water on the Surface of Lithium Aluminum Hydride.—As lithium aluminum hydride is a fine powder, the adsorption of water vapor on its surface must be checked under the experimental conditions.

Standard samples of water with water vapor contents of 0.230 and 0.019% were prepared. The water was decomposed to hydrogen and analysed by the gas chromatograph. The results obtained are shown in Table II. This table shows that the adsorption of water on the surface of lithium aluminum hydride is negligible within the range of experimental error under the present experimental conditions.

The Gas Content of Uranium Dioxide.*—Because of its good heat resistance, good chemical stability, etc., uranium dioxide is widely used as a nuclear fuel. However, uranium dioxide adsorbs various kinds of impurity gases on its surfaces. These gases are released gradually during the reactor operation, which has various harmful effects on the reactor operation, such as reacting with the zirconium used to protect to graphite moderator from the sodium coolant, leading to the deterioration of the physical properties of the zirconium.[10,11]

The analytical method stated above was used to determine the gas content of uranium dioxide, and satisfactory results were obtained. An example of the results is shown in Table III.

The sample of uranium dioxide which was used for the experiments had been stored in a laboratory, sealed in a polyethylene bottle, while the uranium dioxide was purchased from the Yokogawa Kagaku Co., Ltd.

In Table III, the first column shows the

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* The gas content of many samples of uranium dioxide was ascertained. The results will be reported in the Journal of the Atomic Energy Society of Japan.

10) S. Siegel, R. L. Carter, F. E. Bowman and B. R. Hayward, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy," 9 (1956), p. 829.

11) H. J. Anderson and R. J. Anicetti, "Specification for High Density Uranium Dioxide (Nuclear Grade)," HW-74204, July (1962).

degassing temperature; the second, the degassing time; the third, the volume of gas released equivalent to that at S. T. P., and the fourth and other columns, the results of the analysis of the released gases. About 50 g. of uranium dioxide powder was used for this experiment.

The Limitation of the Determination of Water.—Concentrations of hydrogen as low as about 10 p. p.m. could be determined by the present gas chromatographical method. When 10-ml. gas samples are used, the limitation of the determination of water is as follows. In the decomposition of water by lithium aluminum hydride, one mole of hydrogen is obtained from one mole of water. That is, 10 p. p. m. of water in 10-ml. sample gases (0.1 μl. of water) is the limitation of the determination for water. Converting this value to weight, it follows that about 0.1 μg. is the limitation for water.

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