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Coulometric Titration of a Microamount of Water after Conversion to Ammonia

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Sodium amide was used to convert a microamount of water into ammonia in a carrier gas. The ammonia was then titrated with coulometrically generated hypobromite ions. The reaction between water and sodium amide was completed stoichiometrically, and the reaction rate was considerably promoted by heating sodium amide at 80°C. The sample hydrogen was oxidized with copper(II) oxide at 800°C, and the water thus produced was determined by this method. 0.096—0.665 m*l* (8.6—59.8 μg) of hydrogen and 0.055—0.465 mg of water in barium chloride crystals were determined within errors of 3.6% and 3.0% respectively. The water adsorbed on the surfaces of the weights was also determined by this method at various humidities.

Many investigations of the coulometric microdetermination of water are to be found in the literature. Meyer and Boyd[1] proposed first the use of a Karl Fischer reagent for this purpose, and several similar papers have followed theirs.[2–4] In this process, however, the location of the end point of the titration is troublesome for determining a microamount of water. The excess iodine produced after the end point usually disappeared when the reducing material was diffused from the cathode compartment.[2]

Keidel[5] proposed the phosphorous pentoxide cell, which is very useful for the continuous analysis of water in gaseous samples.[6] It was, however, recently pointed out that the cell gave relatively large residual current.[7] This current may disturb the precise determination of microamounts of water. Giegerl[8] proposed a method for the coulometric determination of hydrogen in steel. After the oxidation of the hydrogen, the water was heated with carbon at 1100°C; then the hydrogen and carbon monoxide produced were reoxidized to water and carbon dioxide respectively. The latter was then determined by the coulometric titration method. Martin, Floret, and Lemaitre[9] recommended the following process; the water in the carrier gas was converted into hydrogen chloride with phosphorus pentachloride, and then the gas was allowed to flow through a sodium bicarbonate column. The carbon dioxide thus produced was determined by coulometric titration. These circuitous processes give relatively large blank values, and also a long time is needed to make the values constant.

Sodium amide reacts with water to produce ammonia; this reaction has also been applied to the determination of water.[10] No remarkable advantage can, however, be expected when the ammonia is titrated by the ordinary volumetric method.

In this paper, the authors used the coulometric titration method to determine the ammonia produced by the above reaction; they proved that this process can be adopted to determine a microamount of water or hydrogen in the carrier gas.

Experimental

Apparatus. The apparatus for the dehydration of solid samples is shown in Fig. 1. The heating tube for the dehydration of solid samples was made of Pyrex glass. Two different U-tubes of sodium amide (15 cm × 8 mm i. d. for 20—500 μg H_2O; 10 cm × 5 mm i. d. for less than 20 μg H_2O) were used to convert water into ammonia. The U-tube used was heated in a thermostat (oil bath). In order to pack sodium amide and phosphorus pentoxide in the respective U-tubes, the authors used a moistureless glove box. The air in the U-tube was replaced with argon. Unless these precautions are taken,

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[1] A. S. Meyer and C. M. Boyd, *Anal. Chem.*, **31**, 215 (1959).

[2] Y. Yasumori, M. Ikawa and Y. Nozawa, *Bunseki Kagaku* (*Japan Analyst*), **14**, 871 (1965).

[3] M. R. Lindbeck and H. Freund, *Anal. Chem.*, **37**, 1647 (1965).

[4] R. F. Swensen and D. A. Keyworth, *ibid.*, **35**, 863 (1963).

[5] F. A. Keidel, *ibid.*, **31**, 2043 (1959).

[6] J. J. Engelsman, A. Meyer and J. Visser, *Talanta*, **13**, 409 (1966).

[7] T. Mitsui and K. Nakamura, Lecture to the 16th Analytical Conference Japan, Chiba, Japan (1967).

[8] E. Giegerl, *Arch. Eisenhüttenw.*, **33**, 453 (1962).

[9] F. Martin, A. Floret and J. Lemaitre, *Bull. Soc. Chim. France*, **1964**, 1836.

[10] D. Klamann, *Oesterr. Chemiker Ztg.*, **54**, 165 (1953).

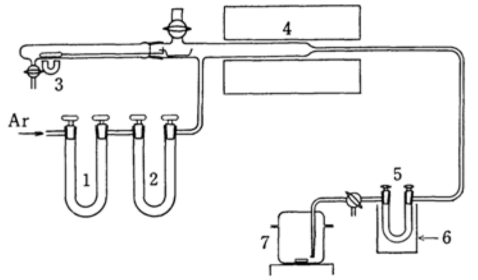

Fig. 1. Apparatus for water determination.
1. $Mg(ClO_4)_2$, 2. P_2O_5, 3. Magnet, 4. Sample heater, 5. $NaNH_2$, 6. Oil bath, 7. Titration cell

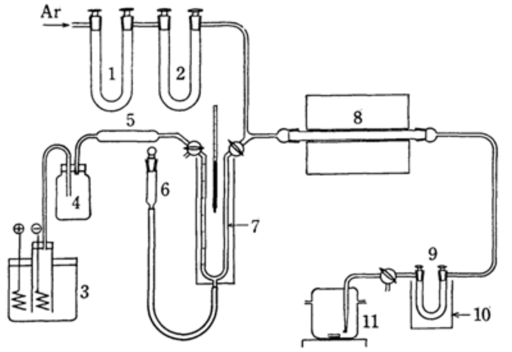

Fig. 2. Apparatus for hydrogen determination.
1. $Mg(ClO_4)_2$, 2. P_2O_5, 3. H_2 generator, 4. Alkaline pyrogallol solution, 5. $CaCl_2$, 6. Mercury reservoir, 7. Gas sampler, 8. CuO, 9. $NaNH_2$, 10. Oil bath (80°C), 11. Titration cell

their expected effectiveness are considerably shortened. The gas-sampling buret proposed by Giegerl[8] (Fig. 2) was advisable for removing the disturbance due to back-pressure of the carrier gas. Copper(II) oxide was used to oxidize the hydrogen. The temperature of the oxide was kept at 800°C.

The coulometric titration cell is shown in Fig. 3. The generator electrode was a platinum foil of 1×1 cm. According to the investigation by Christian, Knoblock, and Purdy,[11] the current density for the generation of hypobromite ions should be less than 9.6 mA/cm^2 in a solution of 1M of bromide ions. Therefore, a current of less than 19 mA was used in this investigation.

The auxiliary electrode was a platinum wire 5 cm in length and 0.5 cm in diameter. The same platinum wires, 0.5 cm in length, were used as the pair of indicator electrodes. The dead-stop method was used to detect the end point of the titration. The indicator current was measured by a microammeter (full scale: 3 μA). The potential difference between the two indicator electrodes was 0.2 V.

The electronic constant current source reported previously[12] and an electric stop clock driven by a synchronous motor were used to measure the electricity. The total error due to the measurements of the electrolytic current and of the time does not exceed 0.5%.

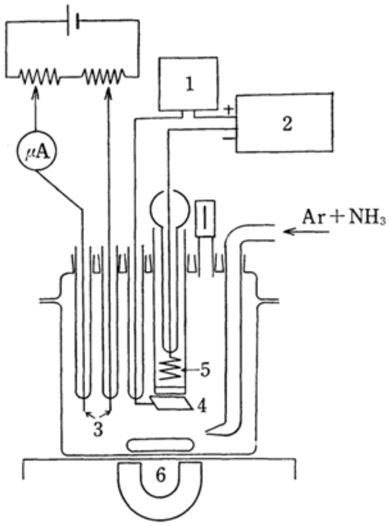

Fig. 3. Coulometric titration apparatus.
1. mA meter (full scale 10 and 30 mA), 2. Constant current source, 3. Indicator electrode pair, 4. Generator electrode, 5. Auxiliary electrode 6. Magnetic stirrer

Reagents. *Sodium Borate Solution.* 38.1 g of sodium borate (Borax) were dissolved in 1 *l* of water; then perchloric acid was added until the pH of the solution decreased to 8.6.

The electrolyte solution was prepared by mixing 25 m*l* of a 5M sodium bromide solution and 50 m*l* of the sodium borate solution, and by then diluting the mixture to 125 m*l* with water. The above mentioned sodium borate solution was used as a catholyte. Sodium amide produced by the Daiichi Pure Chemicals Co., Ltd., could be used without any trouble. All the other reagents used were analytical grade.

Argon was dried with magnesium perchlorate and then with phosphorus pentoxide.

Procedure. *Setup of the Apparatus.* To decrease and to stabilize the blank value quickly, a column of sodium amide was heated at 110°C for half an hour; then it was cooled somewhat and kept at 80°C. During this period, argon was allowed to flow through the apparatus, but it was not introduced into the titration cell. The rate of the flow of argon was 200 or 100 m*l*/min. Argon was then introduced into the column and the cell by turning a three-way cock. The blank values were determined coulometrically every 5 or 10 min until the values became constant.

Introduction of Sample. The process used for sampling gaseous hydrogen was that shown by Giegerl.[8] First, U-tube buret was filled with mercury; then electrolytically generated hydrogen was introduced into the capillary buret on one side of the U-tube. After the measurement of the volume of hydrogen, a small amount of it was transferred to the tube on the other side by lowering the mercury reservoir. The transferred hydrogen was then introduced into the reaction tube containing copper(II) oxide, after which the volume of hydrogen

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11) G. D. Christian, E. C. Knoblock and W. C. Purdy, *Anal. Chem.*, **35**, 2217 (1963).

12) T, Yoshimori, Y. Hino and T. Takeuchi, *Bunseki Kagaku* (*Japan Analyst*), **15**, 1234 (1966).

remaining in the buret was measured again. The difference between the two readings was the volume of hydrogen taken.

A weighed solid sample was dropped into the dried boat in the dehydration tube by the aid of a small glass funnel. The boat was then introduced into a furnace kept at 200°C by the movement of a magnet. After 10 min, the boat was removed from the furnace. Argon was allowed to flow through the apparatus continuously. The rate of the flow of argon should not exceed 200 m*l*/min. Lower results could be obtained at the rate of 400 m*l*/min with the sodium amide column mentioned above. By using a longer column, the rate of argon can perhaps be increased.

Coulometric Titration. The electrolyte prepared as above was electrolyzed with a constant current until the indicator current was raised to a definite value smaller than 1.0 μA. After recording the indicator current, argon containing ammonia was introduced into the cell. After 5 or 10 min, the titrant was generated electrolytically with a constant current until the indicator current was increased to the previous value. This titration was repeated at 5- or 10-min intervals until the electricity of the blank experiment. During the entire course of the titration, argon was allowed to flow through the apparatus and the cell continuously.

Results and Discussion

Determination of Hydrogen. Hydrogen was measured into a reaction tube containing copper(II) oxide and heated at about 800°C using Giegerl's buret.[8] The water thus produced was determined by this method. The results obtained are shown in Table 1.

The reaction of water in a carrier gas with sodium amide is completely stoichiometric. Therefore, a standard sample or a calibration curve is not necessary. This makes it possible to obtain reliable and accurate results in the determination of microamounts of water.

To shorten the time required for a single determination, the heating of sodium amide is quite effective. Blank values, however, increase appreciably over 90°C. The relations obtained in the analysis of hydrogen are shown in Fig. 4. The heating of the column at 80°C is preferable.

TABLE 1. DETERMINATION OF HYDROGEN

H_2 taken (m*l*)	H_2 found (m*l*)	Recovery (%)
0.096	0.092	96
0.126	0.121	96
0.209	0.207	99
0.231	0.217	94
0.241	0.245	102
0.343	0.338	99
0.351	0.348	99
0.490	0.481	98
0.508	0.542	107
0.665	0.680	102
	mean	99.2
	$\sqrt{V}$	3.6

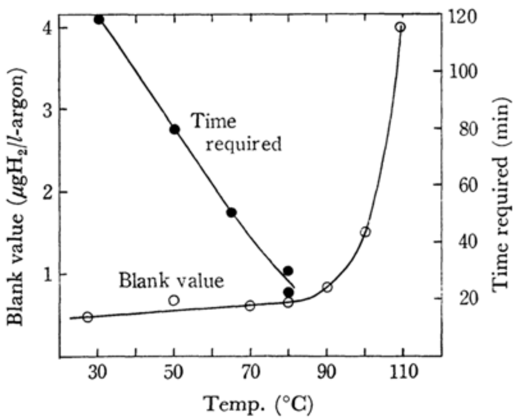

Fig. 4. Effects of heating of $NaNH_2$ column on the blank value and on the time required for single determination of hydrogen.

The increase in the blank value at a temperature higher than 90°C may be based on the some decomposition of the amide.[13] In accounting for the heating effects of the column, the authors considered the following possibility. Some of the water in argon may be adsorbed on the surface of the sodium hydroxide produced by the reaction of water and sodium amide, and the vapor pressure of water on the surface of the hydroxide may be increased at an elevated temperature.[14] These phenomena accelerate the desorption of water on the surface of sodium hydroxide and quickly complete the reaction of water and sodium amide.

In the field of gas chromatography, calcium carbide has sometimes been used for removing the tailing effect due to water in a sample. The present authors tried to use carbide to convert water into acetylene, and then the acetylene was oxidized to carbon dioxide and water. The carbon dioxide thus produced was determined by coulometric titration. This process, however, has the following disadvantages. The calcium hydroxide produced by the reaction between water and the carbide has a relatively high vapor pressure of water. Therefore, it reacts slowly with calcium carbide to produce acetylene. The reaction rate of this process is very slow even at elevated temperatures. More than 3 hr are needed for a single determination even if the carbide has previously been heated at several hundred degrees. The other problem was the purity of the carbide. Different kinds of commercially obtainable carbides and the carbide produced specially by the authors were all used.

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[13] Gmelin, Handbuch für anorg. Chemie, "Natrium," 8 Aufl., s. 211 (1928).

[14] *Ibid.*, s. 255.

The blank values were, however, not decreased enough with these reagents.

Roth and his co-workers[15] has proposed a process to convert water into ammonia with magnesium nitride. This process was also attempted by the present authors with the aid of coulometric titration; they found the same difficulties as in the calcium carbide process.

Since sodium hydroxide does not itself set free water, it is unnecessary to consider these difficulties. By the present method, the time required for a single determination and the blank value of each determination are considerably decreased. Furthermore one mole of water is equivalent to three Faradays of electricity. This ratio is greater than in any of the other processes mentioned above. These advantages show the adaptability of this method to determine microamounts of water and hydrogen in various carrier gases which do not react with sodium amide.

TABLE 2. DETERMINATION OF WATER IN BARIUM CHLORIDE DIHYDRATE

Sample taken (mg)	H_2O calcd (mg)	H_2O found (mg)	H_2O recovery (%)
0.37	0.055	0.054	98
0.50	0.074	0.079	107
0.59	0.087	0.087	100
1.04	0.153	0.148	97
1.09	0.161	0.158	98
1.47	0.217	0.210	97
1.63	0.240	0.232	97
2.13	0.314	0.312	99
3.16	0.466	0.465	100
		mean	99.2
		$\sqrt{V}$	3.0

Determination of Water in Hydrated Barium Chloride Crystal. A weighed crystal of hydrated barium chloride was dropped into the boat in the reaction tube, and then the boat was introduced into the heating furnace by the aid of a magnet. The water content in the crystal was determined by this method. The temperature of the furnace was kept at 200°C, and the rate of flow of argon was 200 m*l*/min. The results obtained are shown in Table 2. In order to recover the water in the crystal completely, a somewhat longer time was needed than for the determination of hydrogen. Because of the water adsorbed on the surface of the crystal, these results were somewhat larger than their theoretical values. Considerably higher results could be obtained when the sample did not consist of a single crystal.

TABLE 3. ADSORBED WATER ON THE SURFACES OF WEIGHTS (in μg)

	Kind of weight (mg)	Relative humidity (%)		
		55		80
Platinum	100	0.22		0.50
	200	0.49		0.62
	500	0.39		0.93
	Kind of weight (mg)	Relative humidity (%)		
		66	76	80
Stainless steel	100*	0.62	0.50	1.03
	200*	0.72	0.62	1.05
	500	0.16	—	0.84
	Kind of weight (mg)	Relative humidity (%)		
		58		
German silver	100	0.43		
	200	0.56		
	500	0.87		

* Surface is somewhat rough.

Determination of Water Adsorbed on the Surfaces of Weights. As an example of the practical use of this method, the water adsorbed on the surfaces of the weights was determined at various humidities. The appratus and the method were the same as in the case of barium chloride. The results obtained for various kinds of weights are shown in Table 3.

These results show that the water adsorbed on the weight depends greatly on the condition of the surface, and not so greatly on the relative humidity. It can be concluded that the water adsorbed on the surfaces of weights does not disturb the ordinary weighings with a microbalance.

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[15] F. Roth and A. Schulz, *Brennstoff Chem.*, **20**, 317 (1939); F. Roth, *ibid.*, **22**, 77 (1941); F. Roth and A. Schnoor, *ibid.*, **22**, 89 (1941).