Yield. An average yield of seven syntheses gave 2 mC of bromoacetic acid-1,2-^{14}C (28 %) from 7 mC of barium carbonate-^{14}C, the formed product carrying twice the specific activity of the original barium carbonate-^{14}C (spec. act. 22.6 mC/mM).

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Quantitative Determination of Crystal Water and Moisture Content by Gaschromatography

INGER LINDGREN

Research Institute of National Defence, Dept. 1, Sundbyberg, Sweden

In the gaschromatographic determination of water some difficulties are encountered due to the polar nature of water and to the resulting tailing, to some absorption in the stationary phase, and to the affinity of water for the support. Rogozinski *et al.*[1] showed that in the direct determination by gaschromatography the detection limit for water in alcoholic solutions is about 10 %. The technique of adding water to the helium carrier gas to reduce tailing is described by Knight.[2] By fitting a gaschromatograph with a trapping arrangement to concentrate the moisture content in butane gas, Carlstrom *et al.*[3] were able to determine trace quantities of water. Smith[4] reports some observations in various stationary phases, and discusses the application of his method to quantitative analyses.

The use of indifferent substances such as Teflon-powder or Fluoropak as supports in gaschromatography of polar components has made possible the construction of columns which give a minimum of tailing.[5,6] When this communication was in preparation, Bennet[7] published a method describing the determination of water in organic solvents, using a column with Teflon-powder as a support, and Schwecke *et al.*[8] reported a way to determine moisture in food with methanol as a water extracting agent on Fluoropak support.

The present investigations were carried out for the determination of (1) crystal water in various compounds, and (2) the moisture content of hygroscopic and thermo-unstable substances. Methanol or acetone were used to extract water from the product to be analyzed, and the water content of the solvent was quantitatively examined on a column prepared by coating Teflon-powder with 20 % Carbowax 1500. Column temperature was 72°C and helium flow rate was 60 ml/min.

Experimental. A gaschromatograph, Perkin-Elmer 116 E, equipped with a hot wire detector, was fitted with an aluminium tubing, 6 mm × 2 m, packed with Teflon-powder (Perkin-Elmer 158–00–906) coated with 20 % Carbowax 1500. The stationary phase was dissolved in methylene chloride, slurried with the support and dried in a Rotavapor.* The new column was heated for 4 h at about 75°C and was then ready for use. It may be used for water determinations in acetone or methanol. The retention time acetone-water is 12 min and methanol-water 10 min at a temperature of 72°C and at a helium carrier gas flow rate of 60 ml/min. The water peak was symmetrical and sharp (Fig. 1).

The quantitative measurements of water in miscellaneous samples was accomplished in the following manner: a calibrated curve was obtained for 0–10 % water in methanol. (Acetone can also be used since the curve will be the same. However, methanol Merck *p.a.* is preferable to acetone Merck *p.a.* The former contains only 0.01 % moisture in a new opened bottle while the latter contains

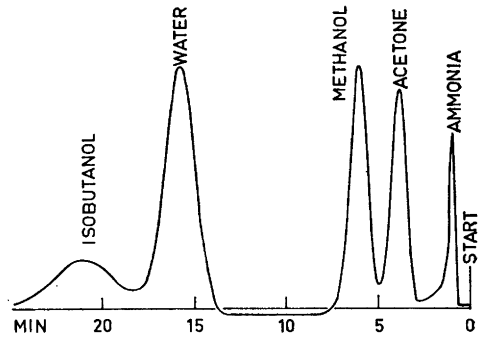

Fig. 1.

* The column is commercially available from Perkin-Elmer & Co, but is not difficult to prepare in the laboratory.

Table 1.

Substance	Number of crystal water	Per cent water		Total error per cent
		found	calculated	
citric acid	1	8.4	8.56	−1.8
sodium acetate	3	39.1	38.68	+ 1.1
cupric sulphate	5	35.0	36.05	−2.8

about 1 % under the same conditions and thus must be dried over Dehydrite and distilled before use.) The product of the peak height and the peak width at half the height [9] was plotted against the concentration, and a straight line was obtained. Under identical experimental conditions the standard deviation at 7 % water was 0.02 %.

When crystal water is determined, the substance must be sufficiently soluble in methanol or in acetone that the water content after dissolution is at least 0.2 %. It is preferable that the matter to be tested gives a total concentration of water in the solvent of 0.2 to 10 %, and that 1 to 5 μl samples from a Hamilton syringe be injected into the gaschromatograph. The per cent of water in the solution may be read off from the calibrated curve. Three substances were examined: citric acid monohydrate, sodium acetate trihydrate and cupric sulphate pentahydrate. The quantitative data are shown in Table 1.

In the attempts made to determine the number of crystal water, it was found that the quantity of substance tested should be at least 10 % lower than its saturation in the solvent. Samples with 90 to 100 % saturation diverge negatively from the theoretical concentrations obtained. In the determination of the moisture content of various substances, it is not necessary that they dissolve in the solvent. Such substances are slurried and vigorously shaken with dry methanol and set aside for an hour. Then a sample of 1 μl of the clear supernatant containing 1 to 10 % water is injected into the gaschromatograph. For example sodium chloride was tested in this way and was found to contain 2.9 % moisture. Sodium chloride determined in the common way in a drying oven contained 3.1 % water.

Results. The technique was employed on samples of hygroscopic and thermounstable substances and on high boiling and viscous liquids. The determination of crystal water had some limitations. The substance to be tested must have such a solubility in acetone or methanol that the total water content in the solvent is 0.2 %.

No degeneration of the column or any ghost peaks were detected in spite of more than 200 injections of solid substances and of high boiling liquids. To avoid the effect of occasional variations in temperature or the carrier gas flow rate, it is recommended that a calibration sample of 3 % water in methanol be injected before the beginning of each experimental series. The accuracy in this method is about ± 1.5 %. In the determination of the crystal water content, this represents a small methodological error since the difference between two units of crystal water is about 10 %. For example, the difference between four and five crystal water in cupric sulphate pentahydrate is 13.6 %. Thus, this method provides a means for a rapid estimation of the moisture content of substances, particularly useful for those substances which cannot be dried in the common way.

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