Determination of Water in Organic Substances

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Two methods for the determination of water in organic compounds, are described. One method uses gas chromatography on Porapak columns and is capable of detecting even ppm amounts of water. The other method is based on reaction of water with CaH_2 and volumetric determination of the evolved hydrogen. The two methods are compared, and their advantages and disadvantages discussed.

Much work has been carried out on the determination of the water content of organic compounds, and many different methods have been proposed.[1] These methods usually have in common that they require relatively large amounts of sample, can be used for a limited range of substances, and are less reliable at water concentrations below 0.1 %. The most widely applicable method, which has been extensively used, is the Karl Fischer titration method.[2] The determination is rapid, and automated commercial equipment is now available which eliminates many possible errors in measurement. The use of Karl Fischer titrations is of great value for routine water determinations, especially in solvents, *etc.*,[3] but has the disadvantage that usually several milliliters of sample are required for each determination. In many cases, especially where novel or high purity substances (purity > 99.9 %) are concerned, this may represent a large proportion of the available substance. Such is often the case with substances to be investigated thermochemically, *e.g.* enthalpy of combustion measurements. Another important requirement here is that the analysis for water content is carried out on exactly the same sample as used in the thermochemical determinations. The K. F. method is also limited to certain classes of compounds.[3]

For these reasons, we have developed two rapid, simple methods for determining small amounts of water in substances, either by taking samples in a syringe, or by analysing the substance in ampoules, filled under vacuum.

GAS CHROMATOGRAPHIC METHOD

Since Hollis[4] introduced the use of porous polymer beads in gas chromatography, such materials have found wide application, especially for analyses of aqueous solutions and polar compounds. Previously, gas chromato-

graphic analysis for water in volatile compounds has proved difficult because of adsorption of water by the solid support and relatively slow elution. Both of these effects lead to tailing and broadening of the water peak and make quantitative determination of trace amounts of water extremely difficult. In a second paper,[5] Hollis indicated that the porous polymer beads, which gave rapid elution of water with excellent peak shape, could be used for quantitative analysis of water in a variety of compounds. While several papers have appeared comparing the separation characteristics of various porous polymers,[6] little attention has been paid to the systematic determination of water in organic compounds. Castrello and Munai[7] have determined traces of water in hydrocarbons, using an electron-capture detector and a column of Porapak Q, but considered it necessary to coat the polymer with a few per cent of SE-30 or Apiezon L and Carbowax 20 M. Neumann[8] has shown that the method is capable of high sensitivity in a study using Porapak R, a polymer normally used for the analysis of amines, and found the detection limits of water to be 150 vol. ppm in gases, and 1 vol. ppm in liquids, using normal injection quantities.

This paper describes the development of a gas chromatographic method for the determination of water in organic substances with special attention to the requirements of thermochemical investigations.

APPARATUS AND MATERIALS

A Varian Aerograph 90-P gas chromatograph fitted with a thermal conductivity detector with WX filaments was used in this study. The porous polymers used were Porapak P and Q, both 80−100 mesh, obtained from Waters Associates. Columns of stainless steel, 5′ × 1/4″, were packed by vibration, and conditioned for 12 h at 180°C. The column temperature was 100° for Porapak P, and 120° for Porapak Q. The detector was held constant at 180° to avoid condensation.

The apparatus was fitted with a backflush valve such that the organic compounds could be quickly flushed out of the column, by-passing the detector.

Hydrogen, dried by passing over molecular sieves 4A, was used as carrier gas (50 ml/min). It has been suggested[9] that a carrier gas with a controlled, constant moisture content is preferable, since this reduces adsorption of water from the sample on metal surfaces. We have found no indication of such adsorption effects, provided sufficiently high temperatures are used, and that the space between the column and the detector is as short as possible, and regard drying of the carrier gas as the best technique.

Method

Calibration. Ethylene chloride (BDH, Ltd.) was dried by a batch process, using molecular sieves 4A. A 20 μl sample was injected into the gas chromatograph and the height of the water peak on the recorder was measured (retention time of water about 1.5 min). The backflush valve was then reversed immediately after elution of the water, and returned to its normal position after the ethylene chloride had been flushed out of the column. This procedure was repeated at least twice. Known amounts of water were then added to the ethylene chloride, using a precision microsyringe, and the resulting solutions were analysed for water as above. Fig. 1 shows a typical calibration curve obtained, where peak height in mm is plotted against vol. % water content. For water contents higher than 0.1 vol. %, similar procedures were carried out, using ethyl acetate as solvent.

The calibration was repeated several times a year, and whenever a new column or detector was installed.

The sensitivity of the detector varied slightly (up to about 3 % from day to day). To avoid the necessity of performing calibration experiments as described above every day, the sensitivity of the apparatus was checked by injecting samples of benzene saturated with water at 25°C. The benzene-water mixture was prepared by shaking
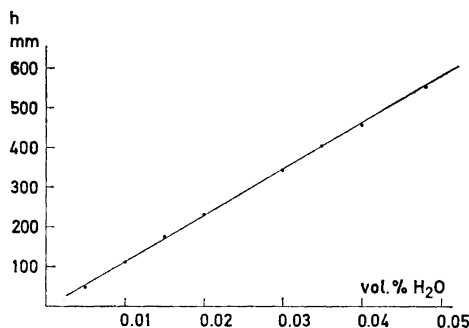

Fig. 1. Calibration of GLC method; 20 μl sample of ethylene chloride.

equal volumes of benzene and water for 24 h at 25°C, and then storing the mixture in a 25°C thermostat. The benzene layer was then analysed for water directly after an absolute calibration of the apparatus as described previously. The solubility of water in benzene at 25°C was found to be 0.061 ± 0.002 vol. %. There is a large variation in the literature values for this solubility, but our value receives support from an independent determination, using a microcoulometric Karl Fischer method.[10] This rapid standardisation is recommended for the method, and is very reliable, provided sufficient care is given to the thermostating of the benzene-water mixture.

Analyses. In routine work, analyses for water were performed as in the calibration by directly injecting a sample of the substance being studied. In connection with calorimetric studies, it was necessary to determine water contents of samples in ampoules of different sizes (~ 1 ml for reaction calorimetry, and ~ 0.5 ml for combustion calorimetry). In these cases, the ampoules were placed in a glass vessel fitted with two taps and a stopper with a silicone rubber membrane. The vessel was first flushed with dry nitrogen. The taps were then closed, the ampoule was broken by inserting the syringe needle through the membrane, and a sample taken and analysed for water in the usual way. In this manner, several runs could be carried out on the same sample without moisture being taken up, and thus enabling the water content measured to be referred directly to the sample being used in the calorimetric investigations.

RESULTS

Water contents were determined from the peak heights and the amount of sample injected. Some results obtained are shown in Table 1 as a comparison with values from the calcium hydride method described below. It should be noted that the figures given in Table 1 are not solubility data, but water contents of the samples filled into ampoules under vacuum. The reproducibility of the method is about ± 3 % over a range of water contents from about 10 ppm to *ca.* 4 vol. %. The method has not been tested at higher water concentrations, but should be applicable up to at least 10 %. In the range $1-10$ ppm, the precision was of the order of $\pm 5 - 10$ %. In this range, for the highest precision, larger samples were injected to increase the peak heights. The system has been tested using sample sizes from 5 to 100 μl and found to be linear in response over the whole of this range. It should thus be possible

in principle to detect fractions of ppm water, but in practice, handling techniques prevent accurate quantitative determinations below 1 ppm. For precision work, especially in the ppm range of water concentrations, it was found vital to evacuate the syringe and needle under vacuum after washing the syringe before each new injection.

Table 1. Water contents of samples determined by the two methods.

Substance	Water content, vol. %, using GLC method	Water content, vol. %, using CaH_2 method
Hexane	0.008 ± 0.0004	0.006 ± 0.0006
Benzene	0.052 ± 0.002	0.055 ± 0.003
Ethylene dichloride	0.124 ± 0.004	0.129 ± 0.005
Ethyl acetate	1.98 ± 0.06	1.92 ± 0.06

The use of the backflush valve greatly reduces the analysis times. Most substances have long retention times on Porapak columns which would make the time for each determination unreasonably long. The backflush technique also helps to prolong the lifetime of the detector, since all organic substances are flushed out of the system without passing through the detector. The column may also be overloaded without affecting the analyses, enabling large samples (100 μl) to be injected.

The lifetime of the column packing is about 6 months when the apparatus is used daily. Porapak becomes miscoloured after prolonged use and tends to form clumps, which leads to tailing of the water peaks and a lowering of the precision of the method.

DISCUSSION

The gas chromatographic method has been found to be rapid, reliable and applicable to almost all classes of compounds. Solids are not easily analysed for water content, unless a suitable solvent is available which is easy to dry and in which the solid has a high solubility.

Some workers prefer to use the measurement of peak areas for quantitative determination. Hogan et al.[11] have used this method with an internal standard technique to eliminate the need for daily area calibrations. Their method is time-consuming and demands large amounts of samples, in order to prepare the solutions containing the internal standard with sufficient accuracy. The use of peak heights as in the present study, instead of areas, puts stringent requirements on the carrier gas flow rate. This should be constant to better than 1 %, since peak heights are dependent on the flow rate, especially for large samples. Peak areas are not affected by the gas flow rate, but require more elaborate equipment for their determination, and it has been concluded [12] that peak height measurements are the more reliable in the type of analyses reported here.

CALCIUM HYDRIDE METHOD

The method consists basically in mixing the sample to be analysed with calcium hydride and determining the amount of hydrogen evolved from the reaction between the hydride and any water present in the substance.

A diagram of the apparatus is shown in Fig. 2. The glass reaction vessel, A, contains the ampoule with the sample, calcium hydride and stirring rod. It is sealed between the brass collars, B, by means of an O-ring, C, compressed by screws between the collars. The hollow ampoule breaker, D, through which carbon dioxide passes from the drying tube into the reaction vessel, is held by the nut, E, and sealed by an O-ring, F. Gas leaves the vessel *via* the tube, G, passing through a cold-trap, H, before flowing into the nitrometer.
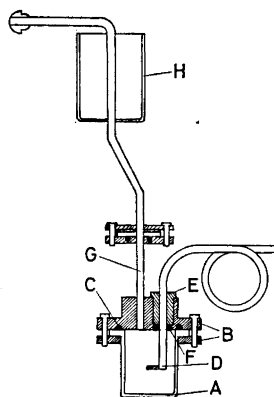

Fig. 2. Diagram of CaH_2 apparatus.

Method. Pure carbon dioxide is passed through a drying tube, containing magnesium perchlorate, into the reaction vessel. From the reaction vessel, the gas flows through the cold-trap and *via* a three-way tap into a nitrometer (Pregel type, vol. 1.5 ml). The nitrometer is filled with ~ 45 % potassium hydroxide solution, which absorbs all the carbon dioxide, but not air and other gases.

First the apparatus is set up, but the nitrometer not connected, and flushed for about 30 min with CO_2. The nitrometer is then connected, and after a further 5 min, readings of the nitrometer are started. When the amount of unabsorbed gas is satisfactorily low and constant (zero-effect, ≤ 0.001 ml/min), the ampoule is broken by pushing down the breaker rod, and the stirrer is started. The rod is drawn up again, and readings of the nitrometer are taken at regular intervals to measure any hydrogen evolved from the reaction between water and calcium hydride. The run is continued until the original zero-effect is again reached, or until the volume change becomes constant, and the volume of hydrogen is calculated.

The cold-trap prevents any substance from being carried over into the nitrometer and interfering with the readings.

Materials. Calcium hydride (Metal Hydrides Inc., 96 %, $-4+40$ mesh) and magnesium perchlorate (Arthur H. Thomas Co.) were used. The calcium hydride was stored in a tightly sealed container.

Especially pure carbon dioxide was obtained in cylinders from which impurities had been removed by a freezing-out procedure.

RESULTS

The measurements were usually complete after 45 − 60 min. Some results are shown in Table 1, compared with data from the gas chromatographic method. Sample quantities were from 0.3 to 0.6 ml, and no significant differences were found in the results for different amounts of samples.

Ampoules must be filled under vacuum, so that the substances are effectively degassed. Most organic compounds usually contain considerable amounts of dissolved hydrogen, oxygen, nitrogen and other gases. The partial pressure of these gases in the apparatus prior to breaking the ampoule will be essentially zero. There will thus be a release of gas from the substance when the ampoule is broken, if the substance has not been degassed, which will lead to large errors in the measured volume of hydrogen evolved from the reaction being studied.

Reproducibility is of the order of ± 4 % when the water content is greater than 0.01 %, and about ± 10 % in the range 0.005 − 0.01 %. The method is not sufficiently sensitive to provide accurate determinations for water contents below 0.005 %.

DISCUSSION

Methods using calcium hydride have been reported previously in the literature, based on the reaction

$$CaH_2 + 2 H_2O \rightarrow Ca(OH)_2 + 2 H_2 \qquad (1)$$
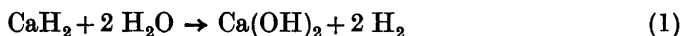
On a stoichiometric basis, 1 ml hydrogen at STP would be equivalent to 0.804 mg of water. However, Perryman [13] found a mean equivalent of 0.841 ± 0.007 mg of water per ml of gas, and recommended that the method be calibrated with distilled water for each batch of calcium hydride used. The agreement between the sets of results shown in Table 1 indicates that such deviations from stoichiometry do not occur with the method described here.

Earlier methods involving calcium hydride, measured the hydrogen evolved by pressure change measurements,[2,14,15] but large samples are required for this type of measurement. Elitzur [14] used ethanol as reaction medium, but it has been shown [16] that calcium hydride reacts with the lower alcohols, forming calcium alkoxides and hydrogen. Rosenbaum's method [15] took at least 12 h for one determination and did not take account of dissolved gases in the samples.

Fischer [2] used a calcium hydride procedure to check the results from his titration method. In general, he obtained fairly good agreement between the two methods, but pointed out that with benzene and CaH_2, stirring for a long time was necessary. We have found that stirring of the reaction mixture is essential if reproducible and accurate results are to be obtained.

Other procedures using calcium hydride, mainly for determining water in gases, have used measurement of the heat of reaction of the hydride with water,[17] and thermal conductivity measurements of the hydrogen evolved,[18] but these methods have not been used for any systematic investigations.

The calcium hydride method has been criticized by Gol'dinov et al.,[19] who stated that the reaction

$$CaH_2 + H_2O \rightarrow CaO + 2 H_2 \tag{2}$$
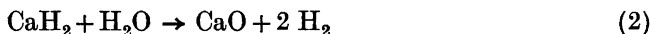
would also occur to a considerable degree. In a later paper, Mikheeva and Kuznetsov [20] reported results from an investigation of the relevant reactions over a wide range of temperatures. They found that up to 150°C, reaction (1) is the sole reaction, and at 400°C reaction (2) goes to completion. Between these temperatures, reaction (2) occurs to an increasing extent as the temperature rises The results presented here, compared with results from the gas chromatographic method, also show the absence of reaction (2) at room temperature, and that calculations based on reaction (1) give correct results.

The method is applicable to many different classes of organic compounds, but can, of course, not be applied to substances which react with CaH_2 giving water or gaseous products, or which react with CO_2, as for example amines.

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