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GAS CHROMATOGRAPHIC DETERMINATION OF WATER: A SOURCE OF SYSTEMATIC ERROR INTRODUCED BY INTERACTIONS OF POLAR COMPOUNDS ON POROUS POLYMER GAS CHROMATOGRAPHIC COLUMNS

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SUMMARY

The accuracy of the determination of water was found to be dependent on two major effects. The first is related to the adsorption properties of porous polymers. Under normal conditions of analysis a considerable amount of water is adsorbed on the column. In a non-polar sample matrix this adsorbed water does not interfere with water introduced by the sample. In a polar matrix, however, a certain amount of water is desorbed, which is seen as a virtual peak. This virtual peak is co-eluted with the first eluted polar compound. The second effect is related to the water content in the carrier gas, which should be controlled to ensure a constant analytical performance. The water concentration in the carrier gas is set by the desired sample blank value.

INTRODUCTION

Porous polymer gas chromatographic (GC) columns have been used for many years in the analysis of water in many kinds of samples. Especially in the analysis of liquid samples with a low water content (0.01–5%) a standard additions method is frequently used. These standard addition methods are based on the assumption of linear behaviour of the measuring system, while the absence of systematic errors can be tested by preparing sample blanks.

Unfortunately, a considerable amount of water can be found even in carefully prepared sample blanks. This phenomenon was noticed by several workers who described analytical procedures for water. In a standard additions procedure for the determination of water in a 2-propanol extract of smoke[1], ethanol was used as an internal standard. The response for water was corrected for the water content of the standard blank solution found by GC using a Porapak Q column. The determination of water in solvents such as isopropanol, toluene and 1,1,2-trichloro-1,1,2-trifluoroethane with methanol as internal standard[2] was corrected for the water content of the

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methanol. With a small sample size non-linear behaviour of the water peak area was observed, which was attributed to contamination[2] of the sample with atmospheric moisture. In a study of the adsorption of water on porous polymer columns[3] a relatively large correction for water found in the sample blanks was also necessary. In a procedure for the determination of water in ketonic solvents[4] no determination of water in the sample blank was made. The method was compared with a similar determination of water in ethyl acetate, which agreed with the results of a Karl Fischer titration method. In 1966 an absolute calibration graph was presented for the range 0–160 ppm for measuring the water content of ethylene dichloride on a Porapak Q column[5], clearly showing a linear response, but also a systematic error relative to the Karl Fischer titration method.

It can be seen from these examples that the accuracy of the determination of water at low concentrations is highly dependent on the response for water in the sample blank. Most workers correct for the water found in the sample blank, as a negligible response for water in a solvent is rarely found. A standard additions procedure can lead to erroneous results, as the assumptions concerning the corrections for water in a sample blank are not valid.

The purpose of this study was to investigate the absolute accuracy of the GC determination of water. Three principles were used in this study to check the reliability of the measuring system. Firstly, the measuring system should have a linear response. Secondly, in a standard additions procedure it should be possible to obtain a sample blank or standard blank with a negligible water content. Thirdly, in an absolute calibration procedure the calibration graph should pass through the origin.

In addition, a gas chromatographic–mass spectrometric (GC–MS) technique was used to study the observed adsorption–desorption phenomena in a qualitative manner.

GC CALIBRATION

Experimental

The GC apparatus was assembled in the Department's workshop for the determination of gas–liquid phase equilibria[6] of ammonia, carbon dioxide and water. An absolute calibration method was chosen[7] rather than the method of internal standardization. This choice was made because the sample was gaseous (rendering the addition of a marker difficult) and because the various components varied greatly in concentration. The use of the absolute calibration method required, however, a reproducible response over a large time scale. Therefore, the volumetric and mass flow-rates in the thermal conductivity cell were kept constant[8] by means of a flow- and pressure-regulating system (see Fig. 1).

The unattenuated bridge signal was recorded with a Hitachi Perkin-Elmer 1-mV recorder and was integrated with an Infotronics Model CR 200 digital integrator.

The ethanol–water standard samples were evaporated in a special device originally developed by Dutch State Mines for this purpose. It consisted of a narrow annular space in an air thermostat. To prepare the water–nitrogen standards a water-saturating device was used. Into a 0.30-m long straight double-walled cooler was introduced a stream of nitrogen, which was pre-saturated at a temperature 20°C

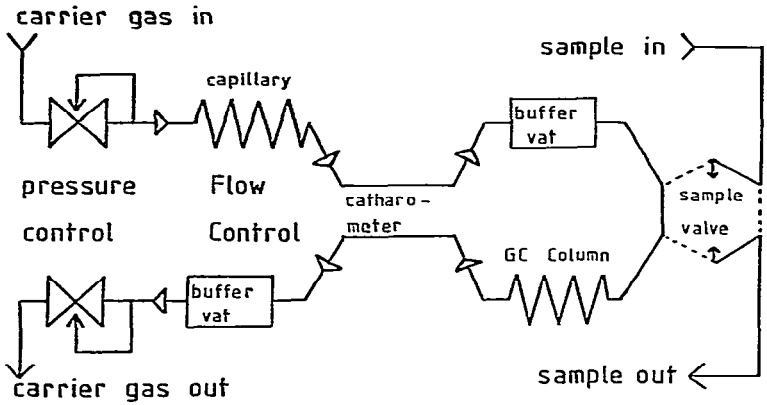

Fig. 1. Flow diagram of GC system.

higher. It appeared to be important that the inner glass surface of the cooler was fully covered with condensed water. The saturating temperature was measured in the gas stream. The thermometer readings were almost equal to the temperature of the thermostating liquid. The stainless-steel transfer line from the saturator to the sample valve was maintained at 200°C.

To minimize heat flux from the steel transfer line to the condensation section a 5-cm long PTFE tube connection was used, which was separately heated a few degrees above the saturating temperature. The stainless-steel column (2.5 m × 4 mm I.D.) was cleaned with *n*-hexane, filled with Chromosorb 104 (80–100 mesh) and conditioned at 250°C for 2 h under a flow of hydrogen. The operating conditions were as follows: detector, thermal conductivity cell; bridge current, 250 mA; carrier gas, hydrogen; carrier gas flow-rate, 44 ml min^{-1} (S.T.P.); column outlet pressure, 0.192 MPa; column temperature, 137°C; detector temperature, 137°C; sample loop volume, *ca.* 1 ml; injection frequency, 4 h^{-1}.

Results and discussion

The calibration graphs obtained are given in Fig. 2a (0–3 mole% H_2O) and b (1–100 mole% H_2O). The water content of the ethanol standards was determined by Karl Fischer titration. The ethanol samples were continuously evaporated and every 15 min an injection was made. A very stable performance could be obtained and the amount of water detected remained constant during the evaporation process for at least 4 h. The data points are mean values of 10 injections (relative standard deviation less than 3%).

The calibration graphs A and B in Fig. 2a are linear and parallel. Curve B shows normal behaviour: the detector response can be extrapolated to zero. Extrapolation of curve A yields a response for water in pure ethanol equivalent to 0.5 mole% H_2O. Ethanol containing a small excess of Karl Fischer reagent (brown colour) was injected on to a Porapak Q column. A constant response for water was obtained equivalent to $\pm$ 0.5 mole% H_2O when the injections took place at regular intervals of about 15 min, and did not disappear even after ten or more injections.

These results led to the conclusion that the determination of water in ethanol

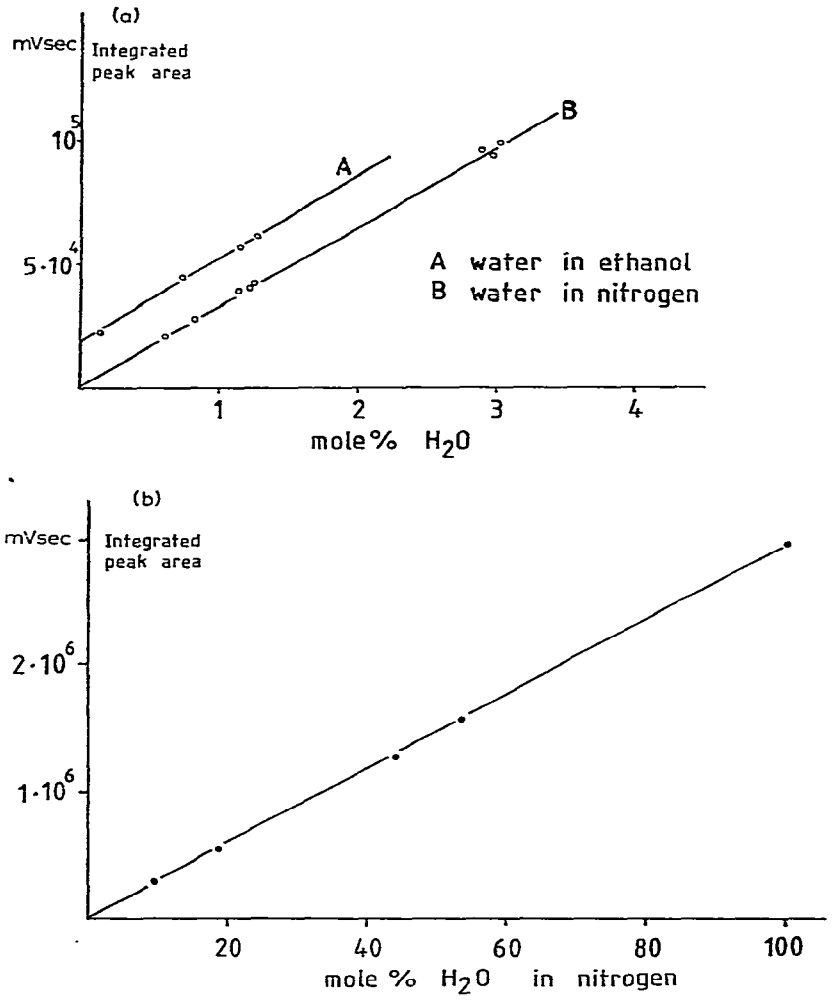

Fig. 2. (a), Calibration graphs for the determination of water in ethanol and nitrogen (0–3 mole % water). (b), Calibration graph for the determination of water in nitrogen (0–100 mole % water). Column, Chromosorb 104.

is disturbed by a small amount of water in the carrier gas. The determination of water in nitrogen gas, however, is not disturbed. Our experiments suggest that ethanol and water compete for the same adsorption sites on Chromosorb 104 and Porapak Q, and that a rapid exchange mechanism occurs. It can be calculated that 7 ppm of water in the carrier gas is sufficient to give a virtual water peak in 1 μl of ethanol equal to 0.5 mole% of water in the sample. The removal of this small amount of water from the carrier gas flow should result in the disappearance of the virtual water peak. However, such a treatment will have a negative effect on the peak shape[5] and a non-linear response due to adsorption losses can be expected.

It is possible to prevent adsorption of water on porous polymer columns by

adding a second polar compound to the carrier gas. We added 50 ppm of ethanol to the carrier gas flow by a technique based on the diffusion principle. Before the addition of ethanol to the carrier gas a constant virtual water peak was obtained with 1-μl ethanol injections. After the addition of ethanol the virtual water peak almost disappeared, and the remaining small peak could represent the real amount of water contained in the sample.

The adsorption–desorption phenomena of water and lower alcohols on Porapak Q were studied by Gassiot-Matas and Monrabal-Bas[9]. They found an increase in the retention volume of ethanol when a second polar compound in the sample mixture was eluted before the ethanol. The retention volume of ethanol was directly dependent on the amount of the second component in the mixture, but no dependence was found when ethanol was eluted first. Thus the amount and kind of adsorbed species is influenced by the peak size and by the adsorption properties of the last component eluted.

The separation process on porous polymer columns is very complex. All types of interaction between adsorbent, first adsorbate and second adsorbate are important and can disturb the quantitative analysis. The appearance of virtual water peaks on injecting polar compounds indicates that an adsorbate can be replaced by another adsorbate, while the results of Gassiot-Matas and Monrabal-Bas[9] can be interpreted as an interaction between the first and second adsorbates taking place in a steady-state situation. It can be seen from the retention values that the displacement effect takes place in the first part of the column only, while the interaction of the first and second adsorbates takes place in the whole column. As a result of the previously described interactions, the retention values of two different compounds can be identical at certain concentrations.

The occurrence of virtual water peaks can now be explained as follows. Before the analysis the adsorption sites on the porous polymer are partly occupied by water only. The adsorbed water is in equilibrium with the water in the carrier gas. An ethanol sample, or any other polar compound, can displace a certain amount of water, and the displaced water is separated with the same retention value as water from the sample. The separation process is facilitated by the adsorbed water on the column material.

Thus, only when water is the first polar component eluted from a sample is a constant performance independent of adsorbate–adsorbate interactions to be expected.

The determination of water in ammonia is an example of an analysis in which water is not eluted first. This means that no virtual water peaks are possible. We studied the separation process for this special case by GC–MS.

GC–MS ANALYSIS

Experimental

The adsorption–desorption effects of water and ammonia were studied in a qualitative manner by GC–MS. A Varian Aerograph gas chromatograph was equipped with a glass column packed with Porapak Q. Via a splitter operating at atmospheric pressure and column temperature, part of the column effluent was fed into a glass capillary interface leading to a Varian-MAT 311A mass spectrometer.

The interface was heated at 220°C. The column material was saturated with water at 130°C by injection of 2 μl of water.

The column effluent following injection of an anhydrous ammonia sample (0.4 ml) was analysed by the mass spectrometer. The peak intensities of the doublet *m/e* 17 (OH^+ and $NH^{+\cdot}$) were measured in a cycle scan (peak match mode), and were recorded on a Kipp 0.5–10-mV recorder (Fig. 3a). To minimize the background level

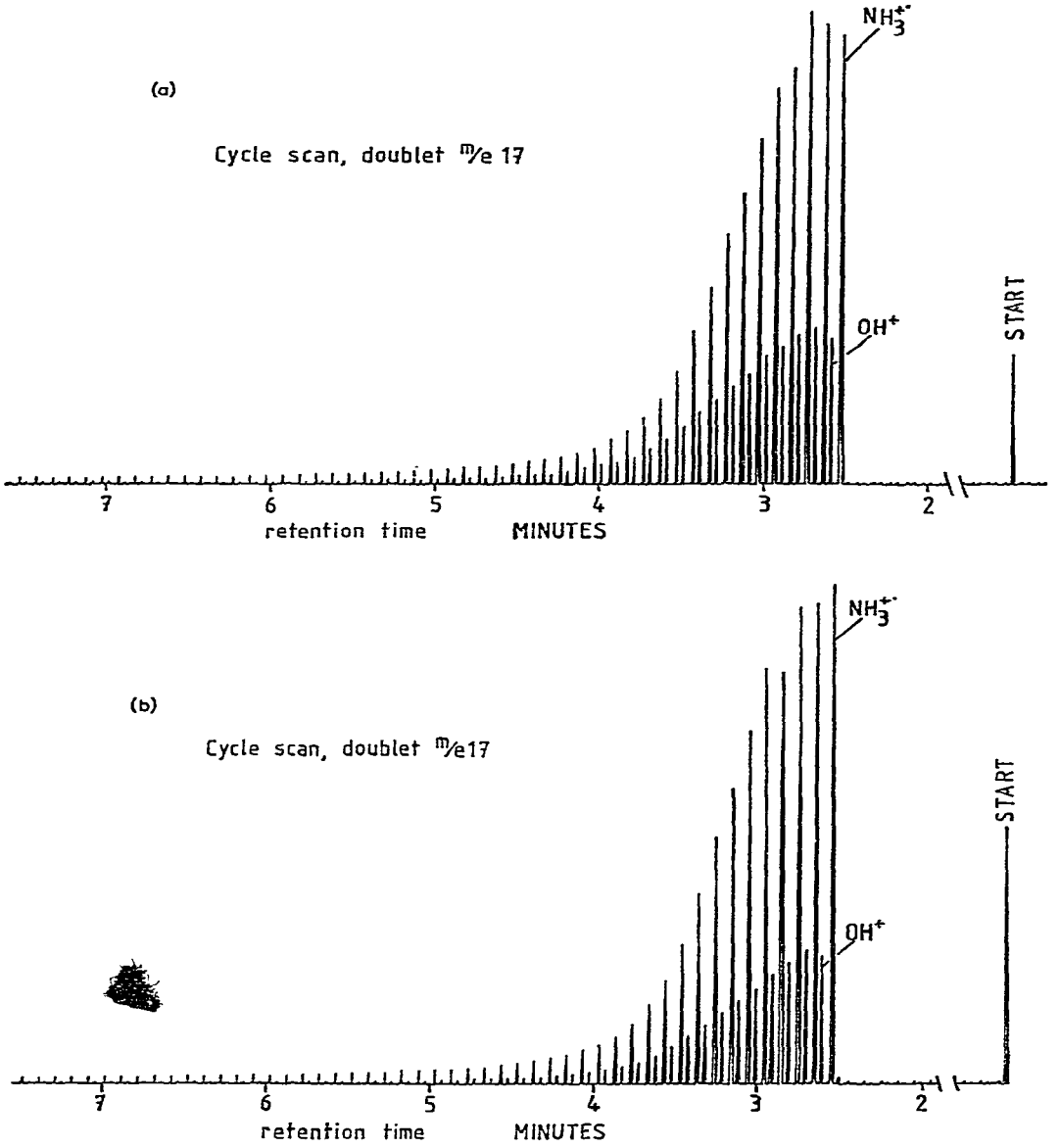

Fig. 3. (a) and (b), High-resolution mass fragmentograms of *m/e* 17. Sample, anhydrous ammonia; column, Porapak Q.

of the OH^+ signal and to prevent unwanted adsorption–desorption effects in the ion source, some deuterated water was introduced via the inlet system of the mass spectrometer. When the peak intensity of doublet *m/e* 17 was again at background level a second anhydrous ammonia sample (0.4 ml) was injected (Fig. 3b).

The adsorption–desorption effects of water and ethanol were studied in a similar manner. Adsorption of deuterated water on the column material was effected by twice injecting 2 μl of D_2O. After elution of the deuterated water the column effluent was fed into the mass spectrometer. While the intensity of the *m/e* 20 signal was recorded continuously, 1 μl of ethanol was injected (Fig. 4).

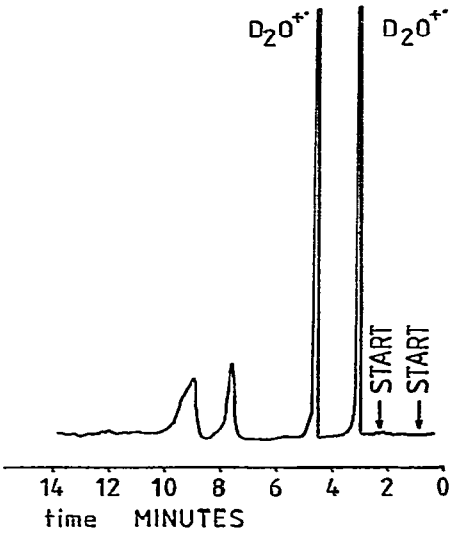

Fig. 4. Mass fragmentogram of *m/e* 20. Sample, anhydrous ethanol; column, Porapak Q; D_2O.

Results and discussion

The mass fragmentograms are shown in Figs. 3 and 4. Injection of 1 μl of dry ethanol gives two peaks in the mass fragmentogram of *m/e* 20. The first peak has the retention time of deuterated water and the second appears at the retention value of ethanol.

Injection of anhydrous ammonia gives only one peak in the mass fragmentogram owing to desorption of water from the column material. The contribution of the ion source to the adsorption–desorption phenomena is very small and cannot explain the relatively large amount of water contained in the ammonia peak. The small intensity of the OH^+ signal after introduction of deuterated water into the ion source is due at least partly to the water content of the deuterated water.

With the second injection of ammonia the released water content is smaller, but the water content of the column material will also be smaller after elution of the first ammonia sample.

The different behaviour of ammonia and ethanol is remarkable. Water released from the column material by ethanol displacement is separated to a certain extent

and cannot be distinguised from water introduced by the sample. Water released from the column material by ammonia is not separated.

It is possible to explain these differences in behaviour when the relative retention times are taken into account. The retention of a small amount of water is dependent on the adsorbed species on the column material. In the case of ethanol adsorption, the desorbed water is eluted before the ethanol. Thus ethanol adsorption has no effect on the retention time of the released water. In the case of ammonia, however, ammonia is eluted first. The water content of the column material changes owing to ammonia displacement, and the retention time of the relatively small amount of water which follows is no longer defined. This effect gives rise to severe peak tailing.

The tailing of the ammonia peak is caused by adsorbate–adsorbate interactions of ammonia and water, which take place on the column material after the passage of the ammonia peak and before the passage of the water peak. Thus the ammonia peak tailing always ends at the true retention time of water.

It should be noted that the ammonia peak tailing is caused by water which is present in the column material before the injection of the sample.

Thus for quantitative ammonia detection, the carrier gas should be as dry as possible. Water introduced by the samples should be removed from the column material in a continuous manner by adding a small amount of anhydrous ammonia to the carrier gas (50 ppm is suitable). With such column conditioning the ammonia peak shape is improved and ammonia adsorption losses are prevented. Thus a linear response for ammonia can be expected, but special attention should be paid to the occurrence of virtual ammonia peaks in polar samples, as was the case in the determination of water in ethanol–water mixtures. Note that water cannot be measured simultaneously with ammonia on such a column.

It will be clear, however, that the quantitative detection of water in ammonia–water mixtures with the previously described column conditioning is not straightforward. Non-linear behaviour for the response of water is very likely to occur.

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