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Note

Trace water analysis in gases using reaction gas chromatography

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The determination of traces of water in gases is one of the most important and at the same time most difficult problems of trace analysis, since water is universally present. Because water is highly polar it adheres to most surfaces, and as a result, surfaces that are normally considered to be dry are, in actuality, usually coated with a thin film of adsorbed moisture.

The determination of water has been the subject of several reviews^{1,2} which show that a wide variety of procedures and instruments are available. These vary in principle from classical wet chemistry, *e.g.*, the Karl Fischer determination, to electric hygrometers and microprocessor controlled instruments using various forms of detection. The dewpoint determination of water in gases is by far the most common and accurate method. However, it is limited to systems containing no condensable species other than water.

Gas chromatography (GC) has been extensively used in various forms for water determination. These methods vary in complexity from simple sample injection and separation by gas-solid chromatography where the sensitivity is low, to reaction GC where the water is converted into another compound which exhibits a greater chromatographic response.

In reaction chromatography, the sample is treated with sodium³, lithium aluminium hydride⁴ or sodium metal² to form hydrogen or with calcium hydride⁵ or calcium carbide⁶ to form acetylene followed by determination of the gaseous product by GC. The practical advantages of calcium carbide when compared with the other reactants has led to this reactant being examined and suggested for a number of purposes.

The microdetermination of carbon and hydrogen in solid organic compounds has been undertaken by the Pregl combustion procedure⁷ where the sample is burnt in a dry carbon dioxide-free oxygen stream. Duswalt and Brandt⁸ employed GC detection by passing the carbon dioxide and water formed through a calcium carbide tube, converting the water vapour into acetylene. The gases were then passed through a liquid nitrogen trap to concentrate them for analysis. After vaporization the gases were swept into the chromatographic system. The combustion has also been carried

out in a helium atmosphere with copper oxide as the oxidant⁹ and subsequent reaction with calcium carbide, product trapping and GC.

The analysis of concentrated aqueous solutions has been reported using an independently heated pre-column containing calcium carbide. This technique was employed to overcome the influence of severe tailing of water in the analysis of alcohol solutions when employing thermal conductivity detection. The acetylene was determined using GC but the precision of the method was not reported¹⁰.

Knight and Weiss¹¹ reported the estimation of traces of water in hydrocarbons by passage through a 12×0.25 in. stainless-steel column packed with calcium carbide and operated at ambient temperature. Detection was by flame ionization rather than thermal conductivity as used previously. This method was optimized for water estimation in hydrocarbon, studies with a gas phase reactor¹² allowed equilibrium times of the order of 1 h, while it was shown that the reaction temperature was important with low acetylene values being obtained at temperatures above 40°C.

A procedure for the estimation of water in gases by the same reaction has been reported by Kaiser¹³ which is applicable to the detection of 1 part in 10^9 . It employed a continuously flowing system with reversion GC. The separating system in temperature gradient chromatography is not uniform and the hotter zone may move during a separation. The mobile phase flows in the direction of the negative temperature gradient. The procedure which has found little utility was described earlier by Kaiser¹⁴ and was based on work by Schuchowizkeff and Turkelturk reported in 1957¹⁵.

The present work presents a simple readily applicable procedure using a simple flow reactor, optimum values of the operating conditions, *e.g.*, temperature and gas flow-rate, being established.

EXPERIMENTAL

The chromatography was conducted using a Packard No. 7300/7400 System with flame ionization detection and a Spectrophysics Computing Integrator Model SP4100.

Calcium carbide (25–50 mesh) was packed in a glass column (1 m \times 2 mm I.D.) which was maintained in a gas chromatograph oven for accurate temperature control. Prior to the analysis, the column was preconditioned for 30 min at 140°C. The generated acetylene was analyzed by using a 2 m \times 2 mm I.D. Porapak P column (80–100 mesh) and a flame ionization detector. The flow-rate through the chromatographic column was varied depending upon the column temperature (which had to follow the calcium carbide column temperature since both were included in the same GC oven). A schematic diagram of the system is shown in Fig. 1.

A mixture of 49.1 ppm water vapour in nitrogen was prepared by weight in a treated aluminium cylinder. This mixture when analyzed by an EG & G Model 300 Optical Dew Point Hygrometer (Leeds & Northrup, Sydney, Australia) gave a dew-point of -45.8°C at 5 p.s.i.g., which is equivalent to 49 ppm water. The mixture was then re-analyzed using a DuPont 510 Quartz crystal hydrometer (DuPont, Wilmington, DE, U.S.A.) to give a water concentration of 50 ppm. From these results the gas in the cylinder was used as a standard containing 49.5 ppm water.

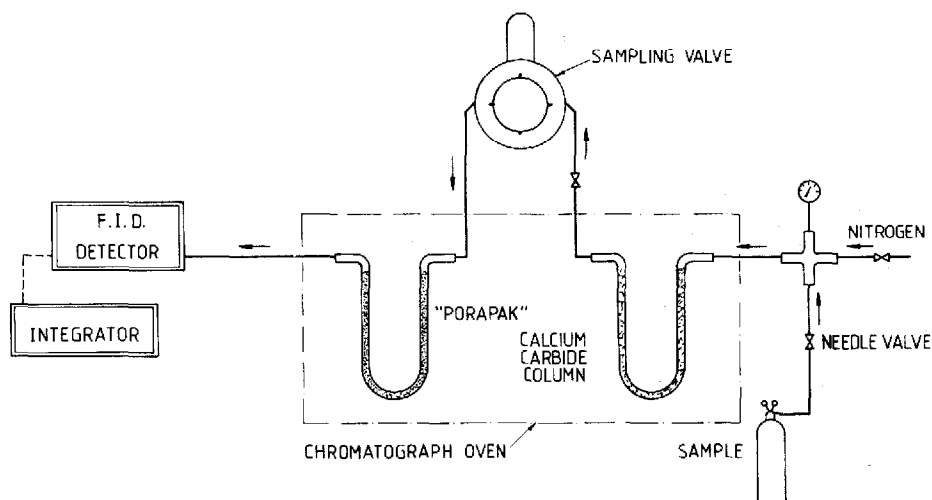


Fig. 1. Schematic diagram of the analytical system.

RESULTS AND DISCUSSION

Due to the contradictory nature of the operating conditions specified by other workers, the effect of temperature and flow-rate was investigated over the ranges 25–100°C and 20–150 ml/min respectively.

TABLE I

EFFECT OF TEMPERATURE AND FLOW-RATE ON EQUILIBRATION TIME

Equilibration time is defined as the time at which four successive results are within 1% of each other and they do not follow a particular pattern, *e.g.*, each result is higher than the previous one by less than 1%.

<i>Temperature 35°C</i>					
Flow-rate (ml/min)	20	40	60	100	150
Equilibration time (min)	—	105	35	25	30
Amount of water (ppm)	—	56.1	51.1	49.4	48.2
<i>Temperature 40°C</i>					
Flow-rate (ml/min)	20	40	60	100	150
Equilibration time (min)	260	90	30	20	25
Amount of water (ppm)	55.7	53.5	50.4	49.0	48.1
<i>Temperature 60°C</i>					
Flow-rate (ml/min)	20	40	60	100	150
Equilibration time (min)	250	75	25	15	35
Amount of water (ppm)	56	54.5	51.6	49.6	48.5
<i>Temperature 100°C</i>					
Flow-rate (ml/min)	20	40	60	100	150
Equilibration time (min)	280	95	35	25	40
Amount of water (ppm)	55.1	52.0	52.3	48.6	48.1

Table I shows the results obtained when the 49.5-ppm standard was used to study the effect of temperature and flow-rate on the equilibration time. These results show good agreement with the assigned moisture content of the cylinder. Variation in temperature (up to 100°C) has a minimal effect on the end results but does affect the equilibration time. The effect of flow-rate is as expected—a low flow requires a long time for steady state to be achieved, but does affect the results for the water assay. From these results it was clear that the equilibration time is a function of both temperature and flow-rate. However, the flow-rate is a function of column length, inner diameter and the packing particle size. For the particular column used in this work the optimum conditions were found to be: temperature 60°C; flow-rate 100 ml/min.

Six cylinders were then prepared in the manner described above and the contents of each were run under these optimum conditions, with 30-min pretreatment with dry nitrogen; samples were taken in increasing order. Table II summarizes the results obtained and shows comparative results obtained with the EG & G 300 Dew point hydrometer and the DuPont crystal hydrometer.

TABLE II

COMPARISON OF ASSAYS FOR WATER USING GC PROCEDURE, EG & G DEWPOINT HYDROMETER AND DUPONT CRYSTAL HYDROMETER

Calculated (ppm)	N ₂ *	11.1	15.6	26.0	55.7	110.5
CaC ₂ (ppm)		6.0	10.7	15.2	25.6	110.3
EG & G (°C at 5 p.s.i.g.) (ppm)		5.7	11.0	15.2	25.8	112.0
DuPont (ppm)		6.0	10.5	15.5	25.5	110
Mean (ppm)		5.9	10.8	15.4	25.7	110.7
S.D.		0.14	0.24	0.18	0.19	0.77
% S.D.		2.4	2.2	1.2	0.75	0.70

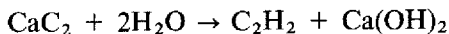
* The moisture content of the nitrogen used as the balance for these mixtures was first named as the average of the three readings; the concentration of each standard was then calculated assuming nitrogen contains zero moisture. The addition of the two figures gives the calculated nominal value.

CONCLUSIONS

The calcium carbide reaction for trace moisture analysis has proved to be an accurate, reproducible and convenient method. Its main advantage lies in its simplicity, yet the detection linearity does not cause loss of resolution at moisture levels up to 100 ppm.

The optimum temperature for the reaction was found to be 60°C and the optimum flow-rate (being a function of column dimensions and the packing size) was found to be 100 ml/min. Under these conditions the results are comparable with those obtained by other accepted methods.

The method relies upon the conversion of water into acetylene by passage through a calcium carbide bed:



Thus each mole of acetylene detected corresponds to 2 moles of water in the mixture.

This assumes that the reaction is quantitative, a fact which previous workers have verified and supported by thermodynamic calculations which indicate that no undesirable reaction should occur below 200°C.

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