GAS CHROMATOGRAPHIC DETERMINATION OF WATER
IN CARBONYL CONTAINING COMPOUNDS ON POLYMER PACKING

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Polymerized macroreticular 2-cyanoethyl methacrylate (KEM) proved to be a good stationary phase in GSC separation of water from some carbonyl containing compounds. The method of water determination throughout the concentration range 0·1 to 50% was worked out at an approximate absolute amount of water about 1 μg. The standard deviation of the method $s_{y,x} = 0·11\%$ rel.

Chemical and physical methods which have been used for determining water in various inorganic and organic materials have already been discussed in review articles[1,2]. Most of these methods are only used to a limited extent. For the determination of water content in organic compounds within the range of ppm to almost 100% the K. Fischer[3] titration with visual or electrometric indication of the end point[1,2], different modifications of Keidel[4] coulometric method, infra-red spectrometry and gas chromatography proved to be the most successful techniques.

The drawback of the Fischer reagent consists in its capability of reacting with aldehydes and ketones producing dimethyl acetals or ketals and water. The extent of this reaction depends on the nature of carbonyl containing compounds. With simple organic substances, however, the carbonyl group in the molecule disturbs the K. Fischer titration even if a volumetric solution is modified by partial or complete replacing of methanol with other solvents. In the near infra-red region, the intensive band of aldehydic or the ketonic carbonyl group (near 1·9 μm) strongly interferes with the absorption band of water.

The paper[5] reviews the state of knowledge up to 1967 concerning the determination of water in organic substances by gas chromatography. In addition to other aspects it includes the application of the organic porous polymers Porapak R as a new stationary phase. Further polymer packings such as *e.g.* Porapacks Q (ref.[6−8] and QS (ref.[7]), Chromosorbs 101 (see[9]), 102 (see[10,11]) and 104 (see[12,13]) and other similar phases[14−16] were tested in some later works.

Up to the present time, however, attention has not been paid to the systematic analytical investigation of water mixtures and simple carbonyl compounds by gas

chromatography. Therefore, in this work our effort was focussed on determining water in aliphatic, cycloaliphatic and aromatic ketones and aldehydes with particular regard to compounds of industrial importance. A macroreticular resin[17] obtained by the copolymerization of 2-cyanoethyl methacrylate and ethylene dimethacrylate was chosen as a column stationary phase. This has already been successfully used[18] for the separation of C_1—C_5 free fatty acids and water. The objective of the present work was to extend its utilization for the determination of water in carbonyl containing compounds where both the Karl Fischer method and the infra-red spectrometry had failed.

EXPERIMENTAL

Apparatus

The measurements were carried out with PYE Heated Dual Thermal Conductivity Detector Programmed Chromatograph, Model 44 (Series 104, Cambridge, Great Britain). It was equipped with a recorder 0—1 mV (Honeywell, model Electronik 194). The columns employed were 170 × 0·4 cm I.D. glass tubes. Nitrogen was used as the carrier gas at the flow rate of approximately 30 ml/min. The samples were introduced with 10 μl Hamilton microsyringe. The injection port and the detector were maintained at 180°C and 150°C respectively. The column temperature was chosen throughout the range 85 to 145°C with respect to the boiling points of the analysed compounds. Most of the measurements were performed at 101°C. Under the given conditions the column exerted significant deteriorating separation efficiency after about 300 analyses.

Column Packing

The macroreticular copolymer of 2-cyanoethyl methacrylate and ethylene dimethacrylate (KEM) of specific surface area of 24 m²/g and of the particle size 0·2—0·4 mm served as the stationary phase. It was extracted with methanol for 16 hours and dried at elevated temperature. The packed columns were preconditioned for 12 hours at 140°C with the carrier gas flowing.

Chemicals

Formaldehyde (23—36%), acetaldehyde (reagent grade, anhydrous, purity at least 99·5%, GC), propionaldehyde (pure, purity at least 99%, GC), n-valeraldehyde (purity at least 98%, GC), paraldehyde (purity at least 97%, GC), phenylacetaldehyde (50% solution in benzyl alcohol) and acetone (reagent grade) were products of Fluka, Switzerland. n-Butyraldehyde and iso-butyl methyl ketone (both at least 98%) were supplied by B.D.H., Great Britain; isobutyraldehyde (the purity 99%, GC) and crotonaldehyde (purity 98%, GC), were products of Schuchardt, B.D.R. n-Butyl methyl ketone, methyl neopentyl ketone and n-amyl methyl ketone were from our laboratory stock. Benzaldehyde, salicylaldehyde, ethyl methyl ketone, isopropyl methyl ketone and acetylacetone (all reagent grade) were supplied by Lachema, Brno. Mesityl oxide (purity at least 95%, GC), cyclopentanone, cyclohexanone and cycloheptanone (the purity of all at least 99%, GC) were products of Koch–Light, Great Britain. The standard amount of water of approximately 1% was added to all the compounds in question. The resulting mixtures were used for the determination of the relative retentions of the individual compounds (Table I).

Calibration and Calculations

The methanol solutions containing $0.1-50\%$ (w/w) of water the content of which was determined by K. Fischer method were used as calibration stock solutions. Other calibration solutions with similar concentration of water in acetone were prepared. Their water contents were determined from the calibration of methanol solutions. The method of direct calibration was employed. A graph was made from the calibration measurements by plotting the retention curve areas of water *versus* the corresponding weighed amounts. The best straight line was calculated by the least square method and the standard deviation of $s_{y,x} = 0.11\%$ rel.

RESULTS AND DISCUSSION

Earlier works concerning the determination of water in organic substances by gas chromatography[1] made use of stationary phases which mostly brought about tailing of the water retention peak[5]. Only the introduction of synthetic porous polymers with particular texture properties could overcome these difficulties. Of the stationary phases in question based mostly on styrene–divinylbenzene or ethyldivinyl-benzene only Porapak Q turned out to be a convenient column packing. However, its low value[19] of mean pore diameters (about 7.5 nm) makes it unfavourable because of the relatively high operating temperature which is required if peak tailing is to be prevented and if a reasonable retention time of analysed compounds is to be achieved. In GC analysis of aliphatic carboxylic acids on the polymerized cyanoethyl metha-crylate (KEM) we noticed[18] that water is sharply separated from other components

TABLE I

Relative Retentions of Some Carbonyl Containing Compounds at 101°C (relative to retention volume of water)

Compound	$r_{1,2}$	Compound	$r_{1,2}$
Formaldehyde	0.24	Acetone	0.65
Acetaldehyde	0.29	Ethyl methyl ketone	1.18
Propionaldehyde	0.51	Isopropyl methyl ketone	1.5
Butyraldehyde	1.00	Butyl methyl ketone	$(1.86)^c$
Isobutyraldehyde	0.12	Isobutyl methyl ketone	$(1.43)^a$ $(1.33)^c$
Crotonaldehyde	2.53 $(2.03)^a$	Methyl pentyl ketone	3.73 $(3.04)^c$
Valeraldehyde	2.11 $(1.35)^a$	Mesityl oxide	3.80
Phenylacetaldehyde	$-^b$	Acetylacetone	5.24
Salicylaldehyde	$-^b$	Cyclopentanone	5.61 $(4.83)^a$ $(4.26)^d$
Benzaldehyde	$-^b$	Cyclohexanone	5.21
		Cycloheptanone	$(12.54)^d$ $(11.00)^c$

[a] At 124°C; [b] is not eluted; [c] at 145°C; [d] at 134°C.

of the mixture. In this work we studied the use of KEM for the determination of water in some volatile organic compounds or in their mixtures. KEM has advantages due to its easy synthesis[17] and the possibility of working at a relatively low temperature. The copolymer employed should possess most frequent pore radii of approximately 60 nm. If the pores are narrower (*e.g.* 20—30 nm) the separated compounds show unsymmetrical retention peaks with significant tailing which becomes worse with increasing polymer surface and lower temperature.

With KEM the determination of water in practically all types of organic substances can be performed. Of the set of all the compounds investigated in this work we did not succeed in determining water in butyraldehyde because of the same retention volume of both compounds throughout the temperature range 86—145°C. Isobutyraldehyde, ethyl methyl ketone, isopropyl methyl ketone, isobutyl methyl ketone and methyl neopentyl ketone were partly superimposed with water. Compared with other organic porous polymers proposed up to the present time KEM showed lower thermal stability[18]. This disadvantage was to a considerable degree compensated by the
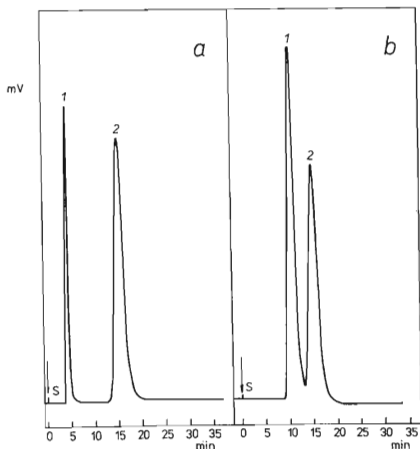

FIG. 1

The Separation of a Mixture of Some Carbonyl Compounds and Water

Column 170 × 0·4 cm (I.D.), KEM 0·2 to 0·4 mm; column temperature 101°C; H_2, $F_m = 30$ ml/min. *a* 1 acetaldehyde, 2 water; *b* 1 acetone, 2 water.

possibility of working at a lower temperature without significantly increasing the retention volume of water and distortion of its retention peak (Fig. 1). Other polymers used for this purpose did not make this possible.

The application of KEM is not restricted to the dermination of water in carbonyl containing compounds only but this resin is convenient for determining water in other kinds of organic substances and their mixtures as well.

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