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DIRECT DETERMINATION OF ORGANIC COMPOUNDS IN WATER USING STEAM–SOLID CHROMATOGRAPHY

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SUMMARY

A method for analysis of organics in water was developed. The principle is the direct injection of water sample into the gas chromatograph using steam as the carrier gas. The steam developer is described. Analyses of natural polluted water containing hydrocarbons, alcohols and ketones are presented. The method is simple, fast and relatively sensitive to the determination of compounds having a wide range of polarities and a wide range of boiling points. The sensitivity of the method was 10 μg/l for hydrocarbons.

The behaviour of the flame ionization detector under conditions of steam–solid chromatography was studied. The detector gives a constant and reproducible response which is, however, lower than that under conventional gas chromatographic conditions. The effect of the hydrogen and steam mobile phase flow-rates upon the detector response differ from those obtained for the flame ionization detector with an inert carrier gas. The other dependences on experimental conditions are similar to those in conventional gas chromatography.

INTRODUCTION

The determination of organic compounds in water is one of the fundamental problems in environmental protection. Water usually contains more than one pollutant; the most suitable methods for analytical determination would therefore seem to be separation methods, especially gas chromatography. However, the direct injection of contaminated water into the gas chromatograph is fraught with difficulties caused by the presence of great quantities of water in the chromatographic system, which, in most cases, makes the application of the method impossible. Many of these problems are eliminated by the use of steam as the carrier gas, *i.e.*, in steam–solid chromatography (SSC).

Steam as an additive to an inert gas[1] and/or steam alone[2] was used as the carrier gas in gas chromatography (GC) of polar compounds to minimize tailing. It was found that steam decreases the sorption of compounds on the sorbent and reduces the

retention times of compounds. Steam was applied as the mobile phase in chromatographic analysis of phenols, amines, organic acids, alcohols, hydrocarbons, steroids and alkaloids. Previous results of SSC have been summarized by Nonaka[3,4] and by Russian authors[5–7].

The flame ionization detector (FID) is often used in SSC but literature data differ as to the response of the FID to water present in the detector. The usual conclusion is that the detector is almost or completely insensitive to water (see, *e.g.*, refs. 8 and 21), so that the presence of water in the detector does not interfere with the detector response to other compounds[8]. Under SSC conditions, the FID sensitivity is reported to be the same as under normal conditions[3,4] and independent of the steam flow-rate[9,10]. On the other hand, some papers indicate that the detector does respond to water[2,11,12] and that FID response to organic compounds in the presence of steam is lower than that obtained with an inert gas[13–16]. Considering the ionization reactions in the FID[17], the detector behaviour under SSC conditions (a large number of water molecules introduced into the flame) would be expected to be different to that under conventional GC conditions.

The problems in designing a steam–solid chromatograph and insufficient knowledge of the FID response under SSC conditions meant that this method was not accepted for the routine analysis of water samples containing organic compounds. We have now developed a SSC method for the analysis of water contaminated with organic compounds and have studied the function of the FID in this system.

EXPERIMENTAL

Apparatus

The chromatographic analysis of organic compounds in water using steam as the mobile phase was studied on a modified Packard-Becker Model 419 gas chromatograph, Delft, The Netherlands, (Fig. 1a). A glass flask (9), volume *ca.* 30 ml, containing distilled water was attached to the injection chamber (1). A supply capillary (400 × 0.3 mm), provided with the apparatus, was connected (8) to a similar capillary from the second injection chamber. Thus the generated steam passes from the flask through the injection chamber (1), the capillaries, the injection chamber (2), through which samples are injected and the chromatographic column (7) into the FID (4). A second FID (3) was not connected. Steam was generated at the column temperature, wich was maintained by the oven within the range $\pm 0.1°$. Distilled water was supplied to the flask by a big syringe through the injection chamber (1). The whole attachment is very simple and does not require complicated modifications of the chromatograph.

The column is placed as near as possible to the septum (12), which is supported by a thin supporting plate (13) (Fig. 1b). The diameter of the first part of the column is reduced (14), so that the needle of the syringe can just pass through. The point of the needle reaches the glass wool layer (15) under which 10–15 cm of inert support for GC is placed (16) Chezasorb AW, 0.16–0.20 mm (Lachema, Brno, Czechoslovakia). This "precolumn" retains inorganic salts and should be changed after about 100 analyses of polluted water. Within a short time, when evaporation of the injected sample proceeds the needle of the syringe is kept in the narrow part of the column inlet so preventing reverse expansion of volatile compounds of the sample against the stream of steam (17). The time during which the needle of the syringe is inserted and the heights

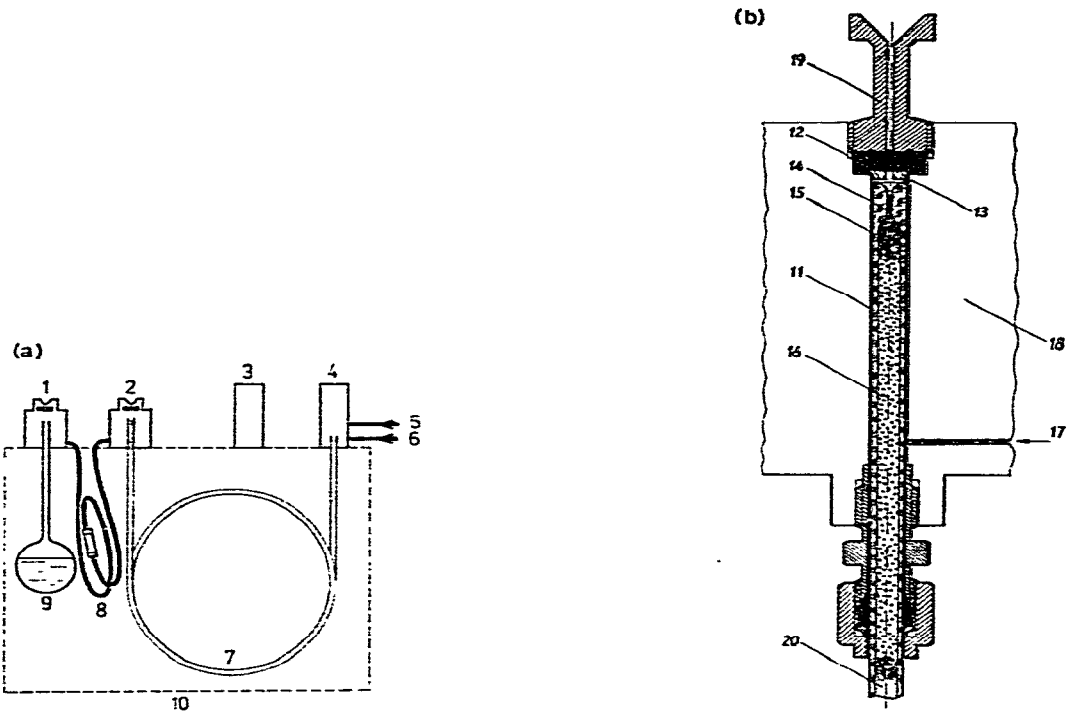

Fig. 1. a, Diagram of the apparatus for steam–solid chromatography: 1,2 = injection chambers; 3,4 = flame ionization detectors; 5 = hydrogen inlet; 6 = air inlet; 7 = chromatographic column; 8 = connecting capillary; 9 = water reservoir; 10 = oven. b, Details of the injection chamber and the first part of the chromatographic column: 11 = wall of the column; 12 = septum; 13 = supporting plate; 14 = first reduced part of the column; 15 = glass wool; 16 = inert GC support; 17 = steam inlet; 18 = injection block; 19 = injection chamber seal; 20 = sorbent.

of the glass wool layer and that of the inert support should be optimized for the experimental conditions used. Unless the modifications and optimalizations are made, after injection, the elution zone of each component may yield several peaks. In the case of a large dead volume between the injection chamber (1) and column inlet, after one sample injection further ghost records of the original whole chromatogram were even observed.

The chromatogram was evaluated using Hewlett-Packard 3380 A digital integrator (Hewlett-Packard, Avondale, Pa., U.S.A.) or a W+W 1100 recorder (W+W Electronic, Basel, Switzerland).

Chromatographic columns

Glass columns (4 mm I.D.) were used. Large porosity silica gel, Spherosil (Supelco, Bellefonte, Pa., U.S.A.), Porasil (Waters Assoc., Milford, Mass., U.S.A.) and Silipor (Lachema), proved to be good packings for analyses of polluted water.

The detector temperature was 200° during all the measurements, and the injection chamber temperature was identical to the oven temperature. All the values of the detector response are given as the average of three measurements. The reproducibility was ±2%.

Preparation of a model solutions

For measuring low concentrations of a compound, its solution in acetone was added to distilled water and then diluted to the required concentration. This process enables solutions of compounds with low water solubility to be prepared accurately[18]. To determine the molar response of the FID, a solution of *o*-xylene in acetone (1.06 g/l) was used. The other aqueous solutions were prepared by adding corresponding amounts of compounds to distilled water.

Steam flow-rate

The steam flow-rate through the chromatographic column is determined by the pressure of water vapour in the generator. Within the temperature range used (127–138°) this pressure varies from $2.47 \cdot 10^5$ to $3.4 \cdot 10^5$ Pa. The steam flow-rate through the detector is not easy to measure directly. It was determined as follows. The mean cross-sectional area of mobile phase, A_m was measured with nitrogen. Then, at a given temperature, the mean linear velocity, $\bar{u}$, of non-adsorbed methane was measured using steam as mobile phase. From the mean linear velocity, the linear velocity of the mobile phase at the column outlet, u_0, was calculated employing the correction factor for the pressure gradient in the column, j (the pressure at the column inlet being considered to be equal to the water vapour pressure at the given temperature T_C). Multiplication of the value of the linear velocity at the column outlet by the mean cross-sectional area of the mobile phase results in the volume flow-rate of steam at the column outlet. Then, this flow-rate was corrected for the detector temperature, T_D:

$$F = \bar{u} \cdot j \cdot A_m \cdot T_D / T_C$$

RESULTS AND DISCUSSION

Fig. 2 shows a chromatogram of a model mixture of various aromatic hydrocarbons in distilled water. The basic requirements for routine analysis of polluted water are rapidity of analysis, simplicity and the possibility of determining compounds with a wide range of boiling points. Apparently (see Fig. 2) SSC satisfies all these requirements. In the present case the range of boiling points of the analyzed compounds was 80–268° (benzene to 1,4-dimethylnaphthalene). The analysis of this mixture required only 6 min. The steam mobile phase considerably reduces the retention of the compounds so that it is possible to analyse them at very low temperatures (in comparison with their boiling points) with a good chromatographic separation. The efficiency of chromatographic columns used in SSC is relatively high (HETP 0.9 mm for 1-methylnaphthalene).

By this method it is possible to analyze aqueous solutions of hydrocarbons down to concentrations of $1 \cdot 10^{-5}$ g/l. This relatively high sensitivity is achieved without any preliminary concentration treatment. Moreover, the determination is not affected by the presence of dissolved or dispersed mineral components in the sample which cause some problems in extraction or head-space analysis[19]. Thus, the simplicity is an important aspect of the application of SSC to the analysis of polluted water.

The analysis of aqueous solution of polar compounds, easily soluble in water, is difficult. These compounds cannot be isolated quantitatively from water, nor

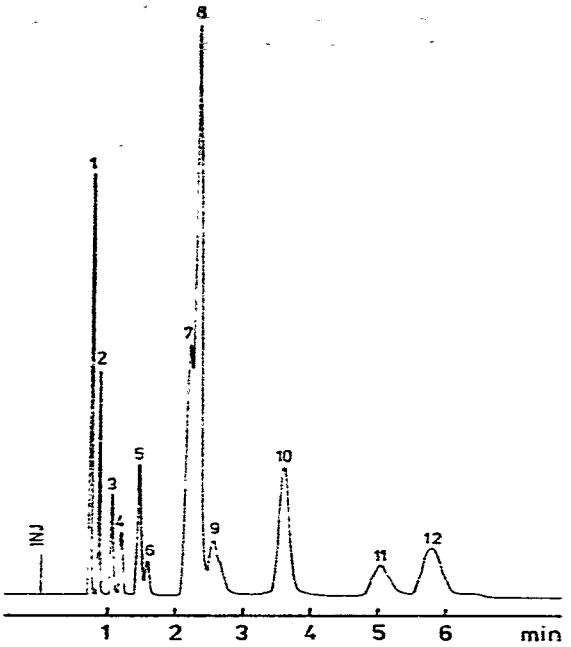

Fig. 2. Chromatogram of a model solution of hydrocarbons in water. Peaks: 1 = benzene (retention time 0.75 min); 2 = toluene (0.87); 3 = *m*-xylene (1.08); 4 = isopropylbenzene (1.21); 5 = 1,2,4-trimethylbenzene (1.49); 6 = *p*-isopropylmethylbenzene (1.61); 7 = 1,2,4,5-tetramethylbenzene (2.21); 8 = naphthalene (2.33); 9 = diisopropylbenzene (2.58); 10 = 1-methylnaphthalene (3.62); 11 = 2,6-dimethylnaphthalene (5.05); 12 = 1,4-dimethylnaphthalene (5.81).

concentrated sufficiently in the gas phase during head-space analysis. SSC enables these polar compounds to be determined very quickly and simply at concentrations of 10^{-4}–10^{-5} g/l, especially when analyzing a not very complicated mixture of several categories or organic pollutants (Table I).

TABLE I

ANALYSIS OF POLAR COMPOUNDS BY SSC

Columns: A = 140 cm Porasil F (0.149–0.177 mm, 2–6 m^2/g), temperature 133°; B = as A but plus 3% H_3PO_4, temperature 136°.

Compounds	*Retention time (min)*	*Limit of determination (g/l)*	*Column*
Alcohols C_1–C_4	0.52–2.00	7×10^{-5}	A
Ketones C_3–C_5	0.89–3.36	7×10^{-5}	A
Phenols C_6–C_8	2.07–4.42	1×10^{-4}	B

Applications

The SSC technique described above has been used for routine analyses of polluted water and thousands of analyses of different types of ground-water have been performed. The analysis of contaminated ground-water taken from a test hole in the area of a pharmaceutical factory (Fig. 3) is one example of the practical utilization of

the method. The identified pollutants (water is polluted simultaneously with hydrocarbons, alcohols and ketones) and their concentrations determined by the external standard method are summarized in Fig. 3.

Another example is chosen from a set of analyses of ground-water from the pumped test well in the area of a petrochemical plant (Fig. 4). In this case the water is contaminated by the petrol fraction of crude oil. The analyses of similar samples required ca. 4–7 min.

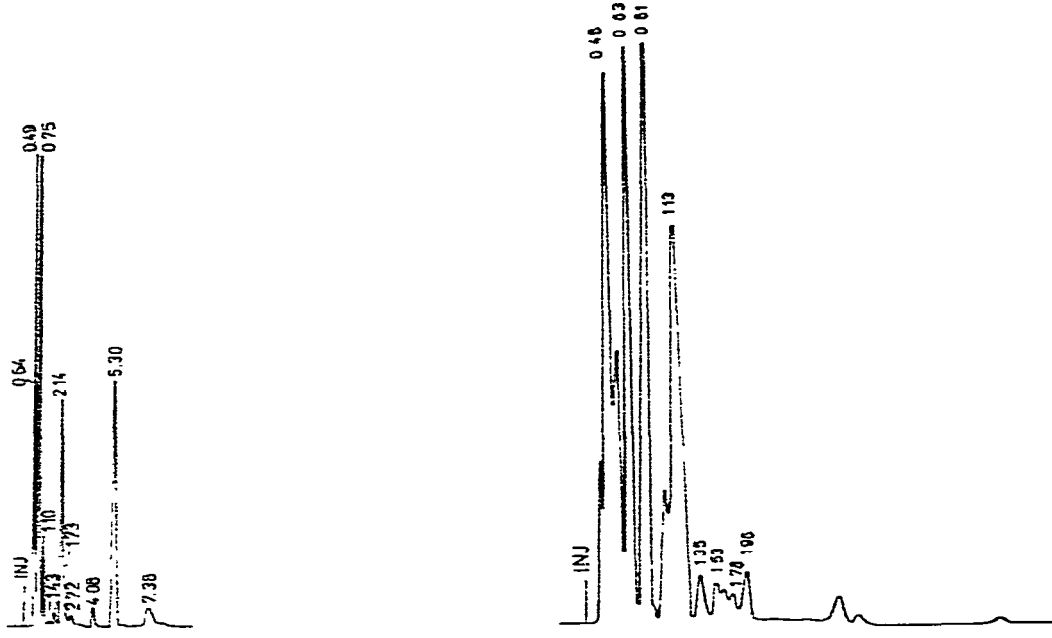

Fig. 3. Analysis of ground-water from a pharmaceutical plant area. Column: 230 cm, Porasil F (0.149–0.177 mm, 2–6 m^2/g), temperature 138°. Retention times (min): 0.49 = alkanes up to C_8 (concentration 27.81 mg/l); 0.64 = benzene (2.11 mg/l); 0.75 = toluene (88.87 mg/l); 1.10 = xylenes + ethylbenzene (1.09 mg/l); 1.43 = methanol (0.40 mg/l); 1.73 = *p*-isopropylmethylbenzene (0.34 mg/l); 2.14 = ethanol + acetone (14.75 mg/l); 2.72 = isopropanol (0.89 = mg/l); 4.08 = methyl ethyl ketone (1.49 mg/l); 5.30 = methyl isopropyl ketone (22.26 mg/l); 7.38 = ethyl isopropyl ketone (2.70 mg/l).

Fig. 4. Analysis of ground-water from a petrochemical plant area. Column: 192 cm, Spherosil XOB 015 (0.10–0.20 mm, 25 m^2/g), temperature 133°. Retention times (min): 0.48 = alkanes up to C_8 (concentration 4.07 mg/l); 0.63 = benzene (6.15 mg/l); 0.81 = toluene (3.60 mg/l); 1.13 = xylenes (3.42 mg/l); 1.35 = isopropylbenzene (0.36 mg/l); 1.53 = *n*-propylbenzene (0.31 mg/l); 1.78 = *tert.*-butylbenzene (0.31 mg/l); 1.96 = *p*-isopropylmethylbenzene (0.58 mg/l)

FID response

In the SSC system the FID response is dependent on the experimental conditions. The effect of hydrogen flow-rate upon the detector response is illustrated in Fig. 5 for four values of the steam flow-rate (the flow-rates of hydrogen and mobile phase are given for the detector temperature). The dependence of the detector response on the hydrogen flow-rate reaches a maximum at all steam flow-rates studied. The higher the steam flow-rate, the higher is the hydrogen flow-rate at which the maximum is reached. The detector background current increases with the

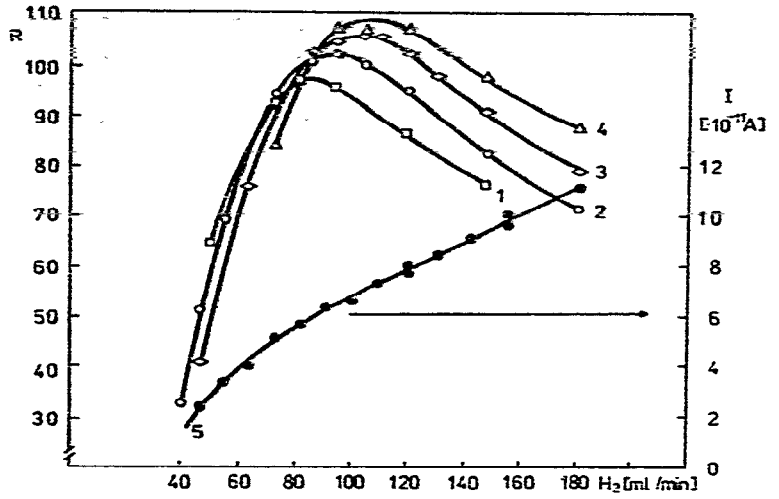

Fig. 5. Dependence of FID response (R in arbitrary units) and background current on the hydrogen flow-rate. Compound: *o*-xylene. Curves: 1 = steam flow-rate 72.5 ml/min, temperature 127°; 2 = steam flow-rate 87.6 ml/min, temperature 130°; 3 = steam flow-rate 96.8 ml/min, temperature 133°; 4 = steam flow-rate 124.5 ml/min, temperature 136°; 5 = background current.

hydrogen flow-rate and is *ca.* 10^{-11} A at the flow-rates studied. The noise level is of the order of 10^{-14} A. Both these parameters are *ca.* 2–5 times higher than those when using nitrogen.

The character of the above flow-rate dependence is similar to the case of an inert carrier gas. In contrast with the conventional conditions, the higher the steam flow-rate, the higher is the detector response at the optimum hydrogen flow-rate. If the inert carrier gas is applied, the maximum FID response is achieved at a certain carrier gas flow-rate[20], which is *ca.* 64.5 ml/min. At the same mobile phase flow-rates, in the case of steam, the optimum hydrogen flow-rates must be higher. For example, if the nitrogen flow-rate is 95.0 ml/min, then the optimum hydrogen flow-rate is 92.5 ml/min, while at a comparable steam flow-rate of 96.8 ml/min the optimum hydrogen flow-rate is 105 ml/min.

TABLE II

BASIC CHARACTERISTICS OF FLAME IONIZATION DETECTOR

		Steam	*Nitrogen flow-rate*	
			Comparable to steam	*Optimum*
Molar response (*o*-xylene)	(C)	1.096	1.872	2.040
Response per gram atom of carbon	(C)	0.137	0.234	0.255
Background current	(A)	$7 \cdot 10^{-11}$		$3.3 \cdot 10^{-11}$
Noise	(A)	$5 \cdot 10^{-14}$		$1 \cdot 10^{-14}$
Flow-rate (ml/min)				
carrier gas		96.8	95.0	64.5
hydrogen		105	92.5	79.8
air		600	600	600

In all previous cases where the FID function was found to be affected by water vapour in the detector[13–16], the detector responses were compared under the same working conditions, the only difference being in the presence or absence of water. This means that no optimal conditions were studied, and no comparison of the detector response, were made under these conditions. However, it follows from our measurements that the optimal conditions for the detector response are dependent on whether steam or an inert gas is used, and the compared response values at equal flow-rates will evidently differ from those obtained at the optimum flow-rates. This is illustrate in Table II, which summarizes basic FID characteristics for the equipment used in this work. The molar response (and hence the response per gram atom of carbon) is lower in the case of steam, by *ca.* 46% for a mobile phases (steam, nitrogen) flow-rate of *ca.* 96 ml/min and at the optimum hydrogen flow-rates for both mobile phases.

The dependence of the detector response and the backgroud current on the air flow-rate is similar to that for conventional FID. At flow-rates higher than *ca.* 500 ml/min both values are constant.

The detector response increases with increasing detector temperature (Table III).

TABLE III

DEPENDENCE OF THE DETECTOR RESPONSE ON THE DETECTOR TEMPERATURE

Temperature (°C)	*Response (arbitrary units)*
150	104,767
180	106,548
250	113,075
280	114,536

Under SSC conditions, the dependence of the FID response on the amount of the sample injected was studied by analyzing aqueous solutions of acetone (Fig. 6). The linear range of the response is five orders of magnitude and the maximum dose at which the response is still linear is $1 \cdot 10^{-5}$ g.

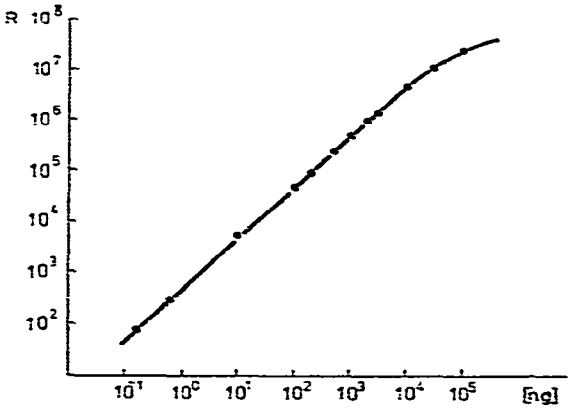

Fig. 6. Dependence of FID response (R in arbitrary units) on the amount of acetone injected.

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