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QUANTITATIVE AND QUALITATIVE HEAD-SPACE GAS ANALYSIS OF PARTS PER BILLION* AMOUNTS OF HYDROCARBONS IN WATER

A STUDY OF MODEL SYSTEMS BY CAPILLARY-COLUMN GAS CHROMATOGRAPHY WITH SPLITLESS SAMPLE INJECTION

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SUMMARY

The reliability of qualitative and quantitative head-space gas analysis of parts per billion* amounts of hydrocarbons in aqueous samples was studied on model systems by capillary-column gas chromatography. A simple all-glass splitless injection system is described that allows the introduction of head-space gas samples with a negligible decrease in efficiency. The applicability of different types of squalane capillary columns for head-space gas analysis was evaluated. The suitability of the standard addition method for quantitative head-space gas analysis is discussed for concentrations in the condensed phase varying from units to hundreds of parts per billion.

INTRODUCTION

The determination of trace amounts of hydrocarbons in aqueous media of various types is an important aspect of environmental analysis[1]. Because of the complexity of the samples and the low concentrations of organic substances in water, gas chromatography is used almost exclusively for the quantitative analysis of the latter. For qualitative analysis, a combination of gas chromatography and mass spectrometry (GC–MS) is required, although precise measurements of retention indices, which permit comparison of measured and tabulated data (table matching) with literature data, can also contribute to the identification of unknown pollutants[2]. To increase the detection limit, many methods and principles have been developed for extraction and concentration of organic constituents prior to GC analysis. An excellent survey of the possibilities and limitations of extraction techniques in combination with capillary-column GC was reported some years ago by Grob[3].

* Throughout this article the American billion (10^9) is meant.

Head-space gas analysis, an essentially different approach, has been widely applied to the determination of various components in samples of different nature[4]. The method has also been used for the quantitative analysis of hydrocarbons in aqueous systems[5–7]. Sensitivities down to 0.1 ppm were achieved and calibration graph methods were employed for the quantitative evaluation. McAuliffe[5] determined hydrocarbons in water by multiple equilibrations (extractions) of a water sample with equal volumes of gas. Each gaseous extract was analysed by GC and the result calculated by extrapolation of the relationship between the peak areas and the number of equilibrations.

The number of reports on the reliability of head-space gas analysis is rather low, probably owing to problems in the calibration procedures used. It should be noted that the partition coefficient of the solute in equilibrated gas–liquid systems depends on its activity coefficient. Consequently, the calibration should be carried out with a mixture the composition of which corresponds as closely as possible to that of the sample. To overcome these difficulties, which can arise with unknown samples that are not available in a pure form[4], the standard addition method was introduced for head-space gas analysis by Drozd and Novák[8,9]. They reported a high reliability of quantitative analysis for both hydrophobic and hydrophilic compounds in gas–aqueous systems at the sub-ppm level.

In this work we have extended the applicability of the standard addition method[8,9] to the determination of complex mixtures of parts per billion concentrations of hydrocarbons in water in combination with capillary columns. A simple all-glass splitless sampling system is described that permits the introduction of large sample volumes on to the capillary column, without a serious decrease in column efficiency. In addition, the possibility of identifying the components by table matching, using high-precision measurements of retention indices, has been considered. The quantitative reliability of the method was studied with model mixtures of aliphatic and aromatic hydrocarbons.

Comparison of extraction methods and head-space gas analyses

Methods suitable for the determination of trace amounts of organic substances in aqueous media can be divided into three basic approaches that differ essentially in the pretreatment of sample and the detection limit. The simplest method, extraction with organic solvents, is used particularly at relatively high concentrations (*ca.* 1 ppm)[10]. For lower concentrations, pre-concentration of the original extract is required. This is a disadvantage because of possible losses of the constituents and the high purity of the solvents necessary in order to prevent contamination[11].

The second method, gas extraction of the organic compounds by stripping them from aqueous samples, requires trapping of the compounds on an adsorptive material. This method offers the possibility of determining trace amounts of organic compounds in water even below the ppt level (1 part in 10^{12}, w/w), particularly for the more volatile compounds[12].

Many factors, such as interference by artifacts because of impurities in the stripping gas, the large amount of water passing the trap, adsorption of less volatile compounds in drying filters, the selection of sorbents and the adsorption and desorption efficiency, are serious drawbacks of the method, particularly for quantitative analyses. However, Grob and co-workers[3,13] recently reported an impressive improve-

ment of the method by using a closed-loop system, provided with a small-volume effective charcoal filter, but several precautions are necessary when working at such low concentrations. The complicated procedure and the sophisticated equipment required result in many more or less unknown factors and a semi-quantitative analysis. In view of the absolute amounts of pollutants involved, their overall results were excellent.

From the point of view of the detection limit the third method, head-space gas analysis lies between the methods discussed above. Because of its simplicity and the absence of problems arising from liquid and gas extraction procedures, head-space gas analysis is an attractive alternative for the quantitative analysis of organic substances in water, and this aspect is discussed in this paper.

EXPERIMENTAL

Model samples and equilibration device

A stock standard solution was prepared containing about 0.1 % of nine hydrocarbons (*n*-hexane, benzene, *n*-heptane, toluene, *n*-octane, ethylbenzene, *o*- and *m*-xylene and *n*-nonane). Appropriate amounts of these solutes were weighed into a 25-ml calibrated vessel and diluted to volume with acetone. All other standard solutions were prepared by dilution of the stock solution in such a way that any required concentration in the equilibration system could be prepared by using the same volume of the appropriate standard solution. The standard solutions were stored in a refrigerator. The total amount of each compound introduced into the equilibration system, containing 50 ml of distilled water and 50 ml of head-space gas, was varied between 0.1 and 15 μg, which corresponds to concentrations of about 2–300 ppb in the liquid phase. Model samples were prepared by addition of 1 μl of an appropriate standard solution to the equilibration system. The same standard solution was always used for the standard addition calibration[8,9].

Although 10 min appeared to be sufficient for equilibration to be achieved, an equilibration time of 30 min was chosen for practical reasons. The equilibration device (Fig. 1) consists of a 100-ml glass vessel with a flat bottom, provided with a jacket, through which thermostated water is pumped with an ultrathermostat (Colora, Tamson, The Netherlands). The thick-walled capillary tube at the top ends in a flange on which a rubber septum is clamped with an aluminium cap. The cap and septum are replaced before every analysis in order to prevent leakage and contamination with possible residues of the standard solution. For the same reasons, care was taken to pierce the septum at the same place only once. During equilibration at 40° the sample is mixed vigorously with a magnetic stirrer.

Gas chromatographic system

The head-space gas samples were analysed on a home-made gas chromatograph described previously[2], equipped with a specially designed splitless sampling system and capillary columns. The column temperature could be controlled to within $\pm 0.02°$ while the inlet pressure variations were within ± 0.002 atm during each analysis. The compounds were detected with a flame-ionization detector (10^{-11} A f.s.d.). Measurements of retention times and peak areas were effected with a digitizer–

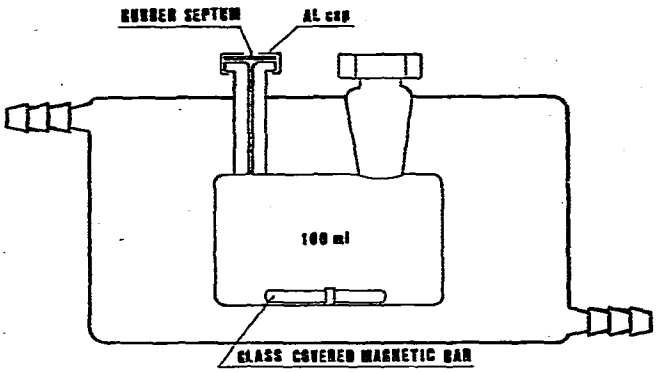

Fig. 1. Equilibration device.

computer system (sampling rate two per second) with subsequent off-line data processing using paper tape.

Splitless sampling system

The splitless sample introduction system is shown schematically in Fig. 2. The all-glass part between the septum and the column (Fig. 2b) consists of a liner, a capillary trap and a second liner that is tapered to match the outside diameter of the column. The capillary trap, coated with a thin film of OV-101 is surrounded by a jacket provided with four fittings to permit the transport of the cooled or heated gas during operation. The pathway of the auxiliary gas flows is controlled by two three-way metal valves. The auxiliary gas lines are made of thin-walled copper tubing (O.D. 3 mm, I.D. 2 mm). They were kept as short as possible and insulated to prevent excessive heat losses. The coiled part of the cooling line was placed in a dry-ice–ethanol bath at about −70°. In the heating line the tube was partly coiled around

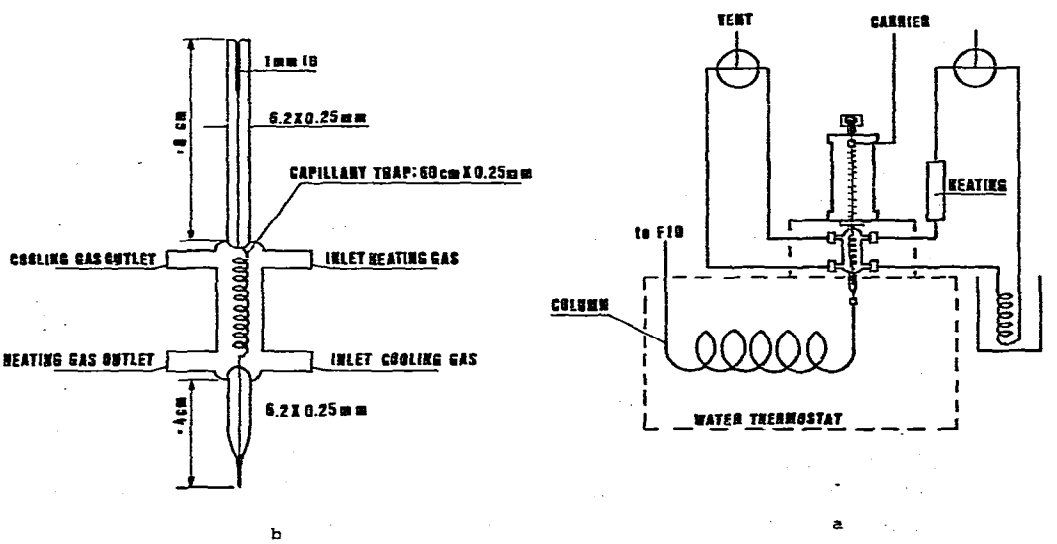

Fig. 2. Schematic diagram of the all-glass splitless injection system.

a massive aluminium cylinder (O.D. 2 cm) provided with two cartridge heaters. Th length of both coils was about 2 m. On applying a flow of dry nitrogen of *ca.* 6 l min a temperature between −50° and −60° was obtained in the centre of the jacke during cooling. After switching to heating, this temperature increased to above 150 within 20 sec. The head-space gas samples were taken from the equilibration systen with a gas-tight syringe provided with a stainless-steel piston (Chirana, Brno, Czecho slovakia), which was pre-heated to about 60°.

Preparation and connection of columns

Three squalane capillary columns were prepared, as follows.

Column 1. A stainless-steel column (10 m × 0.25 mm I.D.) was prepared ac cording to Rijks and Cramers[2], using a 10% solution of squalane in *n*-hexane.

Column 2. An HCl-etched[14] alkali-glass column (73 m × 0.25 mm I.D.), de activated according to Blomberg[15], was coated dynamically with a 60% solution o squalane in *n*-hexane using a slightly modified mercury plug method as reported b Schomburg and Husmann[16].

Column 3. This was a Duran glass column (29 m × 0.25 mm I.D.) provided witl a layer of barium carbonate and deactivated according to Grob and co-workers[17,18] and coated as described by Bouche and Verzele[19] with a 0.6% solution of squalane ir *n*-hexane.

The columns were connected to the injection and detection system either di rectly (metal column) or via a short squalane-coated capillary (O.D. 0.6 mm, I.D 0.25 mm) by means of shrinkable PTFE tubing. The metal column or the metal cap illary protruted into the burner of the detector near to the top so as to avoid a dead volume.

Chemicals

For the preparation of the standard solutions we used API standard hydro carbons and acetone (analytical-reagent grade; Merck, Darmstadt, G.F.R.) as the solvent. Distilled water was used to prepare the model samples.

RESULTS AND DISCUSSION

Splitless injection system

Considering the large volume of the head-space gas sample, it can be expected that direct injection of the sample on to a capillary column will result in a decrease in the column efficiency, and this effect will be greater the shorter is the column. Therefore, the components present in the head-space gas samples were concentrated in a cold trap, coated with a thin film of OV-101. The stationary liquid film was found to be essential to enhance the effective adsorption of the substances in the capillary. To minimize the time required for heating and cooling the concentration trap, the inlet and outlet transfer lines of the cold and hot nitrogen were separated (four-way arrangement). In this way, the heat losses in the connecting lines could be considerably reduced in comparison with a two-way arrangement. In addition, the gas-flow pathways (Fig. 2a) of the cooled and heated nitrogen increase the minimum width of the sample plug in the capillary trap when a temperature gradient is present in

TABLE I

COLUMN PROPERTIES

N = Number of theoretical plates.

Compound	*Column 1*						*Column 2*						*Column 3, freshly prepared*		
	Freshly prepared			*After 2 months of head-space analysis*			*Freshly prepared*			*After 2 weeks of head-space analysis*					
	I^{70}_{sq}	k	N/m	I^{70}_{sq}	k	N/m	I^{70}_{sq}	k	N/m	I^{70}_{sq}	k	N/m	I^{70}_{sq}	k	N/m
Benzene	641.1			641.4			642.3			653.4			642.0		
Toluene	749.2			749.4			749.2			759.3			749.3		
Ethylbenzene	839.0			839.2			838.8			849.7			839.4		
m-Xylene	855.3			855.6			855.3			866.0			855.6		
o-Xylene	874.3			874.5			874.4			885.9			874.6		
n-Nonane		18.6	2900		12.8	2300		5.5	2400		4.9	2400		5.8	2500

the trap. Under the operating conditions (see Experimental) the temperature increased to above 150° in the centre of the trapping system within 20 sec after switching to heating, and this time was therefore taken as the start of the separation process in all experiments.

With the splitless injection system described above, an acceptable decrease in efficiency (less than 10%) was obtained with the shortest capillary column (length 10 m), depending on the capacity ratio of the solutes. For the other columns (lengths 29 and 73 m) the decrease in efficiency was negligible.

Column selection criteria

A high separation efficiency and long-term stability with respect to solute retention, preferably retention indices, are the basic requirements of a column for the reliable routine analysis of complex mixtures of hydrocarbons[20]. The resistance of the column to the high concentration of water vapour is a serious additional complication in the head-space gas analysis of organic compounds in water.

In Table I, three different types of squalane-coated capillary columns (see Experimental) are compared in terms of their efficiency, reproducibility of retention indices and resistance to water vapour. These results were obtained with a split injection system (splitting ratio 1:400) with synthetic mixtures of hydrocarbons using the retention time of methane as the "dead time". Columns 1 (stainless steel) and 3 (Duran glass, covered in advance with a layer of barium carbonate) were acceptable for this application. After continuous use for 2 months for head-space gas analysis under the given experimental conditions their retention properties and their efficiencies had hardly changed, despite the oxygen and water vapour present in the samples. Probably the slight decrease in the capacity ratios of the components occurred during the first period after preparation.

The second column (HCl-etched alkali-glass, deactivated with PEG 20M) was used for routine hydrocarbon analyses at 70° without showing significant changes in efficiency and retention properties. When exposed to head-space gas samples its characteristics changed considerably within a few days. Because of the rapid changes in its polarity, this column was not suitable for qualitative head-space gas analysis by means of retention indices. Possibly this effect is due to the influence of the water vapour on the sodium chloride crystals on the column wall and/or hydroxylation of the bonds between the PEG 20M layer and the column wall.

Qualitative evaluation

Although a detailed discussion about identification by means of retention data is beyond the scope of this paper, it will be evident that retention indices measured with high precision and accuracy provide adequate qualitative information in many instances[20]. With the equipment used in this study in combination with capillary columns and split injection, retention indices can be measured with a precision of about 0.1 index unit for hydrocarbons, using methane for the determination of the "dead time". In head-space gas analysis with capillary columns and splitless injection, the direct measurement of the "dead-time" is not possible. Methane cannot be trapped in the cold capillary and gives broad and asymmetric peaks. Also, the retention time of methane is not representative of the real "dead time". Therefore "dead times"

calculated from the linear relationship between the logarithm of the adjusted retention time and the carbon number of *n*-alkanes were used in this study.

In Table II, retention indices of five aromatic hydrocarbons based on "dead time" measurements with a splitter are compared with those measured during head-space gas analysis either measured directly or calculated as discussed above. Correct results can be achieved by employing "dead times" calculated by the extrapolation method. Retention indices based on the direct measurement of the "dead time" differ markedly for solutes at the beginning of the chromatogram. Compounds with a larger retention time are less sensitive to the method used.

TABLE II

EFFECT OF THE DETERMINATION OF THE "DEAD TIME" ON RETENTION INDICES OF AROMATIC HYDROCARBONS ON A SQUALANE CAPILLARY COLUMN (COLUMN 3)

I_{sq}^{70} values determined (a) directly with split injection, (b) directly with the splitless injection system and (c) calculated by logarithmic extrapolation. n = Number of measurements.

Compound	I_{sq}^{70}		
	a	*b*	*c*
Benzene	641.1	643.3	641.1
Toluene	749.2	749.8	749.0
Ethylbenzene	839.0	839.1	838.8
m-Xylene	855.3	855.5	855.2
o-Xylene	874.3	874.4	874.4
n	3	6	6

Quantitative evaluation

Calculation of results. From the mass balance of a substance *i*, it follows that the total weight of this substance in the sample (W_i) can be calculated according to the equation[8]

$$W_i = \frac{W_s - w_i}{(A_i' v_g / A_i v_g') - 1} \quad (1)$$

It is assumed that the distribution coefficient of a compound *i* in the gas–liquid system as well as the volume of both phases are not influenced by the addition of the standard. The weight of substance *i* in the head-space gas sample (w_i) is usually negligibly small compared with the amount of the added standard (W_s). The peak-area ratio after and before addition of the standard (A_i'/A_i) can be replaced with the ratio of the corresponding peak heights for symmetrical peaks. This is an advantage for concentrations near the detection limit, as will be shown below.

Equilibration time and detection limit. Head-space gas samples (1 ml) were taken from the same model samples after equilibration times of 10 min, 30 min, 2 h and 2½ h. The concentrations in the condensed phase varied between 25 and 100 ppb. The representative chromatogram in Fig. 3 shows that an equilibration time of 10 min is sufficient for equilibrium to be achieved. It appeared that a detection limit of tenths of a part per billion could be obtained under the given experimental conditions

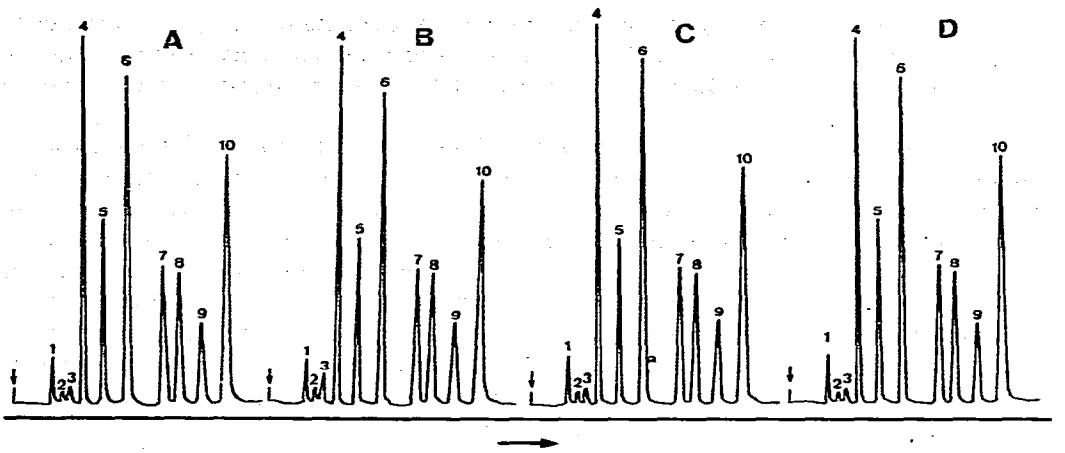

Fig. 3. Chromatograms of 1-ml head-space gas samples, after an equilibration time of (A) 10 min, (B) 30 min, (C) 2 h, and (D) 2½ h at 40°. Peaks: 1 = acetone (10 ppm in the liquid phase); 2 = *n*-hexane (25 ppb); 3 = benzene (46 ppb); 4 = *n*-heptane (27 ppb); 5 = toluene (57 ppb); 6 = *n*-octane (42 ppb); 7 = ethylbenzene (79 ppb); 8 = *m*-xylene (78 ppb); 9 = *o*-xylene (69 ppb); 10 = *n*-nonane (44 ppb). Column 1, carrier gas N_2, inlet pressure 0.11 atm, temperature 70°.

(detector sensitivity setting 10^{-11} A f.s.d. and a noise level of 10^{-14} A) without a serious decrease in quantitative reliability.

Reproducibility of model sample preparation. Some model samples were prepared by injecting 1 μl of an appropriate standard solution into the equilibration system, containing 50 ml distilled water and 50 ml gas. After equilibration for 30 min, 1-ml samples were taken from the gas phase and analysed. The chromatograms were evaluated by means of either peak heights (measured manually) or peak areas (measured with a digitizer–computer system).

From the results presented in Table III, it follows that in this concentration range (25–100 ppb) a slightly better reproducibility can be obtained by peak-area measurements. The relatively large errors for *n*-hexane and benzene are caused by an irreproducible and ineffective trapping at temperatures between −50 and −60°.

TABLE III

REPRODUCIBILITY OF MODEL SAMPLE PREPARATION BY STANDARD ADDITION

Number of model samples: 6.

Component	*h (mm)*	*S.D.$_h$ (%)*	*A (arbitrary units)*	*S.D.$_A$ (%)*
n-Hexane	9.2	47.0	784	46.5
Benzene	16.3	41.6	1.106	47.0
n-Heptane	187.8	11.0	13.600	9.6
Toluene	70.9	12.2	7.229	7.8
n-Octane	127.4	12.7	21.206	6.6
Ethyl benzene	43.3	8.6	11.200	7.8
m-Xylene	38.7	10.0	11.136	2.9
o-Xylene	23.1	8.8	9.734	4.7
n-Nonane	65.9	11.8	23.360	2.2

Considering the many factors that influence these data (*e.g.*, equilibration temperature, transfer of the standard solution and the head-space gas sample and the GC conditions), the reproducibility of the model sample preparation and standard addition is acceptable.

Determination of hydrocarbons in model samples. The results of the determination of hydrocarbons in model water samples by using the standard addition method are presented in Table IV. Each of the samples contained nine hydrocarbons with a concentration varying from units to hundreds of parts per billion in the condensed phase. The concentration of acetone (solvent for the standard solution) was of the order of tens of parts per million in all instances. The results are averages of ten determinations (one determination for one model sample). In the calculation, peak heights measured manually were employed instead of integrator- or computer-measured peak areas for reasons of simplicity and because more reliable results were obtained at low concentrations owing to a low signal-to-noise ratio.

At the highest concentrations studied (hundreds of parts per billion), where

TABLE IV

RESULTS OBTAINED BY HEAD-SPACE GAS ANALYSIS OF HYDROCARBONS IN MODEL WATER SAMPLES WITH THE STANDARD ADDITION METHOD

Number of measurements: 10.

Solute	*Mean W_i (μg)*		*Difference (found–given) (%)*	*S.D.$_{(W_i,\ found)}$ (%)*
	Given	*Found*		
n-Heptane	0.179	0.183	2.2	10.2
	0.358	0.337	−6.0	14.7
	4.476	4.547	7.6	9.1
	8.952	9.247	3.3	8.6
n-Octane	0.281	0.267	−4.7	19.4
	0.561	0.549	−2.2	12.6
	7.016	6.669	−4.9	19.6
	14.03	13.16	−6.2	16.1
n-Nonane	0.292	0.321	10.2	24.1
	0.584	0.598	2.4	15.3
	7.304	6.732	−7.8	18.6
	14.07	12.86	−11.9	14.4
Toluene	0.378	0.358	−5.4	13.7
	0.756	0.722	−4.5	13.7
	9.448	8.612	−8.8	15.0
	18.90	16.82	−10.9	14.2
Ethylbenzene	0.524	0.481	−8.2	22.7
	1.047	0.994	−5.1	11.0
	13.09	10.86	−17.0	21.4
	26.18	22.02	−15.9	19.8
m-Xylene	0.523	0.478	−8.6	18.6
	1.046	0.969	−7.4	20.5
	13.07	11.22	−14.1	14.2
	26.15	22.50	−13.9	24.5
o-Xylene	0.463	0.486	5.1	26.7
	0.925	0.819	−11.5	14.0
	11.57	10.06	−13.1	19.1
	23.14	17.36	−25.0	12.6

peak asymmetry caused by overloading of the column was observed, peak-area measurements offered better results. In all other instances the reliability was either similar or only slightly improved when computer-measured peak areas were used.

It must be realized that systematic and random errors due to the preparation of the model samples are included in these results. In addition, one should also consider variations in the actual temperature of the injection syringe at the moment of sampling. Owing to the thermal expansion of gases, the actual amount of solute within the syringe will vary proportionally to the inverse of the absolute temperature. Considering all of the factors that influence these results, it can be concluded that both the accuracy and the precision are surprisingly good over the whole concentration range. The accuracy for the highest concentrations could be improved considerably by evaluating the results by means of computer-measured peak areas, as illustrated in Table V for a limited number of compounds.

TABLE V

COMPARISON OF QUANTITATIVE RESULTS OBTAINED BY MEASURING PEAK HEIGHTS MANUALLY (a) AND PEAK AREAS BY COMPUTER (b)

n = Number of measurements.

Solute	*Method*	*Mean W_i (μg)*		*Difference (found—given) (%)*	*n*
		Given	*Found*		
Toluene	a	18.90	16.82	−10.9	10
	b		17.78	−5.9	4
Ethylbenzene	a	26.18	22.02	−15.9	10
	b		23.44	−10.5	4
o-Xylene	a	23.14	17.36	−25.0	10
	b		20.37	−11.9	4

CONCLUSIONS

Head-space gas analysis involving quantitation by a standard addition method and capillary-column gas chromatography with splitless sample introduction permits the reliable determination and identification of ultra-trace amounts of volatile hydrocarbons in water. By employing conventional syringes for the head-space gas sampling and with manual measurement of peak heights, an average error below 10% of the value being determined appears possible for concentrations in the condensed phase down to units of parts per billion. Considering the many factors that influence the quantitative results, the reproducibility, corresponding to a relative standard deviation of *ca.* 10%, is surprisingly good. The sensitivity of the analysis is one or two orders higher comparing to that with a packed column. The results obtained with these model systems can reasonably be generalized for most problems concerned with trace amounts of volatile hydrocarbons in aqueous samples.

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REFERENCES

1 J. A. Black, *Water Pollution Technology*, Reston Publ. Co., Reston, Va., 1977, p. 107.
2 J. A. Rijks and C. A. Cramers, *Chromatographia*, 7 (1974) 99.
3 K. Grob, *J. Chromatogr.*, 84 (1973) 255.
4 H. Hachenberg and A. P. Schmidt, *Gas Chromatographic Head-space Gas Analysis*, Heyden & Son, London, New York, Rheine, 1977.
5 C. McAuliffe, *Chem. Technol.*, 1 (1971) 46.
6 H. Miethke, *Deut. Lebensm.-Rundsch.*, 65 (1969) 379.
7 I. Ploder, *Deut. Lebensm.-Rundsch.*, 70 (1974) 401.
8 J. Drozd and J. Novák, *J. Chromatogr.*, 136 (1977) 37.
9 J. Drozd and J. Novák, *J. Chromatogr.*, 152 (1978) 55.
10 R. Jeltes and R. Veldink, *J. Chromatogr.*, 27 (1967) 242.
11 K. Grob, K. Grob, Jr. and G. Grob, *J. Chromatogr.*, 106 (1975) 299.
12 J. Novák, J. Žlutický, V. Kubelka and J. Mostecký, *J. Chromatogr.*, 76 (1973) 45.
13 K. Grob and F. Zürcher, *J. Chromatogr.*, 117 (1976) 285.
14 J. J. Franken, G. A. F. M. Rutten and J. A. Rijks, *J. Chromatogr.*, 126 (1976) 117.
15 L. Blomberg, *J. Chromatogr.*, 115 (1975) 365.
16 G. Schomburg and H. Husmann, *Chromatographia*, 8 (1975) 517.
17 K. Grob and G. Grob, *J. Chromatogr.*, 125 (1976) 471.
18 K. Grob, G. Grob and K. Grob, Jr., *Chromatographia*, 10 (1977) 181.
19 J. Bouche and M. Verzele, *J. Gas Chromatogr.*, 6 (1968) 501.
20 J. A. Rijks, *Thesis*, Eindhoven University of Technology, 1973, p. 20.