COMPARISON OF HEADSPACE-GAS AND LIQUID-EXTRACTION DETERMINATIONS OF HYDROCARBONS IN WATER BY THE STANDARD-ADDITION METHOD

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SUMMARY

The methods of headspace-gas and liquid-extraction analysis, comprising the gas chromatography of samples of the gaseous or liquid-extract phases withdrawn from closed equilibrated systems and involving the standard-addition quantitation, have been examined and compared for the determination of trace amounts of hydrocarbons in water. The liquid-extraction method is more accurate but it yields chromatograms with an interfering background due to the liquid extractant. The sensitivity of determination of volatile hydrocarbons in water is roughly the same for each method, concentrations amenable to reliable determination amounting to tens of $\mu g/l$ on a packed column with a flame-ionization detector.

INTRODUCTION

Headspace-gas analysis, in the variant comprising the analysis of samples taken from the gas present over a liquid in a closed equilibrated gas–liquid system, has been applied by several workers[1,2] to the determination of hydrocarbons and/or halogenated hydrocarbons in water. Analogous procedures involving liquid–liquid rather than gas–liquid equilibration have also been described[3]. Recently, the standard-addition method has been examined as a means of quantitation in headspace-gas analysis of hydrocarbons. The aim of the present paper is to show the possibility of using the standard-addition method for quantitative analysis of liquid–liquid and/or ternary gas–liquid–liquid systems and to compare the headspace-gas–standard-addition method with an analogous procedure involving a single-step liquid extraction and analysis of a sample of the extract. In both cases, systems with water containing trace amounts of several hydrocarbons were chosen as models.

EXPERIMENTAL

The physical arrangement of the system for headspace-gas analysis was the same as that described previously[4]. A 50-ml volume of distilled water was pipetted into a 100-ml flask whereupon the latter was closed with a special ground-glass stopper

and placed in a water-bath, where it was kept at 40° for 20 min while agitating the contents by means of a magnetic stirrer; the volume of the gaseous phase in the stoppered flask was 45 ml. 3.5 μl of a solution containing 0.5769, 1.2156, 1.2615, 1.6208 and 2.0349 μg/μl of hexane, benzene, 2,4-dimethylhexane, octane and 1-nonene, respectively, in acetone were then placed in the flask by use of a 7005 N (5-μl) Hamilton syringe (Hamilton, Micromesure BV, The Hague, The Netherlands).

After allowing 20 min for equilibration, a 1-ml sample of the gaseous phase was withdrawn slowly (ca. 0.5 min) from the system and analyzed by gas chromatography (first analysis). Then another 3.5-μl charge of the above solution of hydrocarbons was placed in the flask and, after 20 min, again a 1-ml sample of the gaseous phase was withdrawn and analyzed (second analysis). From the amounts of standards added after completion of the first analysis and the chromatograms obtained in both analytical steps it is possible to calculate the initial amounts of the solutes in the system. The headspace-gas samples were taken by use of a 1-ml gas-tight syringe (Chirana, Brno, Czechoslovakia) kept at ca. 60°.

The system designed for analysis by the liquid-extraction method was contained in a 20-ml glass ampoule equipped with a short capillary-tube to which an inlet-port head was attached. The inlet-port head was the same as that employed in the arrangement for headspace-gas analysis[4]. Analytical-grade carbon disulphide was employed as the extractant. Volumes of 2 ml CS_2 and 5 ml of distilled water were injected into the ampoule by use of syringes, and the ampoule was closed by the inlet-port head; a schematic representation of the system used in the liquid-extraction analyses is shown in Fig. 1. A 3.5-μl volume of a solution containing 8.241, 17.366, 18.022, 23.154 and 29.070 μg/μl of hexane, benzene, 2,4-dimethylhexane, octane and 1-nonene, respectively, in acetone was then injected into the system using a 5-μl Hamilton syringe and the contents of the ampoule were vigorously shaken for some time in order to promote equilibration. The ampoule was placed in a water-bath at 22° and revolved there for 20 min at 10 rpm about its shorter axis, the latter being positioned horizontally. The ampoule was then removed from the bath, positioned up-side down and a 1-μl charge of the CS_2 phase was withdrawn by a 7001 N (1-μl) Hamilton syringe and injected into the gas chromatograph (first analysis). Another 3.5-μl charge of the standard hydrocarbon solution was placed in the ampoule, the procedure was repeated and a 1-μl sample of the extract was withdrawn and analyzed (second analysis). As with the headspace-gas method, the chromatograms obtained in the two
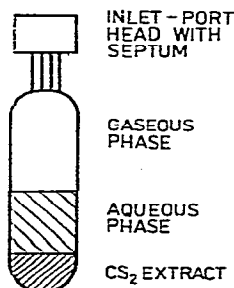

Fig. 1. Representation of the system employed in the liquid-extraction method.

analyses and the knowledge of the amounts of the standards added after completion of the first analytical step enable the initial amounts of the solutes in the system to be calculated.

The standard solutes as well as the acetone and carbon disulphide were analytical grade chemicals from Fluka, Buchs, Switzerland (hexane), Lachema, Brno, Czechoslovakia (benzene, 2,4-dimethylhexane and acetone), VEB Laborchemie, Apolda, G.D.R. (octane), Polyscience, Evanston, Ill., U.S.A. (1-nonene) and Riedel-De Haën, Seelze-Hannover, G.F.R. (CS₂).

With both methods, the chromatographic analyses were carried out on a Hewlett-Packard 402 gas chromatograph (Avondale, Pa., U.S.A.). Conditions: FID, sensitivity attenuation 1/16; glass column (180 cm × 3 mm I.D.) packed with 8.14 g of 10% (w/w) Apiezon K on Chromaton N (0.2–0.25 mm); column temperature, 80°; nitrogen carrier gas; flow-rates of 26, 29.4 and 200 ml/min, for nitrogen, hydrogen and air, respectively. The Chromaton N and Apiezon K were products of Lachema and AEI (Manchester, Great Britain), respectively.

CALCULATION OF RESULTS

A mass balance of solute in the system leads to the following relations[5] for the headspace-gas and liquid-extraction methods of analysis, respectively:

$$W_i = W_{iG}\left(1 + K_{LG} \cdot \frac{V_L}{V_G}\right) = \frac{W_s - w_i}{(A_i' v_G / A_i v_G') - 1} \tag{1}$$

$$W_i = W_{ie}\left(1 + \frac{V_p}{K_{ep} V_e}\right) = \frac{W_s}{(A_i' v_e / A_i v_e') - 1} \tag{2}$$

where W_i is the initial weight of solute i in either system (amount to be determined), W_{iG} is the weight of the solute in the gaseous phase, V_L and V_G are the volumes of the aqueous and the gaseous phase and K_{LG} is the distribution constant of the solute, defined as the ratio of solute concentrations in the liquid and the gaseous phase, W_{ie} is the weight of the solute in the liquid extract, V_p and V_e are the volumes of the parent liquid and the extract, K_{ep} is the distribution constant of solute, defined as the ratio of its concentrations in the extract and parent liquid, W_s is the weight of standard added to the system, w_i is the weight of the solute taken out of the system in sampling the gaseous phase for the first analysis, A_i and A_i' are the solute peak areas in the chromatograms obtained in the first and in the second analyses, v_G and v_G' are the volumes of the gaseous phase and v_e and v_e' are the volumes of the extract used in the gas chromatograph in the first and in the second analyses, respectively.

It is possible to employ peak heights instead of peak areas with the standard-addition method; i.e., the ratios A_i'/A_i can be replaced by the corresponding peak-height ratios, h_i'/h_i, in both the above relations. Further, if $v_G = v_G'$ and $v_e = v_e'$, in the present case, the expressions are simplified accordingly; all the results presented in this work have been calculated from peak heights.

The expression $1 + (V_p/K_{ep}V_e)$ in eqn.2 (a system factor) applies to a system comprising only the parent liquid and the liquid extract. However, the system used in

this work comprised also the gaseous phase, so that the situation has to be expressed by

$$W_1 = W_{1c} \left(1 + \frac{V_p}{K_{cp}V_c} + \frac{V_{Ge}}{K_{cG}V_c} \right) \tag{3}$$

In this case, V_{Ge} and K_{cG} are the volume of the gaseous phase in the ternary parent liquid–extract–gas system and the distribution constant of the solute, defined by the ratio of solute concentrations in the extract and the gaseous phase. The last expression in relation 2 remains unaltered, *i.e.*, the calculation of the results is independent of the form of the system factor[5].

RESULTS AND DISCUSSION

In all the measurements the values of W_s were equal to those of W_1, and the values of w_1 were determined by external calibration. Table I shows the results of the headspace-gas analysis, while the results of liquid-extraction analysis are given in Table II. In both kinds of analysis, chromatograms of comparable sizes were recorded at a fixed detector-sensitivity setting. It is apparent from the data in Tables I and II that the headspace-gas method of analysis is less accurate than its liquid-extraction analogue. On the other hand, a direct comparison of the data suggests that the head-space-gas method is more sensitive. Supposing the entire amounts of solutes (values

TABLE I

RESULTS OBTAINED BY THE HEADSPACE-GAS–STANDARD-ADDITION METHOD

$S/\sqrt{n}$ = Standard deviation of the average, n = number of determinations (9), $t_{exptl.}$ = experimental Student coefficient; t_{crit} = 2.26.

Solute	W_1 (μg)		Error		$S/\sqrt{n}$	$t_{exptl.}$
	Given	Found	μg	%		
Hexane	2.02	1.88	−0.14	6.9	0.08	1.75
Benzene	4.25	4.23	−0.02	0.5	0.20	0.10
2,4-Dimethylhexane	4.42	4.57	0.15	3.4	0.25	0.60
Octane	5.67	6.43	0.76	13.4	0.43	1.77
1-Nonene	7.12	8.36	1.24	17.4	0.63	1.97

TABLE II

RESULTS OBTAINED BY THE LIQUID-EXTRACTION–STANDARD-ADDITION METHOD

For the meaning of symbols see Table I; n = 10, t_{crit} = 2.22.

Solute	W_1 (μg)		Error		$S/\sqrt{n}$	$t_{exptl.}$
	Given	Found	μg	%		
Benzene	60.8	57.2	−3.6	5.9	2.8	1.28
2,4-Dimethylhexane	63.1	60.5	−2.6	4.1	2.4	1.08
Octane	81.0	80.5	−0.5	0.6	3.6	0.14
1-Nonene	101.7	97.7	−4.0	3.9	5.0	0.80

of W_i) had originally been present in the aqueous phase only, as would be the case in an actual analysis of water, it is possible to infer from the data in Tables I and II that concentrations of tenths and tens of $\mu g/ml$ of hydrocarbons in water were determined by the headspace-gas and liquid-extraction standard-addition methods, respectively. This sensitivity is still insufficient for many applications in modern water-pollution control; often it is necessary to determine hydrocarbons in water in concentrations of tenths of $\mu g/l$ or less. This sensitivity could theoretically be attained by employing capillary gas chromatography with unsplit sample injection[6] and utilizing the reserve (about an order of magnitude) in detector sensitivity.

In order to make an unequivocal comparison of the sensitivities of the headspace-gas and liquid-extraction methods, it is necessary to compare situations in which the same amounts of water containing the given contents of hydrocarbons to be determined are analyzed, employing a reasonably small amount of the extractant and injecting into the gas chromatograph the maximum admissible charges of the headspace gas and the extract, respectively. In such a comparison, the measure of the sensitivity of analysis is the solute weight in the charge introduced into the gas chromatograph under the above conditions. It follows from eqns. 1 and 2 that

$$w_{iG} = \frac{W_i v_G}{V_G + K_{LG} V_L} \tag{4}$$

and

$$w_{ie} = \frac{W_i v_e}{V_e + (V_p/K_{ep})} \tag{5}$$

Owing to the low solubility of hydrocarbons in water, except for aromatics, the values of K_{LG} are[1,7] of the order of 10^{-2}. On the other hand, since $K_{ep} = K_{eG}/K_{LG}$, where K_{eG} is the constant of solute distribution between the extract phase and a gas, the values of K_{ep} of hydrocarbons in a nonpolar extractant–water system will be very large. This implies that $K_{LG} V_L \ll V_G$ and $(V_p/K_{ep}) \ll V_e$ even if $V_e \ll V_p$ and $V_L = V_G$ with such systems. Hence, if $V_L = V_p = 50$ ml, $W_i = 1$ μg, $V_G = 50$ ml, $V_e = 100$ μl, $v_G = 5$ ml and $v_e = 10$ μl, calculations by eqns. 4 and 5 with the terms $K_{LG} V_L$ and V_p/K_{ep} being neglected yield $w_{iG} = w_{ie} = 0.1$ μg. It follows from this rough estimate that the sensitivities attainable by either method are approximately the same. However, this situation can be substantially altered by employing different extractants and/or condensing the extract.

A great advantage of the headspace-gas method over the liquid-extraction method is that it is not necessary to introduce into the system any substance that might interfere with the analysis; with the liquid-extraction method the background chromatogram of the extractant may be a source of serious difficulties. This situation is apparent from the chromatograms in Fig. 2 and 3. While the chromatogram of a headspace-gas sample is free from artifact peaks, in the chromatogram of a sample of the liquid extract the peak of hexane is completely obscured by the background response of carbon disulphide. In addition, the peak of benzene had to be corrected for a blank value due to an impurity present in the carbon disulphide. With larger samples of the extract and lower concentrations of the solutes the situation would obviously be worsened accordingly.
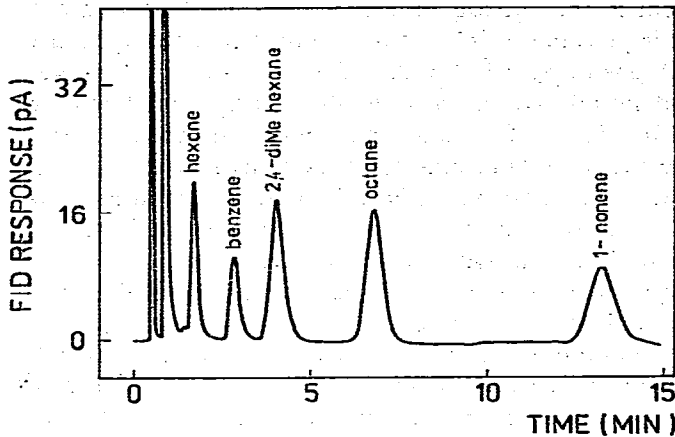
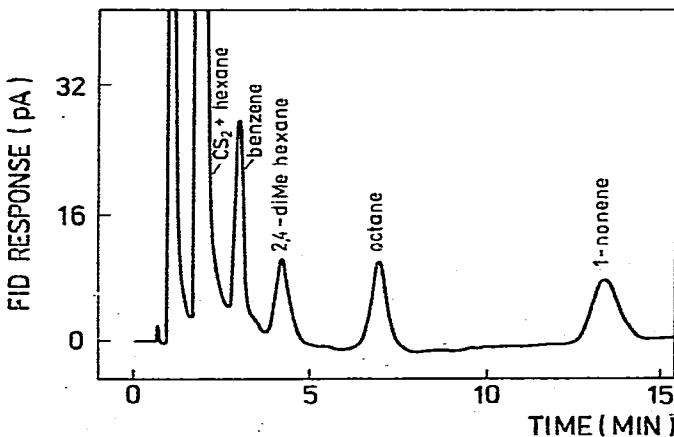Fig. 2. Chromatogram of a 1-ml sample of the headspace gas. FID, sensitivity attenuation $^1/_{16}$.

Fig. 3. Chromatogram of a 1-μl sample of the CS$_2$ extract. Details as in Fig. 2.

CONCLUSIONS

The standard-addition method is a suitable means of quantitation in trace analysis of hydrocarbons in water by both the headspace-gas technique and its analogue involving liquid extraction and analysis of the extract. When sampling the headspace gas and the liquid extract by use of conventional syringes and injecting the samples directly into the gas chromatograph, the accuracy of the results obtained by the headspace-gas method is somewhat lower. If a nonpolar extractant is used with the latter method, both methods render approximately the same sensitivity of analysis. Employing a packed column and a FID, both the methods provide a reliable determination of tens of μg/l of volatile hydrocarbons in water. In contrast to the headspace-gas method, in the liquid-extraction method the chromatograms may be impaired by the interfering background of the extractant.

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