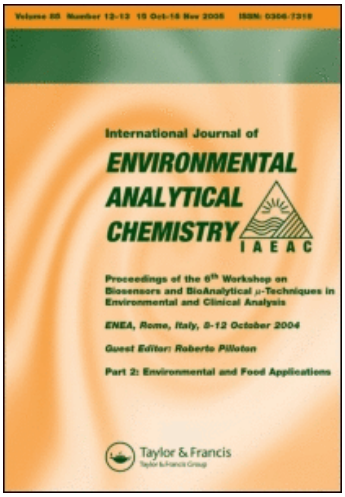

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Josef Drozd[a]; Josef Novák[a]
[a] Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, Brno, Czechoslovakia

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Determination of Trace Hydrophobic Volatiles in Aqueous Media by a Technique of Multiple Stripping and Trapping in a Closed Circuit†

JOSEF DROZD AND JOSEF NOVÁK

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, 611 42 Brno, Czechloslovakia.

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The double-sampling method of quantitative headspace-gas analysis was assayed by analysing model water-gas systems with benzene, toluene, ethylbenzene, *n*-decane, and *n*-dodecane as analytes. With this method, two headspace samples are withdrawn successively from the system and analysed by gas chromatography. The total initial contents of the analytes in the system are calculated by virtue of the decrease in their concentrations in the gaseous phase, brought about by the withdrawal of the first headspace sample. Combined with Grob's closed-loop strip/trap technique, the method provides for the determination of ppb (10^9) concentrations of the above hydrocarbons in water with an average relative error of several percent.

KEY WORDS: Hydrocarbons, hydrophobic volatiles, water, headspace-gas analysis, gas chromatography.

INTRODUCTION

Headspace gas chromatography is mostly employed to measure the so-called characteristic profiles of volatile components of condensed materials. With such applications, the only requirement is that the working conditions be kept invariant during the whole series of

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measurements. Less attention has been paid to the relatively more difficult problem of absolute quantitation in headspace-gas analysis. One of the ways to obtaining absolute quantitative data by headspace gas chromatography is multiple extraction of the material analysed with a gas and gas chromatographic analyses of the extracts. This approach has several versions. The first work on this topic was published by McAuliffe.[1] With his version, a sample of the material to be analysed is placed in an injection syringe and extracted repeatedly by equal volumes of pure gas, each extract being completely pushed out by the syringe piston and analysed by gas chromatography. Plotting the logarithms of the contents of volatiles in the individual extracts against the serial number of extraction steps yields straight lines from the parameters of which the initial contents of the volatiles in the condensed sample can be calculated. Another version, consisting in the successive withdrawal of two headspace-gas samples from a closed gas-condensed phase system, analysis of the samples for the contents of volatiles by gas chromatography, and calculation of the total initial contents of the volatiles in the system from the results of the two headspace-gas analyses, was theoretically outlined by Novák.[2] Recently, Kolb *et al.*[3] suggested a procedure based on the repetitive extraction of a sample of condensed material with a gas, gas chromatographic determination of the contents of volatiles in each extract, and calculation of the initial contents of the volatiles in the condensed sample by summing up the contents found in the individual headspace-gas samples. The linear dependence of the log of headspace-gas contents of volatiles on the number of extractions was used to provide a sufficient amount of data by extrapolation.

The aim of this work is to prove experimentally the concept of the double-sampling method.[2] Model gas-aqueous liquid systems with known trace contents of hydrocarbons were analysed. The Grob's [4-7] closed-loop strip/trap method in both the conservation and equilibration modes of trapping[8] was employed.

PRINCIPLE OF QUANTITATION WITH THE DOUBLE-SAMPLING METHOD

The quantitation with the double-sampling method of headspace-gas analysis is based on the following analyte mass balance:

$$W_i = W_{iG0}[(KV_L/V_G) + 1] \tag{1}$$

$$W_i - w_{iG0} = W_{iG1}[(K'V_L/V_G) + 1] \tag{2}$$

where W_i is the total initial mass of analyte in the system, W_{iG0} and W_{iG1} are the masses of analyte in the gaseous phase of the system before and after the withdrawal of the first headspace sample, w_{iG0} is the mass of analyte in the first headspace sample, K and K' are the liquid/gas partition coefficients of the analyte in the system before and after the withdrawal of the first headspace sample, and V_L and V_G are the volumes of the condensed and gaseous phases of the system, respectively. Provided that $K' = K$, which mostly is the case, Eqs. 1 and 2 yield

$$W_i = \frac{w_{iG0}}{1 - (W_{iG1}/W_{iG0})} \tag{3}$$

Further, if equal volumes of the headspace gas are sampled and analysed under constant conditions, the ratio W_{iG1}/W_{iG0} in Eq. 3 is equal to the ratio of the peak areas or peak heights of the analyte in the chromatograms of the second and the first headspace sample; with the arrangement employed in this work, the W_{iG1}/W_{iG0} ratio is given by the ratio of the analyte peak areas or peak heights in the chromatograms of the second and the first concentrate released from the analyte-enrichment trap, respectively. The quantity w_{iG0} (the amount released from the trap after the first run) is determined by direct calibration of the gas chromatograph.

EXPERIMENTAL

Analytical-grade benzene, toluene, ethylbenzene, *n*-decane, and *n*-dodecane (Fluka AG, Buchs, Switzerland) were employed as model analytes. Analytical-grade acetone (Lachema, Brno, Czechoslovakia) was used as a solvent to prepare standard solutions of the above hydrocarbons. The model systems were prepared with distilled water as the liquid phase, which was always boiled up just before use. Blank experiments, carried out at sensitivities ten-times higher than those set in actual analyses, gave zero values.

Instrumentation

A laboratory-made arrangement for stripping and trapping in a closed circuit was employed. A flow diagram of the arrangement is shown in Figure 1. The main component of the set-up is a drop-ball valve/stainless steel bellows pump (1) actuated with a cam driven by an electric motor (2). The liquid analysed is placed in a 100-ml glass vessel (4) provided with

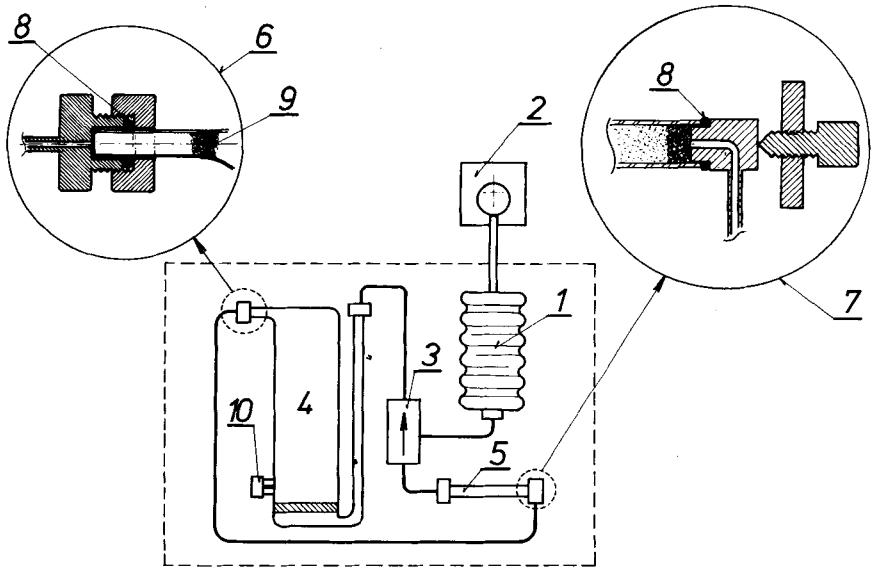

FIGURE 1 Flow diagram of the arrangement for stripping and trapping in a closed circuit.

a sintered-glass frit at the bottom. The gaseous phase of the system is recycled via the valve (3), vessel 4 and trap 5, the latter being a 6 cm/3 mm I.D. glass tube packed with Tenax GC 30/60 mesh (Applied Science Laboratories, State College, PA, U.S.A.). The sorbent was fixed in the tube by two plugs of quartz wool. The individual components of the set-up were interconnected by 2 mm O.D./1 mm I.D. stainless steel capillary. The capillary-to-glass parts connections are shown in detailed representations 6 and 7 in Figure 1. Silicone rubber and/or PTFE rings were used as gaskets (8). A quartz woolplug (9) was placed in the outlet tube of vessel 4 in order to prevent the entrainment of droplets of the liquid phase to the other parts of the circuit. Near the bottom of the vessel there is an inlet port with septum through which samples and/or standards are introduced. The arrangement is fixed to a console and can be immersed into a thermostatting bath.

The analytes captured in the trap are thermally desorbed, and the concentrate obtained is purged by a stream of the carrier gas into the gas chromatograph. The desorption/purge arrangement is illustrated schematically in Figure 2. Oven 2 with controlled temperature is placed around trap 1 while the four-port stopcock 3 is set such as to shortcircuit the trap and direct the carrier gas (4) to the chromatographic column (5).

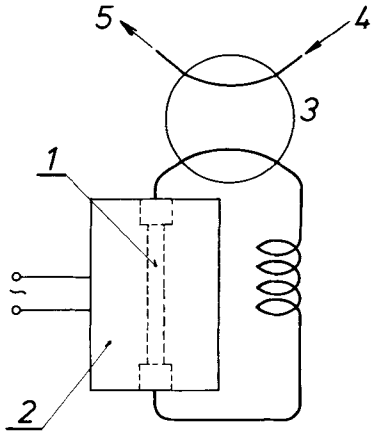

FIGURE 2 Schematic representation of the arrangement for the thermal desorption of captured analytes from the trap and the introduction of the concentrate into the gas chromatograph.

After the trap is brought to the desired temperature, stopcock 3 is turned over to the position allowing the carrier gas to pass via the trap and purge the desorbed analytes into the gas chromatograph. The stopcock and the interconnecting capcillaries are also heated in order to prevent the concentrated analytes from spurious sorption. The outlet of stopcock 3 was connected to column 5 by means of an injection needle pierced through the septum of the inlet port of the gas chromatograph in such a manner that other samples could simultaneously be introduced through the septum by an injection syringe.

The gas chromatographic analyses were carried out on a Shimadzu GC-4A instrument (Shimadzu Seisakusho, Kyoto, Japan) equipped with a flame ionization detector and a 1 m/3 mm I.D. stainless steel column packed with Chromaton N 80/100 mesh (Lachema, Brno, Czechoslovakia) coated with 20% (by wt.) of Carbowax 20 M (Carlo Erba, Milan, Italy). The column and the sample inlet port were kept at 70 and 140°C, respectively. The flow rate of the carrier gas (nitrogen) was 35 ml/min. Before its use, the Tenax trap was kept at 250°C for several hours under a nitrogen stream. An Infotronics CRS-101 integrator (Infotronics, Shannon Airport, Ireland) was used to measure the peak areas.

Procedure

Standard solutions of the model hydrocarbons were prepared by adding known volumes of each of them with a 10-μl Hamilton syringe (Hamilton Micromeasure AG, Bonaduz, Switzerland) to some amounts of acetone in 10-ml measuring flasks and then making up the volumes to the mark with acetone. 0.5-μl volumes of the standard solutions were charged with a 1-μl Hamilton syringe into the gas chromatograph, and the peak areas obtained, A_i^*, were taken as measures of the "given" masses of analytes, W_i^*. Employing the very same 1-μl syringe, 0.5–1 μl of the standard solutions were then introduced into the stripping vessel with 50 ml of distilled water, covering a range of about 1–10 ppb (10^9) of the model hydrocarbons in water. In order to bring the whole circuit into a stationary state before the analysis proper, an empty tube was connected instead of the trap and the pump put on running for 10 min. After that, two traps, each with 16.3 ± 0.1 mg of Tenax GC, were successively connected into the circuit, and the gaseous phase was circulated at a rate of 70 ml/min for 10 min in each run. The whole circuit was thermostatted at 40 ± 0.1°C by means of an ultrathermostat (type 410, VEB Prüfgeräte, Medingen, DDR). The desorptions of the analyte (analytes) captured in the traps were carried out by heating the latter to 160 (and/or 200)°C for 3 min. After each analysis, the vessel was emptied and rinsed with distilled water, and then the whole circuit was purged with a stream of dry nitrogen (about 0.5 1/min), with the pump being running. After 15 minutes, acetone only was detected in blanks.

RESULTS AND DISCUSSION

The quantities W_i^* and A_i^* are related to each other by

$$W_i^* = kA_i^* \tag{4}$$

where k is a calibration factor. With regard to Eq. 3, the "found" mass of analyte, W_i, is given by

$$W_i = kA_i = \frac{W_{it0}}{1-(W_{it1}/W_{it0})} = \frac{kA_{it0}}{1-(A_{it1}/A_{it0})} \tag{5}$$

where A_i is a hypothetical peak area, representing the "found" mass of analyte, W_{it0} and W_{it1} are the masses of analyte in the concentrates released from the traps after the first and the second run, and A_{it0} and

A_{it1} are the respective peak areas. By means of Eqs. 4 and 5, the absolute and relative error can be expressed as

$$W_i - W_i^* = k\left[\frac{A_{it0}}{1-(A_{it1}/A_{it0})} - A_i^*\right], \tag{6}$$

$$\frac{W_i - W_i^*}{W_i} = 1 - \frac{A_i^*[1-(A_{it1}/A_{it0})]}{A_{it0}}, \tag{7}$$

respectively.

The analyte concentrations in the standard solutions were not known precisely, and the results of the analyses were calculated in terms of peak areas by Eqs. 6 and 7. With this way of processing the data, the effects of inaccuracies connected to the preparation of standard solutions were eliminated. For convenience, approximate analyte masses and concentrations were calculated from the measured volumes, densities, and peak areas of the analytes (cf. Table I).

The contents of the analytes in the model systems were too low to be determinable by direct analysis of headspace samples. Therefore, an analyte-enrichment technique had to be employed. We have chosen

TABLE I

Results of the headspace determination of traces of hydrocarbons in model gas-water systems by the closed-loop double-strip/trap method

Analyte	given (ng/50 ml)	given (ppb)	found (ng)	error (ng)	error (%)	stand. deviat. of the mean (ng)	number of measurements
(A)							
Benzene	85.3	1.7	84.0	−1.3	−1.5	2.51	7
(B)							
Benzene	87.9	1.8	90.6	+2.7	+3.1	2.54	5
Toluene	433.5	8.7	418.0	−15.5	−3.6	17.9	5
(C)							
Benzene	439.5	8.8	442.3	+2.8	+0.6	6.07	8
Toluene	86.7	1.7	87.7	+1.0	+1.2	1.56	10
Ethylbenzene	173.4	3.5	169.8	−3.6	−2.1	2.88	11
(D)							
Benzene	87.9	1.8	119.1	+31.2	+35.3	7.65	4
Toluene	433.5	8.7	420.9	−12.6	−2.9	4.21	4
Ethylbenzene	173.4	3.5	181.9	+8.5	+4.9	3.40	4
n-Decane	73.0	1.5	72.7	−0.3	−0.4	1.78	4
n-Dodecane	149.8	3.0	102.8	−47.0	−31.4	1.75	4

Grob's technique of stripping and trapping in a closed circuit, as it appears to constitute a most suitable way of concentrating headspace samples in quantitative headspace trace analysis.

Systems with benzene alone, benzene and toluene, benzene, toluene, and ethylbenzene, and all the three aromatics together with *n*-decane and *n*-dodecane in water were analysed by the above method. The results are summarized in Table I. The "given" and "found" data, obtained by the direct analyses of charges of the standard samples and by the closed-loop double-strip/trap analyses of the model systems, have been calculated by virtue of Eqs. 4 and 5, respectively. The errors, calculated by Eqs. 6 and 7, show the accuracy of the results obtained by the closed-loop double-strip/trap method, the precision of the results being characterized by the standard deviation of the mean.

The results obtained with the systems containing benzene alone, benzene together with toluene, and all the three aromatics (section A, B, and C in Table I) can be considered as excellent, the relative errors and relative standard deviation of the means amounting to some percents only. It is pertinent to note that benzene is equilibrated in the system under the conditions employed. As the retention volume of benzene on 16.3 mg of Tenax GC at 40°C is about 400 ml[9], a two-multiple of the retention volume of benzene approximately is drawn through the trap in each strip/trap run. Under these conditions, the frontal zone of benzene breaks completely through the trap, and the whole circuit becomes practically equilibrated with respect to benzene before the run is finished. About 60 and 23% of the total initial mass of benzene in the system are captured in the trap during the first and the second strip/trap run, respectively, The retention volume of toluene is about 1000 ml under the given conditions, so that its zone breaks through the trap only partially or not at all; about 82 and 14% of the initial mass of toluene are transferred to the trap in the first and the second run. Toluene as well as the other higher boiling hydrocarbons were trapped in a conservation regime. About 99% of ethylbenzene are trapped in the first run, so that practically the entire content of ethylbenzene is recovered in two runs.

At a given flow rate of stripping gas, the fraction of the total initial amount of analyte which is transferred to the trap during a strip/trap run is a function of the water/gas partition coefficient of the analyte and the time of stripping/trapping with conservation trapping and a function of both the water/gas and trapping sorbent/gas partition coefficients of the analyte and the amount of the sorbent in the trap with equilibration trapping.[8] As the water/gas partition coefficients of homologous hydrocarbons decrease with increasing carbon number,[10] the respective rates of stripping increase with increasing carbon number. This is

evidenced by the percentage recoveries in the two successive runs, quoted above for the three homologues of aromatics.

Except for benzene and *n*-dodecane, the results of the simultaneous determination of all the three aromatics together with *n*-decane and *n*-dodecane (section D in Table I) are as accurate as those obtained with the aromatics alone. There are different possible explanations for the 35.3-% positive error with benzene and 31.4-% negative one with *n*-dodecane. An unknown peak which was partially overlapped with that of benzene appeared in the chromatograms in this series of analyses, which could cause an error in the determination of benzene peak area. Another possible cause of the errors may be competitive adsorption of the higher hydrocarbons in the trap, interfering variably with equilibration of benzene. The negative error with *n*-dodecane may be due to irreversible adsorption of the latter in the trap. However, an increase of the desorption temperature to 200°C had no effect on the results, and no rests of *n*-dodecane were released from the trap by repeating the desorption procedure. It is also possible that the errors with benzene and *n*-dodecane are interrelated.

CONCLUSIONS

The double-sampling method of quantitative headspace-gas analysis gives corrent results. Combined with the closed-loop strip/trap technique, the method provides for the determination of ppb (10^9) concentrations of hydrocarbons in water with an average relative error of several percent. With certain systems, mutual interference of the analytes may cause larger errors. This aspect of the method deserves further investigations.

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