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HEADSPACE DETERMINATION OF BENZENE IN GAS–AQUEOUS LIQUID SYSTEMS BY THE STANDARD ADDITIONS METHOD

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SUMMARY

The standard additions method was studied as a means of quantitation in the determination of trace amounts of volatile hydrocarbons in gas–aqueous liquid systems by headspace gas analysis. Amounts of 1–1000 μg of benzene in 50/50-ml air–water systems, corresponding to about 0.02–20 ppm of benzene in the aqueous phase, were determined with errors from about 8 to 2% at these levels, respectively. Analogous systems with milk as the liquid substrate were also studied, and the results obtained by the standard additions method were compared with those obtained by external calibration using a model reference system with water as the liquid phase. While the standard additions method gave correct results, those obtained by the other method suffered from a negative error of about 70%. The sensitivity of the determination of benzene in water by gas chromatographic analysis of head space gas samples was about 100 times higher than that attainable by direct analysis of the liquid phase.

INTRODUCTION

In analytical applications in food quality tests, water pollution control, studying diverse biological materials, etc., it is often necessary to determine trace amounts of hydrocarbons in aqueous substrates. A well tried approach to these problems is the use of headspace gas analysis; in this paper, we consider the version that involves sampling the gaseous phase from an equilibrated gas-condensed phase system rather than stripping the analysed material with a stream of gas.

McAuliffe[1] determined trace amounts of hydrocarbons in water by replicate equilibrations of a given sample of analysed water with several equal volumes of a gas. In each step the headspace gas was separated from the liquid phase and analysed by gas chromatography (GC). The contents of hydrocarbons in the initial sample of water were calculated from the dependence of the contents of hydrocarbons in individual successive gaseous extracts on the number of the extraction step. Kaiser and Oliver[2] analysed aqueous samples for their contents of halogenated hydrocarbons by headspace gas analysis using a calibration graph obtained by means of model reference systems. In a previous work[3], we studied the standard additions method as a means of quantitation in the determination of acetone and some alcohols in gas–aqueous liquid

systems by headspace gas analysis. However, as hydrocarbons have much lower solubilities in water, leading to a different situation from both the physico-chemical and analytical points of view, we decided to try the performance of this method when applied to the determination of trace amounts of hydrocarbons in gas–aqueous liquid systems.

EXPERIMENTAL

Systems studied

Several model systems were studied, consisting of 50 ml of distilled water, 50 ml of head space gas (atmospheric air saturated with the vapour of the condensed phase) and different amounts of benzene as a model compound (1–1000 μg, corresponding to about 0.020–20 ppm in the liquid phase). In order to show the possible effects of small amounts of other substances present in the condensed phase on the equilibrium distribution of benzene between the phases, systems with milk as the liquid phase were also analysed.

Materials and instruments

The systems studied were prepared by using standard solutions of benzene in acetone. Both chemicals (analytical-reagent grade products from Lachema, Brno, Czechoslovakia) were re-distilled and checked for purity by GC. The milk employed as a liquid substrate was a fresh dairy product containing 2 % of fat.

The analyses of the headspace gas samples were carried out on a Hewlett-Packard 402 gas chromatograph (Hewlett-Packard, Avondale, Pa., U.S.A.) with a flame-ionization detector, employing a 180 cm $\times$ 3 mm I.D. glass column packed with Porapak P, 80–100 mesh (Waters Assoc., Milford, Mass., U.S.A.), and kept at 165°C. The peak areas were determined with an Infotronics CRS 101 integrator (Infotronics, Shannon Airport, Ireland).

The systems studied were contained in 100-ml flat-bottomed, short-necked glass flasks with a specially designed ground-in stopper and a side-tube made of a thick-walled capillary of about 1 mm I.D. A similar capillary ran coaxially through the stopper, being fused on its lower face and on its upper face and protruding a short distance above the latter. The outer ends of both the capillary tube passing through the stopper and the capillary side-tube were terminated in flanges to which sampling-port heads were attached. The flask and the stopper, with an exploded view of the sampling-port head, are illustrated in Fig. 1. Both the faces of the flanges and the openings of the nuts and washers were ellipsoidal in shape; the head was connected to the tube by slipping the nut with a washer over the flange, turning the former by 90° and gently tightening the screw against the septum. The side-tube, being fused onto the upper half of the round body of the flask, served for introducing the standard solutions into the system, whereas the headspace gas was sampled from the flask through the tube in the stopper. The use of separate septa for the introduction of the standard and sampling the headspace gas prevented the samples from becoming contaminated by possible traces of the standard substance included in the septum. Moreover, the arrangement ensured that contact between the headspace gas and the septum was reduced to a minimum. The flask was placed in a water-bath maintained thermostatically at 40°C with a U-10 thermostat (VEB Prüfgeräte-Werk, Medingen, Dresden,

A

STOPPER WITH
INLET-PORT HEAD

SIDE-TUBE WITH
INLET-PORT HEAD

HEADSPACE
GAS
CONDENSED
PHASE

WATER
BATH

MAGNETIC
STIRRER

B

HOLLOW BRASS SCREW

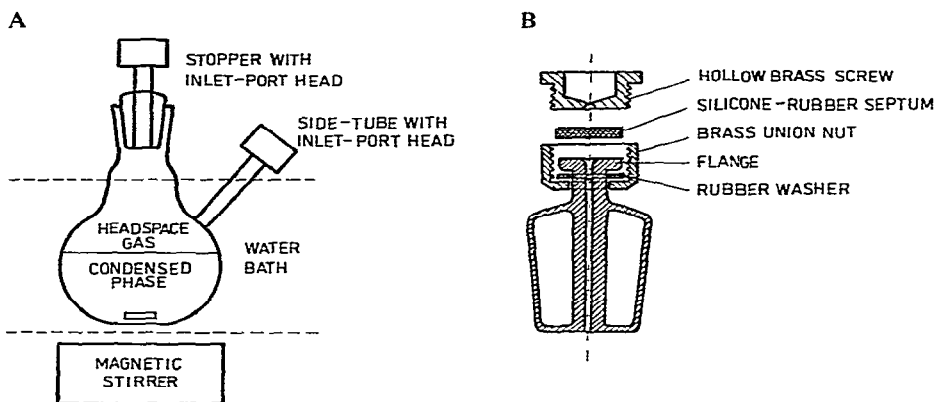SILICONE-RUBBER SEPTUM

BRASS UNION NUT

FLANGE

RUBBER WASHER

Fig. 1. Schematic diagram of equipment: A, equilibrating flask with ground-in stopper and side-tube, provided with sampling-port heads; B, exploded view of stopper with sampling-port head.

G.D.R.) and the liquid phase in the flask was stirred cautiously with an MM-2 magnetic stirrer (Laboratory Equipment, Prague, Czechoslovakia).

Procedure

As in previous work[3], we used the so-called single-sample procedure[4]. The model systems were prepared by injecting into the flask with 50 ml of liquid a defined amount (1–5 μl) of a standard solution of benzene in acetone (about 10, 0.5 and 0.025%, v/v), employing a 7001 N (1 μl) and/or a 7005 N (5 μl) Hamilton syringe (Hamilton Micromesure BV, The Hague, The Netherlands). The same standard solutions were also employed for the standard additions calibrations. In all instances the standard solutions were introduced into the systems after the latter had been brought to equilibrium at 50 °C, the tip of the injection needle being dipped into the liquid and the latter being stirred during discharging the contents of the syringe. About 10 min were allowed for the system to become equilibrated after having introduced the standard solution. Samples of 1 ml of the headspace gas were taken from the equilibrated systems with a 1-ml gas-tight syringe (Chirana, Brno, Czechoslovakia), the latter being kept at about 60 °C in order to prevent condensation of water vapour in the syringe. The results were calculated by using the equation[4]

$$W_i = (W_s - w_i)/[(A_i' v_G / A_i v_G') - 1]$$

where W_i is the total weight of the substances being determined (i) in the initial system, W_s is the weight of substance i added as a standard to the system, w_i is the weight of substance i in the headspace gas sample removed from the system in the first sampling step (usually $w_i \ll W_s$), v_G and v_G' are the volumes injected into the gas chromatograph of the samples of the headspace gas of the initial system and of that enriched by addition of the standard, respectively, and A_i and A_i' are the peak areas of component i in the chromatograms of the samples taken from the initial and the enriched system, respectively.

TABLE I

RESULTS OF THE DETERMINATION OF BENZENE IN AIR–WATER MODEL SYSTEMS
BY THE STANDARD ADDITIONS METHOD

W_i (μg)		Error		$S/\sqrt{n}$ (μg)	W_s (μg)
Given	Found	μg	%		
959.0	971.0	20.0	2.1	39.9	479.5
479.5	493.5	14.0	2.9	29.7	479.5
95.9	93.2	−2.7	2 8	5.66	95.9
24.0	24.9	0.9	3.8	1.90	24.0
4.80	5.04	0.24	5.0	0.50	4.80
1.19	1.29	0.10	8.4	0 21	1.19

RESULTS AND DISCUSSION

The results of the determination of benzene in several model systems with water as the liquid phase are shown in Table I. The range of the values of W_i corresponds to 19.2–0.023 ppm of benzene in water, provided that the entire amount of benzene in the system occurred in the 50-ml amount of the liquid phase. All of the results in Table I are averages of six determinations. The error of the results is surprizingly small; in all instances the experimental Student coefficients (absolute value of error divided by $S/\sqrt{n}$) are markedly smaller than the corresponding critical t-value (for six measurements and a 95% confidence level, $t_{crit.} = 2.44$). With the system containing only 1.19 μg of benzene, the GC analyses had to be carried out at a detector sensitivity setting of 10^{-11} A per full-scale recorder-pen deflection, which was about the maximum sensitivity still compatible with reliable quantitative analysis. As the integrator did not operate properly owing to a small signal-to-noise ratio in
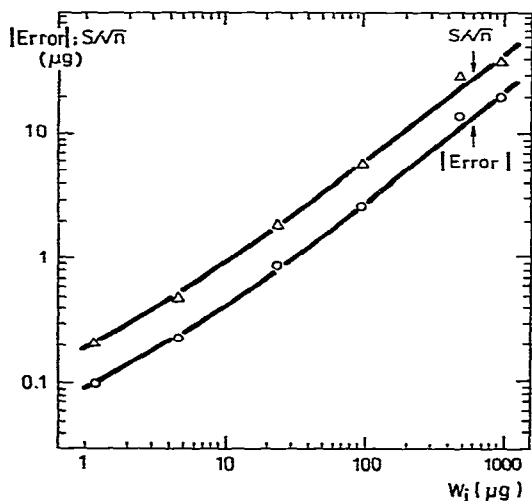

Fig. 2. Standard deviation of average and the absolute values of error plotted against the amount of solute in the system being analyzed.

this instance, peak heights were measured manually from the chromatograms instead of using the integrator data. Both the absolute value of the error and the standard deviation of the average $(S/\sqrt{n}$, where n is the number of measurements) are roughly linearly proportional to W_i; at the lowest values of W_i the error and the standard deviation are somewhat larger. This is illustrated in Fig. 2.

In Fig. 3, the peak heights (actual peak height multiplied by the attenuation factor) of benzene in the chromatograms of 1-ml headspace gas samples are plotted against the corresponding values of W_i. The plot shows that the distribution isotherm of benzene in the system studied is slightly curved; the solubility of benzene decreases with increasing concentration in water.
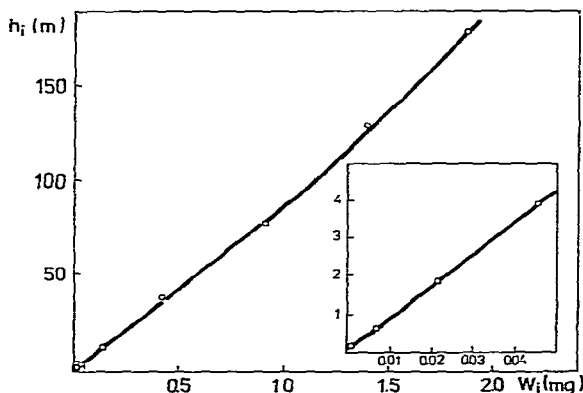

Fig. 3. Plot of the solute peak height in chromatograms of 1-ml headspace gas samples against the amount of solute in the system being analyzed.

The standard additions headspace method was also checked by analysing samples of water containing trace amounts of benzene in concentrations unknown to the analyst. The results obtained by the standard additions method were compared with those obtained by the method of external calibration by means of model reference systems, employing the plot in Fig. 2 as a calibration graph. In these experiments, the solutions to be analysed were prepared in measuring flasks; 50-ml samples of the solutions were pipetted and introduced into the equilibrating flask with its stopper removed, then the flask was closed and the procedure was carried out as described above. The results (averages of three determinations) of these experiments are summarized in Table II.

The results of the determination of benzene in milk are shown in Table III. The procedures employed were the same as in the previous instance, but whereas in the analyses of water the same liquid substrate was used in both the systems being analysed and the reference systems, in this instance reference systems with water were used when analysing systems with milk. As can be seen from the results in Table III, while the standard additions method gave correct results, those obtained by external calibration using model reference systems with water suffered from a large negative error. This comparison confirms the applicability of the standard additions method and also shows how unreliable the method of calibration by means of a model re-

TABLE II

RESULTS OF THE DETERMINATION OF BENZENE IN AIR–WATER SYSTEMS OBTAIN-
ED BY THE STANDARD ADDITIONS METHOD AND BY EXTERNAL CALIBRATION
USING A MODEL REFERENCE SYSTEM WITH WATER AS THE LIQUID SUBSTRATE

Given W_i (μg)	Standard additions method				External calibration		
	Found W_i (μg)	Error		W_x (μg)	Found W_i (μg)	Error	
		μg	%			μg	%
47.95	44 01	3.8	8.0	95.9	49.8	1.9	3.9
76.70	72.9	3.7	4.9	95.9	88.0	11.3	14.7

ference system may be if the condensed phase of the latter differs in composition from
that of the system being analysed.

Knowing the value of W_i and the volumes of the phases in the system, and
having determined by calibration the concentration of benzene in the gaseous phase,
it is possible to calculate the distribution constants of benzene in the systems with
water and with milk. In this way, values of 4.8 and 3.8 were found for the distribution
constant (defined as the ratio of the concentration of solute in the liquid phase to that
in the gaseous phase) of benzene in 50/50-ml air–water systems containing $4.795 \cdot 10^{-6}$
and $4.795 \cdot 10^{-4}$ g of benzene at 40 °C, respectively, whereas in an analogous air–milk
system with $4.795 \cdot 10^{-4}$ g of benzene the distribution constant was 14.2 at the same
temperature. The difference in the distribution constants of benzene in systems with
water and with milk illustrates how significant the matrix effects may be when analysing
such systems. The advantage of the inherent capability of the standard additions
method to eliminate matrix effects was first recognized by Dal Nogare and Juvet[5],
with reference to the analysis of single-phase materials. The results of our work show
that this advantage also applies even if the matrix effects are constituted by the prop-
erties of multi-phase systems. However, the same situation can be also expected with
the method of McAuliffe[1].

The sensitivity of headspace gas analysis is high with the systems studied. With
this procedure, the sensitivity of the determination of benzene is about 100 times
higher than that of the determination of hydrophilic solutes in systems of the same
nature[3]. The increased sensitivity is obviously caused by the high activity coefficient of
benzene in aqueous media; employing the equation $K = RTd_L/\gamma P_i^\circ M_L$, where R is the

TABLE III

RESULTS OF THE DETERMINATION OF BENZENE IN AIR–MILK SYSTEMS OBTAINED
BY THE STANDARD ADDITIONS METHOD AND BY EXTERNAL CALIBRATION USING
A MODEL REFERENCE SYSTEM WITH WATER AS THE LIQUID SUBSTRATE

Given W_i (μg)	Standard additions method				External calibration		
	Found W_i (μg)	Error		W_s (μg)	Found W_i (μg)	Error	
		μg	%			μg	%
479.5	488.2	8.7	1.8	479.5	147.5	322.0	69.2
959.0	962.6	3.6	0.4	479.5	287.5	671.5	70.0

gas constant (82 ml·atm/K·mole), T is the absolute temperature of the system (314 °K), d_L is the density of the liquid phase (0.993 g/ml at 314 °K), γ is the Raoult's law activity coefficient, P_i° is the saturation vapour pressure of benzene (0.59 atm at 314 K) and M_L is the molecular weight of the liquid phase (18 g/mole), we find that for $K = 4.8$, $\gamma \approx 500$. Actually, when analysing the headspace gas, the maximum attainable sensitivity of analysis must be much higher than that which can be attained by analysing the condensed phase directly. If we accept that the ratio of the maximum volumes of the headspace gas (V_G^{max}) and of the liquid phase (V_L^{max}) that can be injected into the gas chromatograph is $V_G^{max}/V_L^{max} = 500$, a simple calculation (with $K = 4.8$) shows that the absolute weight of benzene that can be charged into the gas chromatograph by injecting a headspace gas sample is about 100 times greater than that which could be charged by injecting a sample of the liquid phase.

CONCLUSIONS

The standard additions method is a universal and reliable means of quantitation in the determination of volatile components in complex gas–liquid systems by headspace gas analysis. Provided that the system being analysed is kept under constant conditions during the analytical procedure, the standard additions method eliminates even the matrix effects that occur in multi-component gas–liquid systems. Employing conventional syringes for sampling the headspace gas and analysing the samples on a common GC instrument, less than 100 ppb of benzene can be determined with an error of less than 10%.

The model systems with benzene as a solute component is representative of a large number of analytically important situations. The findings obtained here can reasonably be generalized for most problems in the determination of trace amounts of volatile hydrocarbons in water and aqueous media.

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