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DETERMINATION OF HYDROPHILIC VOLATILES IN GAS–AQUEOUS LIQUID SYSTEMS BY GROB'S CLOSED-LOOP STRIP/TRAP METHOD AND STANDARD-ADDITION CALIBRATION

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SUMMARY

The application of Grob's closed-circuit strip/trap technique to the determination of hydrophilic volatiles in aqueous matrices by the standard-addition method was investigated. Tenax GC was used as the trapping material. Both the conservation and equilibrium alternatives of trapping were assessed, employing butyl acetate and ethanol as model compounds, respectively. With both alternatives the experimentally found dependences of the amount of concentrate recovered from the trap on the total amount of the respective component in the system analyzed were fairly linear. The technique gives an extremely high selectivity of analysis. An application of the procedure to the headspace gas analysis of apple juice is demonstrated.

INTRODUCTION

Grob and co-workers[1–4] recently described an interesting variant of headspace gas analysis, in which volatile components of the condensed phase were trapped in a sorbent by pumping the headspace gas in a closed circuit via the trap and the condensed phase. Until now the method had been applied only to the determination of traces of hydrophobic compounds in water, the quantitation being carried out by means of a reference model system and internal standard; concentrations as low as 1–10 ng/l of hydrophobic organics in water were thus determined. This method is very suitable for such systems because of the low solubilities of hydrophobic compounds in water and the simplicity of the matrix material. With hydrophilic volatiles in aqueous media, however, the problem is more complicated. If, in addition, the matrix is a complex material of unknown composition, which almost always is the case with biological fluids, food products, beverages, etc., it is impossible to prepare an adequate reference model.

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The limitations on the use of the reference model method, combined, if necessary, with the internal-standard method, can be obviated by employing the standard-addition method, as with the latter the material under analysis serves as a reference matrix material in the calibration run. The aim of this paper is to show that the standard-addition method is a general means of calibration with the closed-loop strip/trap method, and to examine the applicability of the technique to the determination of hydrophilic volatiles in aqueous matrices. Model solutions of butyl acetate and ethanol and an apple juice were employed.

THEORETICAL

Considering the situation in the trap, Grob's method can be performed in two ways. In the early stage of the process, frontal chromatography occurs of the components being accumulated in the trap. If the volume of gas pumped through is such that it does not cause the zone of the least sorbed component to leave the trap, the proportions of the components deposited in the trap will be equal to their corresponding mean proportions in the gaseous phase. This case is regarded as conservation trapping. If the volume pumped though is large enough to bring the whole system into equilibrium then we have equilibrium trapping. In the latter case, the proportions of the components entrapped are given by the expression $c^*_{iG}(V_{Gt} + K_{SG}V_S)$, where c_{iG}, V_{Gt}, K_{SG} and V_S are, respectively, the final (equilibrium) concentration of solute i in the gaseous phase, the void volume within the trap, the actual sorbent–gas distribution constant of solute i and the volume of the sorbent in the trap.

From the analytical point of view it is important to know the relations between the total mass of component i in the entire system, *i.e.*, the quantity to be determined, W_i, and the mass of the component accumulated in the trap, W_{it}; the following relations were derived earlier[5] for conservation and equilibrium trapping, respectively

$$W_i = W_{it}\left[1 - \exp\left(-\frac{Ft}{V_G + K_{LG}V_L}\right)\right]^{-1} \tag{1}$$

$$W_i = W_{it}\left[\left(\frac{K_{SG}V_S}{V_{Gt} + K_{SG}V_S}\right)\left(\frac{V_G}{K_{SG}V_G} + \frac{K_{LG}V_L}{K_{SG}V_S} + 1\right)\right] \tag{2}$$

where K_{LG} is the liquid–gas distribution constant of solute i, V_L and V_G are the volumes of the liquid and gaseous phases, F is the volumetric gas flow-rate, as determined by the pump, and t is the stripping/trapping time. Both equations show that a linear dependence of W_i on W_{it} may be expected with both versions of trapping, provided the values of all the parameters in the bracketed terms are invariant. This qualification may well be true in the standard-addition method, as neither the distribution constants of the components of the system nor the volumes of its phases will change significantly upon adding a relatively small amount of the component to be determined. Under these conditions it is possible to employ either the single- or double-system procedure and calculate the results, respectively, by

$$W_i = (W_s - W_{it})/[(A'_i/A_i) - 1] \tag{3}$$

and/or

$$W_i = W_s/[(A'_i/A_i) - 1] \tag{4}$$

where W_s is the mass of the standard (component i) added to the system analyzed and A_i' and A_i are the chromatographic peak areas recorded for component i in the concentrates recovered from the trap after processing the systems with and without the added standard respectively.

EXPERIMENTAL

Apparatus

A schematic representation of the experimental set-up of the strip/trap circuit is shown in Fig. 1. The material to be analyzed was placed in a 350-ml serum bottle, through the septum of which passed two large-diameter injection needles, one of them (140 mm long) reaching into the liquid phase and the other (90 cm long) protruding only into the gaseous phase. The headspace gas was circulated by a modified MP 1 diaphragm pump (Chemoprojekt, Satalice at Prague, Czechoslovakia). The trap was a 120 × 3.5 mm I.D. glass tube with a layer of 51 mg of Tenax GC (Applied Science Labs., State College, PA, U.S.A.). In all instances the flow-rate of the headspace gas through the circuit was set to 100 ml/min by means of a fine needle valve and a flow meter, the latter then being removed from the circuit. The components of the circuit were connected by a copper capillary of 1 mm I.D. Both the serum bottle and the trap were kept at 42°C with the aid of a U-10 water ultrathermostat (Mechanik Prüfgeräte, Medingen, G.D.R.). Except for the experiments in which the time dependence of the amount of solute deposited in the trap was studied, the time of stripping/trapping was 5 min. There were no heaters or desiccators in the circuit.

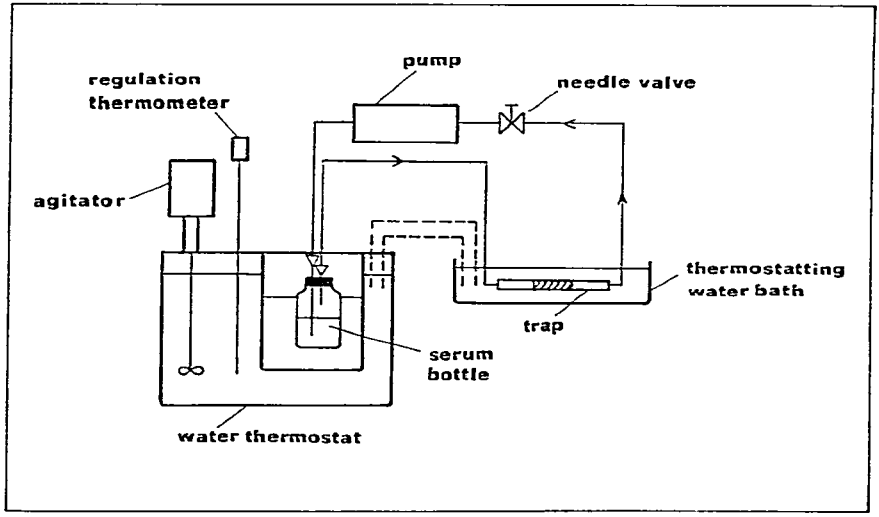

Fig. 1. Schematic representation of the experimental closed-loop strip/trap arrangement.

Preparation and processing of samples

Model solutions. A series of aqueous solutions of butyl acetate and ethanol in concentrations of 0.184–7.52 μg/ml and 0.0512–1.026 mg/ml, respectively, were prepared. In each experiment, 50 ml of the solution to be analyzed were pipetted into

the serum bottle and, after 6 min for stabilization of the temperatures of the bottle and the trap, the stripping/trapping procedure was carried out as described above.

Apple juice. A 30-ml volume of the juice from a Starkrimson apple squash was placed in the serum bottle and either 22.8 ml of distilled water (for runs without the addition of standard) or 20 ml of distilled water and 2.8 ml of a solution containing 39.8 μg/ml of butyl acetate and 18.4 mg/ml of ethanol (for runs with the standard) were added. Both materials were then processed as described above, employing the double-system method of analysis (*cf.*, eqn. 4).

Recovery and analysis of the concentrate from the trap

The substances deposited in the Tenax GC trap were recovered by thermal desorption and transferred into the gas chromatographic (GC) column using a stream of carrier gas. A three-way stopcock was connected by its two inlets in the carrier-gas line before the sample-inlet port of the gas chromatograph, and an oven, kept at 160°C, was situated above the septum. After disconnecting the trap from the strip/trap circuit, one end of it was provided with an injection needle and the other end was connected via a copper capillary to the free inlet of the stopcock. Then the trap was inserted in the oven and the needle was pushed half-way into the inlet-port septum, the carrier gas flow being conducted by the stopcock directly into the GC column. The heating period lasted 3 min, whereupon the needle was pushed through the septum and the carrier gas flow was diverted to pass via the hot trap into the GC column. This purging period lasted 2 min, after which the stopcock was returned to its initial position, and the trap was used for subsequent measurements.

A Chrom 41 gas chromatograph (Laboratory Instruments, Prague, Czechoslovakia) was employed, with a flame ionization detector and a 243 cm × 3 mm I.D. stainless-steel column packed with 10% (w/w) Carbowax 600 on Chromosorb W AW (80–100 mesh) (both components from Carlo Erba, Milan, Italy). The GC column was temperature programmed: after 2 min at 68°C the temperature was raised at 2°/min to 80°C and then at 4°/min to 120°C. The inlet port was kept at 110°C. The column-inlet excess pressure of the carrier gas (N_2) was 0.08 MPa at the initial temperature (68°C); the flow-rates of H_2 and air were 50 and 500 ml/min, respectively. Peak areas were determined from the graphical record of the chromatogram by the height × mid-width method.

RESULTS AND DISCUSSION

The choice of butyl acetate and ethanol as model compounds was made in order to provide conditions for simultaneous assessment of both the conservation and equilibrium versions of trapping. It is apparent from Fig. 2 that, after 5 min of stripping/trapping, ethanol is almost completely equilibrated while the frontal zone of butyl acetate has travelled about half the length of the Tenax trap. Fig. 2 also indicates that, with appropriate choice of the trapping sorbent, the method affords a very high selectivity of analysis, especially when performed in the equilibrium mode. Note that the peak areas of butyl acetate are about five times as large as those of ethanol, while the concentration of butyl acetate in the liquid phase is about three orders of magnitude lower than that of ethanol.

Figs. 3 and 4 show the experimentally determined dependences of the peak

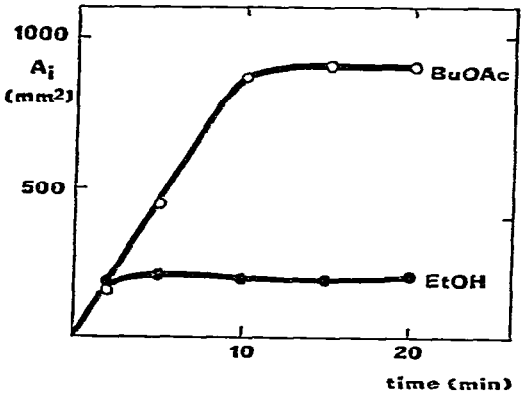

Fig. 2. Dependences of the peak areas of butyl acetate (BuOAc) and ethanol (EtOH) in the chromatogram of concentrate recovered from the trap on the time of stripping/trapping. The concentrations of butyl acetate and ethanol in the liquid phase were 7.1 μg/ml and 4.8 mg/ml, respectively.

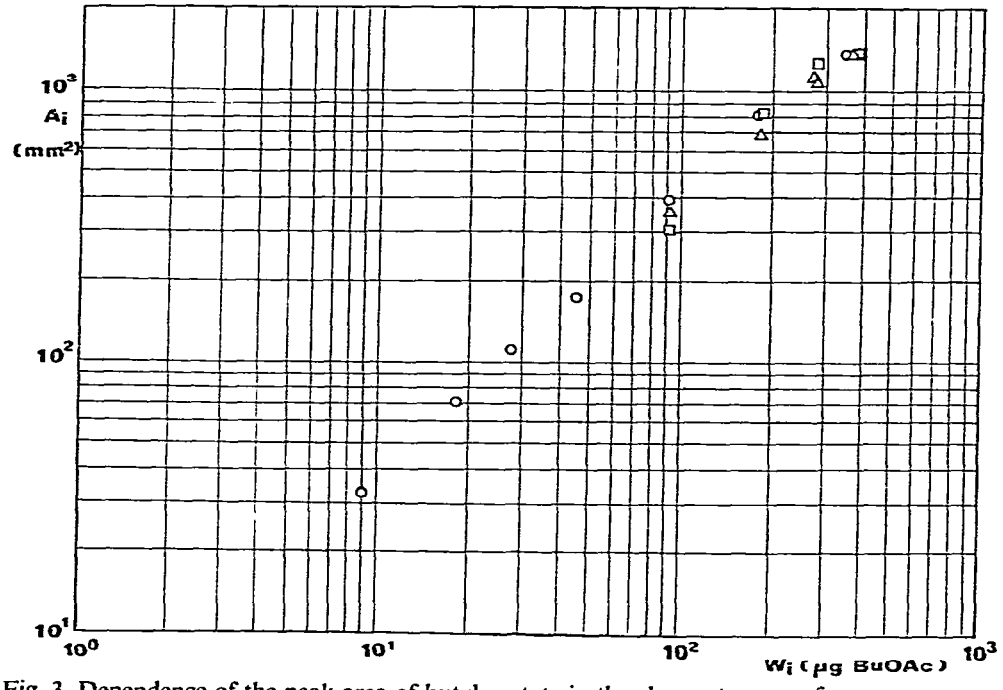

Fig. 3. Dependence of the peak area of butyl acetate in the chromatogram of concentrate recovered from the trap on the total initial mass of butyl acetate in the gas–liquid system analyzed.

areas of butyl acetate and ethanol on the total masses of these components in the system. The circles, squares and triangles refer to measurements carried out on different days. It is seen that both the conservation (butyl acetate) and equilibrium (ethanol) versions yield fairly linear dependences of A_i on W_i. As A_i in the above dependences actually represents W_{it}, the findings comply well with the predictions of eqns. 1 and 2.

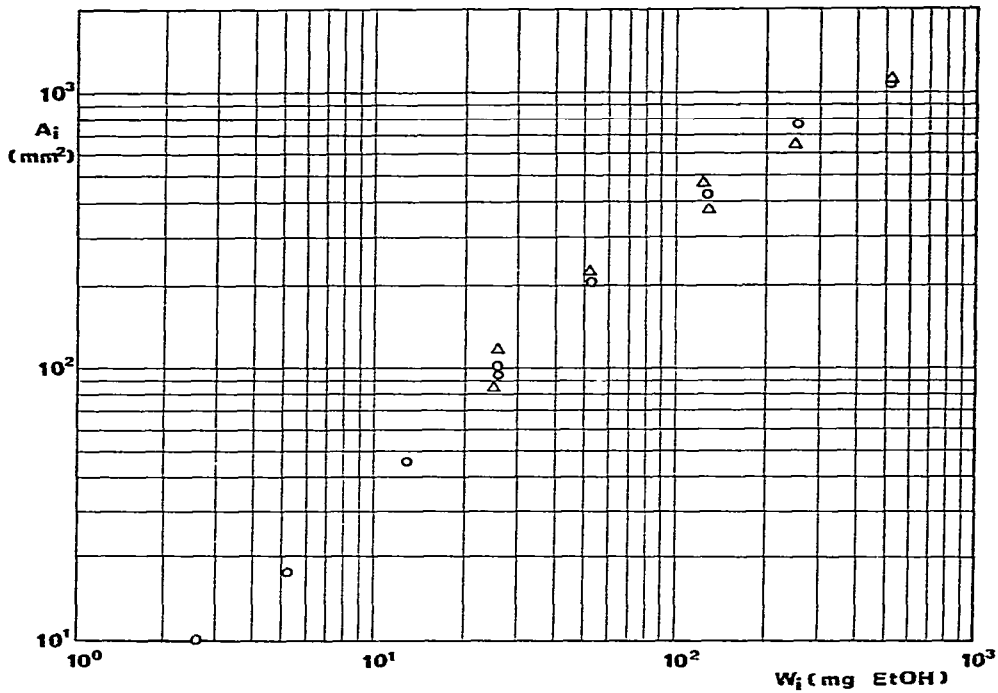

Fig. 4. Dependence of the peak area of ethanol in the chromatogram of concentrate recovered from the trap on the total initial mass of ethanol in the gas–liquid system analyzed.

It is possible to select from the actual data in Figs. 3 and 4 different pairs of $W_{i,j}$, $A_{i,j}$ and $W_{i,k}$, $A_{i,k}$ values with $k > j$, such that $W_{i,k} - W_{i,j} = W_s$, $A_{i,j} = A_i$ and $A_{i,k} = A'_i$, and employ eqn. 4 to calculate for given values of $W_{i,j}$ the corresponding "found" W_i values. Some results obtained in this way are shown in Table I; with butyl acetate and ethanol the average relative errors are 11.0 and 13.8%, respectively.

TABLE I

RESULTS OF THE DETERMINATION OF BUTYL ACETATE AND ETHANOL IN MODEL SYSTEMS

Δ = average $|\ W_i$ (given) $- W_i$ (found) $|$.

W_s	*Butyl acetate (μg in 50 ml of liquid phase)*			W_s	*Ethanol (mg in 50 ml of liquid phase)*		
	W_i *(given)*	W_i *(found)*	$100\,\Delta/W_i$ *(%)*		W_i *(given)*	W_i *(found)*	$100\,\Delta/W_i$ *(%)*
9.2	9.2	8.2		2.6	2.6	3.3	
9.2	18.4	16.1		7.7	5.1	5.0	
18.4	27.6	31.2	11.0	12.9	12.8	10.4	13.8
46.0	46.0	36.6		25.7	25.7	24.9	
92.1	92.1	85.4		77.1	51.4	57.5	
97.8	184.2	180.1					

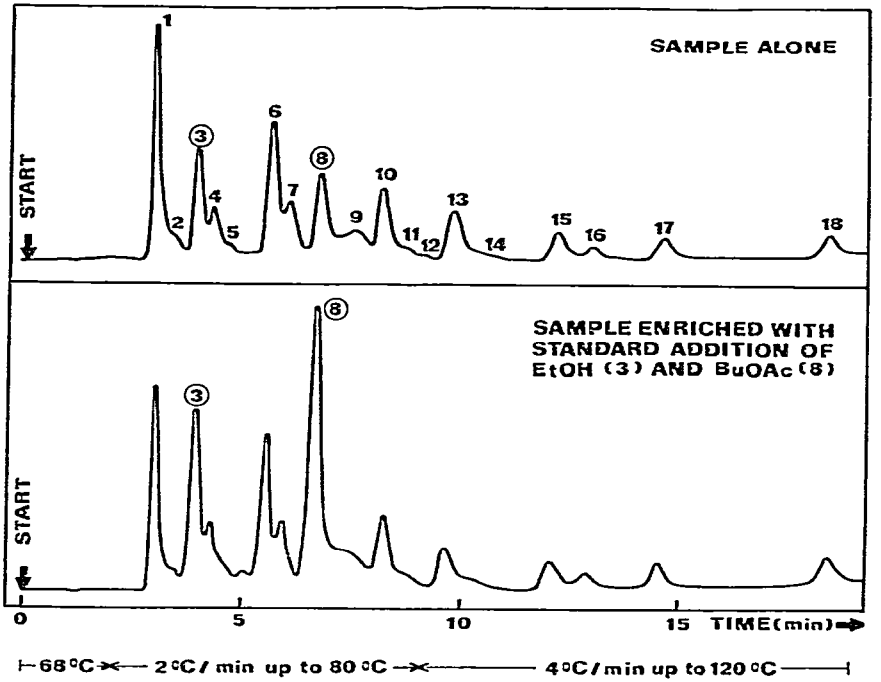

Fig. 5. Chromatograms of the concentrates recovered from the trap after processing a sample of Starkrimson apple juice alone and with addition of the standards butyl acetate and ethanol. Peaks: 1 = ethyl acetate; 2 = methanol; 3 = ethanol; 4 = propyl acetate; 5 = methyl butyrate; 6 = methyl isovalerate; 7 = propanol; 8 = butyl acetate; 9 = isobutanol; 10 = isoamyl acetate; 11 = ethyl valerate; 12 = butanol; 13 = amyl acetate; 14 = isoamyl alcohol; 15 = butyl butyrate; 16 = ethyl capronate; 17 = hexyl acetate; 18 = hexanol. Conditions: 10% Carbowax 600 on Chromosorb W AW; flame-ionization detection; electrometer sensitivity 10^{-11} A f.s.d.; sensitivity attenuation 1/50; recorder chart speed 2 cm/min.

Fig. 5 shows chromatograms obtained by processing a sample of Starkrimson apple juice without (upper chromatogram) and with the addition of the standards butyl acetate and ethanol. The results of five replicate determinations of the two components in the juice are summarized in Table II; the relative standard deviations of

TABLE II

RESULTS OF THE DETERMINATION OF BUTYL ACETATE AND ETHANOL IN STARKRIMSON APPLE JUICE

S = standard deviation of W_i/V_L; $\bar{X}$ = average W_i/V_L.

Butyl acetate			*Ethanol*		
W_s (μg)	W_i/V_L (μg/ml)	$100(S/\bar{X})$ (%)	W_s (mg)	W_i/V_L (mg/ml)	$100(S/\bar{X})$ (%)
111.4	1.22	10.6	51.4	2.62	14.0
	1.42			2.48	
	1.57			3.08	
	1.58			3.44	
	1.54			3.46	

the determination of butyl acetate and ethanol (Dean–Dixon method, five measurements) were 10.6 and 14.0%, respectively.

CONCLUSIONS

Grob's closed-loop strip/trap technique, combined with standard-addition calibration, gives fairly reliable results when applied to the determination of hydrophilic volatiles in complex materials having water as a major constituent. By appropriate choice of the sorbent in the trap and employing the equilibrium version of trapping, it is possible to control the degree of accumulation of different species of compound in the trap, thus enhancing markedly the selectivity of analysis.

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