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QUANTITATIVE HEAD-SPACE GAS ANALYSIS BY THE STANDARD ADDITIONS METHOD

DETERMINATION OF HYDROPHILIC SOLUTES IN EQUILIBRATED GAS–AQUEOUS LIQUID SYSTEMS

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SUMMARY

The use of the standard additions method for the quantitative trace head-space gas analysis of gas–aqueous liquid systems with acetone, methanol, ethanol and propanol as solutes was studied. The method makes it possible to determine the total content of the solute in the equilibrated system by analyzing defined volumes of the head-space gas. When performed under appropriately defined conditions, the procedure provides for the efficient elimination of the system matrix effects. At solute concentrations in the condensed phase of 1–100 ppm, the error in the determination was about 20–3%. With acetone and propanol, the sensitivity of analysis can be markedly increased by saturating the liquid phase with an inorganic salt.

INTRODUCTION

Owing to the properties of equilibrated gas–liquid systems with solutes distributed between the phases, it is possible, in principle, to determine the total content of the solutes in the system by analyzing quantitatively samples of only the gaseous phase. The methods used in such determination must involve either the mass balance of the solutes in the system, taking into account their distribution constants, or a special calibration procedure. In any event, the situation is complicated by the high sensitivity of the equilibrium solute distribution between the phases to the temperature of the system and the composition of the condensed phase, and by the slow recovery of equilibrium after it has been altered. Serious difficulties may occur due to spurious adsorption of the solute within the system and/or the sampling device.

A number of papers describing the analysis of the head-space gas sampled from closed gas–liquid systems involves only qualitative or semi-quantitative assays. The quantitative techniques of head-space gas analysis employed up to now have been based mostly on the use of a calibration graph obtained by means of model solutions. In this way, Weurman[1] determined volatile trace components of raspberry substrates in concentrations of 0.001–0.025%, employing aqueous model solutions for calibra-

tion. Similarly, Bassette and co-workers[2,3] determined less than 1 ppm of various volatile substances in aqueous solutions by analyzing the head-space gas. Kepner *et al.*[4] employed the internal standard method, adding a reference compound to the solution being analyzed and to the model solution and constructing the calibration graph from the ratio of the peak area of the substance being determined to that of the reference compound. Cowen *et al.*[5] discussed the role of the septum used to close the system being analyzed and developed a septumless sampling device. A number of examples of automated head-space gas analysis have recently been described by Kolb[6]. In some instances[2–4], inorganic salts were added to the solution in order to increase the concentration of the solute in the head-space gas.

Head-space gas analysis has been widely applied in the determination of ethanol in blood, using both the method of direct calibration by means of a calibration graph[7–10] and the internal standard method[11]. In most instances inorganic salts were added to the sample being analyzed[8–10]. Some of these methods can be applied to very small amounts of sample[12,13].

Head-space gas methods have also been utilized for studying vapour–liquid[14] and chemical[15] equilibria. Berezkin *et al.*[16] described a method in which the physicochemical aspects of the equilibrium distribution of solutes in a gas–liquid system are utilized analytically in combination with gas chromatography.

The standard additions method has not previously been employed in quantitative head-space gas analysis. In this work, we have studied the possibilities of using this method for the determination of trace amounts of polar solutes in gas–aqueous liquid model systems.

PRINCIPLE AND CALCULATION OF RESULTS

There are several alternative versions of the standard additions method as modified for quantitative head-space gas analysis by gas chromatography and the principles and theory of these alternatives have been described in detail elsewhere[17]. In the present study, we employed the so-called single-sample procedure.

First, a defined volume of the head-space gas is withdrawn from the equilibrated system and injected into the gas chromatograph. Let the volume of the gas sampled be v_G, the weight of the component being determined (i) contained in this volume and the corresponding peak area being w_i and A_i, respectively. In the second step, a defined weight of component i as a standard, W_s, is introduced into the system and, after re-equilibration, a volume v'_G of the head-space gas is again sampled and injected into the gas chromatograph, thus giving a peak area A'_i. The weight of component i contained in the original entire gas + condensed phase system, W_i, is then calculated by

$$W_i = \frac{W_s - w_i}{(A'_i\, v_G / A_i v'_G) - 1}$$

This relationship was derived by virtue of the following mass balance for the solute:

$$W_i = c_{iL} V_L + c_{iG} V_G$$

$$W_i + W_s - w_i = c'_{iL} V_L + c'_{iG} V_G$$

$$c_{iL}/c_{iG} = c'_{iL}/c'_{iG} = K$$

where c_{iL} and c_{iG} are the equilibrium solute concentrations in the liquid and gaseous phase, respectively, of the original system, c'_{iL} and c'_{iG} are the corresponding concentrations in the system after withdrawing the amount w_i and adding the amount W_s of substance i, V_L and V_G are the volumes of the condensed and gaseous phase, respectively, of the system, and K is the distribution constant of the solute in the system. It is assumed that V_L and V_G as well as K are invariable during the procedure; under these circumstances, it also holds that

$$c'_{iG}/c_{iG} = A'_i v_G/A_i v'_G$$

In most instances the value of w_i can be neglected in comparison with that of W_s. It is necessary for the system being analyzed to be kept at the same temperature in both sampling steps, for the samples to be taken slowly and for the amount of the standard added to be not too large compared with the total amount of component i originally present in the system.

EXPERIMENTAL

Systems studied

Two gas–liquid systems were investigated, with condensed phases consisting of (1) aqueous solutions of acetone with concentrations ranging from about 1 to 100 ppm and (2) aqueous solutions of mixtures of about 2–6 ppm of methanol, 2–6 ppm of ethanol, 3–10 ppm of propanol and 1–4 ppm of acetone, containing 0.28 g/ml of sodium carbonate.

Chemicals and instruments

Methanol, ethanol, propanol and acetone were obtained from Lachema (Brno, Czechoslovakia), were redistilled and their purities were checked by gas chromatography. Distilled water was used to prepare the model solutions.

A Hewlett-Packard 402 gas chromatograph with a flame-ionization detector was used to carry out the analyses, employing a 180 × 3 mm I.D. glass column packed with Porapak P, 80–100 mesh (Waters Assoc., Milford, Mass., U.S.A.), and kept at 120 or 130°. The carrier gas was nitrogen. The peak areas were measured with an Infotronics CRS 100 integrator.

Procedure

Standard solutions containing 0.1–1 % of the solutes were prepared by weighing the appropriate amounts of the solutes into 10-ml calibrated vessels and making up the volume with distilled water. The final model systems were prepared by injecting with a 10-μl Hamilton syringe 1–10 μl of the standard solutions into 100-ml serum bottles containing 50 ml of distilled water. The system with higher contents of the solutes were prepared from pure solutes, employing a 1-μl Hamilton syringe. The

serum bottles were closed with rubber septa and thermostatted with a U-10 water ultrathermostat (VEB Prüfgeräte-Werk, Medingen/Dresden, G.D.R.) while agitating the contents with an MM-2 magnetic stirrer (Laboratory Equipment, Prague, Czechoslovakia). The time allowed for the equilibration of the system was 14–40 min, depending on the temperature.

The head-space gas (1–2 ml) was sampled from the system with a 2.5-ml Hamilton syringe. After inserting the needle of the syringe into the head-space of the system, about 0.2 ml was drawn in and then ejected back into the head-space in order to purge the inner space of the needle. Then the sample was drawn in very slowly and injected into the gas chromatograph. Between the individual samplings, the syringe was kept at an elevated temperature in order to suppress the condensation of water vapour in the syringe. The standard was introduced into the serum bottle through its septum by means of an injection syringe.

RESULTS AND DISCUSSION

The results of the measurements with the acetone systems are summarized in Tables I, II and III. In each instance, a 2-ml sample of the head-space gas was chromatographed.

TABLE I

DETERMINATION OF ACETONE IN MODEL SYSTEMS AT 30.4°

W_t = overall weight of acetone in the system; W_s = weight of acetone added as a standard; S = standard deviation; n = number of determinations; t = experimental Student coefficient.

W_t (mg)		Error		$S/\sqrt{n}$	t	W_s (mg)
Taken	*Found*	*mg*	*%*			
6.34	6.18	−0.16	2.5	0.082	1.95	3.17
3.17	3.03	−0.14	4.4	0.076	1.84	3.17
0.790	0.734	−0.056	7.1	0.033	1.70	0.790
0.396	0.348	−0.048	12.1	0.024	2.00	0.396
0.135	0.111	−0.024	17.8	0.013	1.85	0.135

Table I shows the results of the determination of acetone in systems with acetone concentrations in the condensed phase ranging from about 2 to 100 ppm, kept at 30.4°. The results are averages of 7–11 determinations. The percentage error increases as the amount of acetone in the system decreases, which may be due partly to the measurement of smaller peak areas. The experimental values of the Student coefficients show that the errors are not systematic ($t_{0.05}^{\nu=8} = 2.306$); the absolute values of the error and the standard deviations of the average, $S/\sqrt{n}$, vary roughly in the same manner with the solute contents in the system, so that the experimental t-values remain virtually unchanged.

The corresponding distribution isotherm is non-linear; in Fig. 1 the heights of acetone peaks obtained by chromatographing 2-ml samples of head-space gas are plotted against the total weight of acetone in the system. When analyzing, by chromatographing head-space gas samples, a system containing 1.585 mg of acetone by

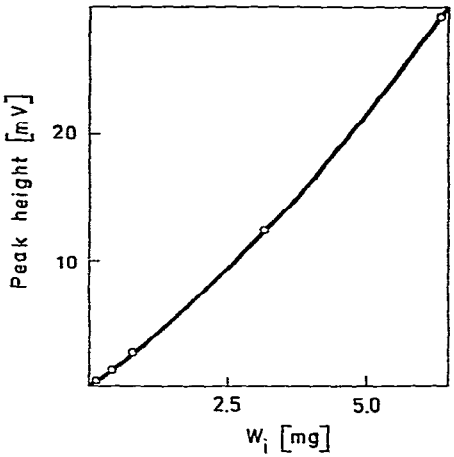

Fig. 1. Plot of the height of acetone peaks in chromatograms of 2-ml samples of head-space gas against the overall content of acetone in the system.

direct calibration using the above plot as a calibration graph, the average of seven replicate determinations was 1.840 mg with a standard deviation of 0.20 mg.

The results in Table II show the effect of the temperature of systems containing about 1–3 ppm of acetone in the condensed phase. The results are averages of about eight determinations. The smallest error and best reproducibility were obtained at 40.4° and this temperature was therefore employed for the other measurements. The use of higher temperatures affords more sensitive analyses, *i.e.*, the determination of acetone concentrations below 1 ppm in the liquid phase, but the syringe would also have to be kept at an appreciably high temperature in order to achieve sufficient reliability of the results.

The variation of pressure within the system, brought about by withdrawal of head-space gas samples, had no serious effect on the reliability of the results, although they could become important with systems of small volumes. When the needle of the syringe filled with the gaseous sample is removed from the head-space of the system, the pressure within the syringe equalizes with the ambient pressure. If there is an excess pressure in the system, which occurred in our work, part of the sample is lost during its transfer from the head-space of the system to the gas chromatograph, the loss in the first sampling being larger than that in the second. This effect is probably

TABLE II

DETERMINATION OF ACETONE IN MODEL SYSTEMS AT DIFFERENT TEMPERATURES

Temperature (°C)	*W_i (mg)*		*Error*		*$S/\sqrt{n}$*	*t*
	Taken	*Found*	*mg*	*%*		
30.4	0.135	0.111	−0.024	17.8	0.0130	1.85
40.5	0.135	0.131	−0.004	3.0	0.0030	1.33
50.4	0.135	0.120	−0.015	11.1	0.0088	1.70
50.4	0.0590	0.0695	0.0105	17.8	0.0068	1.55

TABLE III

COMPARISON OF THE RESULTS OF THE DETERMINATION OF ACETONE IN MODEL SYSTEMS, OBTAINED BY CALCULATING WITH THE VOLUME RATIO v_G/v'_G (a) AND BY EMPLOYING A REFERENCE SUBSTANCE (b)

W_i (mg)		Error		$S/\sqrt{n}$
Taken	*Found*	*mg*	*%*	
0.123	(a) 0.113	−0.010	9.2	0.0083
	(b) 0.127	0.004	3.2	0.0073
0.0615	(a) 0.0715	0.0100	16.4	0.0049
	(b) 0.0580	−0.0035	6.0	0.0037
0.0590	(a) 0.0695	0.0105	17.9	0.0060
	(b) 0.0635	0.0045	7.5	0.0043

the reason why the error is mostly negative. This problem, of course, does not occur with systems with a pressure deficiency. The above effect can be partly eliminated by effecting calculations with the ratio of peak areas of an auxiliary reference substance, present in the system, instead of the ratio of directly measured volumes, v_G and v'_G. In Table III, the results (b) obtained with a reference substance are compared with those (a) obtained by calculating directly with the volume ratio v_G/v'_G. The results are averages of eight determinations. The areas of peaks of an unknown component, probably methane from the atmosphere, were employed as the reference data in case (b). The improvement of the results by employing the reference substance is evident.

The results of analyses of systems containing trace amounts of methanol, ethanol, propanol and acetone are summarized in Table IV. Where the values in the *Error (mg)* column are marked with an asterisk, the ratios of the error to the standard deviation of the average (eight determinations) indicate the possibility of a systematic error. With all of these systems the condensed phase was saturated with sodium carbonate in order to decrease the solubility of the solutes. The effect of the presence of

TABLE IV

ANALYSES OF MODEL SYSTEMS WITH SEVERAL SOLUTES

Solute	W_i (mg)		Error		$S/\sqrt{n}$	W_s (mg)
	Taken	*Found*	*mg*	*%*		
Acetone	0.0615	0.0715	0.010*	16.3	0.0033	0.0620
	0.123	0.113	−0.010	8.1	0.010	0.0620
	0.184	0.175	−0.009	5.4	0.018	0.0620
Methanol	0.0990	0.0790	−0.0200	20.2	0.017	0.099
	0.198	0.134	−0.064	32.3	0.046	0.198
	0.297	0.237	−0.060	20.2	0.092	0.099
Ethanol	0.107	0.0880	−0.019*	17.7	0.0057	0.107
	0.214	0.153	−0.061*	28.5	0.025	0.214
	0.321	0.286	−0.035	10.9	0.050	0.107
Propanol	0.159	0.146	−0.013	8.2	0.017	0.318
	0.318	0.307	−0.011	3.5	0.008	0.318
	0.476	0.434	−0.042	8.8	0.028	0.159

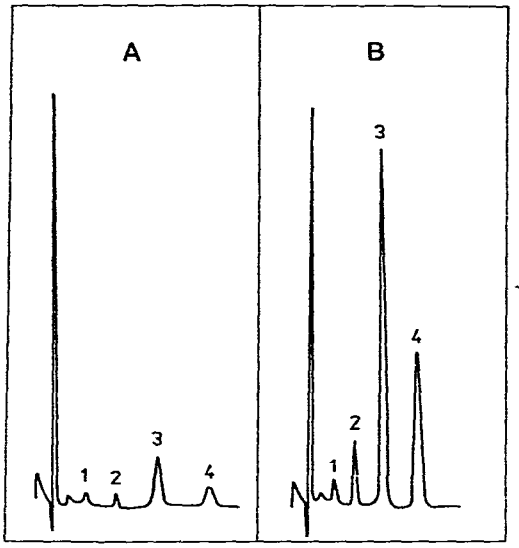

Fig. 2. Chromatograms of 1-ml samples of head-space gas taken from systems containing 3.96, 4.28, 2.46 and 6.36 μg/ml of methanol (1), ethanol (2), acetone (3) and propanol (4), respectively. A, System without Na_2CO_3; B, system with the condensed phase saturated with Na_2CO_3.

sodium carbonate in the liquid phase on the equilibrium concentration of the solutes in the gaseous phase is apparent from the chromatograms in Fig. 2, where A and B refer to systems without and with sodium carbonate, respectively. In both instances the initial concentrations of methanol, ethanol, propanol and acetone in the liquid phase were 3.96, 4.28, 6.36, and 2.46 μg/ml, respectively, and the systems were maintained at 40°. The records A and B were obtained by chromatographing at 120° and 130°, respectively, 1-ml samples of head-space gas at a sensitivity attenuation of 4. It can be seen that with methanol and ethanol the salting-out effect is insignificant and the results of the determination of these components are not very satisfactory. On the other hand, with acetone and propanol the increase in the gas-phase concentration due to salting-out is marked. It can be concluded that there are no significant interferences among the individual solute components at the level of concentrations employed.

CONCLUSIONS

The standard additions method is suitable for quantitative head-space gas analysis. When performed under constant equilibrium conditions, the method provides for the determination of the total content of a solute component in gas–liquid, gas–solid, and/or gas–liquid–solid systems by analyzing only the gaseous phase. The method is especially advantageous in trace analysis; the addition to the system of a small amount of a component already present does not alter the properties of the phases appreciably, so that the distribution constant of the component remains virtually unchanged. From this point of view, the standard additions head-space gas method can be considered as an equivalent of the method of calibration with a defined head-space gas sample taken from over a model solution of the component being deter-

mined dissolved in a solvent the composition of which is identical with that of the matrix material of the condensed phase of the system being analyzed.

It follows from the above considerations that the standard additions method is the only possible choice if an exact quantitative head-space determination of solutes in an equilibrated gas–liquid (solid) system with a multicomponent condensed phase of unknown composition is to be carried out.

When employing the simplest means of sampling (injection syringe), it is possible to determine hydrophilic solutes in gas–aqueous liquid systems containing about 1 ppm of the solute in the liquid phase with an error of about 20% of the value being determined. This error, although acceptable with regard to the nature of the systems being analyzed and the concentrations being determined, could be reduced by employing more sophisticated sampling procedures.

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