

CHROM. 12,402

APPLICATION OF HEAD-SPACE ANALYSIS TO THE STUDY OF VOLATILE ORGANIC IMPURITY CONCENTRATES

GAS CHROMATOGRAPHIC DETERMINATION OF AROMATIC HYDROCARBONS IN ATMOSPHERIC AIR

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SUMMARY

Head-space analysis is suggested for use in the analysis of concentrates of volatile gaseous impurities after their treatment with solvents or reagents that reduce drastically the liquid-gas partition coefficients. Equations are given for calculating the degree of gas enrichment with the components of interest, and it is shown that the sensitivity of analysis can be improved by 2-4 orders of magnitude. The determination of the simplest aromatic hydrocarbons as impurities in atmospheric air, with their preliminary equilibrium concentration in 80% acetic acid and subsequent neutralization of the concentrates with an alkali, is used to show that the detection limit can be lowered by a factor of 50 in comparison with direct analysis of the concentrate, thus making possible the determination of benzene, toluene and xylenes at the level of 0.05-5 mg/m³ to within 5-8%.

The method proposed combines all the advantages of equilibrium concentration with those of head-space analysis, including the possibility of automating the analytical procedure.

INTRODUCTION

The determination of trace impurities in gases normally requires their preliminary concentration by means of sorbents, specific reagents or solvents. Methods currently in use for the analysis of concentrates involve thermal desorption or chemical treatment, with subsequent transfer of all of the evolved adsorbate into a chromatographic column. The method of equilibrium concentration in volatile liquids proposed recently^{1,2} makes it possible to introduce the liquid concentrate directly into the chromatograph, but the increase in the sensitivity of analysis attained in this way is slight. There is, however, another possibility for the gas chromatographic analysis of the concentrates which consists in the use of head-space analysis (HSA) and the determination of the concentration of impurities in the equilibrium gas phase after the transfer into it of most of the adsorbate. An efficient means of ensuring such a transfer would be a substantial reduction in the partition coefficients of the impurities in ques-

tion in the concentrates by chemical treatment of the solvent, by saturation or dilution of the solution with salting-out reagents.

Of the various procedures available for increasing the sensitivity of HSA only salting-out and heating were used (*e.g.*, see papers on the analysis of biological liquids and polymers^{3,4}). Treatment with reagents to change the chemical nature of the concentrator sorbent was not investigated.

The proposed method of the analysis of concentrates (both the concentrates obtained under the conditions of total absorption and those obtained by equilibrium concentration) can have certain advantages.

ADVANTAGES OF THE HSA TECHNIQUE IN THE DETERMINATION OF VOLATILE IMPURITIES IN CONCENTRATES

One of the advantages consists in a considerable improvement in the analytical sensitivity. For concentrates obtained under the conditions of total absorption, the enrichment α of the gaseous sample introduced into the chromatograph in comparison with the original gas under analysis will be

$$\alpha = \frac{C'_G}{C_G} = \frac{V_G}{V'_G + K'V'_L} \quad (1)$$

where V_G is the volume of the gaseous sample from which the analyte has been absorbed, C_G is its concentration, V'_G and V'_L are the volumes of equilibrium vapour above the solution and of the solution itself (after treatment of the concentrate to reduce the partition coefficient to K') and C'_G is the analyte concentration in equilibrium vapour. According to eqn. 1, the limiting degree of enrichment attained with K' close to zero will thus be determined simply by the volume ratio of the gas under analysis and of the equilibrium vapour (V_G/V'_G). As V_G may be as high as a few litres or tens of litres while V'_G can be reduced to a few millilitres, this may entail enrichments of the order of 10^3 . Even for K' close to unity at the volume of the equilibrated liquid phase (V'_L) about equal to that of the vapour phase (V'_G), the degree of enrichment will be less than the limiting value by a factor of two only.

For solutions obtained by the method of equilibrium concentration in volatile liquids, the degree of enrichment at the stage of concentration, C_L/C_G , is not equal to the partition coefficient of the impurity between the liquid and gas phases, K (as has been shown theoretically and confirmed experimentally^{1,2}) and depends on the volatility of the absorbing liquid according to the equation

$$\frac{C_L}{C_G} = \frac{Kf}{1 - AK} \quad (2)$$

The parameters f and A , characterizing the volatility of the absorbing liquid, depend on its vapour pressure, P_L , density, d_L , and molecular weight, M , as well as on temperature, T , and external pressure, P :

$$f = \frac{P - P_L}{P} \quad \text{and} \quad A = \frac{P_L M}{RTd_L}$$

where R is the gas constant.

At the stage of transfer of the volatile compound from the concentrate into the gaseous phase by reducing substantially the partition coefficient to K' by adding salting-out reagents or compounds that change the chemical composition of the solution the concentration ratio will be

$$\frac{C'_G}{C_L} = \frac{V_L}{V'_G + K'V'_L} \quad (3)$$

where V_L and C_L are the volume of the liquid phase and the concentration of the impurities captured in this phase, respectively, the other notations being the same as in eqn. 1.

The total enrichment, equal to the product of intermediate enrichments (2) and (3), will be

$$\alpha = \frac{V_L}{V'_G + K'V'_L} \cdot \frac{Kf}{1 - AK} \quad (4)$$

As can be seen from this equation, optimal conditions ensuring the highest degree of enrichment and, hence, the maximal analytical sensitivity, require K and V_L to be as high as possible at the lowest possible magnitude of K' and V'_G . The current state of the art in HSA involves equilibrium gas-phase volumes not less than a few millilitres. On the other hand, in the equilibrium concentration of impurities with high K it is hardly reasonable to increase the solvent volume V_L to more than a few millilitres in order to avoid an unacceptable increase in the sampling time. Thus, in the ideal case (when $K' = 0$) of equilibrium concentration in a non-volatile solvent ($f = 1$, $A = 0$), the limiting value of the degree of enrichment, according to eqn. 4, will be simply equal to the partition coefficient, K . The values of K that are optimal for the use of equilibrium concentration are of the order of 10^2 – 10^4 , so that the overall gain in the sensitivity of the analysis of equilibrium concentrates by this method can be about the same as when analysing concentrates obtained under the conditions of total absorption.

Another advantage of using the HSA technique for the analysis of concentrates of volatile gaseous impurities that is particularly important when series of analyses are to be made consists in the possibility of automating the procedure using available mass-produced instruments (F-42 and F-45 headspace analysers, and the HS-6 sampler manufactured by Perkin-Elmer (Norwalk, Conn., U.S.A.)).

As can be seen from the above, the major problem for the analysis of concentrates by the proposed method consists in creating conditions that favour a sharp decrease in the partition coefficient of the analyte between the liquid and the gaseous phase. A change in the chemical nature of the condensed phase proper would be the most straightforward means of achieving this goal. Treatment with reagents that interact with liquid concentrates should be a very efficient means of changing the conditions of partition in the liquid-gas systems. Its efficiency and the expedience of applying HSA to the analysis of gas impurity concentrates can be demonstrated in the case of the determination of volatile aromatic hydrocarbons in equilibrium concentrates obtained from atmospheric air.

DETERMINATION OF AROMATIC HYDROCARBONS IN ATMOSPHERIC AIR

It has become evident that aromatic hydrocarbons are always present in the atmosphere of modern cities, and because of their potential toxicity they require constant monitoring in order to ensure that the maximum permissible concentrations are not exceeded. A simple and highly sensitive technique for analysing aromatic hydrocarbons in air which would be suitable for routine use is urgently needed. Sorption on silica gel with subsequent removal of the trapped compounds with glacial acetic acid and chromatographic analysis of the resulting solution^{5,6} yields good results for dry air only. Equilibrium concentration in glacial acetic acid can provide a fairly high selectivity of accumulation of the aromatic hydrocarbons combined with simplicity of sampling and of the analytical procedure proper. However, this again entails the possibility of errors associated with the humidity of the air. The atmospheric moisture dilutes the acetic acid, bringing about a substantial reduction in the partition coefficients. This effect can be taken into account by determining the acid concentration after the sampling⁷, but the reduction in sensitivity makes it necessary to use the most sensitive of the modern chromatographic instruments when analysing urban air.

A transition from direct gas chromatographic analysis of acetic acid concentrates to equilibrium vapour analysis after treatment with alkali greatly improves the analytical possibilities while simplifying the overall procedure (as the absorption of acetic acid in the pre-column is no longer needed⁴). Indeed, the partition coefficients of aromatic hydrocarbons in the aqueous solution of the acetate formed on adding excess of alkali to the acetic acid extract are much smaller than those in water (which is essentially the salting-out effect), and three to four orders of magnitude lower than in acetic acid (Table I). With a gas to liquid sample volume ratio of about 10^3 , eqn. 3 yields an additional increase in sensitivity by a factor of almost 100 if $V'_g/V'_L = 10/2$ and $V_L = 1$ ml.

TABLE I
LIQUID-AIR PARTITION COEFFICIENTS FOR THE SIMPLEST AROMATIC HYDROCARBONS

Hydrocarbon	Temperature (°C)	Acetic acid concentration (%)		Water*	Potassium acetate solution (46%)
		100	80		
Benzene	20	895 ± 62	313 ± 26	4.8 ± 0.2	0.70 ± 0.02
	25	773 ± 41	270 ± 9	4.0 ± 0.1	0.62 ± 0.01
	30	618 ± 44	219 ± 11	3.4 ± 0.1	0.51 ± 0.02
	35	553 ± 21	189 ± 16	2.6 ± 0.2	0.48 ± 0.03
Toluene	20	2479 ± 108	709 ± 42	4.6 ± 0.3	0.57 ± 0.02
	25	2135 ± 94	610 ± 16	3.6 ± 0.2	0.48 ± 0.02
	30	1759 ± 45	488 ± 24	2.9 ± 0.1	0.39 ± 0.03
	35	1480 ± 18	406 ± 37	2.3 ± 0.1	0.33 ± 0.03
<i>m</i> -Xylene	20	6369 ± 643	1577 ± 107	5.9 ± 0.3	0.49 ± 0.02
	25	5574 ± 286	1300 ± 53	4.6 ± 0.3	0.36 ± 0.04
	30	4568 ± 222	1111 ± 88	3.9 ± 0.3	0.28 ± 0.03
	35	3746 ± 65	878 ± 72	2.6 ± 0.3	0.22 ± 0.04

* Data supplied by N. N. Yaglit'skaya.

When determining the simplest aromatic hydrocarbons in atmospheric air, we suggest the use of an 80% aqueous solution of acetic acid as the trapping liquid. Owing to the decrease in K in comparison with the use of glacial acetic acid, the minimal volume of air² required to reach an equilibrium concentration of C_6H_6 - C_8H_{10} hydrocarbon impurities in 2 ml of liquid at 25° is reduced from 20 to 6 l. Passing such a volume of atmospheric air, even at 100% humidity, through 80% acetic acid will dilute it by only 2% with a corresponding change in K of not more than 10-12%. Thus changes in composition of the absorbing liquid⁷ may need to be taken into account only when collecting samples in rainy weather at temperatures above 25°. In addition the 80% acid solidifies at a much lower temperature than the 100% acid, so that sampling at ambient air temperatures down to -7° becomes possible.

A further advantage of using 80% acid rather than glacial acetic acid lies in the possibility of calculating the impurity concentration in the air under study by the simple equation of the partition law

$$C_G = \frac{C_L}{K} \quad (5)$$

without taking into account the volatility of the absorbing liquid, as has been shown previously².

EXPERIMENTAL

Sampling

The air under study is passed through a saturator with a porous glass plate (filter No. 2) shown in Fig. 1, containing 2 ml of 80% acetic acid*, at a rate of 350-450 ml/min until equilibrium partition of the compounds to be studied between the liquid and gaseous phase is obtained. The minimal volume of air required for this purpose varies depending on the sample temperature, from 8 l at 15° to 3.5 l at 40° for benzene, toluene and xylenes.

If storage of a sample is envisaged, it is sealed in a 2-ml glass ampoule.

Analytical procedure

A variable-volume thermostated (25°) flask⁸ based on a 20-ml glass hypodermic syringe was mounted vertically so that the base of the plunger rests against the horizontal surface. The inner volume of the syringe was fixed accurately by means of a special limiter. A 2.00-ml volume of 40% potassium hydroxide solution was transferred into the thermostated flask by puncturing the rubber septum. Next, 1.00 ml of acetic acid saturated with the air impurities was introduced cautiously (because of the pressure change) into the same flask. Accurate sampling of the acid and alkali solutions was effected by the use of calibrated hypodermic syringes, also equipped with limiters.

The flask was shaken periodically for 20 min and then connected to the sampling loop of the heated gas stopcock of the chromatograph. A specially prepared

* After purification by repeated freezing-out, the glacial acetic acid was diluted by weight to $80 \pm 0.5\%$ with doubly distilled water.

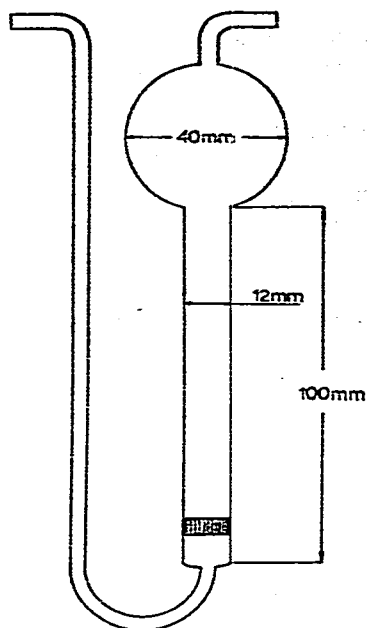


Fig. 1. Saturator for equilibrium concentration in acetic acid.

reference mixture with known concentration of aromatic hydrocarbons in 80% acetic acid was analysed under identical conditions (such mixtures were prepared by successive dilution by weighing). The heights of the corresponding peaks in the chromatograms of the sample and the reference mixture were measured at the same sensitivity of the amplifier and recorder.

From the peak height ratio in the chromatograms of the gaseous phase, we determined the impurity concentration in the liquid (G_L) and calculated C_G by using eqn. 5. The values of K are given in Table I.

The impurity concentration in the air under study can be also calculated by using the equation

$$C_G = C'_G \cdot \frac{V'_G + K'V'_L}{KV'_L} \quad (6)$$

since, as has been mentioned before, for 80% acetic acid $f \approx 1$ and $AK \approx 0$. Although in this instance it is not necessary to analyse reference mixtures, one should calibrate the detector using standard gas mixtures, take into account the partition coefficients (K'), and measure accurately the volumes of the equilibrium phases (rather than reproduce only their ratio with high accuracy).

Conditions of chromatographic analysis

A Tsvet Model 102 chromatograph with a flame-ionization detector was used. The heated gas valve was mounted in the detector thermostat. A 125×0.3 cm glass column containing 10% tripropionitrilamine on 60-80-mesh Chromosorb P was

employed. The column temperature was 80° and the valve temperature 100°. The carrier gas (nitrogen) flow-rate was 20 ml/min and the sample volume 2 ml.

Determination of partition coefficients

The values of K for the aromatic hydrocarbons presented in Table I were determined in water and in potassium acetate solution by the static method⁶ (under the above conditions of gas chromatographic analysis; the volume ratio of the equilibrium phases $V'_G/V'_L = 10$ and $V'_L = 5$ ml). The values of K in the acetic acid were obtained by the continuous gas extraction method⁹. A 15–30-l volume of air was passed through 3–5 ml of a solution of aromatic hydrocarbons in acetic acid (with an initial concentration of 0.4–0.7%) at rate of 50–200 ml/min. A bundle of steel capillaries was used for gas dispersion in the liquid. After 20–30 min, samples of the liquid were collected for gas chromatographic analysis. The sample volume was 1 μ l. A pre-column for the absorption of the acetic acid was placed before the analysis column (see above)⁶. The evaporator temperature was 150°.

The peak areas were measured with a Takeda-Riken Model TR-2213 digital integrator.

RESULTS AND DISCUSSION

The proposed method for the determination of the simplest aromatic hydrocarbons in atmospheric air was tested using humid vapour-air mixtures prepared by

TABLE II
DETERMINATION OF AROMATIC HYDROCARBONS IN HUMIDIFIED AIR MIXTURES

Sampling conditions		Concentration (mg/m ³)								
Temperature (°C)	Moisture content (mg/l)	Benzene			Toluene			<i>m</i> -Xylene		
		Introduced (I)	Found (II)	I–II (%)	Introduced (I)	Found (II)	I–II (%)	Introduced (I)	Found (II)	I–II (%)
25	23	4.50	4.59	–2.0	2.01	1.85	+8.0	1.71	1.72	– 0.6
15	12	4.09	4.40	–7.6	1.86	1.69	+9.1	1.68	1.76	– 4.8
25	23	3.13	3.31	–5.7	1.65	1.73	–4.8	1.43	1.33	+ 7.0
20	17	3.08	3.00	+2.6	1.26	1.34	–6.3	1.42	1.29	+ 9.2
15	12	1.72	1.69	+1.7	0.86	0.79	+8.1	0.90	0.86	+ 4.4
20	17	1.40	1.44	–2.8	0.86	0.86	0.0	0.36	0.35	+ 2.8
20	17	1.40	1.45	–3.6	0.84	0.90	–7.1	0.36	0.39	–11.4
15	12	1.27	1.20	+5.5	0.84	0.86	–2.4	0.34	0.32	+ 6.3
15	12	1.27	1.19	+6.2	0.82	0.81	+1.2	0.28	0.26	+ 7.1
18	15	1.24	1.28	–3.2	0.82	0.84	–2.4	0.34	0.32	+ 6.3
18	15	1.24	1.23	+0.8	0.78	0.82	–5.1	0.28	0.24	+14.3
15	12	1.06	1.04	+1.9	0.78	0.80	–2.6	0.20	0.18	+10.0
15	12	1.06	1.10	–3.8	0.76	0.74	+2.6	0.20	0.20	0.0
25	23	1.06	1.11	–4.7	0.76	0.78	–2.6	0.20	0.21	– 5.0
25	23	1.06	1.11	–4.7	0.76	0.76	0.0	0.29	0.23	–15.0
25	23	1.06	1.07	–0.9	0.75	0.71	+5.3	0.18	0.17	+ 5.6
20	17	0.86	0.86	0.0	0.70	0.72	–2.9	0.18	0.17	+ 5.6
20	17	0.86	0.88	–2.3	0.70	0.20	+2.9	0.18	0.16	+11.1
25	23	0.56	0.59	–5.4	0.21	0.19	+9.5	0.11	0.12	– 9.1
25	23	0.50	0.51	–2.0	0.19	0.68	–5.3	0.091	0.079	+13.2

the diffusion technique⁸. The average difference between the true and measured concentrations of benzene, toluene and *m*-xylene in the range 4.5–0.09 mg/m³* was 4–8% (Table II). Repeated (5–6 times) injections of equilibrium vapour from the same sample into the chromatograph gave a standard deviation of 0.02–0.04 mg/m³.

It may be of interest to compare the results of the determination of impurities in urban air by the proposed method of equilibrium concentrate analysis and by concentration of atmospheric hydrocarbons with complete adsorption on hydrophobic graphitized carbon¹¹. Following thermal desorption, all of the adsorbate from 10 l of air is injected into the chromatographic column and hence is analysed only once (the acetic acid concentrate from a smaller volume of air can be analysed gas chromatographically several times). Gas chromatography–mass spectrometry permits the detection in one sample of concentrate on carbon of more than 100 hydrocarbons contained in air. Fig. 2 shows typical chromatograms of parallel samples of atmospheric impurities obtained by these two methods. One can see clearly the selectivity in determination of the simplest aromatic hydrocarbons by the equilibrium concentration method involving neutralization of the concentrate and analysis of the equilibrium vapour as a result of two factors: firstly, the use of acetic acid at the sampling stage produces a depletion in the solution of impurities with low partition coefficients; and secondly, after neutralization of the concentrate the equilibrium gas phase becomes depleted in substances that do not exhibit such a sharp decrease in the partition coefficients as the aromatic hydrocarbons (*e.g.*, oxygen-containing compounds).

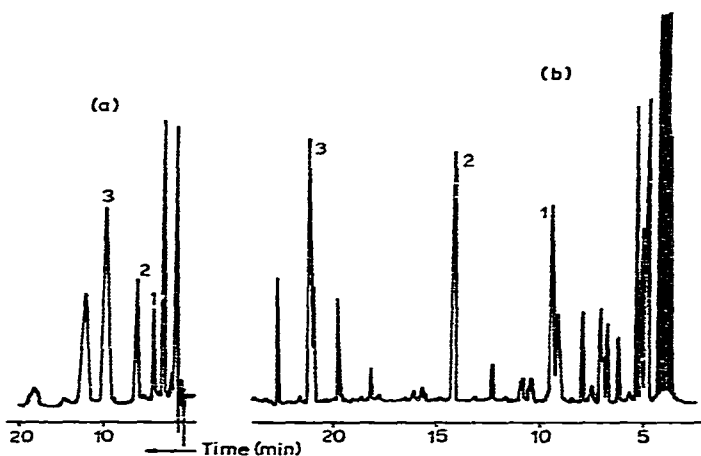


Fig. 2. Chromatograms of (a) equilibrium vapour of neutralized acetic acid concentrate and (b) impurities from the same atmospheric air sample sorbed on carbon. 1 = Benzene (0.056 mg/m³); 2 = toluene (0.062 mg/m³); 3 = *m*- and *p*-xylene (0.055 mg/m³). (a) Current scale $2 \cdot 10^{-12}$ A, other conditions specified in the text; (b) current scale 10^{-10} – $2 \cdot 10^{-10}$ A, copper capillary column (50 m \times 0.35 mm I.D.) containing dinonyl phthalate, carrier gas (nitrogen) flow-rate 4 ml/min, column temperature programmed from 40° at 3°/min.

* The U.S.S.R. environmental standards specify the daily-averaged maximum permissible concentrations of benzene, toluene and xylenes in urban air as 0.8, 0.6 and 0.2 mg/m³, respectively.

Hence the methods under comparison may be considered as complementary: total adsorption on non-selective hydrophobic sorbents is needed for a detailed analysis of air for all volatile impurities in specific research while routine environmental monitoring involves the determination of only the most toxic compounds. Equilibrium concentration and equilibrium vapour analysis considerably simplifies and speeds up the measurement of the content of the benzene series of hydrocarbons in air while retaining the same analytical accuracy (*cf.*, Table III). The minimum detectable concentrations of aromatic hydrocarbons in air are 0.008 mg/m³ for benzene, 0.006 mg/m³ for toluene and 0.003 mg/m³ for xylenes (current range 2·10⁻¹² A, noise level 1.6·10⁻¹⁴ A). Thus both the sensitivity and accuracy of the proposed technique for determining the simplest aromatic hydrocarbons are completely adequate for atmospheric air purity monitoring. The substantial increase in sensitivity achieved by the use of the HSA technique improves the method in some respects while reducing the requirements imposed on the sensitivity of the equipment.

TABLE III

COMPARISON OF AROMATIC HYDROCARBON DETERMINATIONS IN ATMOSPHERIC AIR BY EQUILIBRIUM CONCENTRATION (I) AND ADSORPTION METHODS (II)

Sampling conditions		Concentration (mg/m ³)								
Temperature (°C)	Moisture content (mg/l)	Benzene			Toluene			m- and p-Xylene		
		I	II	I-II (%)	I	II	I-II (%)	I	II	I-II (%)
18	6.1	0.056	0.054	+ 3.7	0.062	0.072	-13.9	0.055	0.052	+ 5.8
19	3.8	0.049	0.047	+ 4.3	0.074	0.060	+23.3	0.055	0.056	+ 1.8
20	5.1	0.050	0.043	+16.3	0.127	0.110	+15.5	0.061	0.076	-19.7
25	11.5	0.102	0.112	- 8.9	0.142	0.135	+ 5.2	0.117	0.113	+ 3.6

ACKNOWLEDGEMENTS

The authors are indebted to V. A. Isidorov and I. G. Zenkevich for providing data on the gas chromatographic analysis of urban air by the adsorption method.

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