THE USE OF THE CHROMATOGRAPHIC EQUILIBRATION PROCEDURE FOR AIR POLLUTION STUDIES

DETERMINATION OF MINUTE AMOUNTS OF BENZENE, CHLOROBENZENE, AND NITROBENZENE IN AIR

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INTRODUCTION

Standard procedures for the determination of benzene in the presence of nitrobenzene in air pollution control are based on polarography, while chlorobenzene is usually determined by photometry. In pyridine, acidified with acetic acid, nitrobenzene gives a well-developed reduction wave whose height is proportional to the concentration of nitrobenzene[1–3], whereas chlorobenzene is determined by photometry of the violet complex of 1-chloro-2,4-dinitrobenzene formed in an alkaline solution of the latter in pyridine[4]. The application of gas chromatography for the analysis of air pollutants has been tackled by several authors[5–7] and seems to be one of the most promising techniques. However, the detection limits, particularly for nitrobenzene, are not satisfactory when using gas chromatography directly, due to the very low vapour pressure of this compound.

Concentration of air pollutants prior to their determination by gas chromatography is, therefore, very often unavoidable**. The most frequent concentration techniques are: condensation[8], chromatographic sorption[9], or chromatographic equilibration[10]. The purpose of the present paper is to show the advantages of chromatographic equilibration, as described by NOVÁK, VAŠÁK AND JANÁK[10], for the determination of minute concentrations of benzene, chlorobenzene and nitrobenzene in chlorobenzene and nitrobenzene producing plants.

EXPERIMENTAL

Artificial mixtures of the above air pollutants with air were obtained by using a conventional assembly with vaporizers for obtaining saturated vapour of the individual components and mixing, in a mixing chamber, the appropriate volumes of the saturated vapours so obtained with air. The various mixtures are obtained by

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** U.S. TLV's (Threshold Limit Values) for benzene, chlorobenzene, and nitrobenzene are, respectively, 80, 350, and 5 mg/m³ (see ref. 11).

controlling the flow rates in the respective branches of the sampling assembly (contaminator) (Fig. 1).

Concentration tubes

The design and packing of the concentration tubes were the same as described elsewhere[10]. The concentration tubes were packed with E 301 (30 % w/w) on Celite 545 (30/60 mesh). The tubes were conditioned in the usual manner for several hours at 150°C and, afterwards, stoppered at both ends.

Sampling and desorption

The necessary volumes of artificially polluted air, as demanded by theory, were drawn through the concentration tubes at room temperature, which was carefully measured; the concentration tubes were then disconnected from the sampling assembly and stoppered at both ends.

The desorption was carried out in a special, electrically heated oven, maintained at a controlled temperature, and positioned adjacent to the injection port of the gas chromatographic apparatus.

Gas chromatography of desorbed samples

Gas chromatographic analyses were carried out with a Chrom II apparatus (Laboratory Instruments, Prague), equipped with a flame ionization detector (FID) and specially adapted for the purposes of the present paper; for details see[10].

Specific retention volumes were measured using a glass column 42 cm long, I.D. 7 mm, packed with 6.00 g of E 301 (30 % by weight) on Celite 545 (30/60 mesh) packing material. The temperature of the column was varied from 30°C to 83°C (*cf.* Table I).

The relative molar response of benzene, chlorobenzene, and nitrobenzene was measured using a stainless steel column 85 cm long, I.D. 6 mm, packed with 5 % by weight of E 301 on Chromosorb W (30/60 mesh) at 65°C. The inlet pressure was 0.175 kp/cm², the chart drive 40 mm/min, and the weight of packing material 7.55 g.

Standard solutions were prepared by weighing the appropriate amounts of individual components and solvent. All solutions were stored in well-stoppered flasks in a refrigerator.

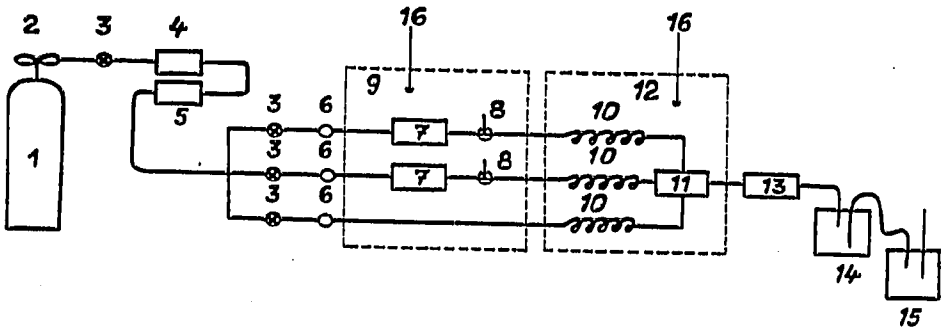


Fig. 1. Contaminator assembly. 1 = Air cylinder; 2 = two-stage reducer; 3 = needle valves; 4 = charcoal filter; 5 = molecular sieve; 6 = pressure gauges; 7 = vaporizers; 8 = stopcocks (T); 9 = thermostatted bath kept at elevated temp.; 10 = cooling coils; 11 = mixing chamber; 12 = cooling bath kept at room temp.; 13 = concentration tube; 14 = volumetric bottle; 15 = levelling bottle; 16 = thermometers.

RESULTS AND DISCUSSION

The main prerequisite of the method used[10] is to achieve equilibrium conditions in the concentration tube. At equilibrium, the concentration of a given component in the gaseous phase, C_G, is equal to the concentration of the same in the sample analysed; this concentration, therefore, can be calculated from $C_G = 273\, m/V_g(T)GT$, where m is the mass of the component trapped in the tube (m can be determined by using a conventional GC procedure), $V_g(T)$ is the specific retention volume of the component as measured on the tube packing at the temperature of sampling, T, and G is the weight of the sorbent liquid. The above relation can be used to calculate the concentration efficiency, as compared with direct injection of sample. The height of the peak of a component, h, can be expressed as

$$h = A \cdot n \cdot v \cdot C_G/V_R \qquad (1)$$

where n is the number of theoretical plates of the chromatographic column, V_R is the retention volume of the component as measured on this column, A is a proportionality constant involving specific features of the instrument and of the substance under analysis, and v is the volume injected.

When using a concentration tube, the amount of substance sorbed in the sorbent liquid is equivalent to its amount contained in its retention volume, and depends upon the tube packing and on the conditions of the determination,

$$V_R = V_g(T)GT/273 \qquad (2)$$

As there is an upper limit, v_{max}, to the volume v directly injected, the ratio

$$v_{max}273/V_g(T)GT \qquad (3)$$

determines the extent to which the actual concentration range amenable to measurements can be decreased when using the equilibration technique as compared with direct injection.

Let us suppose that the maximum injected volume, v_{max}, of the gaseous sample is 10 ml and the weight of sorbent in the concentration tube is about 10^{-1} g. If the specific volume of the component under analysis is about 10^3 ml/g, then the minimum detectable amount of this compound becomes 10^1 times less than on direct injection of the sample. At room temperature and in E 301, the specific retention volume of nitrobenzene is of the order of 10^4 ml/g. Thus, we can increase the sensitivity of determination for nitrobenzene by two orders of magnitude while using an unsophisticated sampling device, and considerably shortening the time necessary for carrying out the actual sampling, because a relatively quick withdrawal of the sample has been proved to be of considerable importance. The volume of nitrobenzene which has to be drawn through the concentration tube is less than about 5 l (with a very fair safety margin for attainment of equilibrium in the tube), which at a flow rate of 5 ml/min represents approximately 17 min or rather less.

The specific retention volumes of benzene, chlorobenzene, and nitrobenzene were measured at several temperatures ranging from 30° to 83°C in order to determine their

temperature dependence. The respective plots were linear, thus making feasible extrapolation to lower temperatures by using equations of the type: $\log V_g(T) = A/T - B$ The data are summarized in Table I.

TABLE I

SPECIFIC RETENTION VOLUMES OF BENZENE, CHLOROBENZENE AND NITROBENZENE AT TEMPERATURES FROM 15°–83°C

E 301 (30% by weight) on Celite 545 (30/60 mesh).
a = Extrapolated values; b = measured values.
Equations for $\log V_g$: benzene, $\log V_g = 1{,}867.4/T - 3.746$; chlorobenzene, $\log V_g = 2{,}291.5/T - 4.434$; nitrobenzene, $\log V_g = 2{,}858.5/T - 5.415$.

t (°C)	T (°K)	$1/T \times 10^3$	V_g (ml/g)		
			C_6H_6	$PhCl$	$PhNO_2$
15	288	3.472	547.1[a]	3,332[a]	32,360[a]
		3.466	533.2	3,228	31,100
16	289	3.460	519.6	3,127	29,990
		3.454	506.4	3,030	28,750
17	290	3.448	493.6	2,936	27,640
		3.442	481.2	2,846	26,580
18	291	3.436	469.1	2,768	25,570
		3.431	457.3	2,674	24,600
19	292	3.425	446.0	2,592	23,660
		3.419	434.9	2,513	22,770
20	293	3.413	424.1	2,437	21,910
		3.407	413.6	2,364	21,090
21	294	3.401	403.4	2,292	20,300
		3.396	393.5	2,224	19,540
22	295	3.390	383.9	2,157	18,810
		3.384	374.6	2,093	18,120
23	296	3.378	365.5	2,031	17,450
		3.373	356.6	1,971	16,810
24	297	3.367	348.0	1,912	16,190
		3.361	339.7	1,856	15,600
25	298	3.356	331.5	1,802	15,030
30	303	3.300	259.3[b]	1,370[b]	—[b]
39	312	3.200	175.5	847	—
40	313	3.195	—	—	5,140
50.5	323.5	3.091	—	—	2,596
51	324	3.086	99.6	423	—
60.5	333.5	2.999	—	—	1,481
63	336	2.976	64.7	237	—
69	342	2.924	—	—	852
77	350	2.857	38.3	132	—
83	356	2.809	—	—	415

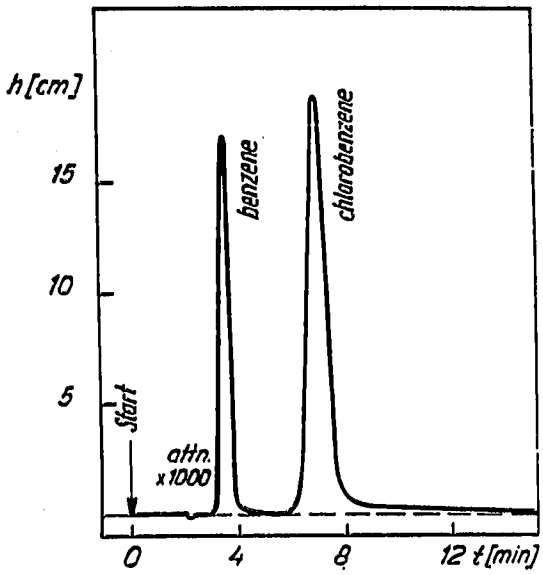
These V_g values were used for the calculation of the concentration, C_G, of the respective pollutants. The mass of the individual compounds was calculated from chromatographic measurements. As the relative molar response of the FID to chlorobenzene and nitrobenzene was not known, it had to be determined. Careful measurements have shown that the relative molar responses for chlorobenzene and nitrobenzene were, respectively, 0.678 and 0.524, when using mesitylene as the reference compound. In other words, the contribution of chlorine and nitro substituents to the total effective carbon number was, respectively, + 0.1 C_{eff} and — 1.3 C_{eff}.

The evaluation of chromatograms obtained for samples of artificially polluted air was performed by the internal standard technique, using a mesitylene standard; in some cases, xylene was used instead. Fig. 2 illustrates a chromatogram obtained for a mixture of benzene and chlorobenzene with air. The concentrations of the compounds were 500 and 450 mg/m³, respectively. The volume of air drawn through the concentration tube was 1.0 l. At a flow rate of approximately 5 ml/sec the sampling lasted approximately 3.5 min. Fig. 3 represents a chromatogram of benzene and nitrobenzene as pollutants, obtained in a similar manner. In this case the concentration of benzene was 400 mg/m³ and that of nitrobenzene 10 mg/m³.

The chromatograms show that the determination of the trace components mentioned can be performed at concentrations which are considerably lower than their TLV's; *e.g.* for a nitrobenzene determination to give fair results, it would be possible to work at concentrations 100 times less than the TLV. This finding prompted an analytical study of the TLV's[12].

As can be seen from Fig. 3, benzene and nitrobenzene can be determined simultaneously in one run; the fact that the content of the more volatile benzene is greater by a factor of 40 does not present any problems. This example shows the main advantage of the equilibration method over other concentration methods. The masses of individual substances become equilibrated and a gas chromatogram of the mixture consists of peaks of comparable areas, which can be evaluated very accurately, since the lower the vapour pressure of the substance under investigation, the larger its partition coefficient and, consequently, the greater the concentration effect. The choice of a non-polar stationary phase eliminated the influence of water vapour present in the usually moist air samples, as the partition coefficient of water, on E 301, is nearly zero.

For the sake of comparison, the chromatogram illustrated in Fig. 4 has been



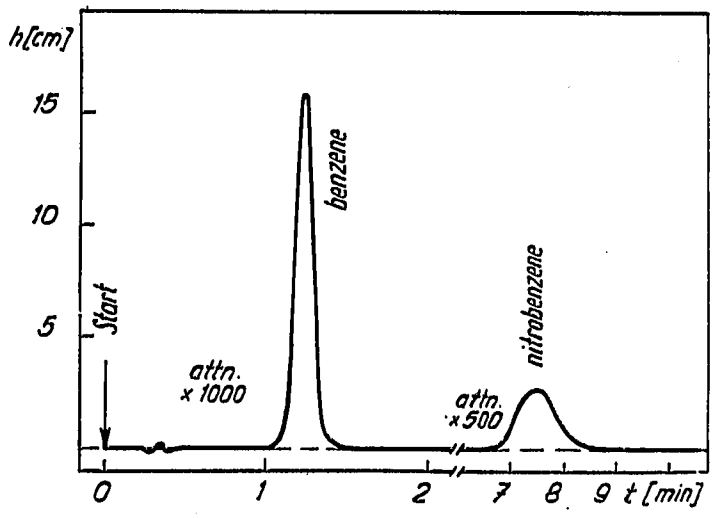


Fig. 2. Determination of chlorobenzene in the presence of benzene. Benzene 500 mg/m³; chlorobenzene 450 mg/m³; FID, E 301 (30% w/w) on Celite 545; concentration tube.

Fig. 3. Determination of nitrobenzene in the presence of benzene. Nitrobenzene 10 mg/m³; benzene 400 mg/m³; FID; E 301 (30% w/w) on Celite 545; concentration tube.

obtained by directly injecting a 5 ml sample taken from the contaminator without previous concentration. The agreement between the concentration expected, *i.e.* as calculated from vapour pressure and dilution data, and a sample equilibrated by the method used, varied within 25 relative %. These variations were due probably to non-equilibrium conditions in the contaminator.

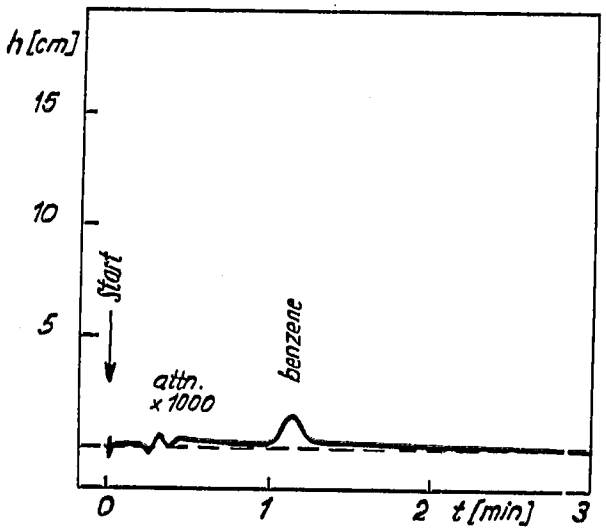


Fig. 4. Determination of benzene and nitrobenzene. Concentrations same as in Fig. 3; direct injection of 5 ml sample from contaminator; other conditions same as in Fig. 3.

Care must be taken also in extrapolating the V_g data. In order to speed up the determinations of V_g, we used, in a preliminary experiment, a column packed with 5 % by weight of E 301 on Chromosorb W (30/60 mesh). Upon comparing the V_g values so obtained with V_g data obtained on a 30 % by weight E 301 on Celite 545 column, it was found that they did not tally. Neither did the use of freshly prepared packing materials for both columns make the V_g values coincide.

The actual amounts of individual components of dilute gaseous mixtures directly withdrawn from the contaminator were calculated from the vapour pressure data taken from literature[13] and summarized, together with the respective concentration data for saturated vapours of pure compounds in Table II.

CONCLUSIONS

The applicability of the chromatographic equilibration technique for air pollution control has been verified for the systems benzene–chlorobenzene, benzene–nitrobenzene, and for a ternary mixture of the three compounds. For field assays, invaluable advantages of the method used, as has already been emphasized, are:

(1) Water does not interfere with the determinations when non-polar phase is used for the concentration-tube packing.

(2) The extent to which individual components are trapped is proportional to their partition coefficients, *i.e.* usually inversely proportional to their volatility. Thus, the least volatile compounds that are present in the atmosphere usually at lowest concentrations, are most efficiently accumulated.

TABLE II

VAPOUR PRESSURES AND CONCENTRATION OF SATURATED VAPOURS OF BENZENE, CHLOROBENZENE AND NITROBENZENE

Temperature		*Benzene*		*Chlorobenzene*		*Nitrobenzene*	
t (°C)	*T* (°K)	$p \times 10^{-2}$ (*atm*)	$g/l \times 10^{-1}$	$p \times 10^{-3}$ (*atm*)	$g/l \times 10^{-2}$	$p \times 10^{-4}$ (*atm*)	$g/l \times 10^{-3}$
15	288	7.734	2.556	9.057	4.314	2.579	1.344
16	289	8.130	2.678	9.626	4.569	2.737	1.421
17	290	8.544	2.805	10.229	4.839	2.908	1.505
18	291	8.974	2.936	10.863	5.121	3.066	1.581
19	292	9.423	3.072	11.534	5.419	3.250	1.670
20	293	9.889	3.213	12.238	5.730	3.447	1.765
21	294	10.374	3.359	12.982	6.057	3.632	1.853
22	295	10.758	3.472	13.766	6.402	3.816	1.941
23	296	11.404	3.668	14.580	6.762	4.026	2.041
24	297	11.950	3.830	15.458	7.140	4.237	2.140
25	298	12.518	3.999	16.371	7.536	4.474	2.252
26	299	13.107	4.173	17.332	7.952	4.658	2.337
27	300	13.719	4.353	18.342	8.388	4.882	2.441
28	301	14.354	4.540	19.404	8.844	5.092	2.538
29	302	15.013	4.733	20.520	9.321	5.316	2.641
30	303	15.780	4.958	21.691	9.821	5.592	2.769

(3) During sampling, care need not be taken of the exact volume drawn through the concentration tube, thus eliminating the use of clumsy-to-operate sampling devices.

(4) The sampling procedure is very versatile and extremely simple, thus rendering the method suitable for field practice. Also the transport of the pocket-size tubular samples is convenient.

(5) The overall time necessary to prepare and analyse samples of benzene in the presence of chloro- or nitrobenzene is about 30 to 40 min as compared with standard procedures, where a complete analysis takes several hours. The equilibration method is therefore of considerable advantage in studying micro-climatic conditions and momentary surges of exhalates.

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SUMMARY

The equilibration technique has been used for the determination of benzene in the presence of nitrobenzene and chlorobenzene.

The advantages of this technique as compared with standard procedures used in air pollution studies, as well as its relative simplicity, make it suitable for routine work.

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