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COMPARISON OF THE DISTRIBUTION CONSTANTS OF BENZENE IN DIFFERENT CHROMATOGRAPHIC SORBENT–GAS SYSTEMS, DETERMINED BY DIRECT MEASUREMENT OF SORPTION EQUILIBRIA AND CALCULATED FROM GAS CHROMATOGRAPHIC RETENTION DATA

JIŘÍ VEJROSTA*, MICHAL ROTH and JOSEF NOVÁK
Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, 61142 Brno (Czechoslovakia)

SUMMARY

The sorbent–gas (nitrogen) distribution constants of benzene on Tenax GC, Porapak Q, P, Apiezon K, QF-1 and Reoplex 400 were determined by direct measurement of sorption equilibria at gas-phase concentrations of benzene ranging from several tens of ppb (10^9) to hundreds of ppm. The concentration limits of the linearity of the sorption isotherms for the individual sorbent–gas systems were estimated, and the limiting distribution constants of benzene, determined by direct measurement of benzene concentrations in the sorbent and in the gaseous phase at concentrations corresponding to linear sections of the isotherms, were compared with the distribution constants calculated from gas chromatographic retention data.

INTRODUCTION

Trapping of trace components of gaseous and/or liquid materials in sorbent-packed traps, followed by the recovery and chromatographic analysis of the concentrate, constitute the most frequently employed steps in trace analysis involving the enrichment of analytes. The actual procedure usually consists in drawing the material to be analyzed through a short column containing a suitable sorbent, in which the components are subject to frontal chromatography. The velocities of migration of the individual frontal zones are given by $u/(1 + k)$ where u and k are the forward velocity of the fluid percolating through the packing of the trap and the capacity ratio of the analyte, respectively. Hence, analytes may be trapped in either a conservation or an equilibration manner, *i.e.*, the drawing of the fluid through the column may be stopped either before the frontal zone of the least strongly sorbed analyte starts to leave the trap or after the zone of the most strongly sorbed analyte has completely broken through. This classification has important analytical implications, as with conservation trapping the proportions of the individual analytes in the trap are identical with those in the original material analyzed, whereas with equilibration trapping the amounts of analytes in the trap are given by $c(V_{Mt} + KW_S)$ where c, V_{Mt}, K and W_S are the concentration of the analyte in the material analyzed, the hold-up volume of the trap, the distribution constant (volume/mass) of the analyte in the given sorbent–

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percolating fluid system and the mass of the sorbent in the trap, respectively. In addition, whereas with conservation trapping it is necessary to measure the volume of the material drawn through the trap in order to obtain absolute quantitative data, with equilibrium trapping this volume need not be known, but it is necessary to know the value of $V_{Mt} + KW_S$. However, with both these alternatives it is necessary to estimate the so-called breakthrough volume.

In the light of these considerations[1–3], it can be shown that the volume of the material to be drawn through the trap, V, should be such that $V \leqslant V_R [1 - (2/\sqrt{N})]$ with conservation trapping and $V \geqslant V_R [1 + (2/\sqrt{N})]$ with equilibration trapping, where N is the number of theoretical plates of the trapping column and $V_R = V_{Mt} + KW_S$. For most practical purposes, a reasonable estimate of the safe sampling volume is within the range $V_R/3$–$V_R/2$ with conservation trapping[3,4] and about $2V_R$ with equilibration trapping[2], and the concentration of the analyte, c, is calculated from $c = W_{it}/V$ and/or $c = W_{it}/V_R$, respectively, W_{it} being the mass of analyte i entrapped.

Owing to the limited capacity of the adsorbent surface, the adsorbent/analyzed material distribution constants and, consequently, the corresponding breakthrough volumes may be practically constant only within certain limits of very low analyte concentrations. Even at such low concentrations, the distribution constants may be drastically influenced by displacement effects of interfering components. Hence, it is often difficult to specify the correct K values, and this is probably why the method of equilibration trapping has not found such a wide application as the currently employed methods of conservation trapping[3–19].

In the first work on quantitative trace analysis involving equilibration trapping[2], use was made of gas–liquid chromatographic (GLC) packings as trapping materials. Dravnieks and Krotoszynski employed open tubes coated with stationary liquids[20] and a stationary liquid-on-Fluoropak 80 packing[21] for equilibration trapping. Janák *et al.*[22] first applied an adsorbent (Tenax GC) to equilibration trapping, having obtained fairly accurate results in the determination of acetone at concentrations of up to about 3 ppm in nitrogen. By virtue of an analysis of the Dubinin–Radushkevich isotherm, Waldman and Vaněček[23] described a universal method for the interpretation of data obtained in equilibration trapping of compounds on microporous adsorbents. A combined procedure was also described[24] for equilibration trapping in a large trap, followed by thermal desorption and conservation trapping of the concentrate in a cooled small trap.

Recently, the effects were shown[25] of the concentration of analyte on the breakthrough volume in trapping volatile organics from air at concentrations ranging from several ppm to hundreds of ppm. However, such high concentrations can easily be determined directly by analysing gaseous samples, and only concentrations below 1 ppm appear to be relevant to analyte enrichment studies. In our work, the sorbent–gas (nitrogen) distribution constants of benzene on Tenax GC, Porapak Q, P, Apiezon K, silicone oil QF-1 and Reoplex 400 were determined by direct measurement of sorption equilibria at gas-phase concentrations of benzene ranging from several tens of ppb (10^9) to hundreds of ppm. An apparatus for the preparation of gaseous mixtures with accurately defined contents of model analytes was employed[26]. The concentration limits of the linearity of the sorption isotherms for the individual sorbent–nitrogen–benzene systems were estimated, and the limiting distribution con-

stants of benzene, corresponding to these linear sections, were compared with distribution constants calculated from gas chromatographic (GC) retention data.

EXPERIMENTAL

Materials

The model solute was benzene, analytical grade (Fluka, Buchs, Switzerland). Tenax GC, 0.175–0.25 mm (Applied Science Labs., State College, PA, U.S.A.), Porapak Q, 0.175–0.31 mm, and P, 0.15–0.175 mm (Waters Assoc., Milford, MA, U.S.A.), were employed as adsorbents. The stationary liquids were: Apiezon K (AEI, Manchester, Great Britain), 9.703% (w/w) on Inerton AW DMCS, 0.125–0.16 mm (Lachema, Brno, Czechoslovakia); silicone oil QF-1 (Carlo Erba, Milan, Italy), 9.764% (w/w) in Inerton AW DMCS; Reoplex 400 (Griffin & George, East Preston, Great Britain), 9.692% (w/w) on Inerton AW DMCS. High-purity nitrogen (Technoplyn, Ostrava, Czechoslovakia) was used as carrier gas.

Measurement of sorption equilibria

Gaseous mixtures with different known concentrations of benzene were drawn through the trap with a known amount of sorbent until equilibrium was attained, whereupon the benzene entrapped was thermally desorbed, purged by a stream of carrier gas into the gas chromatograph and determined by the external standard method. The distribution constants were calculated from $K = (n_t - n_{t,M})/W_S c_g$ where n_t is the total number of moles of benzene entrapped, $n_{t,M}$ is the number of moles of benzene present in the overall (interstices plus connections) dead volume of the trap and c_g is the concentration of benzene in the gaseous phase (number of moles per unit volume). The value of $n_{t,M}$ was approximated as the amount of benzene contained in the empty (without sorbent) trap.

The instrumental set-up (Fig. 1) consisted of a valve system comprising the trap and a pump connected with the gas chromatograph and the apparatus for the

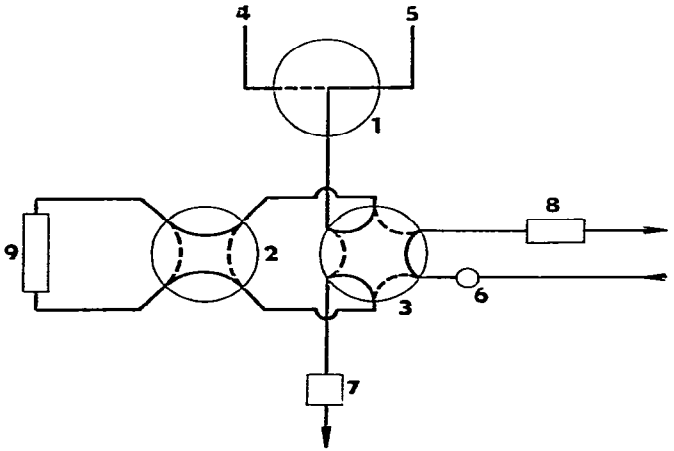
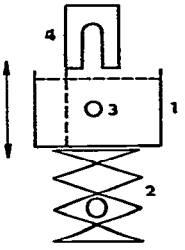


Fig. 1. Flow diagram of the arrangement for the measurement of sorption isotherms. 1 = Three-port valve; 2 = four-port valve; 3 = six-port valve; 4, 5 = inlets for the model gas mixture; 6 = sample-inlet port of the gas chromatograph; 7 = diaphragm pump; 8 = analytical chromatographic column; 9 = trap.

preparation of gaseous model mixtures. Three-port valve 1 is connected by inlets 4 and 5 to the apparatus for the preparation of model gaseous mixtures, the two inlets providing a choice between two mixtures of different concentrations of analyte. In the situation shown in Fig. 1, the carrier gas passes via sample-inlet port 6 of the gas chromatograph directly into analytical column 8, and the model gaseous mixture, entering at position 5, is drawn in by pump 7 via six-port valve 3, two-port valve 2 and trap 9. The arrangement for thermostatting (equilibration) and heating (desorption) of the trap is shown in Fig. 2. Water-bath 1 kept at 35°C is situated on, and heating block 4 is fixed (by a holder of appropriate length) to, lifting jack 2. As soon as equilibrium is reached in the trap (3), the latter is short-circuited by turning valve 2 (Fig. 1), and by suspending the jack the water-bath is moved down while the heating block is set around the trap. After the trap has been brought to the desired temperature, valves 2 and 6 (Fig. 1) are turned and the desorbed concentrate of analyte is swept by the carrier gas into the gas chromatograph. The trap is illustrated in Fig. 3. It is a glass U-tube (1) in which a layer of trapping sorbent (3) is fixed by two quartz wool plugs (2). The ends of the tube are provided with pieces of copper capillary (5) (2 mm O.D.) sealed in by epoxy cement (4); one end of the tube is bent and provided with copper capillary after insertion of the sorbent.



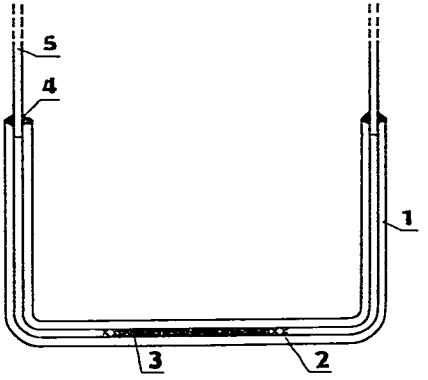


Fig. 2. Arrangement for thermostatting (trapping) and heating (desorption) of the trap. 1 = Thermostatting bath; 2 = lifting jack; 3 = trap; 4 = heater.

Fig. 3. The trap. 1 = Glass tube; 2 = glass-wool plugs; 3 = sorbent; 4 = cement; 5 = copper capillary.

Measurement of chromatographic retention data

A laboratory-made gas chromatograph designed for accurate measurement of specific retention volumes was employed. The chromatographic column was placed in a glass jacket and thermostatted by a water ultrathermostat with a precision of 0.02°C (MLW Prüfgeräte-Werk, Medingen, G.D.R.). The carrier gas flow-rate was controlled by a pressure controller (Porter Instr. Comp., Hatfield, PA, U.S.A.) and a flow controller (Chemoprojekt, Satalice at Prague, Czechoslovakia) connected in series. The excess of pressure and the carrier gas flow-rate were measured at the column inlet by a mercury U-manometer and a differential U-manometer sensing the pressure drop across a capillary, respectively. A flame ionization detector was used. With Tenax GC, Porapak Q and P, the dimensions of the columns and the amounts of the

packings were 280 × 1.8 mm I.D., 230 × 1.5 mm I.D. and 220 × 1.5 mm I.D. and 0.1644, 0.1944 and 0.1256 g, and with Apiezon K, QF-1 and Reoplex 400, 470 × 3.5 mm I.D. columns were employed with 0.3126, 0.2321 and 0.2479 g of the packings, respectively. All the columns were made of glass. The dead retention times were measured by the methane-peak method. With each sorbent, the retention times of benzene were measured at nine different column temperatures between 30 and 95°C, and the corresponding specific retention volumes were calculated as recommended by Desty *et al.*[27].

RESULTS AND DISCUSSION

The distribution constants determined by the direct measurement of sorption equilibria are plotted against log c_g in Figs. 4 (Porapak Q) and 5 (Porapak P and Tenax GC). It can be seen that 1 ppm of benzene in the gaseous phase represents the approximate limit of the linearity of the isotherms. The average values of the distribution constants measured within the linear sections of the isotherms are listed under K_s in Table I. With the liquid sorbents, *i.e.*, Apiezon K, QF-1 and Reoplex 400, the maximum concentrations of benzene in the model gaseous mixtures employed were still within the limits of linearity.

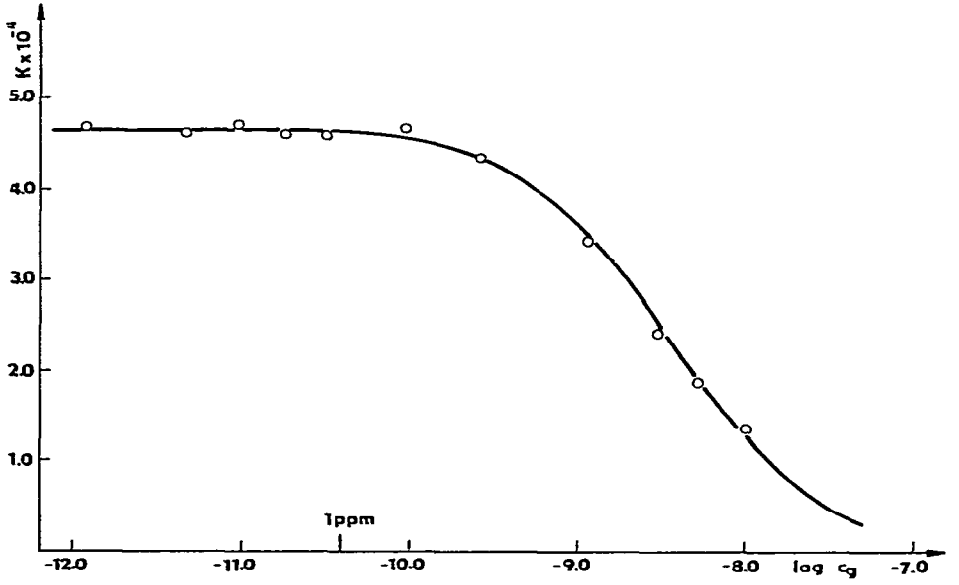


Fig. 4. Dependence of the distribution constant (ml/g) of benzene in the nitrogen–Porapak Q system on the logarithm of the concentration (mole/ml) of benzene in the gaseous phase.

Provided the adsorption of nitrogen can be neglected under the given conditions, the adsorption of benzene from nitrogen–benzene mixtures can advantageously be treated in terms of the Langmuir isotherm[28]. Let the fraction of the sites occupied by adsorbed molecules of analyte be defined as $\alpha = c_s/c_s^*$ where c_s and c_s^* are the actual concentration of analyte in the sorbent and the concentration at which all

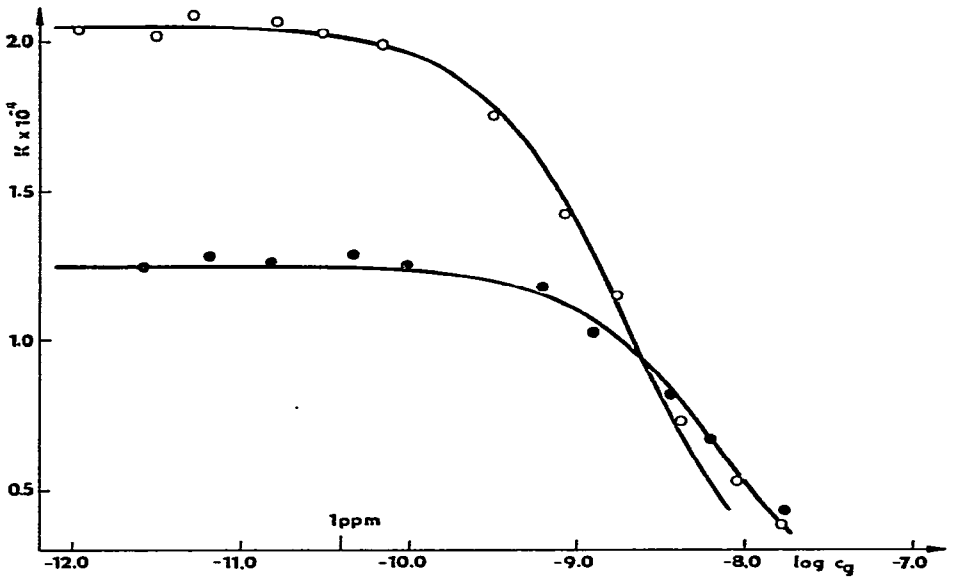


Fig. 5. Dependence of the distribution constant (ml/g) of benzene in the nitrogen–Tenax GC (○) and nitrogen–Porapak P (●) systems on the logarithm of the concentration (mole/ml) of benzene in the gaseous phase.

TABLE I

CHARACTERISTICS OF THE SORPTION ISOTHERMS OF BENZENE

Sorbent	*Linearity limit (ppm)*	K_s *(ml/g)*	K_L *(ml/g)*	K_r *(ml/g)*
Tenax GC	*ca.* 1	20,448.8	20,505.0	20,061.6
Porapak Q	*ca.* 1	46,519.4	46,571.2	46,004.2
Porapak P	*ca.* 1	12,674.2	12,503.8	12,557.3
Apiezon K	>300	324.9	–	329.2
QF-1	>50	151.8	–	149.5
Reoplex 400	>100	347.1	–	344.3

available sites are occupied, respectively. The significance of α is analogous to that of the parameter θ in Langmuir's model. The rates of desorption and sorption are defined as $r_d = k_d \alpha$ and $r_s = k_s(1 - \alpha) c_g$ where k_d and k_s are the respective rate constants. At equilibrium, $r_d = r_s$, and we can write

$$c_s = b c_s^* c_g/(1 + b c_g) \tag{1}$$

where $b = k_s/k_d$. Thus,

$$\frac{c_s}{c_g} = K = \frac{b c_s^*}{1 + b c_g} \tag{2}$$

and:

$$\lim_{c_g \to 0} K = b c_s^* \tag{3}$$

Eqn. 2 can be rearranged as

$$\frac{1}{c_g} = \frac{b c_s^*}{c_s} - b \tag{4}$$

which is a linearized form of the Langmuir isotherm. By plotting $1/c_g$ against $1/c_s$, a straight line of slope

$$\frac{d(1/c_g)}{d(1/c_s)} = b c_s^* = \lim_{c_g \to 0} K \tag{5}$$

should be obtained. The limiting distribution constants determined in this way are listed under K_L in Table I, together with the corresponding values of b. In Figs. 4 and 5, the lines were constructed from K values calculated from eqn. 2 using arbitrarily chosen c_g values, the values of the constants $b c_s^*$ and b being obtained by linear regression analysis of the experimental $1/c_g$ *versus* $1/c_s$ data. There is good agreement between the K_s and K_L values, as well as a fairly close fitting of the experimental data to the Langmuir model within the experimental limits of concentration. With Tenax GC only, the experimental points deviate appreciably from the calculated line at higher concentrations.

The specific retention volumes were treated by linear regression analysis according to the Antoine-type equation $\log V_g^\circ = A + (B/T)$. The constants A and B and specific retention volumes at 35°C are summarized in Table II. With our definition of the distribution constant (amount of solute per gram of sorben/amount of solute per millilitre of gas), K is related to V_g° by

$$K = V_g^\circ \, T/273.15 \tag{6}$$

TABLE II

CONSTANTS OF THE EQN. $\log V_g^\circ = A + (B/T)$ AND THE VALUES OF THE SPECIFIC RETENTION VOLUMES AT 35°C

Sorbent	*A*	*B*	V_g° *(ml/g)*
Apiezon K	−2.592067	1558.35	291.8
QF-1	−3.037330	1589.90	132.5
Reoplex 400	−2.980848	1684.16	305.2
Tenax GC	−6.962881	3455.25	17,783.0
Porapak Q	−5.813332	3212.08	40,779.0
Porapak P	−6.155547	3143.77	11,131.0

where T is the absolute temperature of the chromatographic column. The K values calculated from eqn. 6 are designated K_r in Table I. Again there is a good agreement between K_r and the corresponding values of K_s and K_L.

It can be inferred from the results that, in the absence of compounds showing competitive adsorption, the breakthrough volumes of benzene on Tenax GC, Porapak Q and P are practically independent of benzene concentration in the gaseous phase up to a concentration of about 1 ppm. Within this region, the breakthrough volume as well as the value of $V_{M_l} + KW_S$ can be predicted from GC retention data with fairly good accuracy. However, because of batch-to-batch differences in the properties of a given sorbent and a large error in the estimation of specific retention volumes at lower temperatures due to their extrapolation from those measured at higher temperatures, each individual batch of sorbent should be evaluated by separate measurements in a specified temperature range. For instance, the following data (ml/g) for the V_g° of benzene on Tenax GC at 20°C can be found in literature: 83,368 (ref. 29); 66,641 (this work); 61,538 (ref. 4); 46,446 (ref. 22); *ca.* 40,000 (ref. 18, calculated from a value of 26,000 at 25°C).

Starting from about 10 ppm of benzene in the gaseous phase, there is a sharp decrease of the K value with increasing concentration on all the three adsorbents, whereas with the liquid sorbents the K values are practically independent of concentration even at hundreds of ppm. As is seen from Figs. 4 and 5, simple linear extrapolations from the descending part of the isotherm to K values at 1 ppm or below will lead to serious errors due to the existence of the upper flat section of the isotherm. However, fairly good extrapolations may be obtained by fitting the experimental c_s and c_g data to the equation of a linearized Langmuir isotherm. For the adsorption of different analytes and/or a single analyte at different temperatures, it can be expected that the limits of linearity will shift towards lower c_g values as the limiting K values increase and *vice versa*.

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