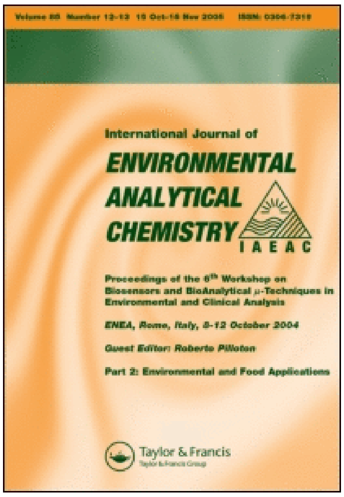

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Investigations of the Influence of Preconcentration Parameters on Sorption Capacity of Solids

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The effect of concentration, for two compounds of very different polarity, on breakthrough volume (BTV), being the measure of sorptive capacity of the examined sorbent bed, has been examined for nine solid sorbents from the porous polymers group. The investigation have been carried out for two flow rates. The effect of granulation (particle size) of sorbent on its sorptive properties has been evaluated for one sorbent as an example. The investigations have been carried out by means of a special apparatus and standard gas mixtures prepared by the permeation method. A simple mathematical equation was employed for extrapolation of the results obtained to very low concentrations of the examined compounds.

KEY WORDS: Solid sorbents, preconcentration of atmospheric pollutants sorption capacity of solids, breakthrough volumes (BTV), standard gaseous mixtures.

INTRODUCTION

The use of adsorption tube samplers for the collection and concentration of trace volatile compounds in air, e.g. air pollutants, contaminants etc., for subsequent detection has been extensively reported and demonstrated.[1-5] A requirement which is necessary for the collection technique to be quantitative is that the volume of sampled air does not exceed the safe sampling volume of an adsorbent for the particular compound being collected. This safe sampling volume, i.e., the adsorbate breakthrough volume (BTV), can be defined as the volume of air containing the adsorbate that may be sampled without the significant amount of adsorbate remaining uncollected. An adsorbate breakthrough volume has been defined as the sampled volume when a certain fraction $f=C_0/C_i \cdot 100\%$ of the inlet adsorbate concentration is detected in the outlet of the sampler.[6] However, it is more realistic to define the adsorbate breakthrough volume (BTV)[7] as the sample volume when a certain fraction of the total collected adsorbate has been allowed to pass through the sampler without collection.

It is usually assumed that the breakthrough of the sorbent bed occurs when the concentration of a compound at the outlet of the trap (C_0) reaches 50%,[18] 10%,[9-11] 5%[12-14] or 1%[15,16] of the concentration at the inlet (C_i) or, alternatively, when C_0 reaches the detection limit for a detector employed.[6,17-20] Typically[21] only ~2% of the compound vapor (adsorbate) has penetrated the sorbent trap at the 10% of breakthrough.

The investigations aiming of determination of BTV are usually comparative character,[5,6,15,22-24] hence it is advisable to express BTV in the units of volume of gas sampled per unit mass of the investigated sorbent.

As expected, the amount of gas and/or vapor sorbed depends on the physical and chemical nature of both the sorbent and sorbate. Unfortunately, no one physical characteristic of the contaminant, or the sorbent has been identified that consistently correlates with adsorption capacity and service life. Thus a dilemma exists, a situation where numerous unknown factors can determine the amount of a particular sorbent needed. Some factors known to be important include:[25]

—rate of flow and flow type (steady state vs cyclic or pulsating, laminar vs turbulent);
—relative humidity of air and water content of sorbent;
—concentration of contaminant;
—temperature;

— physical-chemical properties of the sorbent (surface area, porosity, surface characteristics);
— size of granules and relationship to surface area;
— activity of sorbent;
— capacity of sorbent;
— physical and chemical properties of the gases and vapors (polarizability, dipole moment, quadrupole moment, boiling point, etc.);
— the presence of a number of compounds undergoing adsorption in a competitive manner (coadsorption);
— desorption characteristics;
— void fraction.

GENERAL CONSIDERATIONS

It follows from a recent review[26] that in order to determine the effect of the above discussed parameters on sorptive capacity of the sorbent bed (the measure of it being the breakthrough volume—BTV or corresponding to it breakthrough time—BTT) it is necessary to employ the so-called direct method of determination of BTV. In this case a stream of gas containing a known concentration of a compound or compounds is passed through a tube packed with known amount of a sorbent. The compound is then detected in the effluent from the sorbent trap directly by a FID, FPD, ECD and PID or indirectly by an IR detector (after catalytic oxidation of the compound to the CO_2).[5,6,12,13,15,17-20,27-32] The effect of some of the mentioned parameters on sorptive capacity (BTV) has been discussed in a few papers.[9,25,29,33] For this type of model investigation it is necessary to use suitable standard gas mixtures which can be purchased or self-prepared. Many general reviews[34-36] have appeared in the literature dealing with the preparation and use of calibration standards, hence there is no need to discuss this subject comprehensively. It is only worthwhile to state that the permeation method is particularly suitable for model investigations of the adsorption efficiency of a sorbent bed. Application of this method enables generation of a broad range of concentrations of the measured component as well as generation of multicomponent mixtures.

In the course of the present research, mainly the effect of the concentration of two volatile organic compounds of different polarity such as acetone and *n*-hexane on BTV of 9 solid sorbents from the porous polymers group (Tenax-GC, Chromosorbs and Porapaks) has been determined.

EXPERIMENTAL

Apparatus

The investigations were carried out by means of an apparatus for examination of sorptive capacity of solids described previously.[28] It consists of three basic elements:

— generator of standard gaseous mixtures based on the phenomenon of permeation of a measured component through permeable membrane made of PTFE (Teflon). The generator consists of two-part tightly closed brass housing with a thermostating jacket fed with water from a thermostat. Inside the generator, the permeation tubes are placed, construction and sealing of which are presented[37,38] in Figure 1 or permeation devices described previously.[28,39] It follows from literature data[36,40] that the change in temperature of the PTFE by 1°C results in variation of the permeation rate by ca. 10%. Hence, in order to prepare the mixtures with the accuracy of 1%, excluding other sources of errors, stabilization of temperature to ±0.1°C is necessary. Placing in the generator variable number of permeation tubes or devices the concentration of the measured component can be easily varied.

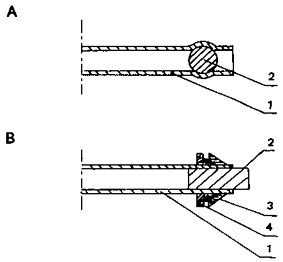

FIGURE 1 Construction and sealing of permeation tubes. (A) 1—PTFE tube; 2—stainless steel ball. (B) 1—PTFE tube; 2—PTFE plug; 3—front ferrule; 4—back ferrule.

It is also evident that changing permeation through the change of membrane surface area and membrane thickness or generator temperature a broad concentration range of the measured component in the diluting gas can be obtained. The stabilization period (T_m), i.e., time necessary to attain a constant permeation rate is determined as described earlier[41] whereas the permeation rate is determined directly by measuring the loss in weight of the permeation tube or permeation device in appropriate time intervals;

— adsorption trap of a controlled and regulated temperature;

— flame-ionization detector with a recorder.

Reagents

Porous polymers used for preconcentration of vapors of volatile organic compounds from a stream of gases were obtained as follows: Tenax-GC (80–100 mesh)—Alltech Assoc. Inc., USA; Chromosorb 101, Chromosorb 103, Chromosorb 105, Chromosorb 107 (80–100 mesh)—Johns-Manville, USA; Porapak R (80–100 mesh)—Alltech Assoc. Inc., USA; Porapaks N (50–80 mesh), (80–100 mesh) and (100–120 mesh), Porapaks Q and T (80–100 mesh)—Waters Assoc. Inc., USA. The method of packing and preparation of a sorbent trap was described previously.[6,28] Volatile organic compounds such as acetone and *n*-hexane used for filling the permeation tubes and permeation devices were of Analytical Reagent grade.

Investigations of the effect of concentration of a preconcentrated compound on breakthrough volume

A stream of nitrogen of known flow rate passed, after purification, through a standard gaseous mixtures generator[28,39] and subsequently through a sorbent bed placed in a trap of special design[20,28] and thermostated at 25 ± 0.1°C and through a gas splitter. A stream of gas of 50 cm^3/min rate was directed continuously to a flame-ionization detector. Sorbent traps were filled with ca. 1.0 g of the studied sorbent which was previously preconditioned.[28] All the investigated sorbents were of 80–100 mesh granulation. The breakthrough was detected by the observation of change in the base-line on a recorder tracing. The breakthrough volumes (BTV in dm^3/g) were determined according to NIOSH[13] recommendations to occur when concentration of the studied component at the outlet from sorbent trap (C_0) reaches 5% of the concentration at the inlet (C_i). Sorbent trap was subsequently heated to 160°C and the concentrated compound was desorbed. After quantitative desorption (base-line on a recorder tracing should reach the same level as before the concentration step) and equilibration at "ambient" temperature (25 ±0.1°C) two additional measurements were carried out for the same conditions (kind of compound concentrated, its concentration and gas flow rate). The obtained three parallel BTV values formed the basis for calculation of average value. The BTV values for 7 various concentrations of acetone (21.2, 42.5, 59.1, 74.7, 131.7, 141.8 and 203.3 ppm v/v) for the flow rate equal to 50 cm^3/min and for 7 concentrations of acetone (10.6, 21.3, 29.6, 37.4, 65.9, 70.9 and 101.6 ppm v/v) for the flow rate equal to 100 cm^3/min were determined in this manner. The 50–100 cm^3/min flow rate range is very often used during preconcentration of various organic compounds from atmosphere.[26] Similar investigations were carried out for *n*-hexane. Breakthrough volumes for 8 various concentrations (13.4, 22.3, 45.1, 83.6, 102.0, 141.1, 302.0 and 494.9 ppm v/v) for 50 cm^3/min flow rate and for the concentrations equal to 6.7, 11.1, 22.6, 41.8, 51.0, 70.6, 151.0 and 247.4 ppm v/v for 100 cm^3/min flow rate were determined.

Investigation of the effect of sorbent granulation on BTV

The investigations were carried out for Porapak N of three various granulations (50–80, 80–100 and 100–120 mesh) for the case of preconcentration of *n*-hexane of various concentrations (13.4, 22.3, 45.1, 83.6, 102.0, 141.1, 302.0 and 494.9 ppm v/v) from the gas stream of 50 cm^3/min flow rate. The procedure was identical to the one described above.

RESULTS AND DISCUSSION

In the course of model investigations, the results of which are presented in this paper, standard gaseous mixtures generated by the permeation method were employed. The advantages of the method, which has gained ever-growing application, need not to be pointed out. Both classical permeation tubes made of Teflon and permeation devices with Teflon membranes described in our previous papers were used for the generation of gaseous mixtures. Common advantage of the employed designs was an ease of change of concentration of the measured component at a given flow rate of gas through the change of temperature of the gaseous mixtures generator. Figure 2 shows an example of a tracing for the recorder obtained during investigations aiming for the determination of stabilization time[28] (T_m) after temperature change of the generator containing permeation devices previously described.[28,39] For the temperature range 20–50°C stabilization time reaches several hours.

After a lapse of time called stabilization time from the moment of temperature change of a generator a new, constant concentration of the measured component in the generated mixture is reached for a very long period of time, since the life-time of the employed

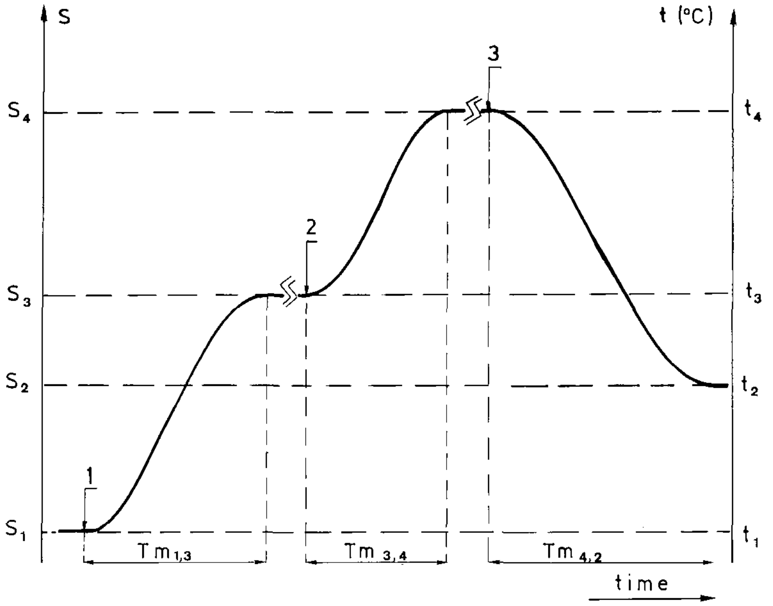

FIGURE 2 Typical experimental recorder output showing stabilization time after a change in standard mixtures generator temperature. 1, 2, 3—a moment of temperature change; T_m—stabilization time.

permeation tubes and devices is of the order of one year for the investigated volatile organic compounds (acetone and *n*-hexane). Naturally, unused filled permeation tubes should be stored at lowered temperature, e.g., in a refrigerator, in order to prolong the life-time.

The effect of concentration of two volatile organic compounds i.e. acetone and *n*-hexane on their breakthrough volume (BTV) for 9 various sorbents from porous polymers group at 25°C for two different gas flow rates (50 and 100 $\mathrm{cm^3/min}$) was examined. The obtained results are depicted in the form of $\mathrm{BTV} = f(C)$ relationship in Figure 3 and Figure 4.

Due to similar shape of the curves representing the dependence $\mathrm{BTV} = f(C)$ for the two employed flow rates (50 and 100 $\mathrm{cm^3/min}$) of the gaseous mixtures containing the compound under study and in order to reduce the volume of this paper, the dependence for the flow rate of 100 $\mathrm{cm^3/min}$ is not depicted here.

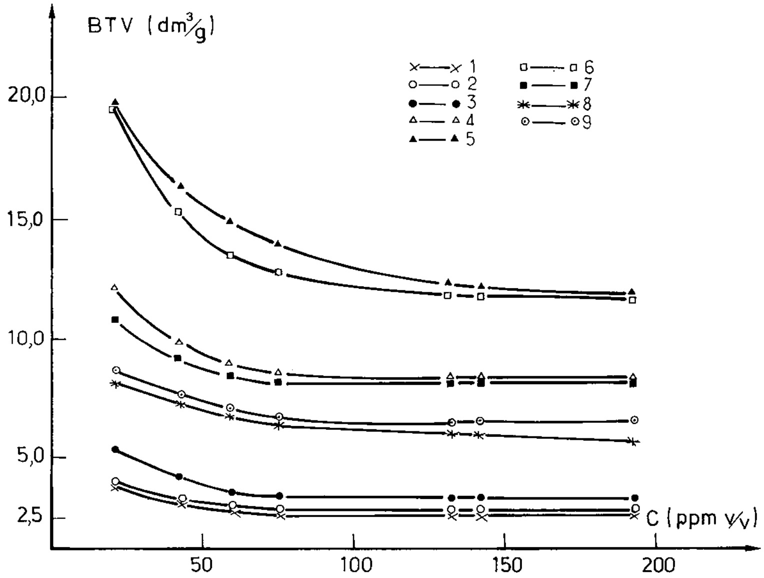

FIGURE 3 The effect of concentration of a preconcentrated compound (acetone) on breakthrough volumes of various sorbents from porous polymers group. Flow rate: 50 $\mathrm{cm^3/min}$. 1—Tenax-GC; 2—Chromosorb 101; 3—Chromosorb 103; 4—Chromosorb 105; 5—Chromosorb 107; 6—Porapak N; 7—Porapak R; 8—Porapak Q; 9—Porapak T.

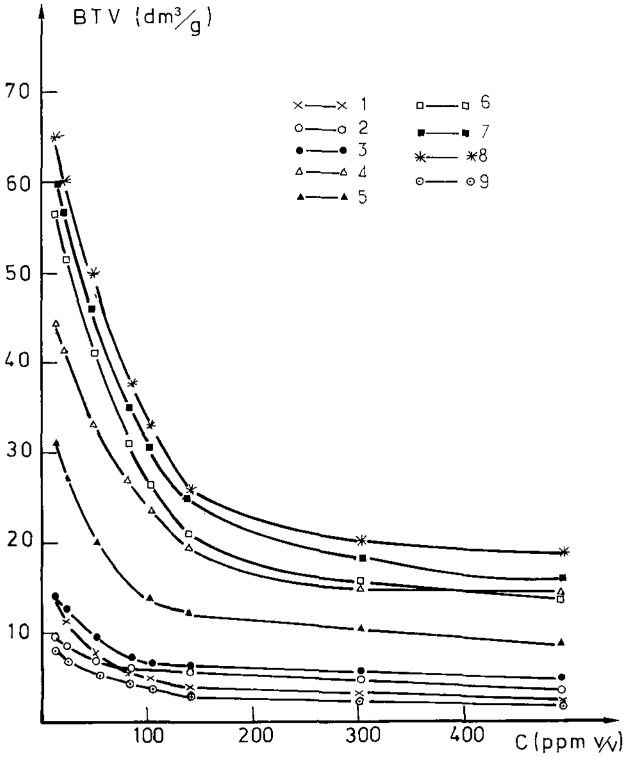

FIGURE 4 The effect of concentration of preconcentrated compound (*n*-hexane) on breakthrough volumes of various sorbents from porous polymers group. Flow rate: 50 cm^3/min. 1—Tenax-GC; 2—Chromosorb 101; 3—Chromosorb 103; 4—Chromosorb 105; 5—Chromosorb 107; 6—Porapak N; 7—Porapak R; 8—Porapak Q; 9—Porapak T.

These compounds differ very much in solvent strength polarity, which is equal to 0.01 and 0.56 for *n*-hexane and acetone, respectively (according to the table published in a catalogue of Alltech Assoc. Inc.[42]). Besides, acetone often serves as an exemplary, volatile organic compound in model investigations of the effect of various parameters on breakthrough volume.[6,30] In case of acetone, the examined sorbents can be divided into three groups (Figure 3):

—sorbents of relatively low BTV (Tenax-GC, Chromosorb 101, Chromosorb 103);

- sorbents of intermediate BTV (Chromosorb 105, Porapaks R, Q and T). For both these groups the dependence of BTV value on concentration is relatively small;
- sorbents of relatively high BTV (Chromosorb 107 and Porapak N). In this case the concentration of acetone influences significantly the BTV values. For all the investigated sorbents at the flow rate of 50 cm^3/min and at the acetone concentration higher than 75 ppm v/v the BTV values practically do not depend on concentration, while at 100 cm^3/min the BTV values are practically independent on acetone concentration starting from concentrations on the order of 40–50 ppm v/v. Some of the examined sorbents were previously employed[6] for much broader concentrations range. It can be emphasized that for the same concentration level they are arranged in the same order as far as BTV values are concerned.

In the case of preconcentration of standard mixtures containing *n*-hexane the investigated sorbents can be divided into two groups (Figure 4):

- sorbents of relatively low BTV values (Tenax-GC, Chromosorbs 101 and 103, Porapak T);
- sorbents of relatively high breakthrough volume (Chromosorb 105 and 107, Porapaks N, R and Q). In comparison with the course of the $BTV = f(C)$ curves for standard mixtures containing acetone, the effect of *n*-hexane concentration on BTV values is much more pronounced. For 50 cm^3/min flow rate the BTV values are practically independent on *n*-hexane concentration starting from 120–130 ppm v/v. For the second applied flow rate (100 cm^3/min) the BTV values are practically independent on *n*-hexane concentration starting from 80–90 ppm v/v.

In practice, the concentrations of the preconcentrated organic compounds are usually considerably lower (ppb, fractions of ppm) than the concentrations used in model investigations. The primary limitations are in this case the difficulties in generation of mixtures of very low concentration of the measured component, despite the existence of a wide variety of methods and techniques[36] and the detection limit of the detectors employed. The application of a direct method of BTV determination is sensible only when the concentration of a measured component of standard mixture is higher than the detection limit of a detector employed. Because of this, the possibility of relating the results of evaluation of sorptive capacity carried out at the relatively high concentrations to the situation when the concentration of this compound is much smaller is of high interest. An equation presenting the dependence of BTV on concentration giving the possibility of extrapolation can be employed for this purpose. It has the following form:[23,43]

$$\mathrm{BTV} = -K \log C + B \qquad (1)$$

where: K and B are constants.

All the group of results of BTV determination that formed the basis for plotting the curves depicted in Figures 3 and 4 were extrapolated to the concentration of the measured component equal to 1.0 ppm v/v which is close to realistic conditions. The $\mathrm{BTV}_{1.0\,\mathrm{ppm}}$ values obtained in this manner, as well as the constants from Eq. (1) and the correlation coefficients (r) are listed in Table I.

In the second part of the presented research, the effect of sorbent granulation on breakthrough volume has been evaluated. The obtained results are presented in the form of BTV$=f(C)$ relationship in Figure 5. Due to too large spread of particle sizes of the particular

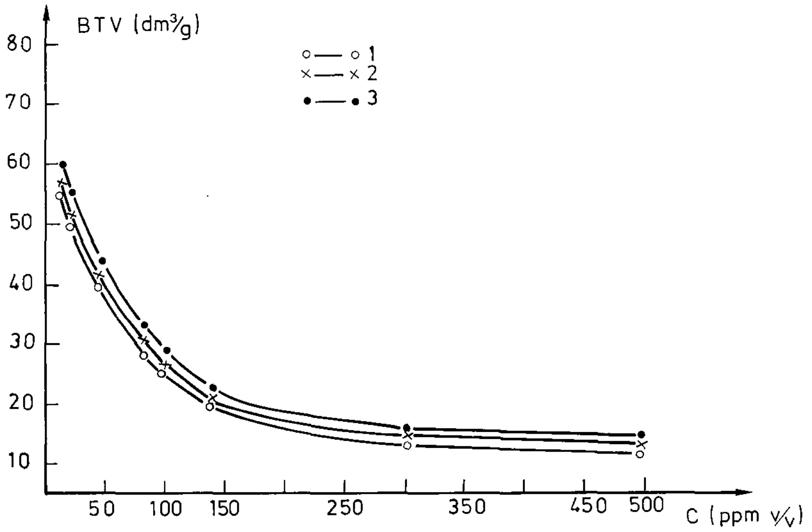

FIGURE 5 The effect of granulation of a sorbent. Porapak N on breakthrough volumes of the preconcentrated compound (n-hexane). Flow rate: 50 cm^3/min. 1—50–80 mesh; 2—80–100 mesh; 3—100–120 mesh.

TABLE I

The results of extrapolation of the obtained BTV values to the 1.0 ppm v/v concentration.

50 cm^3/min	$BTV_{1.0\,ppm}$		K		B		r	
Sorbent 100 cm^3/min	Acetone	*n*-hexane	Acetone	*n*-hexane	Acetone	*n*-hexane	Acetone	*n*-hexane
Tenax-GC	5.10	19.59	1.17	6.81	5.10	19.59	0.934	0.959
	4.83	27.45	1.05	10.60	4.83	27.45	0.970	0.988
Chromosorb 101	5.53	12.96	1.27	3.42	5.53	12.96	0.942	0.983
	5.01	28.44	1.01	10.47	5.01	28.44	0.976	0.990
Chromosorb 103	7.76	19.61	2.10	5.88	7.76	19.61	0.920	0.956
	7.59	31.43	1.76	11.38	7.59	31.43	0.970	0.988
Chromosorb 105	16.05	66.85	3.63	20.71	16.05	66.85	0.892	0.983
	19.53	60.59	4.97	20.06	19.53	60.59	0.990	0.986
Chromosorb 107	29.64	44.91	8.04	14.38	29.64	44.91	0.978	0.968
	33.87	40.53	10.16	12.43	33.87	40.53	0.990	0.984
Porapak N	29.20	89.08	8.13	29.62	29.20	89.08	0.936	0.983
	24.58	78.07	5.87	26.04	24.58	78.07	0.960	0.985
Porapak R	13.57	94.54	2.62	30.59	13.57	94.54	0.880	0.987
	15.08	85.06	2.80	28.45	15.08	85.06	0.988	0.985
Porapak Q	11.32	101.15	2.50	32.52	11.32	101.15	0.979	0.980
	11.28	93.13	2.52	30.67	11.28	93.13	0.992	0.982
Porapak T	14.96	11.87	4.31	3.89	14.96	11.87	0.863	0.981
	11.84	15.71	1.79	5.84	11.84	15.71	0.995	0.979

types of a commercial sorbent Porapak N (50–80, 80–100, 100–120 mesh) and unknown percent fraction of the particular granulations, plotting of the relationship BTV $= f$(mesh) for a given, constant concentration of a preconcentrated compound (n-hexane) was impossible. Only comparison of the course of curves BTV $= f(C)$ for three ranges of particle sizes was possible; this is illustrated in Figure 5. It can be stated that the smaller the particle size of a sorbent, the higher the BTV. This seems quite obvious, because maintaining constant geometrical parameters of the sorbent bed in a sorbent trap, the decrease in grains diameter results in better packing, hence in the decrease of void volume and lengthening the way of preconcentrated compound molecules in the sorbent bed which results in an increase of probability of adsorption.

FINAL REMARKS

The problem of selection of an optimum sorbent for preconcentration of organic air pollutants is gaining an ever-growing importance. In addition to "classical" sorbents such as charcoal, silica gel and alumina more and more new sorbents, mainly from the porous polymers group, are being used for the purpose. Through a judicious selection of a suitable sorbent not only a high enrichment factor but also a relatively high degree of selectivity, already at the preconcentration step, can be obtained. With this ever-growing number of sorbents, the problem of their proper arrangement with respect to sorptive capacity (breakthrough volume—BTV) towards various types of organic compounds present in the investigated atmosphere is gaining importance. Hence, comparative model investigations are necessary before the selected sorbent is used for preconcentration of definite atmospheric components *in situ*.

References

1. P. Ciccioli, G. Bertoni, E. Brancaleoni, R. Fratarcangeli and F. Bruner, *J. Chromatogr.* **126,** 757 (1976).
2. B. Versino, M. De Groot and F. Geiss, *Chromatographia* **7,** 302 (1974).
3. B. Miller, P. O. Kane, D. B. Robinson and P. J. Whittingham, *Analyst* **103,** 1165 (1978).
4. K. Andersson, J. O. Levin and C. A. Nilsson, *Chemosphere* **12,** 377 (1983).
5. L. W. Severs and L. K. Skory, *Am. Ind. Hyg. Assoc. J.* **36,** 669 (1975).
6. J. Namieśnik, L. Torres, E. Kozłowski and J. Mathieu, *J. Chromatogr.* **208,** 239 (1981).

7. G. I. Senum, *Environ. Sci. Technol.* **15,** 1073 (1981).
8. K. J. Krost, E. D. Pellizzari, S. G. Walburn and S. A. Hubbard, *Anal. Chem.* **54,** 810 (1982).
9. J. P. Guenier and J. Muller, Ber. Int. Kolloq. *Verheutung Arbeitsunfaellen Berufskr. Chem. Ind.*, 8th, 1982, p. 355.
10. G. O. Nelson and Ch. A. Harder, *Am. Ind. Hyg. Assoc. J.* **37,** 205 (1976).
11. N. W. Henry III and R. S. Wilhelme, *Am. Ind. Hyg. Assoc. J.* **40,** 101 (1979).
12. R. A. Glaser and W. J. Woodfin, *Am. Ind. Hyg. Assoc. J.* **42,** 18 (1981).
13. D. R. Hemenway, B. J. Fitzgerald and T. Paret, *Am. Ind. Hyg. Assoc. J.* **43,** 686 (1982).
14. K. W. Boyd, M. B. Emory and H. K. Dillon, *ACS Symp. Ser.* **149,** 49 (1981).
15. J. W. Russell, *Environ. Sci. Technol.* **9,** 1175 (1975).
16. E. B. Sansone, Y. B. Tewari and L. A. Jonas, *Environ. Sci. Technol.* **13,** 1511 (1979).
17. J. Namieśnik and E. Kozłowski, *Chem. Anal.* **25,** 301 (1980).
18. B. E. Wilkes, L. J. Pristley and L. K. Scholl, *Microchem. J.* **27,** 420 (1982).
19. L. Torres, M. Frikha, J. Mathieu, M. L. Riba and J. Namieśnik, *Int. J. Environ. Anal. Chem.* **13,** 155 (1983).
20. J. Namieśnik and E. Kozłowski, *Chem. Anal.* **25,** 999 (1980).
21. G. O. Nelson and A. N. Correia, *Am. Ind. Hyg. Assoc. J.* **37,** 514 (1976).
22. S. Seshadri and J. W. Bozzelli, *Chemosphere* **12,** 809 (1983).
23. G. Bertoni, F. Bruner, A. Liberti and C. Perrino, *J. Chromatogr.* **203,** 263 (1981).
24. K. Andersson, J. O. Levin and C. A. Nilsson, *Chemosphere* **12,** 821 (1983).
25. E. S. Moyer, *Am. Ind. Hyg. Assoc. J.* **44,** 46 (1983).
26. J. Namieśnik, *Talanta* (in preparation).
27. S. Van Tassel, N. Amalfitano and R. S. Narang, *Anal. Chem.* **53,** 2130 (1981).
28. J. Namieśnik, L. Torres and J. Mathieu, *Sci. Total Environ.* **39,** 281 (1984).
29. R. G. Melcher, R. R. Langer and R. O. Kagel, *Am. Ind. Hyg. Assoc. J.* **39,** 349 (1978).
30. R. H. Brown and C. J. Purnell, *J. Chromatogr.* **178,** 79 (1979).
31. V. Patzelowa, M. Wurst and V. Catska, *J. Chromatogr.* **190,** 137 (1980).
32. A. T. Saalwaechter, C. S. McCammon, C. P. Roper and K. S. Carlberg, *Am. Ind. Hyg. Assoc. J.* **39,** 476 (1978).
33. J. P. Guenier and J. Muller, *Cah. Notes Doc.* **103,** 197 (1981).
34. R. S. Barratt, *Analyst* **106,** 817 (1981).
35. K. Leichnitz, *Pure Appl. Chem.* **55,** 1239 (1983).
36. J. Namieśnik, *J. Chromatogr.* **300,** 79 (1984).
37. A. E. O'Keeffe and G. C. Ortman, *Anal. Chem.* **38,** 760 (1966).
38. B. E. Saltzman, W. R. Burg and G. Ramaswamy, *Environ. Sci. Technol.* **5,** 1121 (1971).
39. J. Namieśnik, *Chromatographia* **17,** 47 (1983).
40. D. P. Lucero, *Anal. Chem.* **43,** 1744 (1971).
41. L. Torres, J. Mathieu, M. Frikha and J. Namieśnik, *Chromatographia* **14,** 712 (1981).
42. Chromatography, catalog nr. 60, Alltech Assoc., Inc., USA, 1984.
43. J. Namieśnik, E. Kozłowski, L. Torres and J. Mathieu, Proc. VIth World Congress on Air Quality, 1983, Vol. 1, p. 377.