Activated Silicone Rubber as a Sorbent for Solid Phase Extraction of Volatiles from Aqueous Solutions

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Thermally activated polysiloxane resin (silicone rubber) was used as a solid sorbent for direct solid phase extraction of volatiles from aqueous solution prior to GC—MS analysis. Proposed silicone rubber extraction technique (SRE) was compared with widely used and accepted Tenax dynamic head-space preconcentration. SRE provided comparable response for analyzed mixture of aliphatic alcohols and aldehydes (C_4—C_8). Significantly lower response was observed for the studied mixture of aromatic compounds. Shorter time of analysis and higher sensitivity towards less volatile aliphatic compounds were the main advantages of the procedure involving SRE over head-space preconcentration technique.

The determination of volatile organic compounds in complex sample matrices is a fundamental analytical problem widely studied and discussed in the literature. Gas chromatography with prior concentrating step seems to be the most useful combination applied. The choice of suitable preconcentration procedure is usually the most crucial step determining the reliability of obtained results. It is out of scope of this contribution to mention all published papers dealing with the development and application of preconcentration techniques. Excellent reviews covering current trends in this field could be found in the literature [1—3]. Virtually all current protocols involve extraction and preconcentration with organic solvent or solid phase extraction. Liquid-liquid extraction techniques currently in use mostly rely on distillation process and suffer from low recovery for even moderately volatile compounds. The utilization of supercritical fluids greatly reduces this problem. Supercritical fluid extraction methods were successfully applied to the analyses of high volatile and thermally labile solutes [4—6]. The collection and preconcentration of volatiles on solid sorbents could be accomplished in head-space mode [7], when analyzed volatiles are adsorbed from gaseous phase, or as a direct extraction from liquid phase (solid phase extraction) [8, 9]. The decisive factor determining the quality of the method is the choice of suitable sorbent ensuring high recovery, low structurally dependent selectivity and low affinity towards used solvents. Although it is not possible to fulfil all these requirements at the same time, several satisfactory compromises were found among chromatographic sorbents. Charcoal is traditionally used for both direct extraction and head-space procedures [10, 11]. Different porous polymers have been successfully used as sorbents, including Chromosorb [12, 13], Porapak [14, 15], and Ambesorb XE-340

[16]. Tenax-GC [17—19] and Tenax-TA [20] are, at present, the most popular sorbents used for the purposes of preconcentration of the volatiles.

The aim of this paper is to study the properties of thermally treated polymeric polysiloxane resin (silicone rubber) used as a solid sorbent for direct extraction of volatiles from aqueous solution and to compare obtained results with commonly used Tenax head-space (THS) preconcentration technique.

EXPERIMENTAL

1-Butanol (99 %), 1-pentanol (99 %), 1-hexanol (98 %), 1-heptanol (98 %), 1-octanol (99 %), butanal (99 %), pentanal (99 %), hexanal (99 %), heptanal (95 %), octanal (99 %), aniline (99 %), benzyl alcohol (99 %), benzylamine (99 %), p-cresol (99 %), phenol (99 %), acetonitrile and methanol (99.9 % HPLC grade) were purchased from Aldrich (Milwaukee, Wisconsin, USA). 1 M-HCl and 1 M-NaOH were purchased from Fisher Scientific (Fair Lawn, New Jersey, USA).

Tenax-GC (poly(2,6-diphenyl-p-phenylene oxide)) was purchased from Alltech (Avondale, PA, USA) and extracted twice with methanol and dried in vacuum oven (150 °C) overnight before use.

Test mixture I (aliphatic alcohols and aldehydes C_4—C_8) and test mixture II (aromatic compounds — aniline, benzyl alcohol, p-cresol, and phenol) were prepared by dissolving the corresponding compounds in distilled water to desired concentration 5×10^{-5} mol dm^{-3}. All other test solutions used in experiments were prepared by mixing and diluting of 10^{-3} M aqueous stock solutions of corresponding compounds. The pH of the solutions was, when required, adjusted with 1 M-HCl or 1 M-NaOH.

The measurements were carried out with HP 5710A gas chromatograph connected with HP 5980A dodecapole mass spectrometer (Hewlett—Packard, Palo Alto, California, USA). Used capillary column was fused silica nitrophenyl column 50 m × 200 μm i.d. (Lee Scientific, Salt Lake City, Utah, USA).

Preparation of Silicone Rubber Absorber

The membrane used for making the absorber was dimethylvinylsilicone polymer sheet (ASTM : VMQ Dow Corning) with thickness of 0.25 mm. The circles (2 mm diameter), cut from this material with cork borer, were slipped on 100 mm long tungsten wire to obtain configuration given in Fig. 1a. Prepared absorber was carefully washed with acetonitrile, methanol and baked in oven (200 °C) overnight under the inert helium atmosphere.
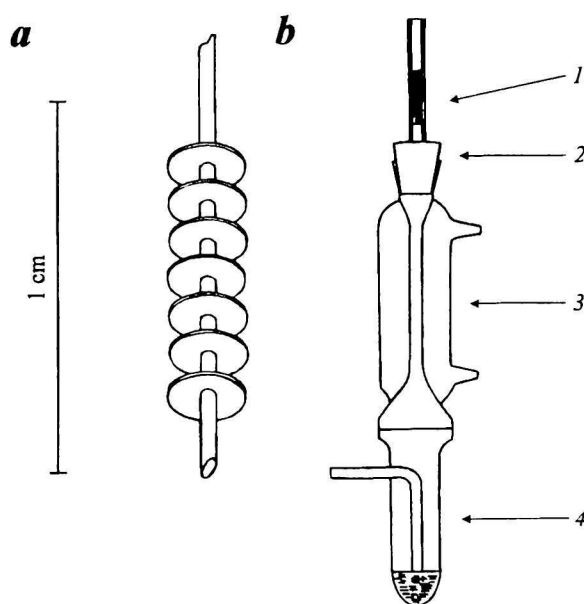

Fig. 1. a) Silicone rubber absorber. b) Tenax head-space glassware. 1. Sampling precolumn; 2. teflon stopper; 3. condenser; 4. sampling vessel.

To obtain maximum sorption capacity of silicone rubber towards analyzed compounds the following activation step proved to be important: the temperature of the oven was decreased to 100 °C and after equilibration the stream of helium was replaced by oxygen. After 1 h the absorber was removed and the free end of tungsten wire was pushed through the septum of injection port end cup.

Although the structural changes of silicone rubber during activation step were not studied, we may presume that oxidative destruction of silicone rubber increases substantially its surface. It possibly leads to sandwich type of sorbent structure with partially oxidized, highly disordered surface layer on intact polymer bead.

Silicone Rubber Extraction Sampling Procedure

The head of the silicone rubber absorber was immersed into the small flask with 2 cm³ aliquot of analyzed sample. To avoid the formation of bubbles on the surface of polymer the solution was stirred with magnetic stirrer during the extraction. After 10 min the absorber was removed from the solution, washed with distilled water, and dried in the stream of nitrogen for 30 s.
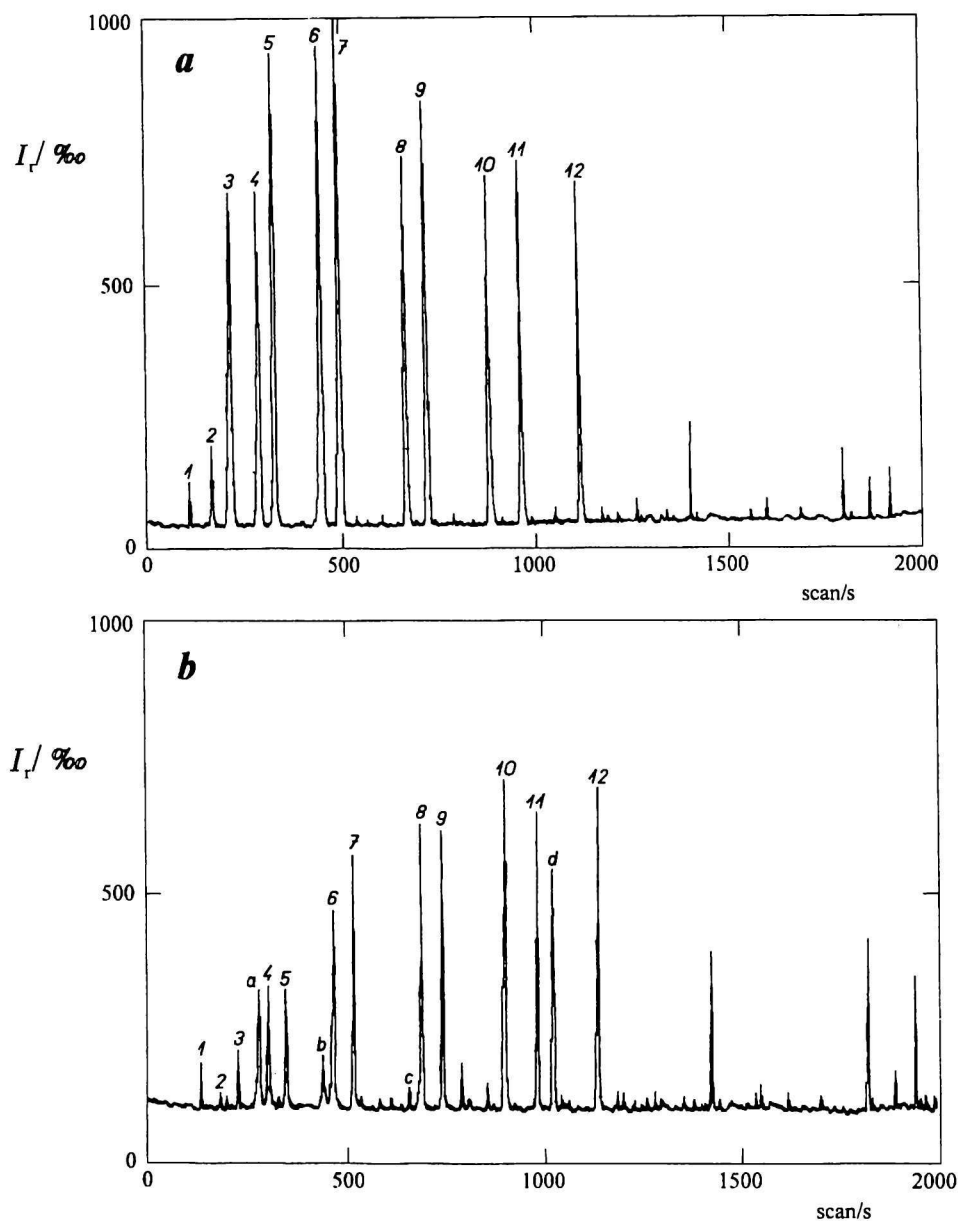
Tenax Head-Space Sampling Procedure

The samples were preconcentrated on Tenax-GC sampling precolumns using glassware shown in Fig. 1b. 2 cm³ aliquot of the sample was placed in the sampling vessel. Purified helium gas was passed through the sample at a flow rate of 80 cm³ min⁻¹. The volatiles swept from the sample were transported into quartz sampling precolumn (3 mm i.d.) packed with 4 mg of Tenax-GC. Cooling water was circulated through the condenser in order to remove some moisture from the gas stream. After 45 min the precolumn was removed from the teflon stopper.

Gas Chromatography—Mass Spectrometry

The procedure is identical for both studied sampling techniques. Either Tenax precolumn or silicone rubber absorber were inserted into the injection port of a gas chromatograph equilibrated to the temperature 250 °C. By capping the injection port and initiating carrier gas flow (He, p_0 = 0.207 MPa), thermally desorbed volatiles were transported onto the analytical column, where they were immediately cryogenically trapped in a w-shaped bend at the front of the column, which was immersed in liquid nitrogen. Chromatography was initiated after 10 min of desorption by removal of the liquid nitrogen flask. Used oven temperature gradient was 4 °C min⁻¹ (30—160 °C). The mass spectrometer was operated in the total ion mode (mass range 35—300 m/z; scan time 1 s) using standard electron impact energy 70 eV.

RESULTS AND DISCUSSION

As shown in Fig. 2 there is a significant quantitative, rather than qualitative difference in the appearance of chromatograms of analyzed mixture I (aliphatic alcohols and aldehydes C_4—C_8) obtained after conventional Tenax head-space (THS) procedure and silicone rubber extraction (SRE). As it was expected, THS procedure, based on dynamic equilibria between gaseous and liquid phase, provides more abundant peaks for low-molecular volatile compounds. With increasing boiling temperature of analyzed com-

Fig. 2. Chromatograms of the analyzed model mixture I (aliphatic alcohols and aldehydes C_4—C_8). a) Tenax head-space procedure; b) silicone rubber extraction. ·1. Carbon dioxide; 2. acetone; 3. butanal; 4. butanol; 5. pentanal; 6. pentanol; 7. hexanal; 8. hexanol; 9. heptanal; 10. heptanol; 11. octanal; 12. octanol; a — hexamethylcyclotrisiloxane; b — octamethylcyclotetrasiloxane; c — decamethylcyclopentasiloxane; d — trimethylsilyl ester of 3-[(trimethylsilyl)oxy]benzoic acid.

pounds the peaks tend to be less significant. Because of lower molar response of mass spectrometer towards low-molecular mass components of the studied mixture such trend is doubtlessly even more prominent than it appears on chromatogram 2a.

SRE procedure is less altered by the volatility of analyzed compounds and tends to suppress peaks of lower molecular mass components (chromatogram 2b). The amount of the compound transferred to polymeric silicone rubber matrix seems to increase with increasing length of the aliphatic chain. Since the mechanism of sorption has not been studied, both hydrophobicity and steric effects should be considered as important factors.
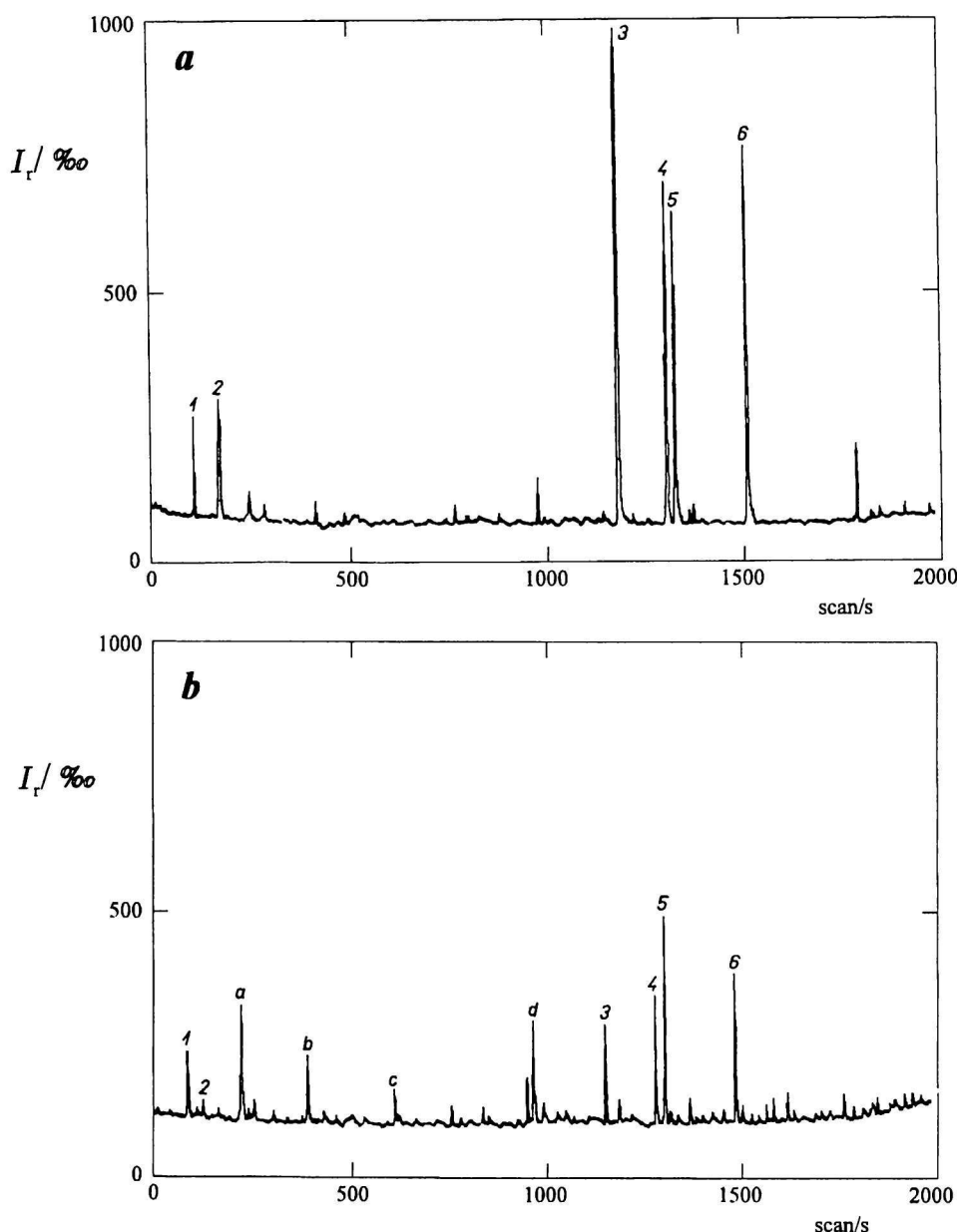
Peaks of carbon dioxide and acetone represent the background common for both used techniques. Peaks a—d on chromatogram 2b, have their origin in thermal degradation of silicone rubber and form the background peaks characteristic only of SRE procedure. Cyclic siloxanes (peaks a—c) are known to be formed by direct thermal cleavage of polysiloxane matrix. Silylated benzoic acid derivative (peak d) arises probably from thermally desorbed and partially degraded residue of plasticizers. The peak area of all three cyclic siloxanes remains almost the same throughout the measurements. While maintaining constant time of desorption, relative standard deviation of peak area does not exceed 3 % for ten con-

Table 1. Reproducibility of the Measurements of Siloxane Background and Octanol Peak Areas

Peak	Number of measurements	Peak area average/a.u.	Relative standard deviation/%
		Blank	
A	8	63481	2.6
B	8	27112	1.7
C	8	6294	2.9
	Extracted 5×10^{-5} M octanol		
A	8	55623	5.4
B	8	22261	6.1
C	8	4671	6.3
Octanol	8	167218	7.8

sequential blank measurements (Table 1). Slightly lower peak areas with higher dispersity were observed during the measurements with absorbed octanol, probably due to lower thermal exposure of the silicone matrix during desorption step. Relative standard deviation of the peak areas of octanol does not exceed 8 %. As the content of plasticizers in thermally exposed silicone rubber decreases, the peak d diminishes and finally completely disappears from the spectrum of detected compounds.

Chromatograms of test mixture II (aromatic compounds) analyzed by using Tenax head-space procedure and SRE are shown in Fig. 3a and 3b. The

Fig. 3. Chromatograms of the model mixture II (aromatic compounds). a) Tenax head-space procedure; b) silicone rubber extraction. 1. Carbon dioxide; 2. acetone; 3. aniline; 4. phenol; 5. benzyl alcohol; 6. p-cresol; a — hexamethylcyclotrisiloxane; b — octamethylcyclotetrasiloxane; c — decamethylcyclopentasiloxane; d — trimethylsilyl ester of 3-[(trimethylsilyl)oxy]benzoic acid.
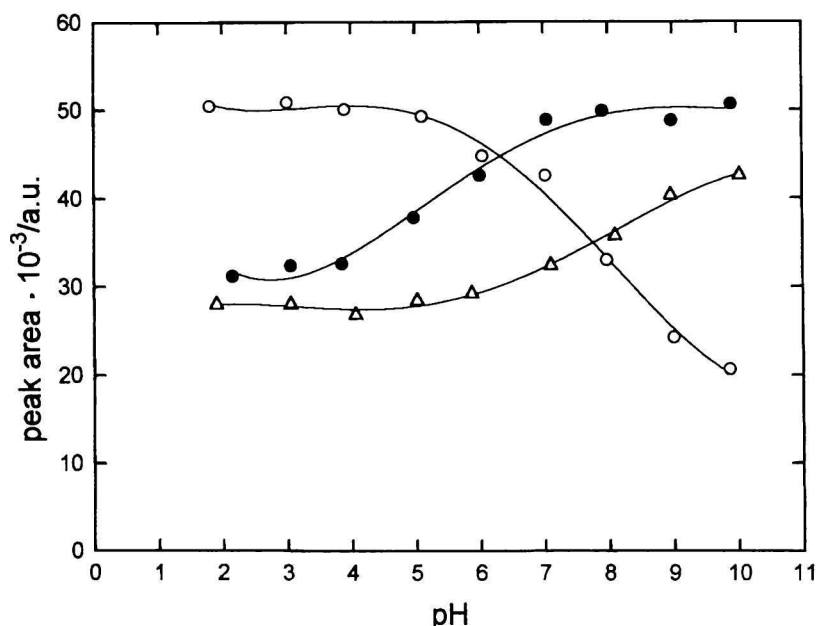
Fig. 4. Silicone rubber extraction technique — the dependence of peak area of some acidic and basic aromatic compounds on pH of analyzed solution. ○ 5×10^{-5} M phenol; ● 5×10^{-5} M aniline; △ 5×10^{-5} M benzylamine.
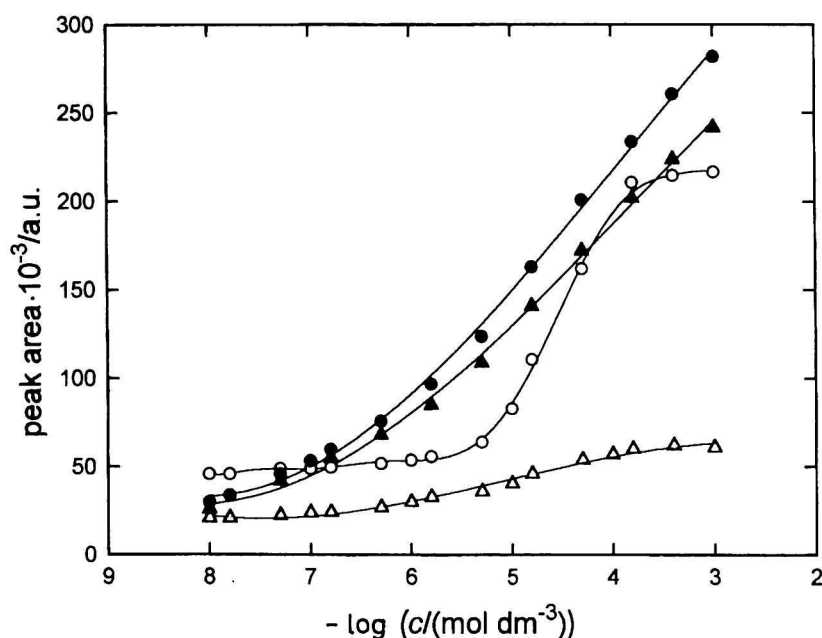

Fig. 5. Calibration curves for octanol and phenol. △ Phenol (silicone rubber extraction); ▲ phenol (Tenax head-space); ○ octanol (silicone rubber extraction); ● octanol (Tenax head-space).

difference between the appearance of both chromatograms is even more striking than in the previously discussed example. Lower affinity of the silicone rubber towards aromatic compounds resulting in less abundant spectrum of peaks may be hypothetically explained by lower accessibility of highly disordered silicone rubber surface with micro cavities and channels for more voluminous molecules. Another important factor may be the presence of charged groups. The dependence of the peak area of phenol, aniline, and benzylamine on pH of the

solution extracted with silicone rubber is shown in Fig. 4. The peak area of slightly acidic phenol significantly decreases with increasing pH value whereas the peaks of basic aniline and benzylamine become more abundant. Such experimental observation supports the idea of lower affinity of hydrophobic polysiloxane matrix towards charged molecules.

Calibration curves for octanol and phenol in the concentration range 10^{-8}—10^{-3} mol dm^{-3} are shown in Fig. 5. SRE of octanol provides well developed
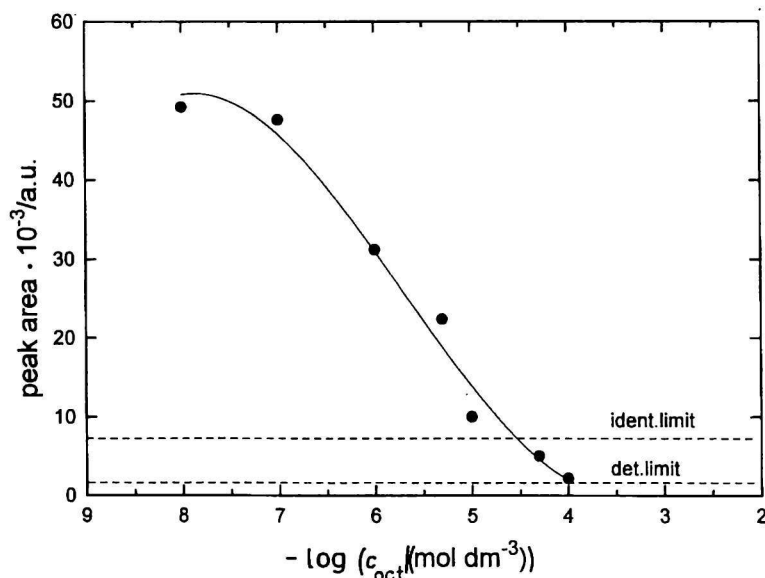
Fig. 6. Silicone rubber extraction technique — the dependence of phenol peak area on the increasing concentration of octanol in 5×10^{-5} M phenol solution.

S-shape curve with characteristic low and high concentration plateau (curve O). Such a nonlinear behaviour in wide concentration range with low response slope at the values 10^{-8} to 10^{-5} mol dm^{-3} was expected. Rather curious is relatively high peak area value for the lowest measured concentrations. This fact confirms strong tendency of silicone rubber to bind and preconcentrate highly diluted hydrophobic compounds.

The slope of the calibration curve in the concentration range 5×10^{-6}—10^{-4} mol dm^{-3} is even higher than that obtained with THS procedure (curve ●). For the concentrations of octanol higher than 10^{-4} mol dm^{-3} the state of saturation is quickly achieved and the slope rapidly decreases.

There is a striking difference between the calibration curves of phenol obtained by using THS and SRE procedures. The second one provides only flat calibration curve with significantly lower slope in the studied concentration range (curve △). Hence, less satisfactory results of the quantitative analysis with higher dispersity should be expected for aromatic compounds.

Easily achieved state of saturation of the silicone rubber and observed differences in affinity towards structurally different compounds may reflect negatively on the accuracy of the measurements. Peak ratios not corresponding to the composition of the sample mixture or even disappearance of some components from observed chromatograms should be expected for unsuitably chosen experimental conditions of the extraction leading to the state of saturation. As shown in Fig. 6 increasing amount of octanol in the two-component octanol—phenol mixture may, in fact, cause phenol peak to disappear from re-

corded chromatogram. For the concentrations of octanol higher than 5×10^{-5} mol dm^{-3}, phenol is not recognized correctly by the standard computer library search procedure. For concentrations higher than 10^{-4} mol dm^{-3} phenol peak completely disappears in the background signal.

CONCLUSION

Main observed advantages of SRE procedure over commonly used THS preconcentration techniques are summarized in the following items:

1. Shorter time of analysis. Complete optimized SRE lasts only about 15 min in comparison with 30—60 min required for THS.

2. Method does not require high-purity helium. The quality of used helium is critical for THS. Trace impurities adsorbed from carrier gas on Tenax may completely distort the analysis.

3. Higher sensitivity towards less volatile aliphatic compounds. Conventional THS does not, in fact, utilize the possibilities of thermally stable gas chromatographic columns capable to analyze less volatile compounds with high boiling temperature.

4. Standard split-splitless GC injection port may be used without any modifications.

Lower sensitivity towards aromatic compounds is probably the main disadvantage of the analysis involving SRE, substantially restricting its possible application area.

The quality of the results obtained with SRE procedure is dependent on various experimental parameters. It should be noted that each extractor has its individual characteristics given by the quality of used

silicone rubber, number and thickness of plates, and geometry of the whole arrangement. The response of each extractor should be tested on model mixture before practical measurements. The arrangement used in our experiments provides reasonable analytical response for a wide range of compounds in a relatively short extraction and desorption time and should be considered as optimal. The use of thicker silicone rubber plates increases the time required for complete thermal desorption without any significant increase in binding capacity. Substantial differences in sensitivity and selectivity were observed for different types and even batches of tested silicone rubber.

The reproducibility of extraction procedure is extremely important for comparative measurements. Gas bubbles which may occasionally appear on the silicone rubber membrane in insufficiently stirred solution change the active surface and substantially decrease the reproducibility of obtained quantitative results.

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