SEPARATION AND DETERMINATION OF SOME AROMATIC SULFONES BY REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

Josef KRALOVSKY[a], Marta KALHOUSOVA[b] and Petr SLOSAR[c]

[a] *Department of Analytical Chemistry, University of Chemical Technology, 532 10 Pardubice, The Czech Republic*
[b] *Synthesia – East Bohemia Chemical Works, 532 17 Pardubice-Semtin, The Czech Republic*
[c] *Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitvi, The Czech Republic*

Received April 5, 1993
Accepted July 24, 1993

The reversed-phase high-performance liquid chromatography of some selected, industrially important aromatic sulfones has been investigated. The chromatographic behaviour of three groups of aromatic sulfones has been studied. The optimum conditions of separation and UV spectra of the sulfones and some of their hydroxy and benzyloxy derivatives are presented. The dependences of capacity factors vs methanol content in mobile phase are mentioned. The results obtained have been applied to the quantitative analysis of different technical-grade samples and isomer mixtures. For all the separation methods mentioned the concentration ranges of linear calibration curves have been determined.

Various methods have been proposed for the analysis of aromatic sulfones and their derivatives such as volumetry[1] and polarography[2,3]. From among separation methods the most frequently adopted are the thin-layer chromatography[4 – 6] and gas-liquid chromatography[7 – 11].

The high-performance liquid chromatography (HPLC) was used in medicine for analysis of dapsone – an antileprotic and antimalarial medicament. The separation of dapsone (4,4′-diaminodiphenyl sulfone) from its metabolites was performed on columns packed with silica gel[12 – 14].

HPLC analyses of aromatic sulfones in mixtures with aromatic sulfonic acids have not been described yet, although aromatic sulfones are known to be by-products in sulfonations of aromatic hydrocarbons. Naphthalene sulfonic acids ($C_{10}H_7SO_3H$) are important intermediates in the production of synthetic dyes. The formation of dinaphthyl sulfones as possible by-products of sulfonation of naphthalene is known to consist in secondary reactions of naphthalene sulfonic acid.

$$C_{10}H_7SO_3H + C_{10}H_8 \xrightarrow{-H_2O} (C_{10}H_7)_2SO_2$$

$$2\,C_{10}H_7SO_3H \xrightarrow{-H_2SO_4} (C_{10}H_7)_2SO_2$$

The reaction course, amount and ratio of dinaphthyl sulfone isomers depend upon the sulfonation conditions.

Hydroxy derivatives of diphenyl sulfone are intermediates in syntheses of some important colour components in photochemistry.

Diaryl sulfones Ar_2SO_2 can also be found as by-products of syntheses of arenesulfonyl chlorides due to subsequent reaction of sulfonyl chloride with aromatic hydrocarbon.

$$ArH + 2\,HOSO_2Cl \longrightarrow ArSO_2Cl + H_2SO_4 + HCl$$

$$ArSO_2Cl + ArH \longrightarrow Ar_2SO_2 + HCl$$

The present paper describes in detail the separation of the following diaryl sulfones $Ar–SO_2–Ar'$:

I, Ar = Ar′ = 1-naphthyl
IIa, Ar = 1-naphthyl; Ar′ = 2-naphthyl
IIb, Ar = Ar′ = 2-naphthyl
IIc, Ar = phenyl; Ar′ = 2-naphthyl
IId, Ar = 4-methylphenyl; Ar′ = 2-naphthyl
IIe, Ar = 2-methylphenyl; Ar′ = 2-naphthyl
IIf, Ar = 2,5-dimethylphenyl; Ar′ = 2-naphthyl
IIIa, Ar = Ar′ = phenyl
IIIb, Ar = Ar′ = 4-hydroxyphenyl
IIIc, Ar = 2-hydroxyphenyl; Ar′ = 4-hydroxyphenyl
IIId, Ar = 4-hydroxyphenyl; Ar′ = 4-benzyloxyphenyl.

EXPERIMENTAL

The analyses were carried out on the HPLC systems HP 1090 M equipped with diode-array detector and ChemStation HP 9000 Model 310 and Varian 5020 with a UV-50 photometric detector. The col-

umn of 150 mm length and 3 mm i.d. was packed with Separon SGX C 18, 5 μm grain size. The methanol–water mobile phase was used at a flow rate of 0.5 ml min^{-1}. All the sulfones were synthesized in the Research Institute of Organic Syntheses where also their structure and purity were checked with the help of NMR spectrometry[15].

RESULTS AND DISCUSSION

An isocratic separation of the dinaphthyl sulfone isomers and their UV spectra are shown in Figs 1*a*, 1*b*. As it can be seen, the retention times of the isomers increase in the order: 1,1′ < 1,2′ < 2,2′.

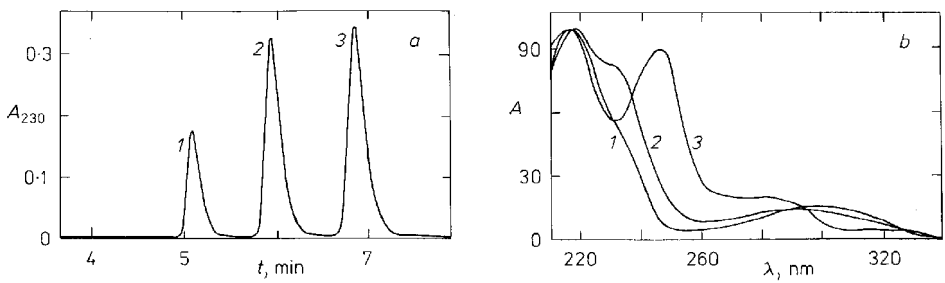

FIG. 1
Separation (*a*) and UV spectra (*b*) of dinaphthyl sulfones: mobile phase methanol–water (80 : 20 v/v), UV detection (230 nm); curves and peaks: *1 I*, *2 IIa*, *3 IIb*

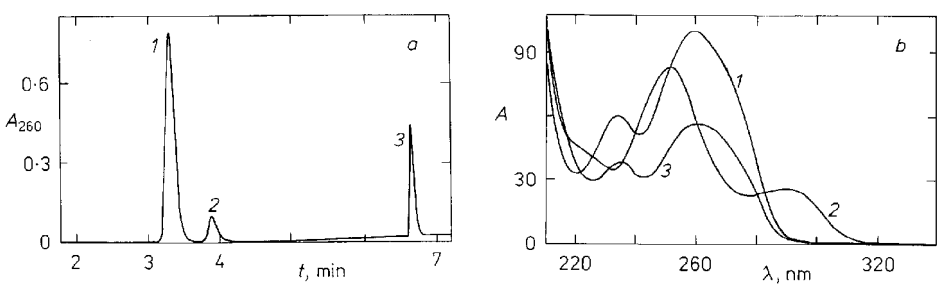

FIG. 2
Separation (*a*) and UV spectra (*b*) of hydroxydiphenyl sulfones: mobile phase methanol–water, gradient program: 50 vol.% methanol isocratically for 2 min and then from 50 to 100 vol.% methanol linearly during 3 min; UV detection (260 nm); curves and peaks: *1 IIIb*, *2 IIIc*, *3 IIId*

All the three dinaphthyl sulfones were detected in samples of crude 2-naphthalenesulfonate before hydrolysis. On the other hand, no dinaphthyl sulfones were found in samples taken from the production of 1,3,6-naphthalenetrisulfonic acid where the sulfonation of naphthalene is carried out at different conditions (higher temperature and stronger oleum).

In the analyses of technical samples the aromatic sulfonic acids (being highly polar) are eluted nonseparated in a short time. At the above-mentioned conditions of chromatographic separation, the residual unreacted naphthalene present in the samples remains trapped in the column and must be removed after several analyses. The individual separated dinaphthyl sulfones were determined by the method of calibration curve. The calibration curves are linear in the required interval of dinaphthyl sulfone concentrations, the detection limit being 5 μg ml^{-1}.

The separation of hydroxy and benzyloxy derivatives of diphenyl sulfone using the gradient elution and the corresponding spectra are shown in Figs 2*a*, 2*b*. The lower polarity and higher molecular weight of the benzyloxy derivative significantly increase its retention time. 4,4′-Dihydroxydiphenyl sulfone is an intermediate in the production of 4-benzyloxy-4′-hydroxydiphenyl sulfone where the presence of the 2,4′-dihydroxy isomer is undesirable. Therefore the separation and determination of the individual dihydroxydiphenyl sulfones is of considerable practical importance.

Figure 3 presents the chromatogram of a mixture of diphenyl sulfone, phenyl-, methylphenyl-, and dimethylphenyl-2-naphthyl sulfones. The 2-naphthyl derivatives were synthesized by the reaction of 2-naphthalenesulfonyl chloride with benzene, toluene, and *p*-xylene, respectively, in the presence of anhydrous ferric chloride[15]. The above-mentioned separation method was applied to quantitative analysis, the detection limits being 5 μg ml^{-1} for all the sulfones.

4-Methylphenyl-2-naphthyl sulfone contains the 2-methyl isomer as an impurity which was separated by decreasing the elution strength of the mobile phase, identified by its UV spectrum (Figs 4*a*, 4*b*), and verified by NMR spectrometry.

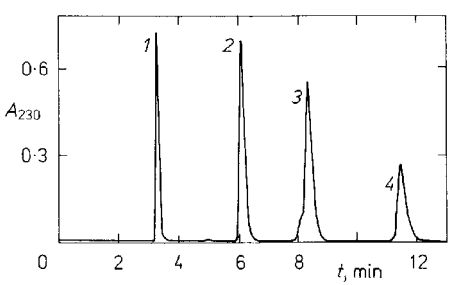

FIG. 3
Separation of diaryl sulfones: mobile phase methanol–water (70 : 30 v/v); UV detection (230 nm); peaks: *1 IIIa*, *2 IIc*, *3 IId*, *4 IIf*

The dependences of capacity ratios (k) vs methanol content in mobile phase are linear in all the cases (Fig. 5).

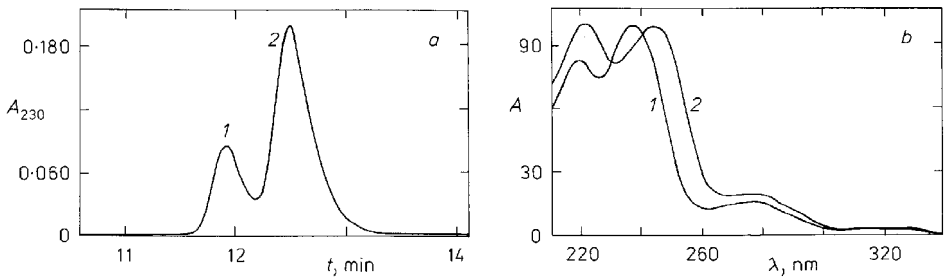

FIG. 4
Separation (*a*) and UV spectra (*b*) of methylphenyl-2-naphthyl sulfone isomers: mobile phase methanol–water (62 : 38 v/v); UV detection (230 nm); curves and peaks: *1 IIe*, *2 IId*

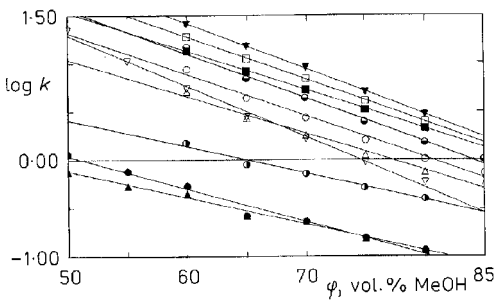

FIG. 5
Dependence of capacity ratio (k) of aromatic sulfones vs methanol content (vol.%) in methanol–water mobile phase: ■ *I*, ❐ *IIa*, ▼ *IIb*, Δ *IIc*, ❍ *IId*, ❍ *IIf*, ❍ *IIIa*, ▲ *IIIb*, ● *IIIc*, ∇ *IIId*

REFERENCES

1. Ganapathy K., Ramanujam M.: J. Indian Chem. Soc. *60*, 511 (1983).
2. Cox J. A., Przyjazny A.: Anal. Lett. *10*, 1131 (1977).
3. Filimonova M. M., Gorbunova V. E., Durneva V. F.: Zh. Anal. Khim. *33*, 1829 (1978).
4. Schogl K., Mohar A.: Monatsh. Chem. *93*, 861 (1962).
5. Cheung A. P., Lim P.: J. Pharm. Sci. *66*, 1723 (1977).
6. Sighal R. K., Kumar S., Grover R., Joshi B. C.: Acta Scienc. Indica *4*, 122 (1978).
7. Krasuska E., Celler W.: Chem. Anal. (Warsaw) *23*, 371 (1978).

8. Przyjazny A., Staszewski R., Cox J. A.: Chem. Anal. (Warsaw) *26*, 147 (1981).
9. Lindstrom K., Schubert R.: J. High Resolut. Chromatogr., Chromatogr. Commun. *7*, 68 (1984).
10. Ventre E. R.: J. Chromatogr. *333*, 253 (1985).
11. Wilkins J. P. G., Hill A. R. C., Lee D. F.: Analyst *110*, 1045 (1985).
12. Murray J. F., Gordon G. R., Culedge C. C., Peters J. H.: J. Chromatogr. *107*, 67 (1975).
13. Gordon G. R., Peters J. H.: J. Chromatogr. *47*, 269 (1970).
14. Jones C. R., Ovenell S. M.: J. Chromatogr. *163*, 179 (1979).
15. Slosar P., Hojer J., Snobl D.: Czech. 230 942; Chem. Abstr. *106*, 4693 (1987).

Translation revised by J. Panchartek.