Journal of Chromatography, 331 (1985) 321–330
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17 849

TRACE ANALYSIS OF AMINES AND ISOCYANATES USING GLASS CAPILLARY GAS CHROMATOGRAPHY AND SELECTIVE DETECTION

IV. DETERMINATION OF FREE AROMATIC AMINES USING NITROGEN-SELECTIVE DETECTION

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(Received April 25th, 1985)

SUMMARY

A method for trace analysis of free aromatic amines of special interest in relation to the rubber industry is presented. It involves separation of the amines by high temperature glass capillary gas chromatography on an OV-73 stationary phase, using on-column injection and nitrogen-selective detection. The necessary inertness of the column was achieved by deactivation with octamethylcyclotetrasiloxane. Linear calibration plots were obtained over the range 50–1600 pg and detection limits in the range 10–20 pg.

INTRODUCTION

Several papers dealing with the gas chromatographic (GC) analysis of amines were previously presented from these laboratories. In most of the methods developed, the amines were converted into the corresponding perfluoro fatty acid amides before packed or glass capillary column GC analysis[1–4]. However, the analysis of the amines themselves by packed column GC was also successful[5,6]. In the present paper, the possibilities for assay of trace free aromatic amines by glass capillary GC and nitrogen-selective detection are examined in some detail.

Few attempts have been made to apply glass capillary GC to the assay of trace free amines. This is undoubtedly due to the tendency of these compounds to become adsorbed in the analytical system, which is related *inter alia* to the basicity of the amines and to the number of hydrogen atoms bonded to nitrogen. Hence, it is generally more difficult to chromatograph aliphatic than aromatic amines and the adsorption tendency is in the order primary > secondary > tertiary amines. Accord-

0021-9673/85/$03.30

ingly, aromatic and tertiary aliphatic amines should be best suited to separation by capillary column GC.

Trace analysis for these kinds of amines is of interest in many fields. Per example, they are employed in the rubber industry as antioxidants and antiozonants[7] and as components in epoxy and polyurethane polymers[8]. Since most of them are poisonous and several are carcinogenic, it is important to be able to assay low concentrations of them. The amines studied in this paper are mainly used in the rubber industry (see Table I). They include 15 aromatic mono- and diamines containing either free or alkylated or arylated amino groups. Compounds 1–4 can appear as

TABLE I

LIST OF AMINES INVESTIGATED

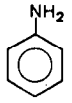
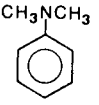
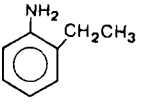
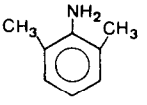
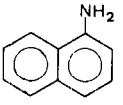
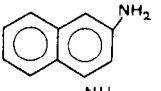
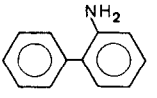
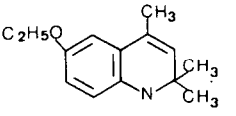
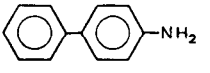
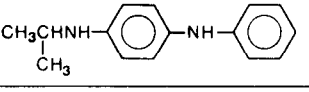
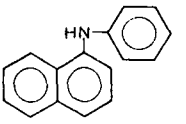
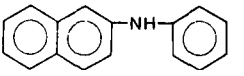
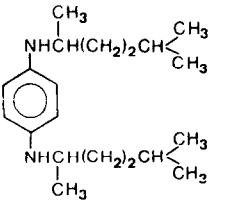
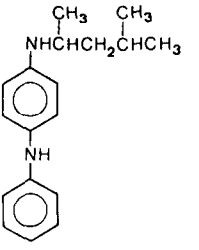
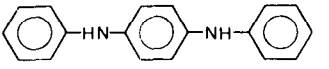
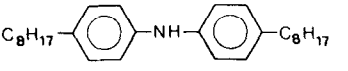
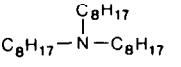
No.	*Amine*	*Formula*
1	Aniline CA No. 62-53-3*	
2	N,N-dimethylaniline CA No. 121-69-7	
3	2-Ethylaniline CA No. 578-54-1	
4	2,6-Dimethylaniline CA No. 87-62-7	
5	1-Naphthylamine CA No. 134-32-7	
6	2-Naphthylamine CA No. 91-59-8	
7	2-Aminobiphenyl CA No. 90-41-5	
8	6-Ethoxy-1,2-dihydro-2,2,4-trimethylquinoline ETMQ CA No. 91-53-2	
9	4-Aminobiphenyl CA No. 92-67-1	
10	4-Isopropylaminophenyl(phenyl)amine IPPD CA No. 60457-56-9	

TABLE I (*continued*)

No.	*Amine*	*Formula*
11	1-Phenylaminonaphthalene (PAN) CA No. 90-30-2	
12	2-Phenylaminonaphthalene (PBN) CA No. 135-88-6	
13	1,4-Bis(1,4-dimethylpentylamino)benzene 77PD CA No. 42738-31-8	
14	4-(1,3-Dimethylbutylamino)phenyl(phenyl)amine 6PPD CA No. 793-24-8	
15	4-Phenylaminophenyl(phenyl)amine DPPD CA No. 74-31-7	
16	Bis(4-octylphenyl)amine OCD CA No. 28929-90-0	
17	Trioctylamine CA No. 1116-80-9	

* CA = Chemical Abstracts Registry Number.

contaminants in the other aromatic amines. Quinoline and trioctylamine are also included.

A review of the chromatographic analysis of this kind of amines has recently been published by Vimalasiri *et al.*[9]. From this review and our own literature search it appears that, although packed column GC has frequently been used, glass capillary GC has not hitherto been applied to the trace assay of free antioxidant amines of the kinds used in the rubber industry.

Previous attempts to separate free amines on glass capillary columns nearly all involved aromatic amines and, to our knowledge, none in the low pg range. In 1971

Franken *et al.*[10], in a quantitative study, separated mixtures of aromatic amines and pyridines by gas–solid chromatography using glass capillaries coated with graphitized carbon black and with cobalt phthalocyanine as stationary phase; flame ionization detection (FID) was used. Glass capillaries with graphitized carbon black were also employed by Goretti *et al.*[11] for the separation of aromatic amines; in this instance; however, the stationary phase was polyethylene glycol (PEG) made alkaline by the addition of potassium hydroxide. As before, detection was accomplished by FID.

Alkaline PEG seems to be the most often used stationary phase for the assay of aromatic amines and related nitrogen compounds by glass capillary GC. Thus, this phase was utilized by Tesařík and Ghyczy[12] for the separation of methylanilines and methylpyridines in coal-tar light oil with FID, and by Olufsen[13], Becher[14] and Becher *et al.*[15] for the determination of airborne aromatic amines. In the last cases, monitoring was achieved with nitrogen-selective detection (NPD), which made possible a decrease in the detection limits: *ca.* 600 pg with a signal-to-noise ratio of 2; linear relationships were observed between 2 and 250 ng. A disadvantage of the alkaline PEG phase is its tendency to deteriorate at temperatures slightly above 200°C with consequent bleeding of the phase. This makes this and similar phases useless for high temperature GC of free amines.

Recently, a GC method for the assay of aniline and halogen and nitrogen derivatives of aniline in waste water was presented by Riggin *et al.*[16]. They employed commercial SE-54 glass and SE-30 fused-silica capillary columns and NPD. The detection limits were in the range 40–2000 pg and linear calibration curves were obtained between 2 and 50 ng. We are not aware of any other reports dealing with the GC of trace amines on commercial glass or fused-silica capillary columns and our own experiences with such columns are not favourable. It might be that the low basicity of the amines studied by Riggin *et al.*, caused by the presence of halogen atoms and nitro groups in the aromatic ring, makes them more easy to chromatograph than the kinds of aromatic amines discussed in this paper. Fused-silica columns should be less suited to GC of trace amines because of the acidic properties of these columns[17].

An interesting report dealing with the separation of amines and other nitrogen compounds on glass capillary columns with stationary phases polymerized *in situ* was published by Blomberg *et al.*[17]. The columns, AR-glass or fused silica, were silanized using octamethylcyclotetrasiloxane and trifluoropropyl(methyl) cyclosiloxane and coated with various phases (SE-30, SE-52, SE-54, OV-215) which were cured with dicumyl peroxide. On separation of test mixtures containing about 1 ng of such difficult substances as primary mono- and diaminoalkanes, symmetrical peaks were obtained on some of the phases. Our own experience with dicumyl peroxide-cured phases is, however, that they tend to become more active towards amines than conventional stationary phases. Further references to works on the separation of amines by capillary column GC can be found in a recent book by Lee *et al.*[18].

EXPERIMENTAL

Apparatus

Chromatograph and detector. A Varian Model 3700 gas chromatograph equipped with a Carlo Erba on-column injection system and a Varian thermionic

specific detector was used. The detector was optimized for maximum sensitivity to nitrogen-containing compounds. Typical settings for the detector were: gas flow-rates, 4.0 ml/min of hydrogen and 180 ml/min of air; bead heating current, 6.8 scale divisions; bias voltage, −10 V; temperature, 290°C.

Gases. The carrier gas was helium, with an inlet pressure of 1 kg/cm^2. The make-up gas was nitrogen at a flow-rate of 22 ml/min. These gases were dried over molecular sieve 5 A and deoxygenated using an "Indicating Oxytrap" (Chrompack, Middleburg, The Netherlands). Hydrogen and air for thermionic specific detection (TSD) were used without extra purification.

Materials

The amines listed in Table I were obtained from the following suppliers: A. Bayer, Leverkusen, F.R.G. (IPPD, PAN, PBN, OCD, 6PPD); Monsanto, St. Louis, MI, U.S.A. (ETMQ, 77PD, DPPD); E. Merck, Darmstadt, F.R.G. (N,N-dimethylaniline, 1-naphthylamine, 2-naphthylamine, trioctylamine); Fluka, Buchs, Switzerland (2-ethylaniline, 2,6-dimethylaniline, 2-aminobiphenyl, 4-aminobiphenyl) and Mallinckrodt, St. Louis, MI, U.S.A. (aniline).

2,4-Toluenediamine (2,4-TDA) was from E. Merck and pentafluoropropionic acid anhydride (PFPAA) from Pierce (Rockford, IL, U.S.A.). OV-73 stationary phase and octamethylcyclotetrasiloxane (D_4) were obtained from Ohio Valley Speciality Chemicals (Marietta, OH, U.S.A.), and N,N-diethylaminotrimethylsilane (DEATMS) from Petrarch Systems (Bristol, PA, U.S.A.).

The solvents used were all of pro analys grade.

Procedure

Standard solutions and derivative preparation. Standard solutions were prepared by dissolving accurately weighed amounts of each amine in toluene and further dilution in toluene to the appropriate concentrations. The PFPA amide of 2,4-TDA was prepared as previously described[2].

Column preparation. Duran 50 borosilicate glass capillary columns were drawn on a Carlo Erba GCDM Model 60 glass capillary drawing machine and leached according to Grob *et al.*[19]. The columns were dried by purging with nitrogen for 2 h at 250°C. Deactivation was achieved by dynamic coating with pure D_4 or DEATMS, followed by flame sealing and thermal treatment overnight at 400 and 350°C, respectively. After rinsing with toluene, methanol and diethyl ether, OV-73 stationary phase was applied by static coating from pentane solution. The film thickness was 0.4 μm.

A commercial OV-73 capillary column was obtained from Chrompack.

Column end straightening. In order to fit into the chromatograph, the first part of the glass capillary column has to be straightened at the softening temperature of the glass, *ca.* 600°C. If the straightening is performed without previously removing the stationary phase the column is seriously impaired. Thus, the phase has to be removed from the first part of the column, as follows.

About 20 cm of the inlet end of the column were carefully flushed with dichloromethane using a 2-ml syringe connected to a 20 cm × 0.23 mm O.D. needle. The needle was inserted into the column and at the same time helium pressure was applied to the outlet end in order to prevent the solvent from penetrating deeper into

the column. By this procedure, the stationary phase was removed and the column end could be straightened in a flame without formation of decomposition products. After straightening, the naked part of the column was deactivated with D_4 or DEATMS and then heated for a short time at 400°C while simultaneously flushing with helium. Application of stationary phase is unnecessary.

When applying the on-column injection technique the column tends to deteriorate during prolonged use. However, it is easily restored by breaking off the straight inlet end and then treating the remaining part as described above.

Quantitative analysis. This was based on peak-height measurements. Typical volumes injected were 2 μl. The linear response range was established by plotting peak height per pg *versus* the amount of amine in pg injected for standard solutions, see Fig. 3.

RESULTS AND DISCUSSION

Gas chromatography

Capillary column. In our previous investigations of glass capillary GC of perfluoroacylated aromatic amines, several silylating agents were tested in order to get optimum column performance in the picogram range[2–4]. The most effective deactivation was given by octamethylcyclotetrasiloxane (D_4), which in combination with the OV-73 stationary phase, made possible the separation and quantitation of aromatic and aliphatic perfluoro amides in amounts as low as 10–20 pg.

This column was also sufficiently inert towards free aromatic amines of the kind studied in this work. Several other silylating agents were tested, but none gave as high column inertness as D_4. The Grob test of the D_4-deactivated OV-73 column demonstrated excellent performance for the amine (2,6-dimethylaniline) and also for the alcohol and phenol present in the test mixture. Furthermore, the column has a good long-term stability when used at temperatures up to 300°C, and the column end was easy to straighten without adsorptive sites being formed. Experiments were also made with dicumyl peroxide and azo-*tert.*-butane as cross-linking agents for the OV-73 and SE-54 stationary phases. However, the results were unsatisfactory because of increased adsorption due to the acidic character of the resulting phase. Difficulties in end-straightening the columns without impairing their performance were also encountered.

It was previously pointed out[2] that the Grob test, which is performed at the nanogram level, is of limited value for testing the suitability of a capillary column for trace analysis at picogram levels. A simple method was therefore developed for practical column testing in the picogram range, utilizing TSD. In this test, 10–1000 pg of the test compound, 2,4-TDA, were injected on to the column and the peak heights measured. The heights corresponding to 1 pg were plotted *vs.* the amount injected on a relative scale, putting the 1000-pg injection equal to 100%. The results obtained for three OV-73 columns are shown in Fig. 1.

Of the three columns, two were prepared at these laboratories and deactivated with D_4 and DEATMS, respectively. The third column was a commercial OV-73 column, the nature of the deactivation procedure being unknown. A straight horizontal line in the 2,4-TDA test implies little or no adsorption. This result is obtained

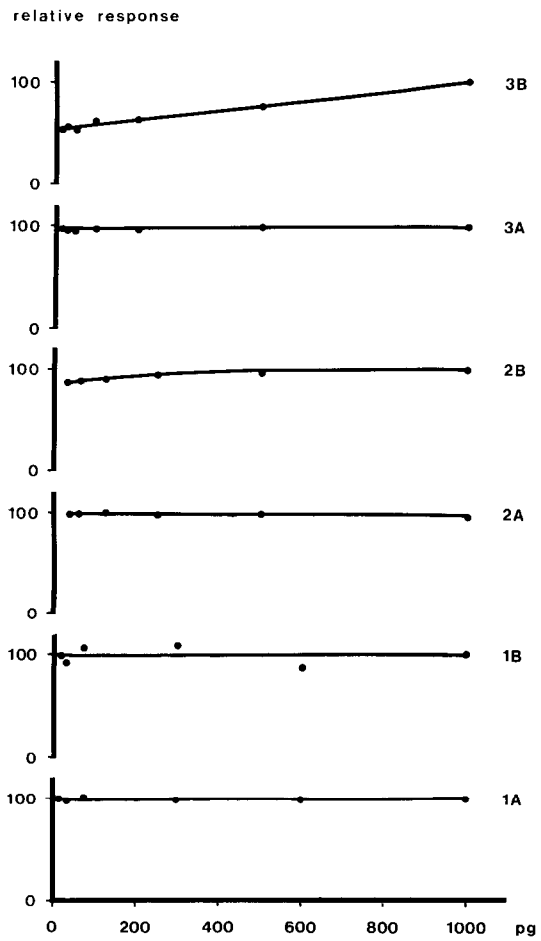


Fig. 1. 2,4-TDA tests of three OV-73 columns. 1B = D_4-deactivated column; 2B = DEATMS-deactivated column; 3B = commercial column; 1A, 2A, 3A = experiments with the pentafluoropropionic amide of 2,4-TDA on the above three columns.

only for the D_4-deactivated column, whereas the DEATMS-deactivated and commercial columns give sloping or curved lines. In the former case, adsorption is discernible below *ca.* 300 pg, and ion the latter, over the whole range investigated. Obviously, caution should be exercised when using these two columns for the quantitative analysis of free amines in the picogram range. The results obtained with the D_4- and DEATMS-deactivated columns are representatives of a considerable number of such columns tested.

For comparison, the test was also applied to the pentafluoropropionic amide of 2,4-TDA. As shown in Fig. 1, straight horizontal lines result for all three columns, indicating negligible adsorption, due to the fluoroacylation of the amino groups. At the same time, the proper functioning of the detector is established by this 2,4-TDA amide test. This manner of plotting is also convenient for illustrating the extent of linearity of the calibration graphs in trace analysis of easily adsorbed compounds like amines (see Fig. 3).

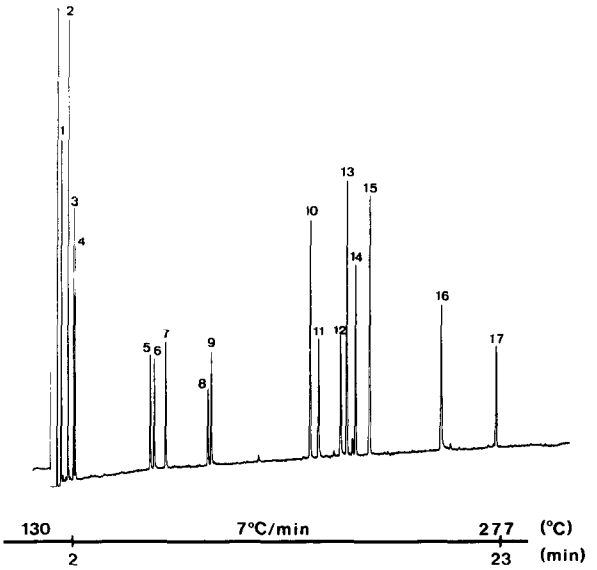


Fig. 2. Chromatogram with TSD of all investigated amines. On-column injection of 1 μl of a 0.5 pmol/μl toluene solution. Peak identities according to Table I. Column: 20 m × 0.32 mm I.D. Duran 50 glass capillary column, D_4-deactivated, with OV-73 stationary phase (film thickness 0.4 μm). Temperature programming as shown. Carrier gas: helium at 0.5 kg/cm^2. Thermionic specific detector: bead heating current, 6.0 scale divisions; bias voltage, −10 V; temperature, 290°C; hydrogen flow-rate, 4 ml/min; air flow-rate, 180 ml/min; make-up gas, nitrogen (flow-rate 20 ml/min).

Amine separation and TSD response. Fig. 2 shows the chromatogram obtained for the amine mixture on the OV-73 capillary column with TSD monitoring. The symmetry of the peaks is remarkably good considering the small amounts injected (0.5 pmol) and the wide temperature range (130–290°C).

As the same number of picomoles of the various amines were injected, the height of the peaks in Fig. 2 gives a measure of the relative TSD response of not too early eluting compounds (nos. 5–17). It is evident that the molar TSD response to aromatic amines is mainly a function of the number of nitrogen atoms present in the

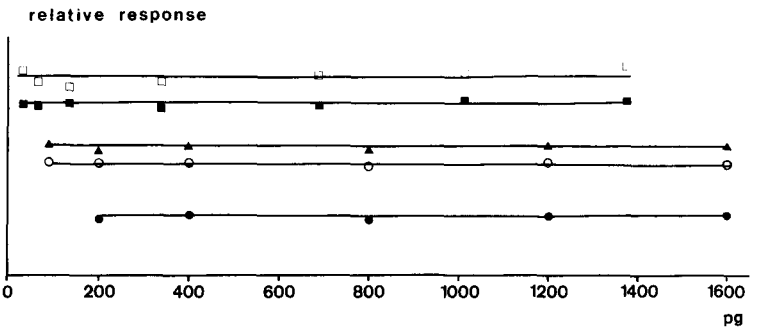


Fig. 3. Calibration curves with TSD (relative response *vs.* pg injected) for 1-naphthylamine (●), 2,6-dimethylaniline (○), OCD (▲), 2-aminobiphenyl (■) and PAN (□). Chromatographic conditions as in Fig. 2.

molecule. Hence, the TSD response to diamines (nos. 10, 13–15) is approximately twice that to monoamines (nos. 5–7, 9, 11, 12 and 16). The structural influence is slight. Most remarkable is the low response to the diamine 14 and the high response to the monoamine 16. A difference in molar response in relation to adjacent monoamines is also noted for compound 8, which is a dihydroquinoline. The response to the only purely aliphatic amine present, the tertiary amine 17, is similar to that for aromatic monoamines.

Linear range and detection limits. Calibration plots for some of the amines are given in Fig. 3, demonstrating linear responses in the range 50–1600 pg. TSD detection limits for the investigated free amines are of the order of 10–20 pg for a signal-to-noise ratio of 2:1. As discussed previously[3], the TSD response to a nitrogen-containing compound is dependent on several factors such as bead identity, bead heating current, detector base temperature, bias voltage and hydrogen, air, make-up and carrier gas flow-rates. It is not easy do decide to what extent the detection limit is set by these instrumental factors or by adsorption of the amines in the analytical system. However, the calibration curves in Fig. 3 indicate that little adsorption takes place.

CONCLUSIONS AND APPLICATIONS

Aromatic amines used as antioxidants in the rubber industry can be determined in trace amounts by glass capillary GC and TSD monitoring. A necessary provision is an inert capillary column with a low adsorption tendency for the amines in question.

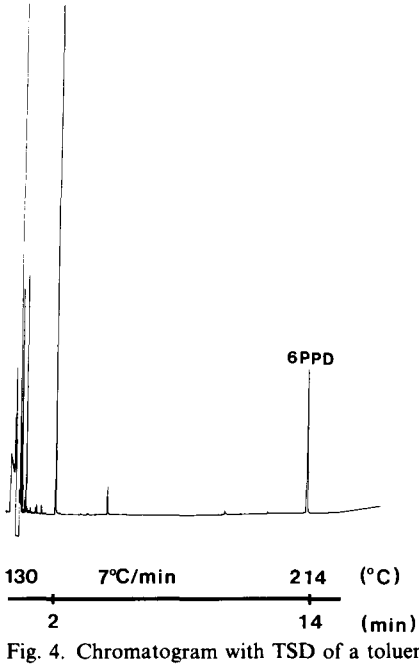


Fig. 4. Chromatogram with TSD of a toluene extract of smoke from vulcanization of a rubber sample, containing 6PPD (10 ng). Chromatographic conditions as in Fig. 2.

Amines can be liberated during the manufacture of rubber, especially on vulcanization or by other thermal degradations. Thus, on pyrolysis of rubber, fumes are formed which contain amines and a great number of other compounds. The amines can be absorbed in an acidic solution and, after making alkaline, extracted with toluene and the toluene solution chromatographed.

Fig. 4 shows a chromatogram obtained on pyrolysis of a rubber sample containing 6PPD as antioxidant (with sampling and sample treatment as above). It is evident that the great selectivity of TSD for nitrogen-containing compounds is a considerable advantage and contributes to the production of a clean chromatogram.

ACKNOWLEDGEMENTS

We are indebted to Professor Bengt Smith for valuable discussions during the course of this work. This work was supported by grants from the Swedish Work Environment Fund.

REFERENCES

1 G. Skarping, C. Sangö and B. E. F. Smith, *J. Chromatogr.*, 208 (1981) 313.
2 G. Skarping, L. Renman and B. E. F. Smith, *J. Chromatogr.*, 267 (1983) 315.
3 G. Skarping, L. Renman and M. Dalene, *J. Chromatogr.*, 270 (1983) 207.
4 G. Skarping, B. E. F. Smith and M. Dalene, *J. Chromatogr.*, 303 (1984) 89.
5 M. Dalene, L. Mathiasson and J. Å. Jönsson, *J. Chromatogr.*, 207 (1981) 37.
6 G. Audunsson and L. Mathiasson, *J. Chromatogr.*, 261 (1983) 253.
7 L. Parmeggiani (Editor), *Encyclopaedia of Occupational Health and Safety*, Vol. 1, International Labour Office, Geneva, 1983.
8 G. D. Clayton and F. E. Clayton (Editors), *Patty's Industruial Hygiene and Toxicology*, Vol. 28, Wiley-Interscience, New York, 1981.
9 P. A. D. T. Vimalasiri, J. K. Haken and R. P. Burford, *J. Chromatogr.*, 300 (1984) 303.
10 J. J. Franken, C. Vidal-Madjar and G. Guiochon, *Anal. Chem.*, 43 (1971) 2034.
11 G. Goretti, M. Ciardi and C. Di Palo, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 523.
12 K. Tesařík and S. Ghyczy, *J. Chromatogr.*, 91 (1974) 723.
13 B. Olufsen, *J. Chromatogr.*, 179 (1979) 97.
14 G. Becher, *J. Chromatogr.*, 211 (1981) 103.
15 G. Becher, A. Bjørseth and B. Olufsen, *ACS Symp. Ser.*, 149 (1981) 369.
16 R. M. Riggin, T. F. Cole and S. Billets, *Anal. Chem.*, 55 (1983) 1862.
17 L. Blomberg, J. Buijten, K. Markides and T. Wännman, *J. Chromatogr.*, 239 (1982) 51.
18 M. L. Lee, F. J. Yang and K. D. Bartle, in *Open Tubular Column Gas Chromatography*, Wiley, New York, 1984, p. 263.
19 K. Grob, G. Grob, W. Blum and W. Walther, *J. Chromatogr.*, 244 (1982) 197.