Journal of Chromatography, 211 (1981) 103–110
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,734

GLASS CAPILLARY COLUMNS IN THE GAS CHROMATOGRAPHIC SEPARATION OF AROMATIC AMINES

II. APPLICATION TO SAMPLES FROM WORKPLACE ATMOSPHERES USING NITROGEN-SELECTIVE DETECTION

GEORG BECHER
Central Institute for Industrial Research, Blindern, Oslo 3 (Norway)
(Received January 21st, 1981)

SUMMARY

A gas chromatographic method for the analysis of airborne aromatic amines on glass capillary columns is described. Sampling is achieved by silica gel adsorption tubes. Aromatic amines are subsequently desorbed using 2-butanone and directly injected into the gas chromatographic system. Application of a nitrogen-selective detector increases sensitivity and facilitates identification of relevant compounds in complex mixtures. The method has been applied to samples from different work environments.

INTRODUCTION

Aromatic amines are of considerable industrial and commercial importance. They are used as intermediates in the synthesis of a large number of organic compounds including dyes, drugs, pesticides and plastics. Furthermore, they are constituents of several consumer goods such as most rubber products and hair dyes.

Some aromatic amines have been shown to have toxicological properties[1] and there is much concern from an occupational and environmental point of view with regard to their carcinogenicity[2,3]. It has been established that 2-naphthylamine, benzidine and 4-biphenylamine are responsible for almost all of the known industrial cases of bladder cancer[4]. Whereas the production of the most hazardous compounds has now ceased, other aromatic amines are produced continuously.

Glass capillary gas chromatography has been successfully used in the characterization of potentially harmful chemicals in workplace atmospheres[5]. The analysis of aromatic amines, however, presents a challenging problem. These basic polar compounds may give rise to adsorption on the glass surface, leading to severe tailing of peaks or even loss of the component. Derivatization of the amines is therefore usually employed. Olufsen[6] has recently reported preliminary results of the direct gas chromatographic analysis of aromatic amines on glass capillary columns coated with Carbowax 20M on a basic support. Later Goretti *et al.*[7] described a similar separation of aromatic amines using graphitized capillary columns.

0021-9673/81/0000–0000/$02.50

The objective of this paper is to demonstrate the usefulness of simultaneous detection of aromatic amines in capillary gas chromatography using a flame ionization detector (FID) and a nitrogen-selective detector; applications to samples from workplace atmospheres are also presented.

MATERIALS AND METHODS

Chemicals

All solvents were purified by distillation in glass apparatus. Standard compounds were commercial samples and were purified by distillation under reduced pressure or by conventional recrystallization. Standard solutions were prepared by dissolving weighed amounts of aromatic amines in 2-butanone. The standard mixtures were stored at −20°C in the dark.

Sampling

Samples of airborne aromatic amines were collected in three-section silica gel tubes (NIOSH type; Supelco, Bellefonte, PA, U.S.A.). Only stationary sampling was used. Air was drawn through the adsorption tube by means of a Casella pump, Type 13051/2, at a rate of *ca.* 1.2–1.4 l/min for 5–6 h. The adsorption tubes were capped immediately after sampling and stored at −20°C in the dark until analyzed.

Analytical procedure

Aromatic amines collected on the silica gel adsorption tubes were removed for analysis by elution with 2-butanone containing internal standards. The three adsorbent sections were desorbed separately with 1 and 3 ml of solvent for the 150-mg and 600-mg sections, respectively, using ultrasonication for 30 min.

Desorption efficiencies were determined by spiking adsorption tubes with standard samples of aromatic amines. After spiking, a stream of highly purified nitrogen was blown through the silica gel tubes at a rate of 200 ml/min. The tubes were sealed and allowed to stand overnight at room temperature. The silica gel sections were eluted as described above and analyzed using N,N-diphenylamine as internal standard.

The gas chromatographic (GC) analysis was carried out on a Hewlett-Packard Model 5730 A gas chromatograph equipped with a FID and a nitrogen/phosphorus-sensitive detector (NPD), Model 18789 A. About 2 μl of the 2-butanone solution were injected using the splitless injection technique. The glass capillary column, prepared in our laboratory especially for the separation of aromatic amines, has been described previously[6]. The chromatographic conditions were as follows: column, glass capillary (37 m × 0.32 mm I.D. or 23 m × 0.28 mm I.D.) coated with Carbowax 20M on KOH; carrier gas, helium at pressures resulting in a linear gas flow-rate of 29 cm/sec at room temperature; injector/detector temperature, 300°C; initial column temperature, 80°C, programmed at 3°C/min. The chromatographic peaks were displayed on a Perkin-Elmer 56 two-channel recorder. Peak areas were integrated electronically using a Minigrator (Spectra-Physics).

The column effluent was split by means of Pt/Ir tubing (Chrompack, Middelburg, The Netherlands) according to Etzweiler and Neuner-Jehle[8]. The FID/NPD splitting ratio was 1.05 measured at room temperature. The NPD required 30 ml/min of He as make-up gas and the FID had 40 ml/min of N_2 as make-up gas.

A Finnigan Model 4021 gas chromatographic–mass spectrometer system was used for identification of aromatic amines. The GC conditions were as described above. The following experimental conditions were chosen: ionization mode, electron impact; ionization energy, 70 eV; ion source temperature, 250°C; mass range, 35–300; scan time, 2 sec.

RESULTS AND DISCUSSION

Simultaneous application of FID and NPD

Simultaneous, multiple detection in capillary GC has been reported by several authors[9–11] using a general detector such as a FID and a specific detector such as an electron-capture detector (ECD). This technique was applied to the analysis of aromatic amines using an FID and an NPD.

The selectivity of the NPD will depend on the instrumental conditions used and on the quality and age of the source; however, it usually exceeds 10^4 g C per g N. Simultaneous flame ionization–nitrogen/phosphorus detection therefore offers a great advantage in the determination of aromatic amines in complex environmental samples. Furthermore, with the FID, a large solvent peak can cause interference with rapidly eluting compounds, but with the NPD, the solvent peak is negligible, as illustrated in Fig. 1. This chromatogram also shows enhanced sensitivity of the NPD towards the aromatic amines in comparison with the FID. NPD:FID response ratios

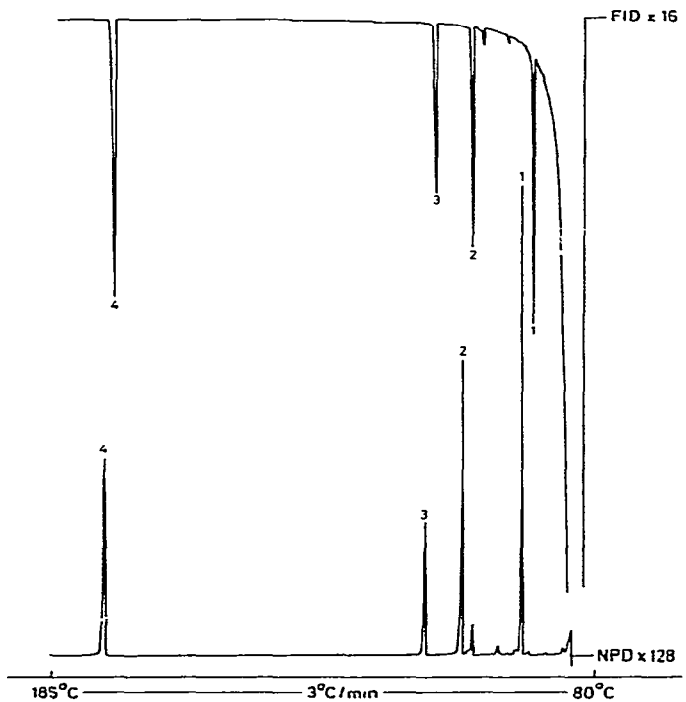

Fig. 1. Glass capillary gas chromatogram of aromatic amines using simultaneous flame ionization and nitrogen-selective detection. Column: Carbowax 20M on basic support, splitless injection at 80°C. Peaks: 1 = N,N-dimethylaniline; 2 = aniline; 3 = 2,6-dimethylaniline; 4 = N,N-diphenylamine.

for selected aromatic amines are listed in Table I. The average ratio is of the order of 10, the actual value depending on the type of aromatic amine and the condition of the detector.

As already reported by Baker[12], the NPD response is not necessarily correlated with the number of nitrogen atoms in the molecule. Thus the aromatic diamines in Table I do not give double the response of the monoamines. On the contrary, the NPD response of aromatic amines seems to be more dependent on the substitution at the nitrogen atom. The tertiary amine N,N-dimethylaniline, for example, shows an NPD response approximately twice that of its primary isomer 2,6-dimethylaniline.

From this it is clear that careful calibration is required for each compound to be quantified. N,N-Diphenylamine was chosen as internal standard because it is chemically stable and interferes little with other aromatic amines of interest.

TABLE I

FID AND NPD RESPONSES FOR SELECTED AROMATIC AMINES

Compound	*Detector response**		*NPD:FID*
	FID	*NPD*	
N,N-Dimethylaniline	78	1061	13.6
Aniline	75	780	10.4
2,6-Dimethylaniline	78	561	7.2
N,N-Diphenylaniline	100	570	5.7
N,N-Diethyl-1,4-diaminobenzene	53	811	15.3
2,4-Diaminotoluene	43	662	15.4
2,4-Diamino-1-methoxybenzene	23	382	16.6

* Peak area per μg compound, in arbitrary units.

Evaluation of the analysis procedure

Ethanol is recommended for the desorption of aromatic amines from silica gel[13]; however, this solvent is not suitable for splitless injection on the glass capillary column. 2-Butanone proved to be a good solvent for aromatic amines and its low polarity favours a longer column life. Recoveries of aromatic amines from silica gel sampling tubes after desorption with 2-butanone were found to be 76 $\pm$ 2% at a loading of 3–30 μg aromatic amine per sampling tube. No breakthrough was found for the front sections of the silica gel tubes over the concentration range investigated.

In the analysis of aromatic amine standards, a linear relationship was observed between 2 and 250 ng. Calibration plots for some aromatic amines are shown in Fig. 2.

The sensitivity of the method has also been investigated. Splitless injections of 2 μl of 2-butanone solutions containing six aromatic amines gave peaks with a signal-to-noise ratio of 10 for concentrations as low as 0.3 μg/ml. Assuming that 0.1 m^3 of air is sampled, the sensitivity corresponds to at least 3 $\mu g/m^3$.

Separation of a standard mixture of aromatic amines in 2-butanone is shown in Fig. 3. Although the compounds were not derivatized, the peaks are eluted with negligible tailing. The high resolving power allows good separation of isomers, such as 1- and 2-aminonaphthalene, and yields accurate results in quantification work.

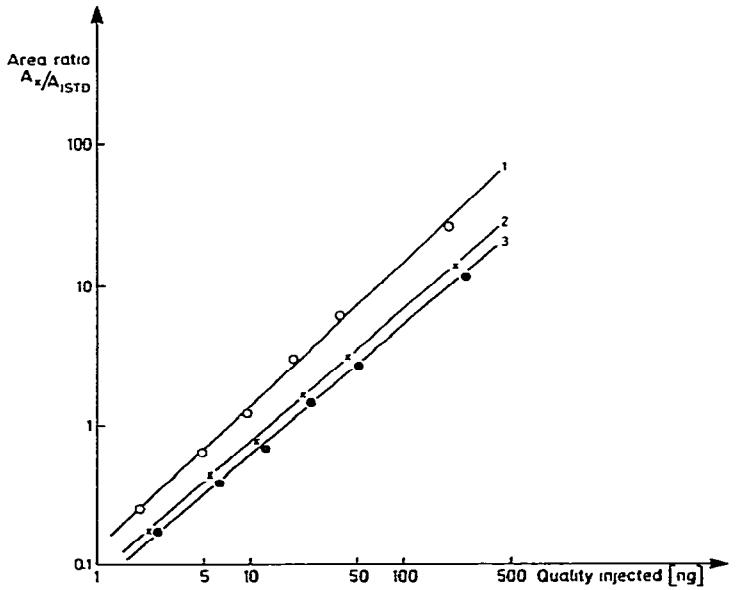

Fig. 2. Calibration plots for some aromatic amines using N,N-diphenylamine as internal standard. 1 = 2,4-Diaminotoluene; 2 = 2-aminonaphthalene; 3 = 1-aminonaphthalene.

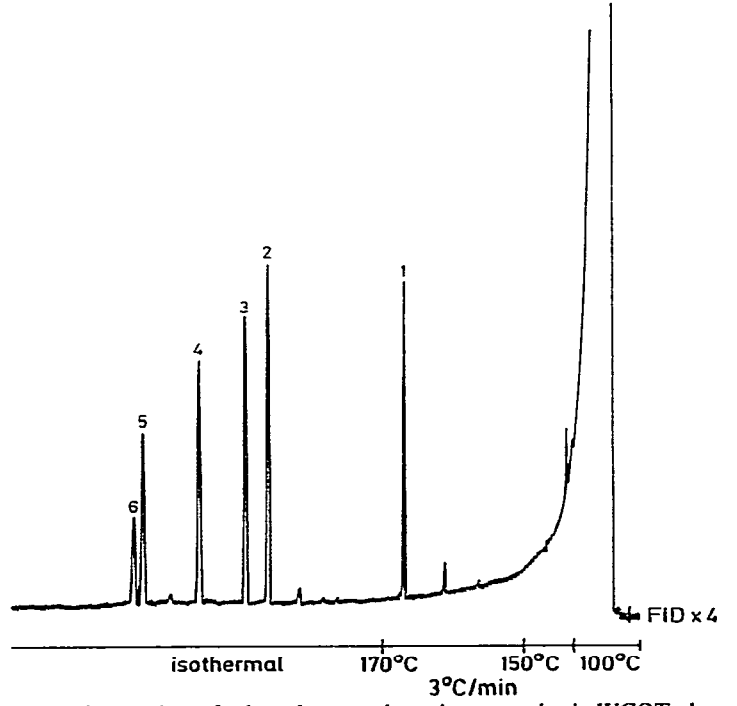

Fig. 3. Separation of selected aromatic amines on a basic WCOT glass capillary column with Carbowax 20M as stationary phase. Splitless injection of 1 μl at 100°C. Peaks: 1 = 1,2-diaminobenzene; 2 = 2,4-diaminotoluene; 3 = N,N-diphenylamine; 4 = 1-aminonaphthalene; 5 = 2-aminonaphthalene; 6 = 2,4-diamino-1-methoxybenzene.

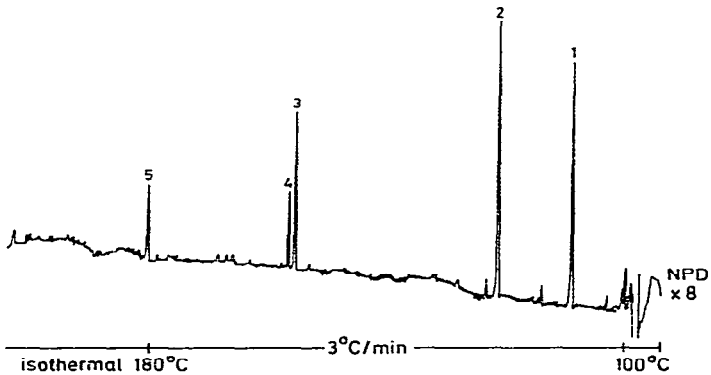

Fig. 4. Glass capillary gas chromatogram of airborne aromatic amines from a film-processing laboratory using nitrogen-selective detection. Peaks: 1 = N,N-diethylaniline; 2 = 2,6-dimethylaniline; 3 = N,N-diethyl-1,4-diaminobenzene; 4 = N,N'-diisopropyl-1,4-diaminobenzene; 5 = not identified (*m/e* = 180).

Analysis of aromatic amines from workplace atmospheres

To test the feasibility of the method, samples from workplace environments were analyzed. Fig. 4 shows a chromatogram of airborne aromatic amines from a film-processing laboratory, using a nitrogen-selective detector. Four nitrogen-containing compounds were detected, of which three were positively identified by gas chromatography–mass spectrometry (GC–MS). Quantitative results are given in Table II. No threshold limit values (TLVs) exist for these particular compounds in workroom atmospheres. However, the concentrations found may be compared with the TLCs of related aromatic amines. At present the time weighted-average TLVs in most countries are set at 25 mg/m^3 and 0.1 mg/m^3 for N,N-dimethylaniline and 1,4-diaminobenzene, respectively[14]. The concentrations of aromatic mono- and diamines found in this investigation are far below these TLVs.

Aromatic amines are widely used as curing agents for epoxy resins[15]. The curing agent (hardener) converts the epoxy resin into a hard solid and is mixed with

TABLE II

RESULTS FOR SAMPLES OF AIRBORNE AROMATIC AMINES FROM A FILM-PROCESSING LABORATORY

Peak No.	*Peak identity*	*Amount in sample (μg/ml)*	*Airborne concentration (μg/m^3)*
1	N,N-Dimethylaniline	5.6	13.4
2	2,6-Dimethylaniline	10.0	Internal standard
3	N,N-Diethyl-1,4-diaminobenzene	2.5	6.0
4	N,N'-Diisopropyl-1,4-diaminobenzene	1.4	3.4
5	Not identified	—	—

the resin just prior to use. One of the main applications of epoxy resins is in protective coatings. The possibility of occupational exposure to aromatic amines during this process was therefore studied.

Air samples were taken during coating of the concrete top of a road bridge. A tent had been built over the coating area which was heated by hot air. Fig. 5 shows the glass capillary chromatogram using simultaneous flame ionization (upper trace) and nitrogen-selective (lower trace) detection. The NPD trace shows a number of compounds with strong NPD responses, however the total number of peaks is considerably reduced compared to the FID trace, thus facilitating the identification of relevant compounds by GC–MS. Table III shows the main compounds having NPD

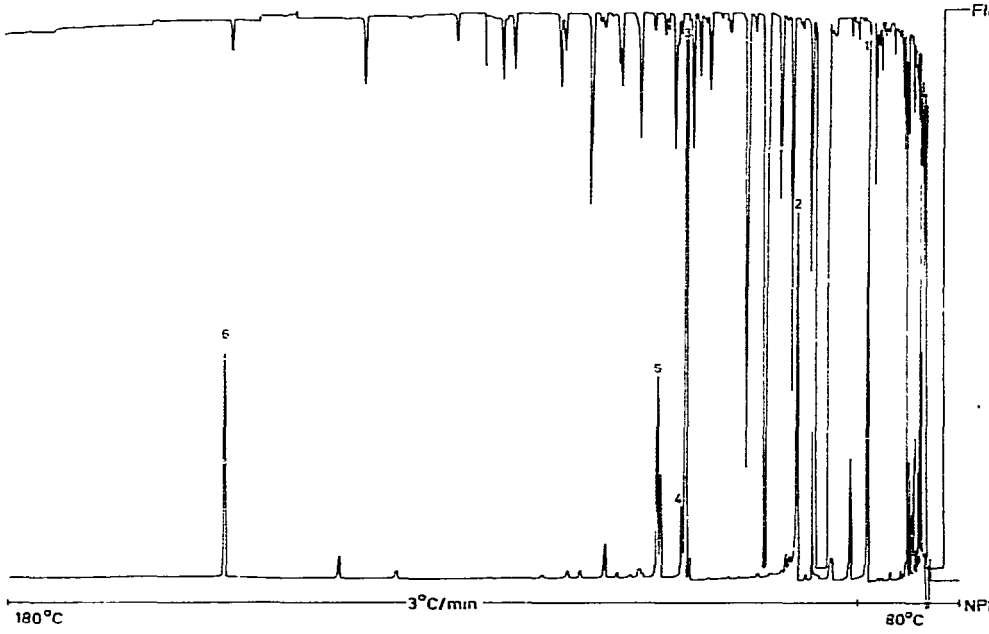

Fig. 5. Glass capillary gas chromatogram of an air sample obtained during epoxy coating. Simultaneous detection by FID (upper trace) and NPD (lower trace). For peak identities see Table III.

TABLE III

NITROGEN-CONTAINING COMPOUNDS IDENTIFIED IN AN AIR SAMPLE TAKEN DURING EPOXY COATING

Peak No.	*Compounds identified by GC–MS*
1	Benzonitrile*
2	Aliphatic amine**
3	Quinoline/isoquinoline
4	Benzothiazole
5	Isoquinoline/quinoline
6	N,N-Diphenylamine***

* Tentative assignment. The peak is obscured by a major, non-nitrogen-containing compound.
** No molecular ion is observed; however the fragments are characteristic of aliphatic amines.
*** Internal standard corresponding to 8.25 μg/ml.

responses. Volatile aromatic amines were not detected in the sample. The quinolines observed are constituents of tar contained in this particular epoxy resin. Basic azaarenes have been observed in a great variety of environmental samples such as urban particulates, automobile exhausts and tobacco smoke[16]. Quinoline is potentially dangerous in occupational environments because of its volatility and its carcinogenicity in experimental animals[17]. The total amount of quinoline and isoquinoline found in the air sample corresponds to *ca.* 175 $\mu g/m^3$.

CONCLUSION

It is shown that glass capillary gas chromatography may be successfully used in the characterization of aromatic amines and other basic nitrogen-containing compounds in workplace atmospheres. The method gives high resolution and good sensitivity. The use of both general and nitrogen-selective detectors provides additional information about the sample composition and facilitates the identification of components. The GC method may also be used for other types of samples such as water and biological material.

ACKNOWLEDGEMENTS

The financial support from the Royal Norwegian Council for Scientific and Industrial Research under contract 0311.7615 is gratefully acknowledged. B. Sortland is thanked for technical assistance and helpful suggestions.

REFERENCES

1 T. S. Scott, *Carcinogenic and Chronic Toxic Hazards of Aromatic Amines*, Elsevier, Amsterdam, New York, 1962.
2 *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Vol. 16, IARC, Lyon, 1978.
3 D. B. Clayson and R. C. Garner, in C. E. Searle (Editor), *Chemical Carcinogens*, ACS Monograph 173, American Chemical Society, Washington, DC, 1976, p. 366.
4 H. G. Parkes, in C. E. Searle (Editor), *Chemical Carginogens*, ACS Monograph 173, American Chemical Society, Washington, DC, 1976, p. 462.
5 G. Becher, A. Bjørseth and B. Olufsen, in G. Choudhary (Editor), *Chemical Hazards in the Workplace: Measurement and Control, ACS Symposium Series No. 149*, American Chemical Society, Washington, DC, 1981.
6 B. Olufsen, *J. Chromatogr.*, 179 (1979) 97.
7 G. Goretti, M. Ciardi and C. Di Palo, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 523.
8 F. Etzweiler and N. Neuner-Jehle, *Chromatographia*, 6 (1973) 503.
9 K. Bäckmann, W. Emig, J. Rudolph and D. Tsotos, *Chromatographia*, 10 (1977) 684.
10 A. Bjørseth and G. Eklund, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 22.
11 A. Bjørseth, G. E. Carlberg, N. Gjøs, M. Møller and G. Tveten, in L. H. Keith, *Advances in the Identification and Analysis of Organic Pollutants in Water*, Ann Arbor Science Publishers, 1981.
12 J. K. Baker, *Anal. Chem.*, 49 (1977) 906.
13 G. O. Wood and R. G. Anderson, *Amer. Ind. Hyg. Ass., J.*, 36 (1975) 538.
14 *Occupational Exposure Limits For Airborne Toxic Substances*, International Labour Office, Geneva, 1977.
15 H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967.
16 M. Dong, I. Schmeltz, E. LaVoie and D. Hoffmann, in P. W. Jones and R. I. Freudenthal (Editors), *Carcinogenesis —A Comprehensive Survey*, Vol. 3, Raven Press, New York, 1978, p. 97.
17 K. Hirao, Y. Shinohara, H. Tsuda, S. Fukushima, M. Takahashi and N. Ito, *Cancer Res.*, 36 (1976) 329.