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

I. DETERMINATION OF AROMATIC AMINES AS PERFLUORO FATTY ACID AMIDES USING ELECTRON-CAPTURE DETECTION

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SUMMARY

A method for the trace analysis of aromatic amines is presented. It involved conversion of the amines into the corresponding amides by reaction with a perfluoro fatty acid anhydride. The amides were separated by glass capillary gas chromatography and quantitation was achieved using on-column injection and electron-capture detection.

The method was applied to amines of interest from work environment health aspects. Detection limits were in the low picogram range. Columns suitable for this application and their preparation are discussed together with detector behaviour and the mass spectra of investigated perfluoro fatty acid amides.

INTRODUCTION

Recently a gas chromatographic (GC) method for the trace analysis of isocyanates in air, developed at this laboratory, was presented[1]. It involved absorption of the isocyanates in acidic solution, where they were hydrolysed to the corresponding amines. After addition of excess base, the amines were extracted with toluene and reacted with a perfluoro fatty acid anhydride to yield the corresponding amides. These were separated by packed column GC and monitored with an electron-capture detector. The method was applied to a small number of aromatic isocyanates.

In this continuation work, our attention was focused on the assay of aromatic amines that are encountered in industrial atmospheres, thus being of interest from work environmental health aspects. In order to increase selectivity and versatility, capillary instead of packed column GC was applied to the separation of the amides.

The amines in toluene solution are converted into the corresponding amides by treatment with a perfluoro fatty acid anhydride, preferably pentafluoropropionic acid anhydride (PFPAA), according to the reaction

$$RNH_2 + (C_2F_5CO)_2O \rightarrow RNHCOC_2F_5 + C_2F_5COOH \quad (1)$$

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TABLE I

AMINES INVESTIGATED

No.	*Amine*	*Abbreviation*	*Abbreviation of corresponding isocyanate**
1	Aniline	–	PhI
2	2,6-Toluenediamine	2,6-TDA	2,6-TDI
3	2,4-Toluenediamine	2,4-TDA	2,4-TDI
4	2,4-Diaminoanisole	2,4-DAA	–
5	α-Naphthylamine	–	–
6	β-Naphthylamine	–	–
7	4-Aminobiphenyl	–	–
8	1,5-Naphthalenediamine	NDA	NDI
9	4,4′-Diaminobiphenyl (benzidine)	–	–
10	4,4′-Methylenedianiline	MDA	MDI
11	*o*-Tolidine (4,4′-diamino-3,3′-dimethyl-biphenyl)	TODA	TODI
12	4,4′-Methylenebis-(*o*-chloroaniline)	MOCA	–
13	4,4′-Diamino-3,3′-dimeth-oxybiphenyl (*o*-dianisidine)	DADA	DADI

* The isocyanate formula is obtained by exchange of NH_2 groups in the amine for NCO groups.

Excess reagent and pentafluoropropionic acid formed in the reaction are extracted with a pH 7.0 phosphate buffer and the remaining toluene solution of amides is analysed by glass capillary GC using on-column injection and an electron-capture detector.

The method is also applicable, as will be described in a forthcoming paper, to the determination of aromatic isocyanates after absorption in acidic solution and extraction of the amines formed. Table I lists the investigated amines and corresponding isocyanates currently encountered in industrial atmospheres. Amines without counterparts among the isocyanates are carcinogenic substances, being entered on the A and B lists of the Swedish Work Environment Board.

EXPERIMENTAL

Apparatus

Chromatograph. A Carlo Erba Fractovap Model 4160 chromatograph with on-column injection system was employed.

Detector. A ^{63}Ni (10 mCi) Carlo Erba Model HT-25 electron-capture detector with a control module 251 was used in the constant-current mode (voltage 50 V, pulse width 0.1 μsec, standing current 2.0 nA).

Glass capillaries. Glass capillaries were drawn from Pyrex or Duran 50 borosilicate glass tubes on a Carlo Erba Model 60 Glass Capillary Drawing Machine.

Column. A capillary Pyrex glass column (30 m × 0.3 mm I.D.) with 1.0 μm OV-73 stationary phase was employed, together with several other capillary columns,

all prepared in this laboratory as described below.

Recorder. A Servogor Model 310 recorder was used.

Integrator. A Hewlett-Packard Model 3390A Reporting Integrator was employed for peak evaluation.

Gases. The carrier gas used was helium and the make-up gas was argon–methane (95:5). Both were dried over activated molecular sieve 5A and deoxygenated using an Indicating Oxytrap (Chrompack, Middelburg, The Netherlands). The gas pressure regulators used were equipped with steel membranes (l'Air Liquide; provided by Alfax, Stockholm, Sweden).

Mass spectrometer. Mass spectrometric data were obtained on a Finnigan Model 4021 mass spectrometer operated in the electron impact mode with positive ion monitoring or in the chemical ionization mode using methane as ionization agent and negative ion monitoring.

Materials

Chemicals. Aniline, 2,4- and 2,6-toluenediamine (2,4- and 2,6-TDA), 2,4-diaminoanisole (DAA), 4,4′-diaminodiphenylmethane (MDA), benzidine and α- and β-naphthylamine were obtained from E. Merck (Darmstadt, F.R.G.). 4-Aminobiphenyl (BPA), 3,3-dimethoxybenzidine (DADA), 3,3′-dimethylbenzidine (TODA) and 1,5-diaminonaphthalene (NDA) were obtained from Fluka (Buchs, Switzerland) and 4,4′-diamino-3,3′-dichlorodiphenylmethane (MOCA) from Aldrich-Europe (Beerse, Belgium). Heptafluorobutyric (HFBAA), pentafluoropropionic (PFPAA) and trifluoroacetic (TFAAA) anhydrides were obtained from Pierce (Rockford, IL, U.S.A.) and, depending on batch quality, were distilled over phosphorus pentoxide (E. Merck). Hydrochloric acid, min. 37% (w/w), potassium dihydrogen phosphate and p.a. grade pentane were purchased from E. Merck and sodium hydroxide (p.a.) pellets from EKA (Bohus, Sweden).

Silylating agents for column deactivation, hexamethyldisilazane (HMDS), diphenyltetramethyldisilazane (DPTMDS), tetraphenyldimethyldisilazane (TPDMDS) and triphenylsilylamine (TPSA) were all obtained from Fluka. All stationary phases used were purchased from Chrompack.

Solvents and solutions. All water used was doubly distilled. Toluene was of glass-distilled grade (Rathburn Chemicals, Walkerburn, U.K.). Pentane, diethyl ether and methanol, all of p.a. grade, were from E. Merck. Saturated sodium hydroxide solution was obtained by addition of 150 g of sodium hydroxide to 100 ml of water. Phosphate buffer was prepared from potassium dihydrogen phosphate (136 g, 1 mol) and 1000 ml of water. The pH was adjusted to 7.0 with saturated sodium hydroxide solution.

Procedure

Standard solutions. Standard solutions of the amines were prepared by dissolving accurately weighed amounts (*ca.* 50 mg) in 100 ml of acetonitrile; 100-μl aliquots of this solution were then diluted to 100 ml with toluene to produce a solution with an amine concentration of *ca.* 500 pg/μl. This solution was further diluted with toluene to desired concentrations.

Derivative preparation. A 1-ml aliquot of the sample solution was transferred into a ground-glass stoppered test-tube, followed by the addition of 20 μl of the

appropriate perfluoro fatty acid anhydride. The contents of the test-tube were shaken for 1 min and then allowed to stand for 5 min. The excess reagent and the acid formed were removed by shaking with 1 ml of phosphate buffer (pH 7.0). The toluene layer containing the amide was then transferred into another test-tube, ready for injection into the gas chromatograph.

Column preparation. Columns with apolar stationary phases (OV-73, OV-1, SE-52 and SE-54) were prepared by the persilylation procedures described by Grob *et al.*[2]. Coiled Pyrex or Duran 50 glass columns with pre-straightened ends were rinsed and filled to 92% with 20% hydrochloric acid, flame-sealed and heated at 180°C for 16–18 h. After rinsing with water and drying under vacuum at 250°C the columns were treated by dynamic coating with a mixture of HMDS and DPTMDS (1 part of each in 2 parts of pentane), subjected to vacuum, sealed and heated at 400°C overnight. After rinsing with toluene, methanol and diethyl ether, the columns were coated by the static coating procedure at room temperature, using pentane solutions (1.3%, w/v, to produce a *ca.* 1.0 μm stationary phase thickness) employing a sealing technique developed at this laboratory[3]. A similar procedure was applied to fused silica columns (obtained from Hewlett-Packard, Avondale, PA, U.S.A.), differing only in that the leaching procedure was replaced by merely rinsing with 20% hydrochloric acid.

In the on-column injection method, the stationary phase is gradually flushed away from the first part of the column, and involatile substances will also be deposited at the inlet end of the column, thus impairing its performance. On that account, the inlet end has to be renewed from time to time. This is achieved in the following way: *ca.* 1 m of the column is cut off and stationary phase is removed from the first 7 cm of the remaining part of the column by the slow injection of 5 ml of solvent (pentane for apolar phases) against a nitrogen gas stream by means of a 5-ml syringe equipped with an on-column injection needle inserted as far as possible into the column. The column end is then straightened at a minimum temperature using an alcohol flame, as suggested by Grob *et al.*[4] or using a glass capillary straightener (Carlo Erba GESM Model 102-20). Occasionally the same procedure has to be applied to the outlet end of the column, where the column tends to deteriorate because of the high detector temperature (300°C).

Gas chromatography. Samples were analysed by on-column injection at a starting temperature near the solvent's boiling point (115°C for toluene). After elution of the solvent (*ca.* 2 min), the column temperature was programmed at 10°C/min to 300°C, where it was held for 5 min.

Quantitative analysis. The quantitative analysis was based on peak-height measurement. The linear response range for each derivative was established by plotting peak heights against concentration (Fig. 2) for injected standard solutions. In the applied mode, the response of the electron-capture detector is linear up to *ca.* 50% of its dynamic range (see discussion below).

RESULTS AND DISCUSSION

Procedure

Formation of amides. Three perfluoroacylating agents, HFBAA, PFPAA and TFAAA, were investigated with regard to yield, separation properties and sensitivity.

The TFAA derivatives were discarded at an early stage of the investigation owing to their low sensitivities, being 10–20 times lower than for the HFBA and PFPA derivatives. This is also evident from recent work by Ebell *et al.*[5], who employed TFAAA for the assay of 2,4-TDA, 2,6-TDA and MOCA.

The sensitivity difference between the PFPA and HFBA derivatives is surprisingly small considering the difference in the number of electron-withdrawing fluorine atoms in these derivaties. However, the increased distance between the trifluoromethyl group and the electron-capturing carbonyl group in the HFBA derivative should diminish its electron-attracting effect compared with that in the PFPA derivative, as has been discussed by Clarke *et al.*[6].

The same derivatization procedure could be used for the two kinds of derivatives and the amines were fully converted into the amides in less than 1 min at room temperature. It was shown by GC–mass spectrometry (MS) that only one hydrogen atom at each amino group was replaced by a pentafluoropropionyl (PFP) or a heptafluorobutyryl (HFB) group (see Fig. 4).

Chromatograms of HFBA and PFBA derivatives of the investigated amines are shown in Fig. 1. The main difference between the chromatograms is the lower elution temperatures for the PFPA derivatives and the better separation between the PFPA derivatives of the two TDA isomers. It is therefore considered that PFPAA is the best derivatization reagent for the present application, in spite of the higher sensitivity of the HFBA derivatives. The fact that PFPAA can be obtained in a higher purity is an added advantage.

Extraction of excess reagent and liberated acid. Excess reagent and liberated acid are removed by extraction with a pH 7.0 phosphate buffer. Higher pH values will result in losses of derivatives, as demonstrated in earlier work in this laboratory[1], and lower pH values will give incomplete removal.

Chromatographic system

Capillary column. Trace analysis of the perfluoracylated amines requires glass capillary columns with high inertness and good temperature stability. On that account, polar stationary phases are less suitable because of more active surfaces and lower maximum temperatures. This is specially the case for the high-boiling derivatives of benzidine, MDA, TODA, MOCA and DADA, as shown by tests with OV-225 and Carbowax 20M stationary phases. Apolar columns prepared by the persilylation procedures described above, on the other hand, although requiring the same high elution temperatures as the polar columns, have shown remarkably good inertness and long-term stability.

Several silylating agents were tested in order to achieve optimal column performance. The agents finally chosen were a mixture of HMDS and DPTMDS as suggested by Grob *et al.*[2]. Attempts to use HMDS alone, as recently proposed by Godefroot *et al.*[8], gave columns with a durability of only a few days of high-temperature use. Other silylating agents suggested by Grob[7], namely TPDMDS and TPSA, did not give even initially acceptable columns.

Fused-silica columns were also prepared using the HMDS–DPTMDS mixture for deactivation, but although the initial inertness was acceptable, these columns rapidly deteriorated. This is probably due to the fact that persilylation temperatures above 330°C cannot be used, owing to the temperature limit set by the outer coatings

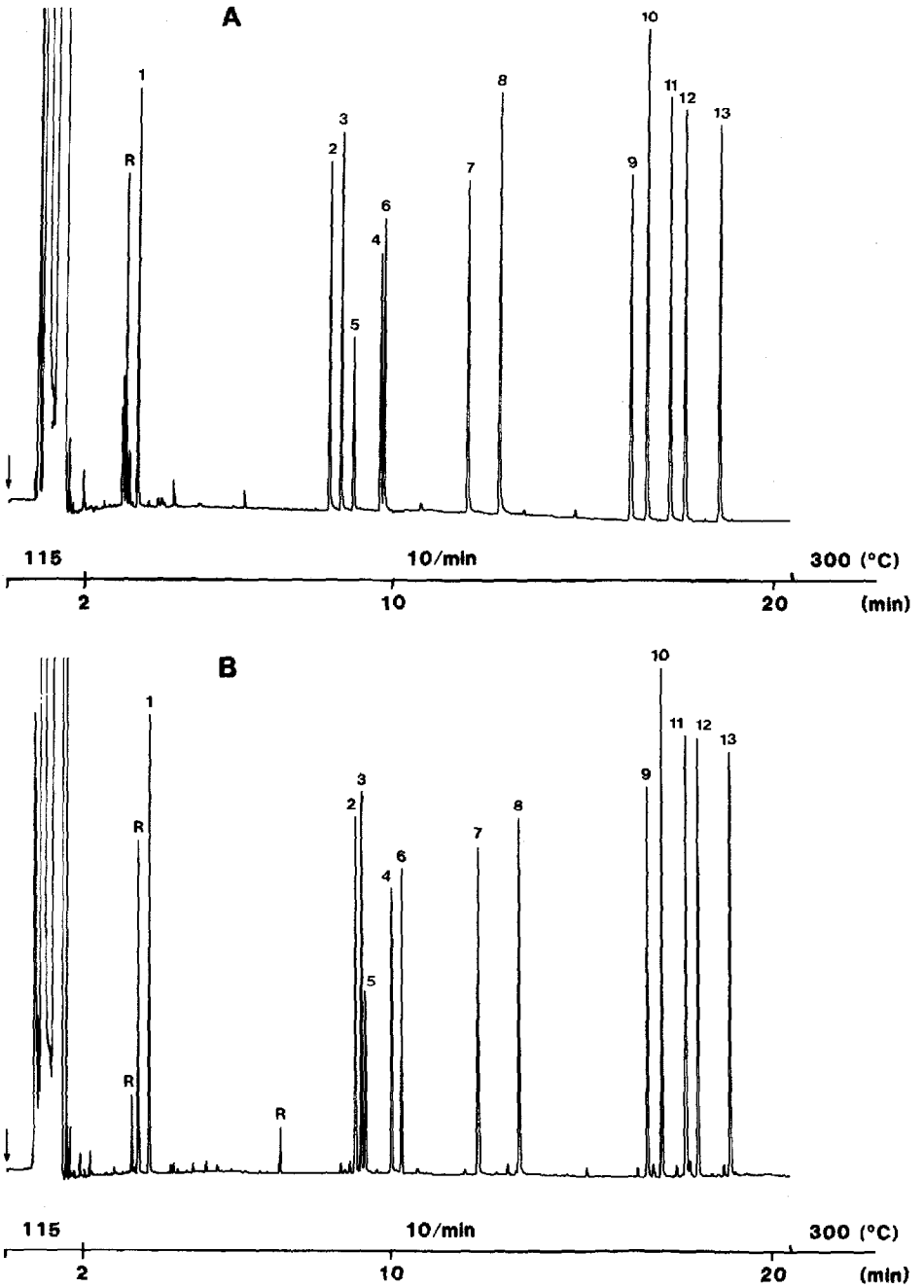

Fig. 1. Chromatograms of amine derivatives. (A) PFPA derivatives; (B) HFBA derivatives. Column, 25 m × 0.32 mm I.D. Pyrex glass capillary with OV-73 stationary phase, film thickness 1.0 μm. On-column injection of 2 μl of toluene solution at 115°C; after 2 min the temperature was programmed at 10°C/min to 300°C, where it was held for 5 min. Carrier gas, helium at 0.8 kg/cm^2. Electron-capture detector, constant-current mode; standing current, 2.0 nA; voltage, 50 V; pulse width, 0.1 μsec; temperature, 300°C; make-up gas, argon–methane (95:5); flow-rate, 55 ml/min. Peak identities according to Table I, each peak corresponding to 20–80 pg of amine. Peaks denoted R refer to reagent and solvent impurities.

of these columns. Initial work with polysiloxane deactivated columns, employing octamethylcyclotetrasiloxane (D4)[9] as deactivating agent, indicates that these columns may be well suited for the present application.

It should be emphasized that almost all of the *ca.* 50 columns prepared for this investigation were of acceptable quality when tested at nanogram levels with amide standard solutions or a "Grob test" mixture[10] and a flame-ionization detector, but only when tested at picogram levels with an electron-capture detector was their true suitability for the trace analysis of perfluoro fatty acid amides revealed.

One important factor with regard to the high inertness of the column finally chosen is the relatively high stationary phase film thickness (1 μm) used. Of the stationary phases tested (OV-73, OV-1, SE-52 and SE-54), OV-73 was selected as having very good long-term stability (one column was in constant use for 6 months) and separation efficiency, although differences between the tested phases in the latter respect were small. All stationary phases used were gum phases, being preferable in conjunction with on-column injection because of low solubility[11], and electron-capture detection, because of the low bleed rate[12].

The columns were fitted into the chromatograph using Vespel graphite ferrules (obtained from Carlo Erba, Milan, Italy). The use of Teflon or Viton ferrules was found to give ghost peaks, even when used at the cool injector end.

Carrier gas. Although hydrogen is generally the most suitable carrier gas in capillary GC, helium was employed because of the higher response and better linearity in conjunction with the electron-capture detector[13], although this meant about 20–30°C higher elution temperatures. Use of the make-up gas (argon–methane) as the carrier gas was not considered, as this would result in even higher elution temperatures, although the detector performance might be improved.

On-column injection. The on-column injection technique is the most reliable injection technique for quantitative analysis by capillary GC. The reproducibility of our chromatographic system was found to be acceptable, in that repeated injections of 2-μl aliquots of a 25 pg/μl standard solution of all PFPA derivatives at 115°C gave peak height standard deviations of 0.3% for the aniline derivative and 0.8–1.7% for the other derivatives, eluted at temperatures of up to 300°C.

Problems with removal of the stationary phase by solvent flushing were dealt with as described above. When renewing the capillary inlet end, both removal of the stationary phase prior to and the use of a protective atmosphere (nitrogen or helium) during straightening are essential, as increased column adsorption of samples will otherwise occur, as demonstrated by Grob *et al.*[4].

It has been demonstrated that non-extractable stationary phases can be prepared *in situ* from, *e.g.*, OV-73 by using dicumyl or dibenzoyl peroxide and other cross-linking agents[9,14–16]. For such stationary phases, the need to renew the inlet end of the column generally does not arise, as the phase is not flushed from the column during injection and involatile deposits can be removed with a suitable solvent. Deterioration of column ends due to high temperatures can not be prevented, however, and as renewal of the column end is not possible, the column life is considerably shortened. In addition, these stationary phases have a greater tendency to adsorb samples. On that account, non-extractable stationary phases are at present not recommended for the trace analysis of the amides in question.

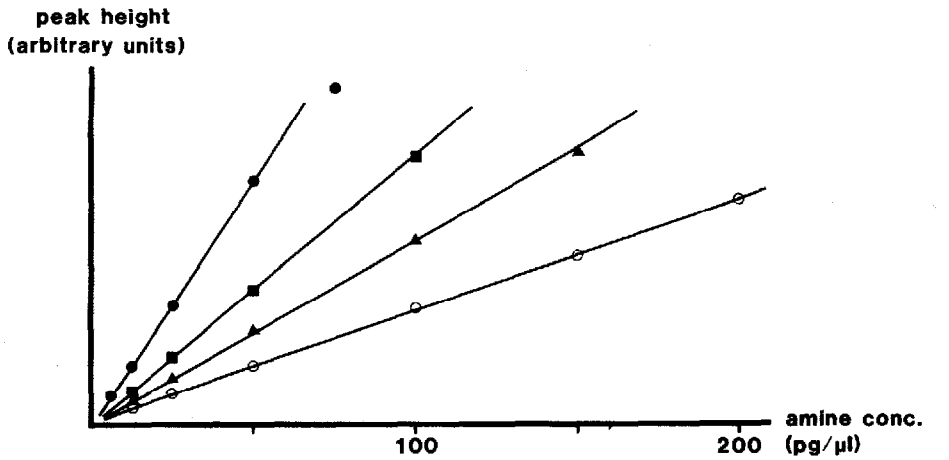

Fig. 2. Calibration graphs for some amine PFPA derivatives in toluene. ● = 2,4 TDA; ■ = MDA; ▲ = benzidine; ○ = DADA.

Quantitative analysis

Linear range and detection limits. Fig. 2 demonstrates the linear range for some of the PFPA derivatives investigated. By the use of a high make-up gas flow-rate (60 ml/min), compared with the 10–20 ml/min recommended[17], the linear range was improved. By modification of the detector flow geometry, whereby the inner diameter of the detector jet and the area of the collector electrode were reduced, the linearity was further improved (Fig. 3).

The detection limits for the compounds investigated, calculated as the amount of amine giving a signal-to-noise ratio of 2:1, are in the region of 0.1–0.4 pg, but adsorption effects restrict practical detection limits to *ca.* 1 pg. Peak evaluation could be based on either peak height or peak area measurements, giving equivalent results.

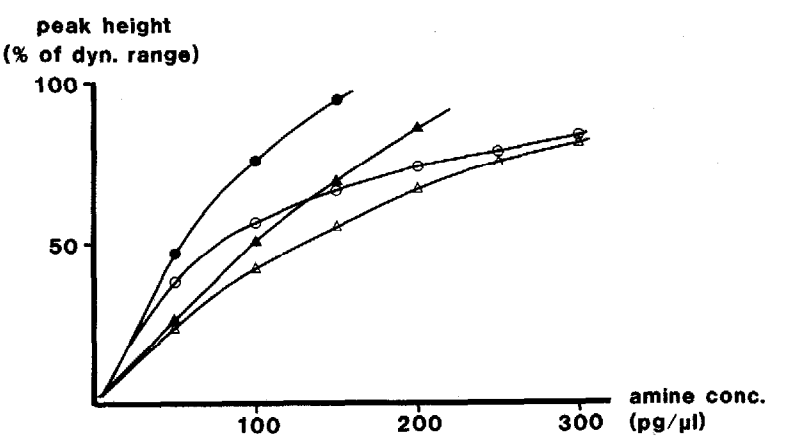

Fig. 3. Effect of make-up gas flow-rate and detector modifications (see text) on response for PFPA derivative of 2,4-TDA. ○ = Original detector and ● = modified detector, flow-rate 20 ml/min; △ = original detector and ▲ = modified detector, flow-rate 55 ml/min.

Mass spectrometry

The structures of all PFPA derivatives were confirmed by GC–MS spectrometry using a Finnigan Model 4021 mass spectrometer in the electron impact mode. It was shown that one hydrogen was substituted at each amino group. Mass numbers (*m/z*) *versus* relative abundance of fragments of interest for the interpretation of the spectra are given in Table II.

As can be seen, a molecular ion is obtained in all instances, varying in relative abundance from 15 to 100%. CF_3^+ and $C_2F_5^+$ ions are also always split off, although the relative abundance of the latter is low in some instances. The structure of a major part of the fragments formed, $(M - X)^+$, can be formally interpreted as that of residual ions appearing when C_2F_5, C_2F_5CO and C_2F_5CONH alone, or in various combinations for difunctional derivatives, are split off from the molecular ion. In the case of 2,4-DAA, TODA and DADA, methyl groups are in addition lost. There is also an indication that hydrogen is eliminated from the methyl group in 2,4- and 2,6-TDA, a reaction that is known to occur with toluene (ref. 18, pp. 76 and 86).

The ions Y^+ in Table II are considered to be formed by rearrangement of the basic aromatic structure. Thus the PFPA derivatives of aniline, α- and β-naphthylamine, 1,5-NDA and 4-aminobiphenyl can give rise to cyclopentadienyl cations by expulsion of HCN from a residual ion (ref. 18, p. 323). For PFPA-DADA, the same kind of ion can, by analogy with anisole, be formed by abstraction of a methyl group followed by expulsion of carbon monoxide (ref. 18, p. 237). The appearance of tropylium ions in the mass spectra of diphenylmethanes is well known (ref. 18, pp. 87–89). On that account, the structural assignments given in Table II for the Y^+ ions of the PFPA derivatives of MDA and MOCA are considered to be well founded.

In most of the spectra, clusters of ions are found in the region of *m/e* 51–52, 63–65, 77–78, 89–92 and 101–107, which are known to arise from the decomposition of aromatic structures[18]. The base peak, *i.e.*, the highest peak in the spectrum, is formed in one instance by the molecular ion (M^+) and in four instances each by the $C_2F_5^+$ ion, an $(M - X)^+$ ion or a Y^+ ion.

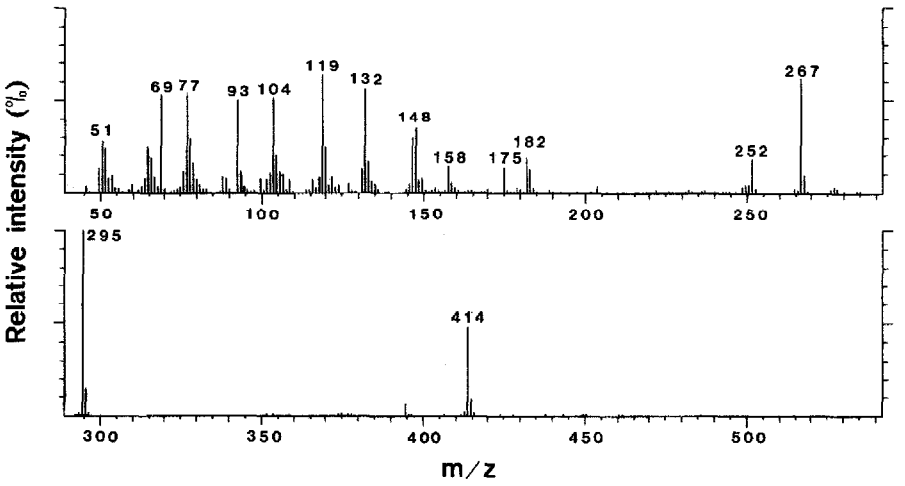

Fig. 4. Mass spectrum of PFPA derivative of 2,4-TDA, obtained by electron impact ionization and positive ion monitoring. For interpretation, see text and Table II.

TABLE II

MASS NUMBER (m/z)/RELATIVE ABUNDANCE (%) OF CERTAIN DIAGNOSTIC IONS FORMED ON ELECTRON IMPACT MASS SPECTROMETRY OF PFPA DERIVATIVES OF AROMATIC AMINES

One PFA group is substituted at each amino group.

PFPA derivative of	*Base peak*	M^+	CF_3^+	$C_2F_5^+$	$(M-C_2F_5)^+$	$(M-C_2F_5CO)^+$	$(M-X)^{+\star}$	Y^+	*Tentative assignment for* Y^+
Aniline	$(M-X)^+$	239/45	69/20	119/20	120/50	92/45	77/100[1]	65/65	Cyclopentadienyl ion $(C_5H_5)^+$
2,4-TDA	$(M-C_2F_5)^+$	414/45	69/45	119/60	295/100	267/35	252/20[1] 148/20[2] 132/25[3] 104/45[4]	–	
2,6-TDA	$(M-C_2F_5)^+$	414/50	69/50	119/60	295/100	267/60	252/20[1] 148/40[2] 132/60[3] 104/50[4]	–	
2,4-DAA	$C_2F_5^+$	430/30	69/95	119/100	311/5	283/20	415/12[5] 296/50[6] 149/70[7] 106/40[8]	–	
α-Naphthylamine	Y^+	289/25	69/20	119/4	170/15	142/40	127/30[1]	115/100	Cyclopentadienyl ion $(C_9H_7)^+$
β-Naphthylamine	Y^+	289/35	69/23	119/4	170/8	142/55	127/50[1]	115/100	Cyclopentadienyl ion $(C_9H_7)^+$

1,5-NDA	M^+	450/100	69/40	119/40	331/20	303/40	184/50[2] 156/50[9]	114/30	Cyclopentadienyl ion $(C_9H_6)^+$
4-Aminobiphenyl	$(M - C_2F_5CO)^+$	315/50	69/20	119/8	196/8	168/100	153/20[1]	141/50	Cyclopentadienyl ion $C_6H_5(C_5H_4)^+$
Benzidine	$C_2F_5^+$	476/45	69/60	119/100	357/3	329/80	182/25[9] 167/20[10]	–	
TODA	$C_2F_5^+$	504/70	69/50	119/100	385/10	357/60	342/4[1] 210/25[9] 195/30[10] 180/30[8] 165/30[11]	–	
DADA	$C_2F_5^+$	536/95	69/70	119/100	417/trace	389/8	402/20[6] 268/40[12] 242/8[9] 227/25[10] 212/25[8] 197/34[11]	169/20	Cyclopentadienyl ion $CH_3OC_6H_3(C_5H_3)^+$
MDA	Y^+	490/30	69/16	119/trace	371/trace	343/12	328/10[1]	165/20	Tropylium ion $C_6H_4(C_7H_5)^+$
								132/100	Tropylium ion $(C_7H_5)^+NHCO$
MOCA	Y^+	558/15	69/45	119/50	439/trace	411/trace	523/20[13]	166/100	Tropylium ion $Cl(C_7H_4)^+NHCO$**
							250/75[14]		

* [1]X = C_2F_5CONH. [2]X = C_2F_5CO. [3]X = $C_2F_5CONH + C_2F_5 + H$. [4]X = $C_2F_5CONH + C_2F_5CO + H$. [5]X = CH_3. [6]X = $C_2F_5 + CH_3$. [7]X = $C_2F_5 + C_2F_5CO + CH_3$. [8]X = $2C_2F_5CONH$. [9]X = $2C_2F_5CO$. [10]X = $C_2F_5CO + C_2F_5CONH$. [11]X = $2C_2F_5CONH + CH_3$. [12]X = $2C_2F_5 + 2CH_3$. [13]X = Cl. [14]X = $2C_2F_5 + 2Cl$.

** The presence of one chlorine atom is shown by the simultaneous appearance of an ion 168/34.

For comparison, the mass spectra of the corresponding HFBA derivatives were also run. It appears that qualitatively they differ only slightly from those of the PFPA derivatives. However, in addition to CF_3^+ and $C_2F_5^+$ ions, $C_3F_7^+$ ions, of course, were formed. It is of interest that the abundance of CF_3^+ is considerably greater than for the PFPA derivatives. Thus, CF_3^+ is the base peak ion in seven cases, compared with none for the PFPA derivatives. Among the $(M - X)^+$ ions, no ions with $X = CF_3$ or $X = C_2F_5$ were found, only those with $X = C_3F_7$ being formed. Their abundance was generally lower than that for the corresponding $(M - C_2F_5)^+$ ions in the spectra of PFPA derivatives. Other $(M - X)^+$ ions present in the spectra of the HFBA derivatives were the same or corresponded to those given in Table II.

Selected ion monitoring (SIM), focusing the instrument on an ion in a mass spectrum, is a valuable technique for the quantitative and qualitative assay of complex mixtures of organic compounds, affording increased sensitivity and selectivity. The highest sensitivity for a given compound is achieved by focusing on the base ion, while monitoring on the basis of the molecular ion gives a high selectivity. Pairs of isomers such as derivatives of 2,4- and 2,6-TDA and α- and β-naphthylamine cannot be separately monitored using SIM technique, as their mass spectra are essentially identical. Focusing on common ions such as CF_3^+ and $C_2F_5^+$ could be suitable for recording chromatograms of PFPA derivatives of amines after separation by GC.

The data referred to above were all obtained by electron impact ionization and positive ion monitoring. For the SIM technique, preliminary work suggests that chemical ionization by methane and negative ion monitoring will give superior sensitivity and selectivity for the compounds investigated. Fig. 5 demonstrates a spectrum obtained in this mode.

CONCLUSION

The proposed trace analysis method for aromatic amines permits the simultaneous assay of many amines of special interest from work environmental health aspects. The high selectivity and sensitivity of the method makes it potentially useful for the analysis of complex industrial atmospheres.

The method is also applicable to the determination of aromatic isocyanates

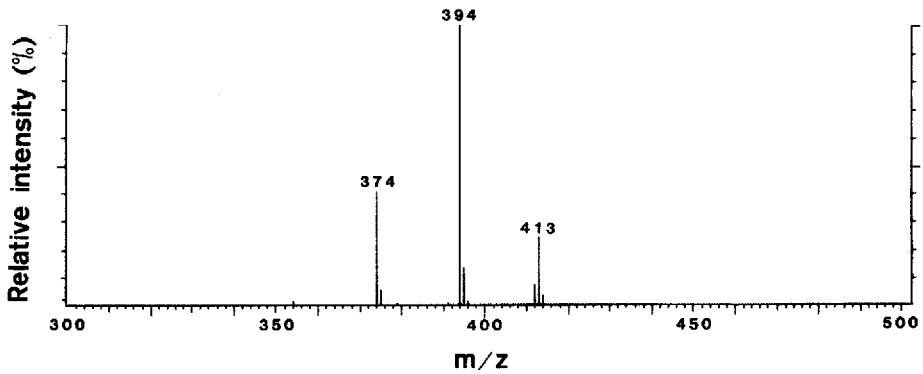

Fig. 5. Mass spectrum of PFPA derivative of 2,4-TDA, obtained by methane chemical ionization and negative ion monitoring.

after sampling in acidic solutions, where they are converted into the corresponding amines. This problem will be discussed in a forthcoming paper.

Further applications of the method will include determination of aliphatic amines and isocyanates in working atmospheres and analytical studies in connection with moulding, welding etc. of polyurethane-based materials.

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