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

III. DETERMINATION OF ALIPHATIC AND ALICYCLIC AMINES AS PERFLUORO FATTY ACID AMIDES USING ELECTRON-CAPTURE AND NITROGEN-SELECTIVE DETECTION

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SUMMARY

A method for the trace analysis of aliphatic and alicyclic amines is presented. It involves derivatization of the amines to the corresponding amides by reaction with a perfluoro fatty acid anhydride. The amines were separated by glass capillary gas chromatography and picogram amounts were quantitated using on-column injection and electron-capture or nitrogen-selective detection.

The method was applied to amines of interest from work environment health aspects. Detection limits were in the 2–30 fmol range with electron-capture detection and in the 40–60 fmol range with nitrogen-selective detection. Linear ranges for the quantitative analysis were established and electron impact and methane chemical ionization mass spectra of investigated heptafluorobutyric acid amides were registered and discussed.

INTRODUCTION

Two gas chromatographic (GC) methods for the trace analysis of aromatic amines, developed at this laboratory, were recently presented[1,2]. They were based on the transformation of the amines into perfluoro fatty acid amides, which were separated and quantitated by glass capillary column GC and electron-capture detection (ECD)[1] or nitrogen-selective detection (thermionic specific detection, TSD)[2]. It was demonstrated that the methods in question were useful for the trace assay of several aromatic amines related to isocyanates, encountered in industrial atmospheres and thus of special interest from work environmental health aspects. Since isocyanates

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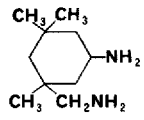
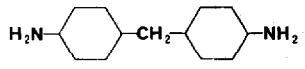
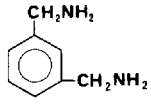
can be hydrolysed to the corresponding amines, the methods were also usable for the determination of aromatic isocyanates after sampling in aqueous acidic solution, where they were converted into the corresponding amine salts.

In this paper, the problem of analysing some aliphatic and alicyclic amines as perfluoro fatty acid amides after reaction with a perfluoro fatty acid anhydride, preferably heptafluorobutyric acid anhydride (HFBAA), is treated in some detail. The methodology is essentially the same as that previously used for the analysis of aromatic amines[1–3]. The amine or isocyanate is sampled from a stream of air into dilute hydrochloric acid and the free amine extracted with toluene after alkalization. After conversion of the amine into the corresponding HFBA derivative and removal of excess reagent and HFBA formed in the reaction, the amide solution is analysed by glass capillary GC, using on-column injection and ECD or TSD. A similar method for the determination of airborne 1,6-hexamethylene diisocyanate by packed column GC and ECD was recently described by Esposito and Dolzine[4].

Table I lists the amines studied and the corresponding isocyanates. The latter are starting materials for the preparation of various polyurethane-based products such as lacquers, glues, foam rubbers, etc. Accordingly, it is of importance to be able to assay them in trace amounts in industrial atmospheres.

TABLE I

AMINES INVESTIGATED

Amine	*Abbreviation*	*Abbreviation corresponding isocyanate***	*Formula*
Hexamethylenediamine 1,6-Hexanediamine CA* 124-09-4	HDA	HDI	$H_2N(CH_2)_6NH_2$
2,2,4-Trimethylhexamethylenediamine CA 25497-66-9	TMHDA	TMHDI	$H_2NCH_2C(CH_3)_2CH_2CHCH_3(CH_2)_2NH_2$
Isophorondiamine CA 2855-13-2	IPDA	IPDI	
4,4'-Methylenebiscyclohexylamine CA 1761-71-3	MCA	MCI	
1,3-Xylenediamine CA 1477-55-0	XDA	XDI	

* CA = *Chemical Abstracts.*

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

EXPERIMENTAL

Apparatus

Chromatographs and detectors. A Varian Model 3700 gas chromatograph equipped with a Carlo Erba on-column injection system and a Varian thermionic specific detector was used for the nitrogen-selective detection. Typical settings for the detector were: gas flow-rates, 4.0 ml/min of hydrogen and 180 ml/min of air; bead-heating current, 5.3 A; bias voltage, −10 V; temperature, 290°C. For ECD a Carlo Erba Fractovap Model 4160 gas chromatograph equipped with a Model HT-25 electron-capture detector and Control Module 251 was used in the constant-current mode, voltage 50 V, pulse width 0.1 μsec, standing current 2.0 nA, temperature 300°C.

Gases. Carrier gas was helium for both TSD and ECD measurements with inlet pressure 0.3 kg/cm^2. Make-up gas for TSD was nitrogen at a flow-rate of 20 ml/min and for ECD argon–methane (95:5), at 60 ml/min. These gases were dried over molecular sieve 5 A and deoxygenated using an "Indicating Oxytrap" (Chrompack, Middelburg, The Netherlands). Hydrogen and air for TSD were used without extra purification.

Materials

Chemicals. Amines were obtained from the following suppliers: HDA from E. Merck (Darmstadt, F.R.G.); TMHDA and IPDA from ICN Pharmaceuticals (Plainview, NJ, U.S.A.); MCA from Aldrich-Europe (Beerse, Belgium) and XDA from Fluka (Buchs, Switzerland). HDI was from Merck and HFBAA from Pierce (Rockford, IL, U.S.A.). Octamethylcyclotetrasiloxane (D_4) and OV-73 stationary phase were from Ohio Valley Specialty Chemicals (Marietta, OH, U.S.A.).

Solvents and solutions. Solvents used were all of p.a. grade (see ref. 1). 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.

Standard solutions of amides were prepared by dissolving accurately weighed amounts of amines (*ca.* 50 mg, except for XDA where *ca.* 10 mg were weighed) in 100 ml of 10% hydrochloric acid. To a 1-ml aliquot of this solution were added 2 ml of saturated sodium hydroxide solution and the free amine then extracted with toluene. To 1 ml of the toluene solution, containing *ca.* 20 μg of the amine, were added 60 μl of HFBAA, and after 10 min at room temperature the excess of HFBAA and the acid formed were removed by shaking with 1 ml of phosphate buffer solution (pH 7). Standard amide solutions of desired composition were then made up from this solution by dilution with toluene.

Procedure

Sampling, extraction and derivative preparation. A midget impinger was utilized for the absorption of isocyanates into 10 ml of dilute hydrochloric acid. This part of the procedure will be treated in more detail in a forthcoming paper. Extraction and derivative preparation were performed in the same way as previously described for standard solutions except that 20 μl of HFBAA were added to 1 ml of the toluene solution of amine.

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.*[5]. The columns were dried by nitrogen purging for 2 h at 250°C. Deactivation was achieved by dynamic coating with a plug of pure D_4 followed by flame-sealing and thermal treatment at 400°C overnight. After rinsing with toluene, methanol and diethyl ether, OV-73 stationary phase was applied by static coating from pentane solutions, 1.3% w/v and 0.13% w/v, to produce stationary phase thicknesses of 1.0 μm and 0.1 μm, respectively.

Quantitative analysis. Quantitative analysis with TSD was based on peak height measurements and with ECD on peak area measurements.

RESULTS AND DISCUSSION

Procedure

Formation of amides. Aliphatic and alicyclic amines are less reactive towards HFBAA than aromatic amines. In order to compensate for the decreased reactivity, the reaction time was increased from 5 to 10 min at room temperature. The amount of reagent as before was 20 μl per ml of amine solution. Addition of a catalyst was found to be unnecessary.

Theoretically several isomeric amides can be formed from each amine. We have, however, found that under the conditions used with a moderate excess of anhydride present only the symmetrical diamides are formed from the diamines in Table I.

Gas chromatography

Capillary columns and separation of HFBA amides. In Part II of this series[2] it was shown that trace analysis by glass capillary GC of perfluoroacylated aromatic amines could be performed on D_4 deactivated thin-film OV-73 columns. In the present case it was found on comparison between D_4 deactivated columns with 0.1 and 1.0 μm film thicknesses, respectively, that thin-film columns are also well suited for the separation of perfluoroacylated aliphatic amines. In addition to improved separation characteristics compared to thick-film columns, lower elution temperatures and column bleeding were obtained.

The results of the GC separation of the HFBA derivatives of the Table I amines are presented in Fig. 1 (ECD) and Fig. 2 (TSD). As can be seen, several of the amides furnish more than one peak. Thus, two peaks are obtained for each of the HFBA derivatives of TMHDA and IPDA and three peaks for the MCA derivative.

In the case of THMDA the amine, although labelled 2,2,4-trimethylhexamethylenediamine, is a mixture of this compound and the 2,4,4-isomer. The other multiple peaks in the chromatograms are due to the existence of amine stereoisomers, *viz. cis-trans* isomers of IPDA and *cis-cis, cis-trans* and *trans-trans* isomers of MCA (8, 41 and 51% w/w, respectively, according to the manufacturer).

The elution order of the HFBA derivatives of the MCA isomers is *cis-cis, trans-trans* and *cis-trans* on the OV-73 stationary phase. On a more polar phase, *e.g.* OV-225, the last two peaks are reversed. GC separation of the methylated MCA isomers and of their N-dimethylaminomethylene derivatives has previously been achiewed by Scoggins *et al.*[6,7].

Linear range and detection limits. Calibration plots for HFBA derivatives of

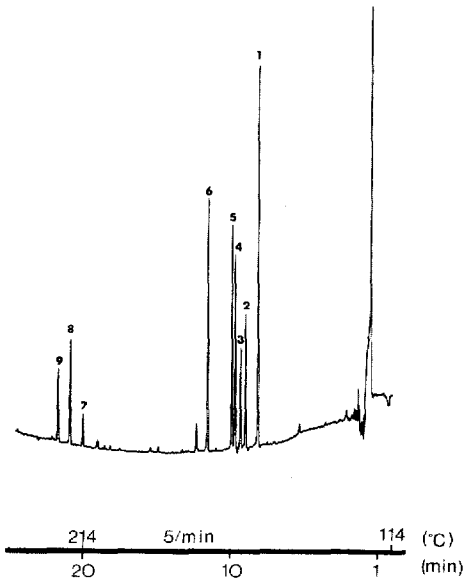


Fig. 1. Chromatogram with ECD of HFBA derivatives of the Table I amines. Peak identities: 1 = HDA; 2,4 = TMHDA; 3,5 = IPDA; 6 = XDA; 7,8,9 = MCA. On-column injection of 113 pg each of HDA and IPDA, 108 pg of TMHDA, 33 pg of XDA and 440 pg of MCA. Column, 13 m × 0.32 mm I.D. Duran 50 glass capillary, D_4 deactivated with OV-73 stationary phase, film thickness, 0.1 μm. Temperature programming as shown. Carrier gas helium at 0.3 kg/cm². 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, 60 ml/min.

the amines investigated are given in Fig. 3 (ECD) and in Fig. 4 (TSD). They demonstrate linear response in a wide range of amines for both ECD and TSD. The amine samples used for calibration were dissolved in 10% hydrochloric acid and then subjected to the extraction and derivatization procedures.

Detection limits for the HFBA amides investigated using ECD or TSD and calculated as the amount giving a signal-to-noise ratio of 2:1 are listed in Table II. For IPDA and MCA the detection limits given refer to the most abundant isomer and have been recalculated to 100%. For comparison, detection limits for the HFBA amides of two aromatic amines, *viz.* 2,4-toluenediamine (2,4-TDA) and 4,4'-methylenedianiline (MDA), are also given.

It is demonstrated that the response with ECD is 2–25 times greater than with TSD for aliphatic amides, but up to *ca.* 100 times greater for aromatic amides. It is also seen that aromatic amides are more sensitive to ECD than aliphatic of similar structure, whereas their sensitivity to TSD is more equal. That the presence of an aromatic group also increases sensitivity to ECD for aliphatic amides is shown by the XDA amide, which is the most sensitive member of the group of aliphatic amides. This fact is also demonstrated by the calibration plots in Fig. 3.

Mass spectrometry

The structures of the HBFA amides were confirmed by GC–mass spectrometry using a Finnigan Model 4021 mass spectrometer in the electron impact (EI) mode or

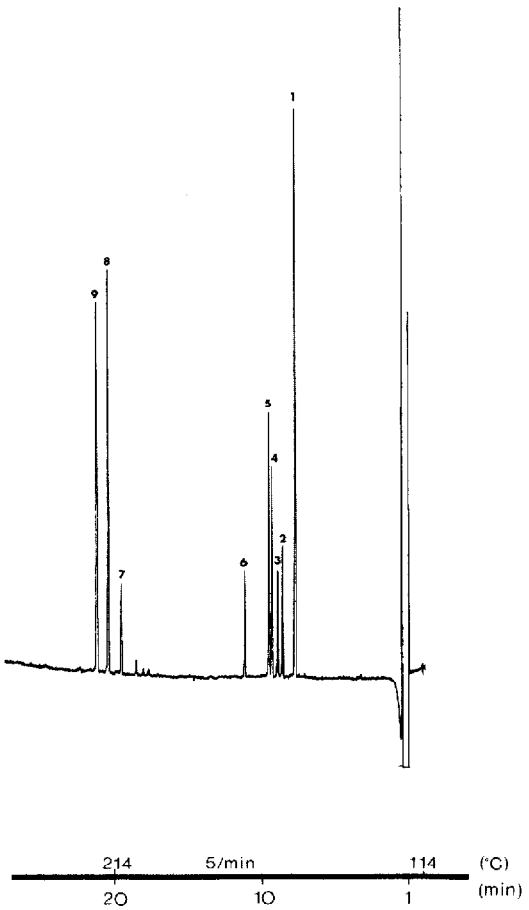


Fig. 2. Chromatogram with TSD of HFBA derivatives of the Table I amines. On-column injection of 450 pg each of HDA and IPDA, 430 pg of TMHDA, 130 pg of XDA and 1760 pg of MCA. Peak identities according to Fig. 1. Thermionic specific detector; bead-heating current, 5.3 A; bias voltage, −10 V; temperature, 290°C; hydrogen flow-rate, 4 ml/min; air flow-rate, 180 ml/min; make-up gas, nitrogen; flow-rate, 20 ml/min. Other conditions as in Fig. 1.

by methane chemical ionization (CI) with positive ion monitoring. Typical spectra are given in Figs. 5 and 6 for the HFBA amide of HDA.

CI mass spectra. The ions in the CI mass spectrum are predominantly in the high-molecular-weight region of the spectrum, whereas the converse is true for the EI mass spectrum. The main part of the former spectrum can be interpreted by comparison with the basic work of Munson and Field[8]. The base ion, *i.e.* the most intense ion in the spectrum (*m/e* 509), is due to monoprotonation of the amide molecule (M) in a reaction with CH_5^+ and $C_2H_5^+$ ions present in the reaction gas, whereby a $(M + 1)^+$ ion is formed. The parent M^+ ion with *m/e* 508 is probably the result of a charge exchange with the ethyl ion.

It is well known that a $(M - 1)^+$ ion is formed in the methane plasma (*m/e* 507) by splitting off hydrogen from the $(M + 1)^+$ ion or by hydride-transfer from

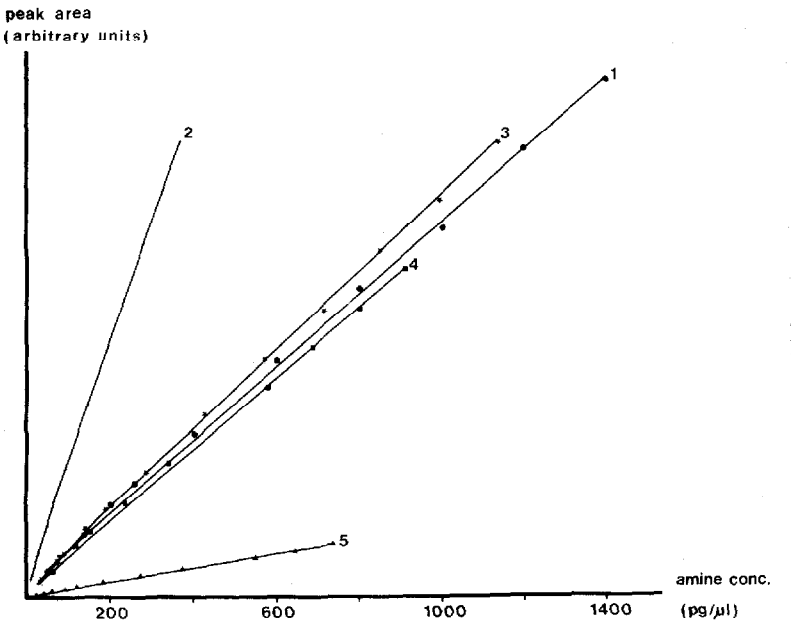


Fig. 3. Calibration curves for HFBA derivatives of HDA (1), XDA (2), IPDA (3), TMHDA (4) and MCA (5). On-column injection on an OV-73 capillary column with EC detection. Other conditions as in Fig. 1.

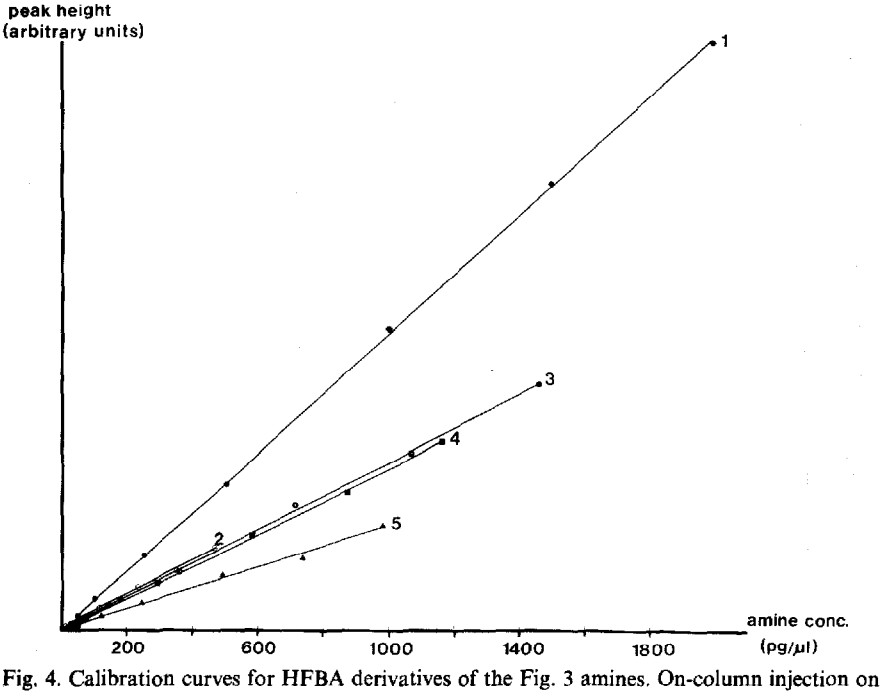


Fig. 4. Calibration curves for HFBA derivatives of the Fig. 3 amines. On-column injection on an OV-73 capillary column with TSD. Other conditions as in Fig. 2.

TABLE II

DETECTION LIMITS WITH TSD AND ECD FOR HFBA AMIDES OF SOME AMINES

Amine	*Detection limit (fmol)*	
	TSD	*ECD*
HDA	40	7
TMHDA	50	5
IPDA	50	5
XDA	50	2
MCA	60	30
TDA	80	0.8
MDA	80	0.7

M to an ethyl ion. The ion with *m/e* 489 is most likely due to abstraction of HF from the molecule ion, and the ions with *m/e* 537 and 549 to addition of $C_2H_5^+$ and $C_3H_5^+$, respectively, to the amide molecule. Only a few ions of low abundance appear outside this range. These ions generally coincide with such found in the EI spectrum (see below).

EI mass spectra. In a previous investigation of EI mass spectra of HFBA amides of aromatic amines[1] it was found that characteristic CF_3^+, $C_2F_5^+$ and $C_3F_7^+$ ions were split off and registered and that residual ions $(M - X)^+$ appeared in the spectra. X corresponded *inter alia* to C_3F_7, C_3F_7CO, or C_3F_7CONH alone or in

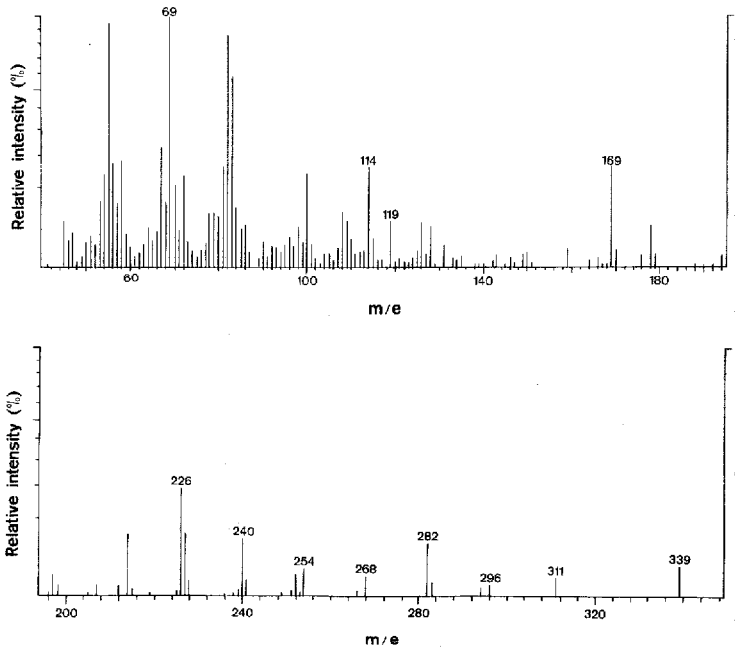


Fig. 5. Mass spectrum of HFBA derivative of HDA, obtained by EI ionization and positive ion monitoring. For interpretation see text.

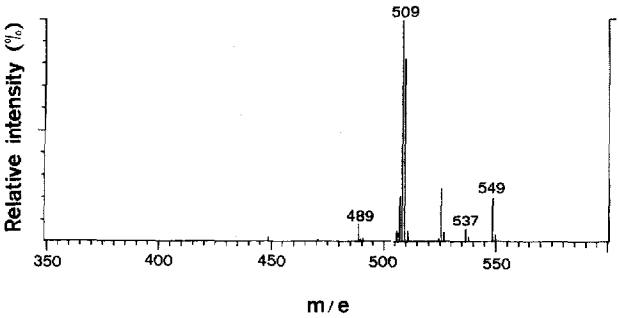


Fig. 6. Mass spectrum of HFBA derivative of HDA, obtained by methane CI and positive ion monitoring. For interpretation see text.

various combinations for difunctional derivatives. Inspection of the present EI spectra reveals, that the same pattern is followed (see Fig. 5).

Hence, for the HFBA amide of HDA we get CF_3^+, $C_2F_5^+$ and $C_3F_7^+$ ions with *m/e* 69, 119, and 169, respectively. Among the $(M - X)^+$ ions are found those with X = C_3F_7 (*m/e* 339), C_3F_7CO (*m/e* 311), C_3F_7CONH (*m/e* 296) and $2C_3F_7CO$ (*m/e* 114). In addition, the carbon chain is split leaving fragment ions $[C_3F_7CONH(CH_2)_n]^+$ (n = 1-5) with *m/e* 226, 240, 254, 268 and 282. Ions with *m/e* 282, 296 and 339 also appear in the CI mass spectrum. The base peak is the CF_3^+ ion, as was also found to be the case with many of the HFBA amides of the aromatic amines.

A difference between the present EI spectrum and those of aromatic amides is the absence of a molecular ion in the former case. In fact, the highest ion registered in Fig. 5 has *m/e* 339. This behaviour seems to be typical of aliphatic and alicyclic HFBA amides. It thus appears that the CI and EI mass spectra of the present amides complement each other in a fortunate way, in that the former mainly gives information about the upper part of the spectrum and the latter about its lower and middle part.

CONCLUSIONS

The method previously developed for the assay of aromatic amines and isocyanates in air[1-3], *viz.* GC analysis of the compounds in question after transformation to the corresponding perfluoro fatty acid amides, is also suitable for the trace analysis of aliphatic and alicyclic amines and isocyanates of interest in relation to the manufacture and utilization of polyurethanes. The use of highly selective glass capillary GC makes it possible to distinguish between isomers of the various compounds and application of ECD or TSD allows trace analysis in the low picogram range.

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