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SELECTIVE DETECTION OF POLYAROMATIC AND POLYCHLORINATED ISOMERS IN AEROSOL EXTRACTS BY CAPILLARY GAS CHROMATOGRAPHY COMBINED WITH NEGATIVE-ION DETECTION

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SUMMARY

High-resolution gas chromatography combined with negative-ion chemical ionization mass spectrometry has been used to analyse air extracts for polyaromatic and polychlorinated isomeric compounds. Nanogram amounts of isomers could be differentiated by using methane–nitrous oxide reaction gas mixtures. Resonance electron-capture ionization is a very useful technique for the detection of nitrated polyaromatics. The total ion current chromatograms are compared with those obtained by electron-capture detection.

INTRODUCTION

High-resolution gas chromatography (HRGC) has become an indispensable tool in the analysis of complex air sample extracts. Some applications are the separation of polychlorinated biphenyls, polyaromatic hydrocarbons (PAHs) and polychlorinated dibenzo-*p*-dioxins. Although the separation efficiency of capillary columns has been improved considerably in recent years, there are still some problems in the separation of isomeric compounds. One example is the separation of the benzofluoranthenes in aerosol extracts.

Another well known problem in air analysis is the interference from major compound groups (such as aliphatic hydrocarbons and aromatics), when minor or trace compounds with biological activity or toxicological properties are to be detected. The resolving power of high-quality capillary columns is still not sufficient to eliminate these problems completely. One way to reduce interferences is by pre-fractionation, *e.g.*, by high-performance liquid chromatography. However, losses of trace compounds cannot always be avoided.

Electron-capture detection (ECD) is a very useful tool for obtaining information on compounds with high electron affinity and for reducing interferences from the sample matrix. As reported elsewhere[1], there is a strong correlation between biological activity (such as mutagenic or carcinogenic properties) and the ability to form stable negative ions. However, the major drawback of ECD is that no structural information can be obtained.

When HRGC is used with negative-ion chemical ionization (NICI) mass spec-

trometry, the resolving power of capillary GC is combined with a detection method of great flexibility and selectivity[2]:

(1) When methane is used as a reagent gas to form thermal electrons in the ion source, compounds with electron affinity factors $E_a > 0.5$ eV easily can be detected by resonance capture ionization. Interferences from the sample matrix, containing aliphatics, aliphatic-substituted benzenes, phthalates, silicones, etc., are strongly suppressed. Complete mass spectra can be recorded with only 50–100 pg of compound. However, normally, only information about molecular weight and isotope clusters can be obtained. In a dissociative electron-capture mechanism a fragment with high electron affinity is often cleaved off (e.g., Cl^-, NO_2^-). Monitoring of these fragments helps to confirm the compound class or to use the mass spectrometer as a group-selective detector. Using the selected-ion detection mode, trace amounts of less than 50–100 fg are detectable. As there is a strong correlation between biological activity and response in the NICI electron-capture mode, this method is very useful in the search for mutagenic compounds or metabolites in different kind of samples[3].

(2) The application of reagent gas mixtures such as methane–nitrous oxide, hydrogen–nitrous oxide or methane–acetylene allows the formation of different Brønsted bases(OH^-, $CH \equiv C^-$, etc.) and reagent gas ions in the ion source[4]. Apart from resonance capture ionization, the main reaction pathways in the ion source are then deprotonation of the compound $(M - H)^-$ and ion–molecule adduct formation, e.g., $(M + OH)^-$, $(M - H + NO)^-$ and $(M - H + H_2O)^-$. These reactions produce significant differences in the mass spectra of many isomeric polyaromatic hydrocarbons. Different mass spectra are also obtained for polychlorinated dioxins. For a complete mass spectrogram of these compound classes, 100–300 pg are sufficient. The discrimination of aliphatic compounds, phthalates, substituted benzenes, etc., is inferior to that obtained by NICI with methane, but still sufficient for many applications. The number of compound classes that can be detected by NICI is considerably extended (including terpenes, phenols, etc.). Another advantage is that the total ion current gas chromatograms are very similar to those obtained by electron-capture detection.

Both techniques, combined with HRGC, have been used to characterize aerosol extracts. Useful additional information about polyaromatic and polychlorinated isomeric compounds could be obtained. Some examples are presented in the Results and discussion section.

EXPERIMENTAL

Gas chromatography

A Carlo Erba 4160 gas chromatograph, equipped with an HT-25 ^{63}Ni electron-capture detector and a Model 251 control unit, was used. The separation columns were fused silica, 25 m × 0.32 mm I.D., coated with SE-52 or SE-54 of film thickness 0.1 or 0.17 µm (Hewlett-Packard or Prolab, Espoo, Finland). The same instrumental parameters and separation conditions as described in ref. 5 were used.

Mass spectrometry

A Hewlett-Packard Model 5985B GC–MS system, equipped with the capability

to detect negative ions and with a laboratory-built interface, having a fused-silica transfer line, was used. The reagent gases were methane (0.4 Torr ion-source pressure) or methane–nitrous oxide (0.2 + 0.3 Torr). The following conditions were used:
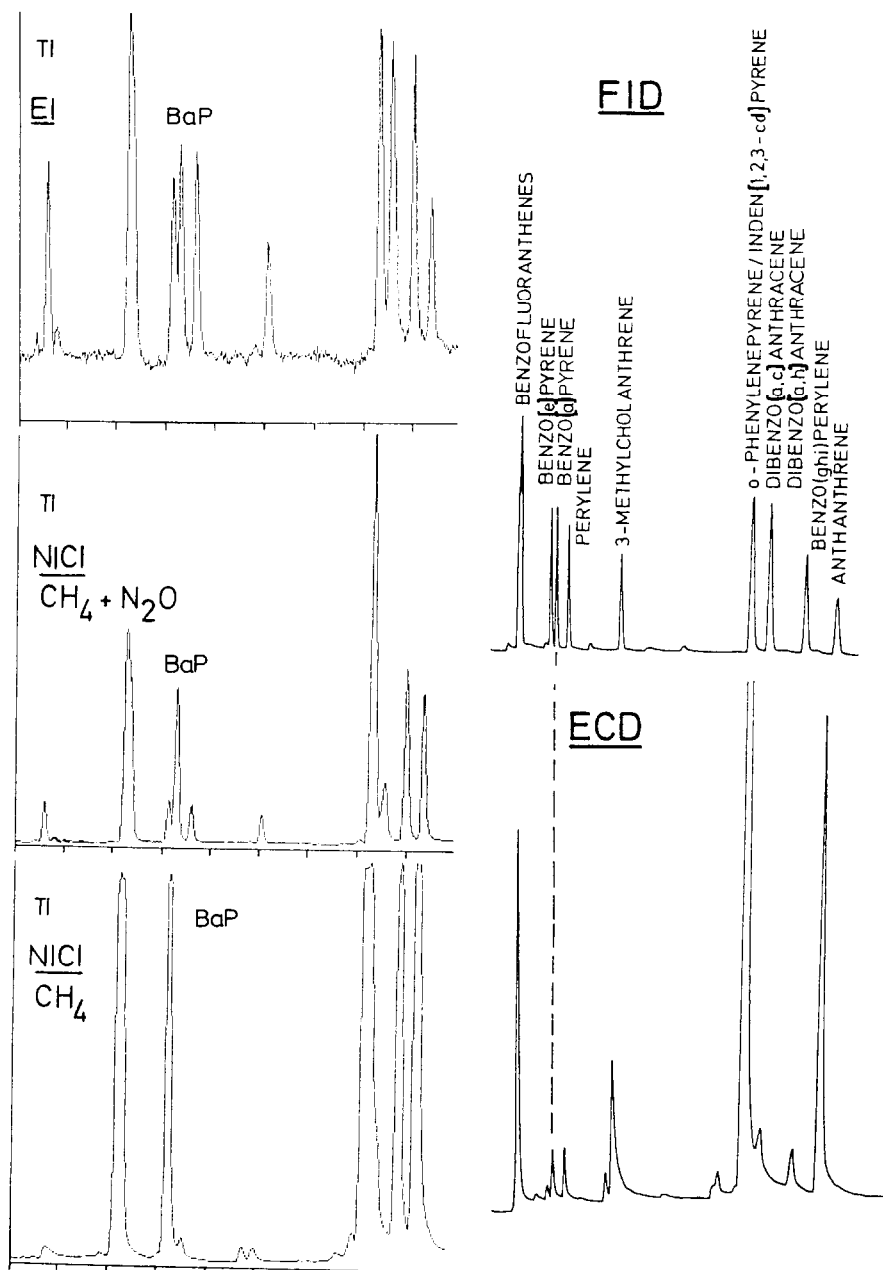

Fig. 1. Gas chromatograms of PAHs with molecular weight 252 and 278 obtained by ECD, FID, NICI with CH₄ and NICI with CH₄ N₂O. Amount of sample injected, 4 6 ng per compound. BaP = benzo[a]-pyrene. TI is total ion current.

TABLE I

NICI MASS SPECTRA OF SOME ISOMERIC PAHs OF MOLECULAR WEIGHT 252

CH_4, N_2O was used as the reaction gas mixture. Relative abundance is given as a percentage of the base peak.

Compound	Ion abundance (%)[*,***]				Response factors[**,***]		Carcinogenic activity
	$(M - H)^-$	M^-	$(M + OH)^-$	$(M - H + N_2O)^-$	$NICI/CH_4$	$NICI/CH_4$-N_2O	
Benzo[b]fluoranthene	16.0	100	4.2	1.9	48	21	+ +
Benzo[j]fluoranthene	33.9	100	31.5	5.5	31	18	+ +
Benzo[k]fluoranthene	16.5	100	3.6	4.4	52	17	+ +
Benzo[e]pyrene	100	74.0	2.1	24.5	0.01	5.5	0/+
Benzo[a]pyrene	10.5	100	2.1	1.6	120	31	+ + +
Perylene	100	53.0	32.0	22.1	1.5	5.3	0

* Other ions not presented in this table are $(M + 1)^-$, $(M + 15)^-$ and $(M - H + NO)^-$.
** Averages of five measurements; relative standard deviation 4–5%.
*** Response factors relative to EI.

ion-source temperature, 175–200°C; electron energy, 75–95 eV; emission current, 200–300 μA; separation columns, glass, 30 m × 0.32 mm I.D.; stationary phase, SE-52; film thickness, 0.1 μm (60 m × 0.25 mm I.D., coated with OV-1, 0.1 μm, for polychlorinated dioxins).

Aerosol sampling and clean-up

For details see ref. 5. Samples were extracted with liquid carbondioxide, as described in ref. 6.

RESULTS AND DISCUSSION

The different response patterns of some five-ring PAHs detected by flame-ionization (FID), ECD, NICI (see above) and electron-impact ionization (EI) methods
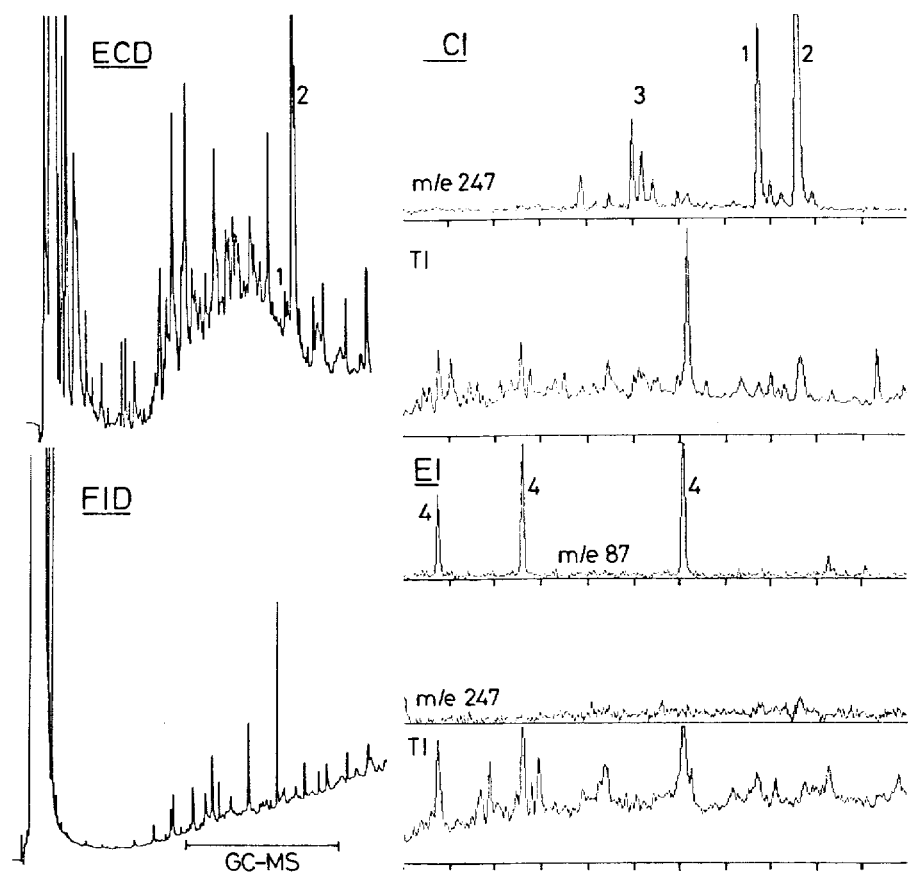

Fig. 2. Fraction of an aerosol extract (sample volume *ca.* 72 m³) containing NO₂-PAHs. 1 = 3-Nitro-fluoranthene; 2 = 1-nitropyrene; 3 = dimethyldinitronaphthalenes (mol. wt. 246); 4 = alicyclic alcohols. By FID and EI no NO₂-PAHs could be found. Identification by ECD is also difficult. The mass fragmentogram for *m/e* 247 (mol. wt. of nitrofluoranthene/pyrene) clearly shows the presence of these compounds. The range of the total ion-current chromatograms is marked in the FID chromatogram. Volume of sample extract, 60 μl; volume injected, 1 μl.

are compared in Fig. 1. The electron-capture detector gives an increased response for some PAHs (see also ref. 7) but, in general, no additional information can be obtained. Resonance electron-capture ionization gives a considerably increased sensitivity for most compounds with carcinogenic properties (see also Table I and ref. 8). The correlation between biological activity and the ability to form stable negative ions by resonance capture is about 90% for the 3- to 6-ring PAHs that were tested. The method is well suited for screening of samples for PAHs with more than 3 rings. NICI with methane–nitrous oxide mixtures given a response increased by a factor of 5–60 for all 2- to 6-ring PAHs compared with EI. In addition, many isomeric PAHs can be differentiated by differences in the abundance of the ion–molecule adducts formed (see Table I and ref. 8).

The search for nitrated PAHs in urban air is another application. These compounds can also be formed as sampling artefacts when large amounts of air, con-
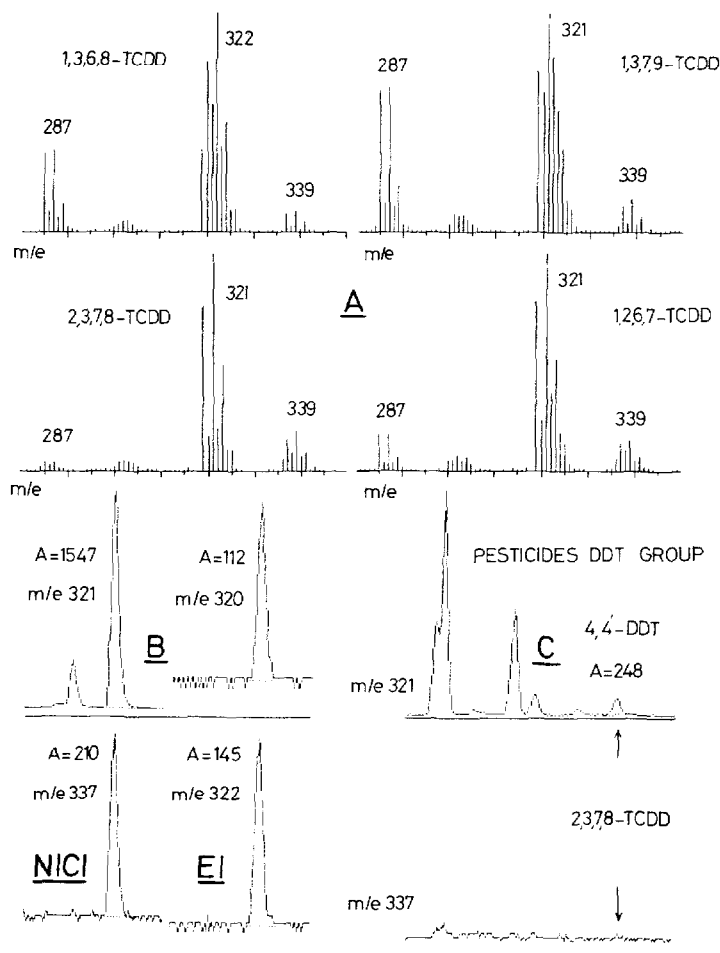

Fig. 3. (A) Mass spectra of some TCDD isomers, obtained by the NICI/CH₄–N₂O technique. (B) Comparison of the response factors of 2,3,7,8-TCDD with EI and by NICI with CH₄–N₂O. Amount injected, 50 pg. (C) Interference of some pesticides at m/e 321 is completely eliminated at m/e 337.

taining nitrogen oxides, are sucked through the filter on which PAHs are deposited. Short sampling periods are therefore desirable. As shown in Fig. 2, neither the FID or the EI method is able to detect nitrated PAHs in such a sample. The identities of compounds with the same retention time as 3-nitrofluoranthene and 1-nitropyrene, which were detected by ECD in the same sample, could be confirmed by NICI. As little as 50–100 pg compound still gives a mass spectrum with the molecular weight information. Dinitro-PAH compounds give, in addition, fragment ions $(M - O)^-$, $(M - NO)^-$, $(M - NO_2)^-$ and NO_2^-, which facilitate their identification. Some unknown dimethyldinitronaphthalenes could be found in the same sample with help of these ions.

Preliminary results indicate that NICI with methane–nitrous oxide is also useful for the detection and identification of tetrachlorodibenzo-*p*-dioxin (TCDD) isomers (see Fig. 3). The OH^- ions formed attack the dioxin ring. Opening of the ring by OH^- attachment is followed by loss of H_2O. This gives two additional isotope clusters at m/e 337 $[(M + OH)^-]$ and 319 $[(M + OH - H_2O)^-]$. As can be seen in Fig. 3, these chlorine clusters can be used to improve the discrimination against pesticides and other polychlorinated compounds, which are eluted with the same retention time as 2,3,7,8-TCDD on columns with average separation efficiency (*e.g.*, 30 m × 0.3 mm I.D., coated with OV-1). When the same instrument tuning optimization is used for both EI and NICI, the sensitivity in the NICI mode is increased by a factor of about 10 in comparison with EI.

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