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ANALYSIS OF ORGANICS IN THE ENVIRONMENT BY FUNCTIONAL GROUP USING A TRIPLE QUADRUPOLE MASS SPECTROMETER

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SUMMARY

A comprehensive scheme for the direct analysis of organics in the environment is described. The technique of collision-activated dissociation on a triple quadrupole mass spectrometer is employed for the characterization of both knowns and unknowns by both molecular weight and functional group Neutral loss scans are used for the analysis of carboxylic acids, phenols, polynuclear aromatic hydrocarbons, amines and chlorocarbons Parent ion scans are used for detection of aldehydes, ketones and phthalates The total analysis time per sample is typically 25–30 min by this approach.

INTRODUCTION

Analysis of water samples for the 114 toxic organic chemicals on the U.S. Environmental Protection Agency (EPA) priority pollutant list presently involves separation of the organics from the matrix using a combination of wet chemical extraction steps, sample concentration and clean-up by various types of chromatography, and final analysis by a gas chromatograph–mass spectrometer–data system[1] This approach has proved to be highly reliable and applicable to a variety of different matrices. Efforts to extend the methodology and develop a master analytical scheme for the analysis of all organics in water that can be made to pass through a gas chromatograph are presently in progress[2].

Disadvantages of the above approach include: (a) the inability to detect highly polar compounds too involatile or thermally labile to pass through the gas chromatograph, (b) the high labor costs dictated by the need for extensive sample clean-up and preseparation prior to analysis, and (c) the large amount of time required to perform even a single analysis on a relatively expensive gas chromatograph–mass spectrometer–data system.

To overcome these problems, we have initiated research to develop an alternate comprehensive analytical scheme that uses the technique of collision-activated dissociation on a triple quadrupole mass spectrometer for the direct, rapid, qualitative–semiquantitative analysis of organics in liquid and solid environmental matrices Elimination of all or most wet chemical and chromatographic separation steps,

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characterization of both knowns and unknowns by molecular weight and functional group at the 0 1–1 0-ppm level, and a total analysis time per sample of under 30 min are additional objectives of this effort

Here we describe the instrumentation employed in this analytical scheme and outline the approach used for the direct analysis of phthalates, chlorocarbons, polycyclic aromatic hydrocarbons, phenols, amines, carboxylic acids, ketones, and aldehydes in environmental matrices

Additional examples of mixture analysis by tandem mass spectrometry can be found in two excellent reviews[3,4]

EXPERIMENTAL

All experiments were performed on a Finnigan triple stage quadrupole mass spectrometer–data system This instrument consists of a conventional electron ionization chemical ionization ion source, three quadrupole filters, Q1, Q2, and Q3, and a conversion dynode electron multiplier detector (Fig 1)[5]. Mixture analysis on this instrumentation can be accomplished with or without prior chromatographic separation of the components

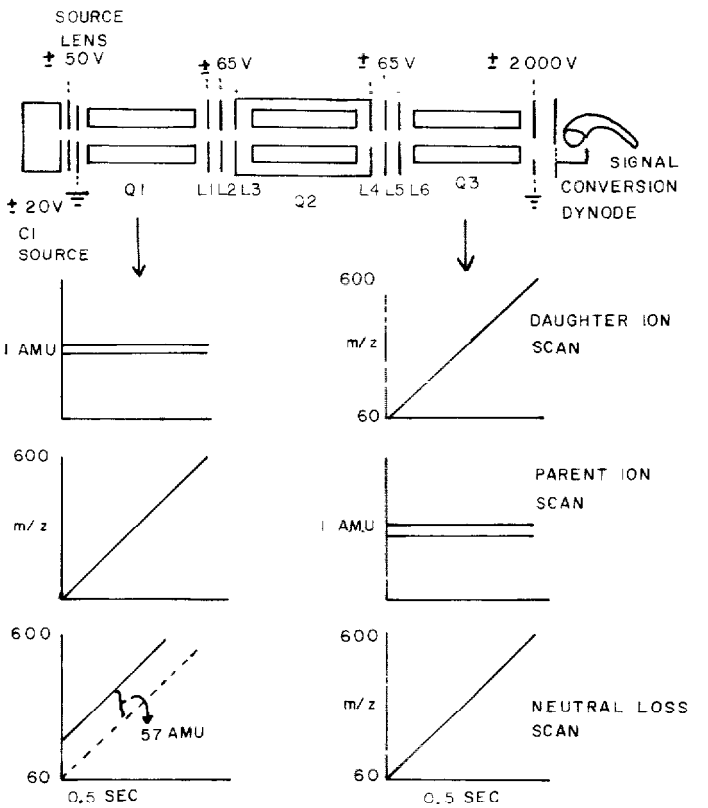


Fig 1 The Finnigan triple quadrupole mass spectrometer and its various modes of operation

Operation of the triple quadrupole mass spectrometer as a conventional single analyzer instrument

When a quadrupole mass filter operates with only low radiofrequency (r.f.) potential on the rods, it functions as an ion-focusing device and transmits ions of all m/z ratios. Accordingly, if Q1 and Q2 function in the r.f. only mode, and Q3 is operated with both r.f. and d.c. potentials on the rods, the triple quadrupole mass spectrometer behaves like a conventional single analyzer instrument. All ions exiting the ion source are transmitted through Q1 and Q2 and are mass analyzed in Q3. Standard electron ionization or chemical ionization mass spectra of each component eluting from the gas chromatograph result.

Operation of the triple quadrupole mass spectrometer in the daughter ion scan mode

Daughter ion scans (Fig. 1) are particularly useful when a complex matrix is to be analyzed for the presence or absence of a small number of known compounds. To obtain collission-activated dissociation mass spectra, matrix components are volatilized into the ion source and Q2 is filled with argon gas to a pressure of 1–4 mTorr and operated in the r.f. only mode. The r.f. and d.c. potentials on Q1 are then set to pass ions with a particular m/z value (Fig. 1). When the selected ions enter Q2, they suffer collisions with argon atoms, become vibrationally excited, and dissociate to produce ions characteristic of their structure. In the presence of a weak r.f. field, all of these fragment ions are transmitted to Q3 where they undergo mass analysis. A mass spectrum of the fragment ions derived from each ion entering Q2 results. Other matrix components will usually contribute to the total signal at the particular m/z value selected by Q1 and the resulting collision activated dissociation mass spectrum will contain fragment ions derived from several components. All ions in the collision-activated dissociation mass spectrum of the pure analyte should be present in the mixture spectrum if the known compound is present in the matrix.

Previous reports from this laboratory have described the use of this approach for the detection of nitrophenols and phthalates in industrial sludge at the 100-ppb* level[6] and for sequence analysis of polypeptides in mixtures[7].

Operation of the triple quadrupole mass spectrometer in the parent ion scan mode

If Q3 is set at a particular m/z value, Q2 is operated as a collision cell, and Q1 is scanned over the desired mass range, the resulting spectra contain all of the parent ions that afford a particular fragment in the collision-activated dissociation process. This is referred to as a parent ion scan and is particularly useful for the analysis of either a homologous series of compounds or a class of compounds containing the same functional group. In the present work, phthalates are analyzed using this scan mode.

Operation of the triple quadrupole mass spectrometer in the neutral loss scan mode

Neutral loss scans are employed for the rapid analysis of complex mixtures for members of a class of compounds that undergo the same type of fragmentation, loss of the same neutral moiety, under collision-activated dissociation conditions. Q2 is employed as a collision chamber and both Q1 and Q3 are set to scan repetitively at a fixed mass separation over the desired mass range (Fig. 1). Mixture components are

* Throughout this article, the American billion (10^9) is meant.

volatilized into the ion source and converted into ions characteristic of sample molecular weight under either positive or negative chemical ionization conditions. At any point in the scan of Q1, all ions of a particular *m/z* value will be transmitted to Q2. Only those ions that lose a particular neutral of specified mass will have the right *m/z* ratio for transmission through Q3. Nitroaromatic compounds, for example, form abundant $(M + H)^+$ ions under methane positive ion chemical ionization conditions and then suffer loss of 17 a.m.u. $OH^{\cdot}$, on collision-activated dissociation in Q2. Since loss of 17 a.m.u. is highly characteristic of nitroaromatic compounds, the neutral loss scan with Q1 and Q3 separated by 17 a.m.u facilitates detection of these compounds and is transparent to most other matrix components. Fragment ions produced by loss of neutrals having masses other than 17 a.m.u. fail to pass through Q3 and are never detected. Spectra recorded in the neutral loss scan mode yield both the molecular weight and relative abundance of all members of a particular class of compounds in the matrix.

Recently this approach has been used for the analysis of heterocyclic organosulfur compounds in hydrocarbon matrices[8] and carboxylic acids in urine[9]. Here, neutral loss scans are employed for the analysis of chlorocarbons, polycyclic aromatic hydrocarbons, amines and phenols.

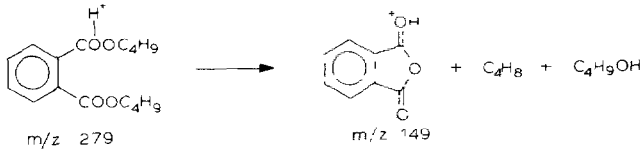
Analysis of phthalates, polycyclic aromatic hydrocarbons, chlorocarbons, phenols and amines

Solid matrices (5–10 mg) and residues from lyophilized aqueous samples are placed on or between glass-wool plugs in a 4.5-cm piece of 4 mm O.D. × 2.5 mm I.D. glass tubing. Amines and phenols in the matrix are converted into ureas and carbamates, respectively, by saturating the sample with 10 μl of ethyl acetate–methyl isocyanate (4:1) containing 100 ppm of triethylamine. After 5 min at room temperature, excess reagents are removed by purging the sample with a stream of nitrogen for 10–15 sec at a flow-rate of 20 ml/min. Polycyclic aromatic hydrocarbons are then converted into nitroaromatic compounds by exposing the sample matrix to gaseous dinitrogen tetroxide for 3–5 sec[10]. A stream of nitrogen is employed to remove excess reagent and the sample is then placed on the end of a modified solids probe and inserted into the removable ion source volume on the Finnigan triple stage quadrupole mass spectrometer. A mixture of methane and nitrous oxide sufficient to maintain a pressure of 500 microns in the ion source is employed as both the carrier gas and to generate the chemical ionization reactants, CH_5^+ and OH^-. Gas flows through the sample tube into the ion source at all times. Slow thermal volatilization of organics from the matrix is facilitated by heating the sample from 25 to 360°C over a period of 5–9 min. During this period the instrument, under computer control, is cycled repetitively through a series of six 0.5-sec experiments, one parent ion scan at *m/z* 149 for phthalates and five neutral loss scans for the other four classes of compounds studied. At the end of the heating period all data acquired from each type of scan is summed together and printed out in conventional bar graph format. The result is a plot of molecular weight *vs.* relative abundance for all mixture components containing the particular functional group being detected. Total time for sample derivatization, data acquisition, and data processing in the above procedure is typically 25 min.

RESULTS AND DISCUSSION

Success of the functional group analysis approach depends on the assumption that ions characteristic of the molecular weight of all members of a particular class of organic compounds will suffer collision-activated dissociation with high efficiency and either lose a highly characteristic neutral or form a highly characteristic charged fragment Unfortunately this is not the case for several types of organic compound under the low-energy conditions employed in the collision cell of the triple quadrupole instrument (10–20 eV). Those compounds that fail to meet the above criteria must be derivatized in order to promote the desired behavior in the collision-activated dissociation process. Ideally the derivatization reaction should (a) employ volatile reagents that can be removed easily from the matrix, (b) proceed in high yield under mild conditions. and (c) introduce a functional group that is sufficiently basic or acidic to localize proton addition or abstraction at the site of the newly introduced substituent

Phthalates



Collision-activated dissociation of $(M + H)^+$ ions from all phthalates except dimethylphthalate affords the protonated anhydride, *m/z* 149, in high yield. Since this fragment is highly characteristic of phthalate esters, members of this class of compounds can be monitored in mixtures using parent ion scans on the triple quadrupole instrument. Results from the analysis of an uncharacterized sample of industrial sludge are shown in Fig. 2. Signals at *m/z* 223. 279, 313, and 391 correspond to $(M + H)^+$ ions of diethyl-, dibutyl-, butylbenzyl-, and either di-2-ethylhexyl- or di-*n*-octylphthalate, respectively. Fragment ions in the main beam chemical ionization (CH_4) spectrum of these four phthalates at *m/z* 167. 177, and 205 are also observed in the parent ion scan because they too undergo further dissociation in the collision chamber to produce *m/z* 149 The signal at *m/z* 149 represents that fraction of the protonated anhydride species generated in the ion source that passes through the collision chamber intact. An unknown. perhaps the phthalate ester of propyleneglycol, ap-

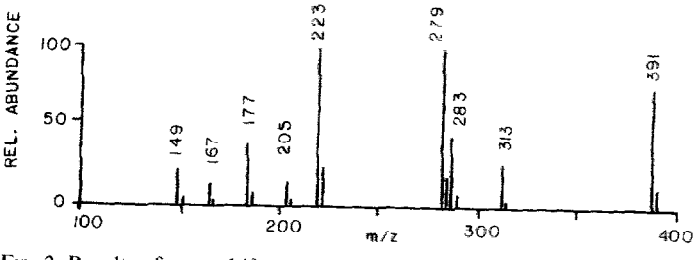
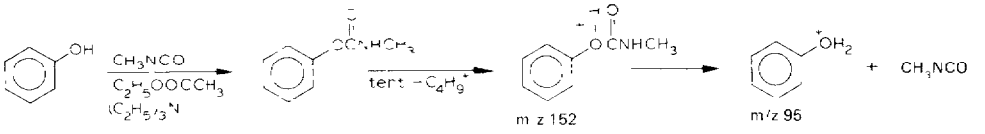


Fig. 2. Results of a *m/z* 149 parent ion scan for detection of phthalates in an uncharacterized sample of industrial sludge

pears in the spectrum at *m/z* 283 Comparison of spectra recorded on spiked and unspiked samples indicated that the phthalates in this particular sludge matrix are present at the 1–5-ppm level

Phenols



Collision-activated dissociation of either M^+ or $(M + H)^+$ ions from phenols is highly inefficient under the low-energy conditions employed in the triple quadrupole instrument Accordingly, members of this class of compounds are derivatized prior to analysis. Treatment of the lyophilized sludge with methyl isocyanate converts phenols into carbamates. This derivative is highly basic and readily forms $(M + H)^+$ ions that in turn suffer facile dissociation with loss of methyl isocyanate (57 a.m.u) in the collision cell Analysis of phenols in mixtures is accomplished, therefore, using 57 a.m u. neutral loss scans on the carbamate derivatives Results obtained on sludge spiked at the 1-ppm level with seven phenols from the EPA priority pollutant list are shown in Fig. 3 The signals observed correspond to $(M + H)^+$ ions of the parent phenols since these are the ions transmitted through the second mass analyzer. Ions at *m/z* 95, 123, 129, 143, 163, 197, and 265 are assigned to phenol, dimethylphenol, chlorophenol, chloromethylphenol, dichlorophenol, trichlorophenol and pentachlorophenol, respectively Phenols of unknown structure are also detected at *m/z* 134, 140, 157, 171, and 205

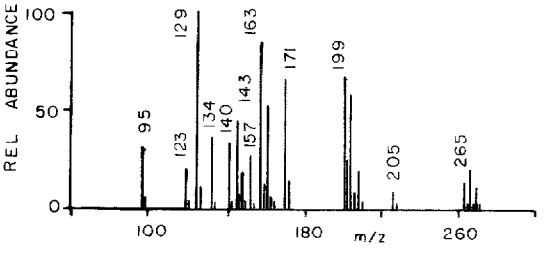


Fig 3 Results of a 57 a m u neutral loss scan for detection of phenols in an uncharacterized sample of industrial sludge spiked with seven phenols from the U S EPA priority pollutant list

Polynuclear aromatic hydrocarbons

Like the situation with phenols, M^+ and $(M + H)^+$ ions from polynuclear aromatic hydrocarbons also dissociate with low efficiency during collision experiments conducted with ion energies in the range 10–20 eV. Derivatization of this class of compounds for analysis on the triple quadrupole is accomplished by exposing the sample matrix to gaseous N_2O_4 for 3–5 sec. Under these conditions mono- and/or dinitro derivatives are formed in good yield from all polynuclear aromatic hydrocarbons on the EPA priority pollutant list Carbamate derivatives of phenols on the same list are not nitrated in the above procedure.

Nitroaromatic compounds make excellent derivatives for analysis by the

tandem mass spectrometry approach since the nitro group is highly basic and easily protonated when methane is used as the chemical ionization reagent gas. The resulting $(M + H)^+$ ions dissociate readily in the collision cell with loss of one or more of the neutrals, OH, NO, NO_2 and HNO_2 (Fig. 4). Loss of OH (17 a.m.u.), NO (30 a.m u.), NO_2 (46 a.m.u.) and HNO_2 (47 a.m.u.) is highly characteristic of the nitro functional group and one or more of these pathways is observed for all of the polynuclear aromatic hydrocarbons on the priority pollutant list. Analysis of this class of compounds can be carried out, therefore, using neutral loss scans for one of the above losses. If it is necessary to distinguish between nitro polynuclear aromatic hydrocarbons already in the environmental matrix from those produced in the derivatization step, a second sample of the untreated matrix must be examined directly.

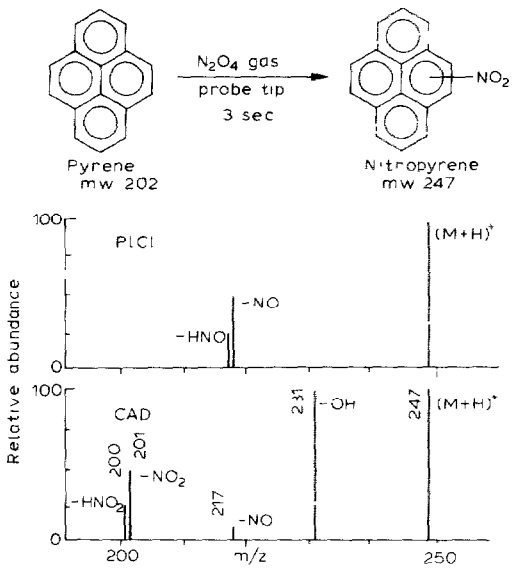


Fig 4. (Top) Main beam positive-ion chemical ionization methane mass spectrum of nitropyrene (Bottom) Collision-activated dissociation (CAD) mass spectrum of the $(M + H)^+$ ion from nitropyrene

Results of 17 a.m.u. neutral loss scans on a sample of lyophilized industrial sludge spiked with a standard mixture of nine polynuclear aromatic hydrocarbons are presented in Fig. 5. Most of the ions in the spectrum occur at *m/z* values 16 a m.u. $(M + H - OH)^+$ below the molecular weight of the nitro derivative and therefore 29 a.m.u. above the molecular weight of the parent aromatic hydrocarbon. Signals at even *m/z* values contain an even number of nitrogen atoms and are formed by loss of OH from either $(M + H)^+$ ions or $(M + H - NO)^+$ fragment ions in the main beam chemical ionization spectrum of the corresponding dinitro derivatives. Dinitration is observed for most polynuclear aromatic hydrocarbons and is particularly facile for fluorene, pyrene, fluoranthene and benzopyrene.

All components of the standard mixture are readily identified in Fig. 5. Signals at *m/z* 157, 181, 183, 195, 207, 231, 257 and 281 correspond to $(M + H - OH)^+$ fragments from mononitro derivatives of naphthalene, acenaphthalene, acenaphthene, fluorene, anthracene-phenanthrene, pyrene-fluoranthene, chrysene and

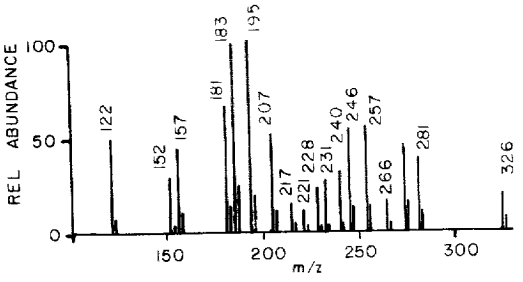


Fig 5 Results of a 17 a.m u neutral loss scan for detection of nitro derivatives of polynuclear aromatic hydrocarbons in an uncharacterized sample of industrial sludge spiked with nine standards from the U.S. EPA priority pollutant list

benzopyrene, respectively. Dinitro derivatives of fluorene, pyrene-fluoranthene, and benzopyrene give rise to the signals at *m/z* 240, 246–276, and 326, respectively. Signals due to unknowns at *m/z* 122, 152, 221–266, and 245 can be assigned to nitroaniline, dinitrobenzene, methylphenanthrene, and methylpyrene Comparison of spectra obtained from spiked and unspiked samples indicates that acenaphthalene, fluorene, phenanthrene-anthracene, pyrene-fluoranthene, chrysene, and benzopyrene are all present in this particular sludge matrix at the 100–500-ppb level.

Amines

Derivatization of phenols with methyl isocyanate as described above also converts amines into N-methylureas. These latter derivatives form abundant $(M + H)^+$ and $(M - H)^-$ ions under chemical ionization conditions when CH_5^+ and OH^- are employed as the reactant ions. Pathways observed for collision-activated dissociation of both these types of ion are shown in Fig 6. Elimination of the neutral, CH_3NCO (57 a.m u.) is essentially the only pathway observed for dissociation of $(M + H)^+$ and $(M - H)^-$ ions from primary and secondary amines in which the nitrogen atom is attached directly to an aromatic ring. Loss of CH_3NCO from the $(M - H)^-$ ion is also a major pathway for collision-activated dissociation of aliphatic secondary amines. For urea derivatives of primary amines, formation of the $NHCONHCH_3$ anion at *m/z* 73 competes favorably with elimination of CH_3NCO from the $(M - H)^-$ ion since the latter pathway is considerably more endothermic when the product ion is stabilized by one rather than two alkyl groups.

In the positive-ion mode, loss of olefin rather than CH_3NCO frequently dominates the dissociation process for $(M + H)^+$ ions of secondary amines. Elimination of CH_3NCO is the preferred pathway for dissociation of $(M + H)^+$ ions derived from primary amine derivatives

Based on a study of more than 100 compounds, we conclude that most amines can be analyzed effectively under tandem mass spectrometry conditions using 57 a.m.u neutral loss scans to monitor collision-activated dissociation of $(M - H)^-$ ions from N-methyl urea derivatives Results of such an experiment on a standard mixture of amine derivatives are shown in Fig. 7. Spectra from neutral loss scans of 57 a m u. in both the positive- and negative-ion modes are displayed The ions that exit the collision cell and reach the detector correspond to the $(M + H)^+$ and $(M - H)^-$ species from the underivatized amines. Carbamate derivatives of the phenols ex-

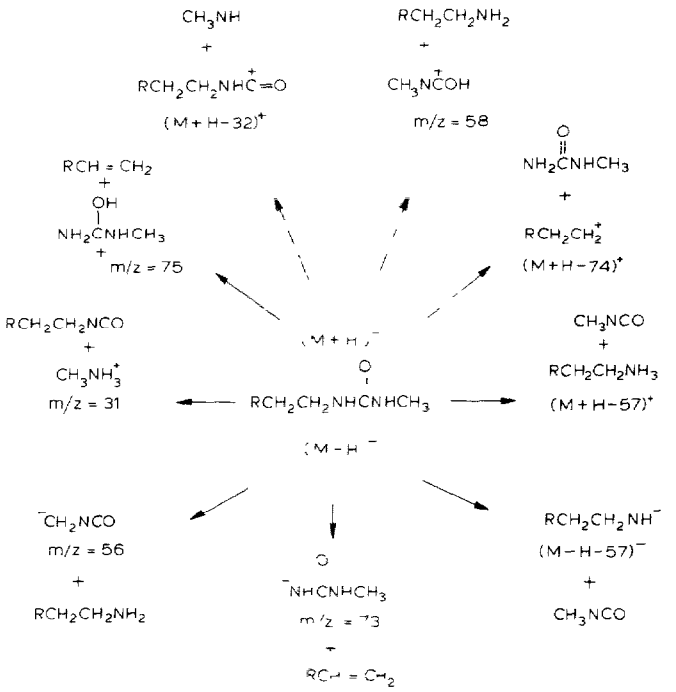


Fig 6 Pathways observed for fragmentation of $(M + H)^-$ and $(M - H)^-$ ions from N-methylurea derivatives of amines under collision-activated dissociation conditions on the triple quadrupole mass spectrometer

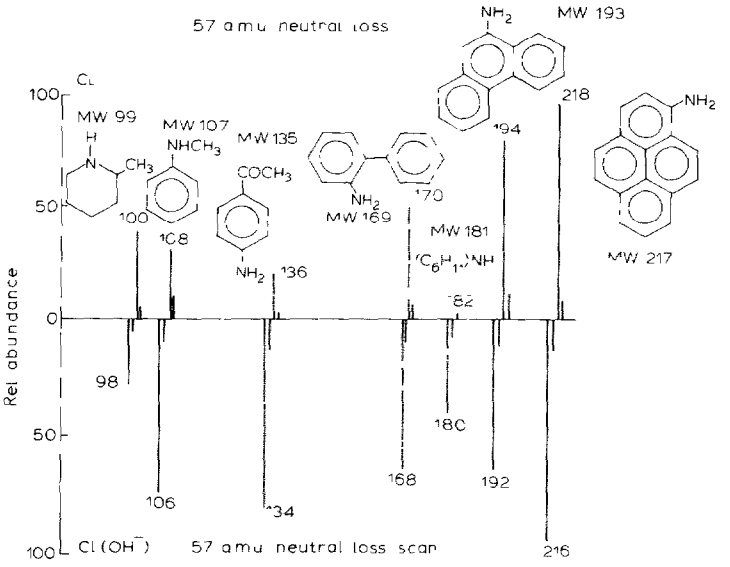


Fig 7 Results of a 57 a m u neutral loss scans in both the positive (top) and negative (bottom) mode on a standard mixture of N-methylurea derivatives of amines

amined to date dissociate completely with loss of CH_3NCO (57 a.m.u.) in the ion source rather than in the collision cell and therefore, do not interfere with the above analysis for amines using negative ions. Signals due to both phenols and amines appear on the positive-ion 57 a.m u. neutral loss scan, but only the amine affords signals on the negative-ion trace at a position 2 a.m.u. lower than the corresponding signal on the positive-ion trace.

Chlorocarbons

The EPA priority pollutant list contains *ca.* 40 chlorocarbon compounds and/or preparations. We find that these can be analyzed under positive-ion chemical

TABLE I

CHLORINE-CONTAINING COMPOUNDS ANALYZED BY NEUTRAL LOSS SCANS OF 35 a m u. AND 36 a m.u , RESPECTIVELY

Compound	*Neutral loss scan*	
	35 a.m u	*36 a m.u*
Hexachlorobenzene	Yes	No
Hexachlorobutadiene	Yes	No
Hexachloroethane	Yes	No
Heptachlor	Yes	Yes
Chloronaphthalene	Yes	Yes
3,3′-Dichlorobenzidine	Yes	Yes
1,2,4-Trichlorobenzene	Yes	Yes
Arochlor 1242, 1254	Yes	Yes
2-Chlorophenol	Yes	Yes
4-Chloro-3-methylphenol	Yes	Yes
2,4-Dichlorophenol	Yes	Yes
2,4,6-Trichlorophenol	Yes	Yes
Pentachlorophenol	Yes	Yes
DDT	Yes	Yes
DDE	Yes	Yes
DDD	Yes	Yes
Chlorobenzene	No	Yes
1,2-Dichlorobenzene	No	Yes
1,3-Dichlorobenzene	No	Yes
1,4-Dichlorobenzene	No	Yes
trans-1,2-Dichloroethylene	No	Yes
1,1-Dichloroethylene	No	Yes
Trichloroethylene	No	Yes
Tetrachloroethylene	No	Yes
1,1-Dichloroethane	No	Yes
1,2-Dichloroethane	No	Yes
1,1,2-Trichloroethane	No	Yes
1,1,1-Trichloroethane	No	Yes
1,1,2,2-Tetrachloroethane	No	Yes
1,2-Dichloropropane	No	Yes
Chlordane	Yes	Yes
Aldrin	Yes	Yes
Endrin	Yes	Yes
Dieldrin	Yes	Yes
Heptachlorepoxide	Yes	Yes

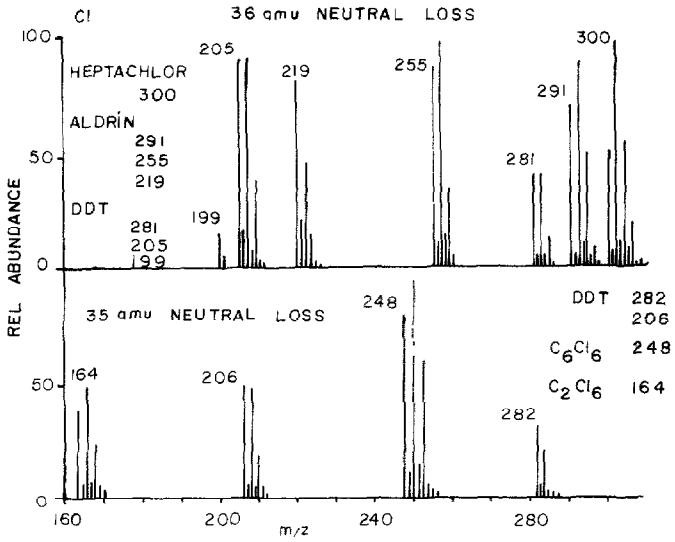


Fig. 8 Results of 36 a m u. and 35 a m u neutral loss scans on standard mixtures of chlorocarbons containing heptachlor, aldrin, and DDT in one case and DDT. hexachlorobenzene, and hexachloroethane in the other

ionization conditions using neutral loss scans that monitor for the loss of either Cl (35 a.m.u.) or HCl (36 a.m.u.) (Table I). Results obtained using 35 and 36 a.m.u. neutral loss scans to analyze a standard mixture of halogenated compounds are presented in Fig. 8 In the 36 a.m.u. neutral loss spectrum. ions due to aldrin appear at *m/z* 291, 255, and 219. Loss of HCl during collision-activated dissociation of the $(M + H - HCl)^+$, $(M + H - 2HCl)^+$, and $(M + H - 3HCl)^+$ ions in the main beam spectrum account for the observed pattern of signals.

The main beam chemical ionization spectrum of heptachlor is considerably less

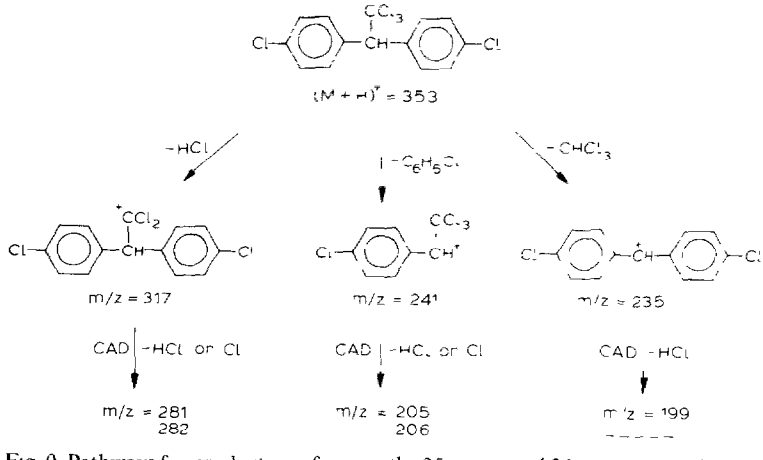


Fig 9 Pathways for production of ions in the 35 a m u and 36 a m u neutral loss scans on ions in the main beam spectrum of DDT

complicated and accordingly only one group of peaks appears in the 36 a.m.u. neutral loss scan. $(M + H - HCl)^+$ dissociates to $(M + H - 2HCl)^+$. The three ions observed in the DDT spectrum result from loss of HCl from the $(M + H - HCl)^+$, $(M + H - C_6H_5Cl)^+$ and $(M + H - CHCl_3)^+$ ions in the main beam spectrum.

DDT is one of the compounds in Table I that can be monitored by either 35 or 36 a.m.u neutral loss scans (Fig 9). The two signals at *m/z* 282 and 206 in Fig. 8 result from loss of Cl from the $(M + H - HCl)^+$ and $(M + H - C_6H_5Cl)^+$ ions and therefore appear at a position 1 a.m.u. higher than the DDT signals in the top half of Fig. 8. Ions characteristic of hexachlorobenzene and hexachloroethane in Fig. 8 are found at *m/z* 248 and 264 and are generated by loss of Cl from the $(M + H)^+$ and $(M + H - HCl)^+$ ions, respectively, in the main beam spectrum of the sample mixture.

Carboxylic acids

Negative-ion collision-activated dissociation mass spectra have been recorded for more than 90 carboxylic acids. Abundant fragments corresponding to loss of CO_2 (44 a.m.u.) from the $(M - H)^-$ ion are observed for most of these acids. Hydroxy acids and dicarboxyl acids lose both CO_2 and H_2O to form $(M - H - 62)^-$ ions. The utility of 44 and 62 a m.u neutral loss scans for monitoring carboxylic acids in urine has already been demonstrated[9] Experiments to evaluate the procedure on environmental matrices are in progress.

Aldehydes and ketones

One approach to the analysis of aldehydes and ketones by triple quadrupole mass spectrometry is outlined below. Treatment of aldehydes and ketones with benzyloxylamine affords derivatives whose $(M + H)^+$ ions readily dissociate to the benzyl cation (*m/z* 91) under collision-activated dissociation conditions. Formation of *m/z* 91 is highly characteristic of the benzyloxylamine derivatives but is also observed in the mass spectra of many other molecules containing the benzyl moiety. An increase in the specificity of the above reaction pathway can be achieved by using either $[^2H_5]$benzyloxylamine or pentafluorobenzyloxylamine in the derivatization step. This would shift the mass of the benzyl cation from *m/z* 91 to *m/z* 96 and *m/z* 181, respectively, and remove any ambiguity about the origin of the characteristic fragment Use of *m/z* 96 or *m/z* 181 parent ion scans on benzyloxylamine derivatives should facilitate the analysis of aldehydes and ketones in a variety of environmental matrices.

$$RCHO + C_6H_5CH_2ONH_2 \rightarrow RCH{=}NOCH_2C_6H_5$$

$$RCH{=}NOCH_2C_6H_5 \xrightarrow{CH_5^+} RCH{=}\overset{+}{N}(H)OCH_2C_6H_5 \xrightarrow{CAD} RCH{=}NOH + C_6H_5CH_2^+$$

m/z 91

ACKNOWLEDGEMENT

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REFERENCES

1 R B Medz, *Fed Reg.*, 44 (1979) 69,464–69,551
2 J E Ryan, L E Gebhart, L C Rando, D L Perry, K B Tomer, E D Pellizzari and J T Bursey, in L Keith (Editor), *Advances in the Identification of Organic Pollutants in Water*, Ann Arbor Sci Publ, Ann Arbor, MI, 1981
3 F W McLafferty, *Science*, 214 (1981) 280–286
4 F W McLafferty (Editor), *Tandem Mass Spectrometry*, Wiley, New York, in press
5 J R B Slayback and M S Story *Ind. Res. Dev*, (1981) 129.
6 D F Hunt, J Shabanowitz and A B Giordani, *Anal Chem.*, 52 (1980) 386–390
7 D F Hunt, A M Buko, J M Ballard, J Shabanowitz and A B Giordani, *Biomed. Mass Spectrom.*, 8 (1981) 397–408
8 D F Hunt and J Shabanowitz, *Anal Chem*, 54 (1982) 574–578
9 D F Hunt, A B Giordani, G Rhodes and D A Herold, *Clin Chem*, 28 (1982) 2387–2392.
10 J N Pitts, Jr., K A Van Cauwenberghe, D Grosjean, J P Schmid, D R Fitz, W L Belser, Jr., G B Knudson and P M Hynds, *Science*, 202 (1978) 515–519