# MASS SPECTROMETRY OF PRIORITY POLLUTANTS

Brian S. Middleditch

Stephen R. Missler

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**Brian S. Middleditch**
**Stephen R. Missler**
**and**
**Harry B. Hines**

*University of Houston*
*Houston, Texas*

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# PREFACE

When the list of organic priority pollutants was first published, many mass spectroscopists went scrambling to their reference books. GC–MS was mandated for the analysis of 114 compounds, yet the spectra of many of them, if they had been recorded at all, were scattered throughout the literature. Moreover, it soon became apparent that, even if a sufficient number of instruments could be made available to undertake the task of monitoring 114 substances in the effluents of 21 categories of industry, the personnel could not be trained to perform the analyses and interpret the results.

The solution to this problem has been the development of highly automated mass spectrometers which can be operated by personnel without the traditional research training. This book is for the new breed of mass spectroscopist who is not interested in the esoteric details of mass spectral fragmentation, but who merely wishes to identify specific pollutants in effluents. Our inclusion of comprehensive lists of synonyms and bibliographic data should make the book of even greater value to the reader who is not too familiar with the idiosyncrasies of chemical nomenclature and the scientific literature. The experienced mass spectroscopist should also benefit from having all of the data collected together in one volume.

This is a book to be used, rather than deposited in a library distant from the laboratory: we would hope that it will find a place on top of every mass spectrometer used for the analysis of priority pollutants.

We are indebted to Pamela Milton for typing the manuscript. Ellis Rosenberg and Betty Bruhns of Plenum have performed an admirable job of implementing the publication of the book. Our wives, to whom this volume is dedicated, have provided the additional sacrifice, support, and encouragement needed for the prompt completion of the manuscript.

*Houston*

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# INTRODUCTION

The Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500) required the U.S. Environmental Protection Agency to develop a comprehensive program to improve the quality of the nation's waterways. Section 307(a) mandated publication of a list of toxic pollutants for which effluent standards were being established. There was substantial delay in implementing this task. It was not until June 7, 1976 that the National Resources Defense Council, Environmental Defense Fund, Businessmen for the Public Interest, National Audubon Society, and Citizens for a Better Environment were able to reach an agreement with the EPA under which timetables and procedures for implementation of certain sections of P.L. 92-500 were delineated. One of the terms of the consent decree related to the study of 65 substances or groups of substances (totaling 129 individual substances) in industrial effluents, and the development of appropriate regulations for their control. These substances (known as "priority pollutants," "consent decree pollutants," or "toxic pollutants") were selected on the basis of their known occurrence in effluents, their presence in drinking water or fish, their known or suspected carcinogenic, mutagenic, or teratogenic properties, their likelihood of human exposure, their persistence in the aquatic food web, their propensity for bioaccumulation, and their toxicity to aquatic organisms and those (including humans) which might feed on such organisms.

Combined gas chromatography–mass spectrometry (GC–MS) was required for the analysis of the 114 organic priority pollutants, according to guidelines for sampling and analysis distributed by the EPA in early 1977.

There are four categories of organic priority pollutants (volatiles, base–neutral extractables, acid extractables, and pesticides), each requiring a different analytical procedure.

The volatile priority pollutants are listed in Table 1. They are analyzed by the purge-and-trap method. The pollutants are purged from solution by helium onto a trap containing Tenax-GC and silica gel. After an appropriate purging time, the trapped compounds are desorbed onto a GC column for analysis by GC–MS. Bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane are employed as internal standards. There is some overlap between the compounds that can be analyzed by the purge-and-trap method and those that can be analyzed by liquid–liquid extraction methods. Some of the compounds listed in Table 1 are not easily determined by the purge-and-trap method; these are noted in the text.

The base–neutral extractable priority pollutants are listed in Table 2. The sample is adjusted to pH 11 using sodium hydroxide, and extraction with

## Table 1. Volatile Priority Pollutants

| | |
|---|---|
| Acrolein | 1,2-Dichloroethane |
| Acrylonitrile | 1,1-Dichloroethylene |
| Benzene | *trans*-1,2-Dichloroethylene |
| Bis(chloromethyl) ether | 1,2-Dichloropropane |
| Bromodichloromethane | *cis*-1,3-Dichloropropene |
| Bromoform | *trans*-1,3-Dichloropropene |
| Bromomethane | Ethylbenzene |
| Carbon tetrachloride | Methylene chloride |
| Chlorobenzene | 1,1,2,2-Tetrachloroethane |
| Chloroethane | 1,1,2,2-Tetrachloroethene |
| 2-Chloroethyl vinyl ether | Toluene |
| Chloroform | 1,1,1-Trichloroethane |
| Chloromethane | 1,1,2-Trichloroethane |
| Dibromochloromethane | Trichloroethylene |
| Dichlorodifluoromethane | Trichlorofluoromethane |
| 1,1-Dichloroethane | Vinyl chloride |

## Table 2. Base–Neutral Extractable Priority Pollutants

| | |
|---|---|
| Acenaphthene | Diethyl phthalate |
| Acenaphthylene | Dimethyl phthalate |
| Anthracene | 2,4-Dinitrotoluene |
| Benzidine | 2,6-Dinitrotoluene |
| Benzo[*a*]anthracene | Di-n-octyl phthalate |
| Benzo[*b*]fluoranthene | 1,2-Diphenylhydrazine |
| Benzo[*k*]fluoranthene | Fluoranthene |
| Benzo[*ghi*]perylene | Fluorene |
| Benzo[*a*]pyrene | Hexachlorobenzene |
| Bis(2-chloroethoxy)methane | Hexachlorobutadiene |
| Bis(2-chloroethyl) ether | Hexachlorocyclopentadiene |
| Bis(2-chloroisopropyl) ether | Hexachloroethane |
| Bis(2-ethylhexyl) phthalate | Indeno[1,2,3-*cd*]pyrene |
| 4-Bromophenyl phenyl ether | Isophorone |
| Butyl benzyl phthalate | Naphthalene |
| 2-Chloronaphthalene | Nitrobenzene |
| 4-Chlorophenyl phenyl ether | *N*-Nitrosodimethylamine |
| Chrysene | *N*-Nitrosodiphenylamine |
| Dibenzo[*a*,*h*]anthracene | *N*-Nitrosodi-n-propylamine |
| Di-n-butyl phthalate | Phenanthrene |
| 1,2-Dichlorobenzene | Pyrene |
| 1,3-Dichlorobenzene | 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin |
| 1,4-Dichlorobenzene | 1,2,4-Trichlorobenzene |
| 3,3′-Dichlorobenzidine | |

**Table 3. Acid Extractable Priority Pollutants[a]**

| | |
|---|---|
| *p*-Chloro-*m*-cresol | 2-Nitrophenol |
| 2-Chlorophenol | 4-Nitrophenol |
| 2,4-Dichlorophenol | Pentachlorophenol |
| 2,4-Dimethylphenol | Phenol |
| 4,6-Dinitro-*o*-cresol | 2,4,6-Trichlorophenol |
| 2,4-Dinitrophenol | |

[a]"Total phenols" are also to be measured.

methylene chloride affords these compounds. They are analyzed by GC–MS, using anthracene-$d_{10}$ as an internal standard.

The acid extractable priority pollutants are listed in Table 3. After extracting the base–neutrals, the remaining water sample is adjusted to pH 2 using hydrochloric acid. Extraction with methylene chloride affords the phenols. They are analyzed by GC–MS, also using anthracene-$d_{10}$ as an internal standard. Some of the phenols do not possess good gas chromatographic properties.

The pesticide priority pollutants are listed in Table 4. The PCBs are included in this category even though they are not pesticides. These compounds are analyzed by gas chromatography with electron capture detection. If pesticides are detected, their identities are confirmed by GC–MS.

**Table 4. Pesticide Priority Pollutants**

| | | |
|---|---|---|
| Aldrin | Dieldrin | PCB-1016[a] |
| α-BHC | α-Endosulfan | PCB-1221[a] |
| β-BHC | β-Endosulfan | PCB-1232[a] |
| γ-BHC | Endosulfan sulfate | PCB-1242[a] |
| δ-BHC | Endrin | PCB-1248[a] |
| Chlordane[a] | Endrin aldehyde | PCB-1254[a] |
| 4,4′-DDD | Heptachlor | PCB-1260[a] |
| 4,4′-DDE | Heptachlor epoxide | Toxaphene[a] |
| 4,4′-DDT | | |

[a]These substances are mixtures.

**Table 5. Inorganic Priority Pollutants[a]**

| | | |
|---|---|---|
| Antimony | Chromium | Nickel |
| Arsenic | Copper | Selenium |
| Asbestos | Cyanide | Silver |
| Beryllium | Lead | Thallium |
| Cadmium | Mercury | Zinc |

[a]This category includes salts of each of these substances (except asbestos). Ammonia has also been proposed as a member of this category.

The inorganic priority pollutants are listed in Table 5. Mass spectrometry is not used in their analysis.

Complete details of sampling and analysis procedures are obtainable from the EPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, so they are not repeated here.

## Data Compilations

Our data compilations contain mass spectra (line diagrams and tabulated data), lists of synonyms, brief notes on analyses and uses, selected bibliographies, and additional information useful in searching the literature for further data on each compound.

The information given is listed in the order normally used by the EPA. The EPA nomenclature has been adhered to even though, in some instances, it deviates from the IUPAC or CAS conventions. For each substance or group of substances the following data are given.

**Class of Pollutant.** This is the description of the pollutant (or group of pollutants) as stated in the consent decree. An indication is given of the use (if any) of each individual substance. Some compounds, particularly the halogenated compounds, are formed during chlorination of drinking water, although this is not always mentioned. Salient details of analytical procedures or mass spectra are given where warranted.

**Individual Pollutant.** The EPA name, molecular formula, and molecular weight (calculated using integral atomic weights of most abundant isomers, as is conventional in mass spectrometry) are given.

The category of pollutant follows.

The name assigned for the *Eighth Collective Index* of Chemical Abstracts (CAS name) and other synonyms are followed by the CAS registry number. The registry number is a unique identifier which is invaluable in searching the literature for further information about each compound.

References are also given to the Registry of Toxic Effects of Chemical Substances (which provides toxicity data) and the ninth edition of the Merck Index (which provides chemical and pharmaceutical data).

**Spectral Data.** The eight most abundant ions in each spectrum are given, as are the ions considered by the EPA to be characteristic of each compound or useful for quantitation. Mass spectral data are given, in tabulated form and as line diagrams, for ions greater in relative abundance than 2% of the base peak. The minimum $m/e$ value for volatiles is $m/e$ 20, while for nonvolatiles it is $m/e$ 40. Ions of nonintegral mass are not tabulated.

Reference compounds were obtained from Aldrich Chemical Co., Analabs, Inc., Chem-Service, Nanogens Co., RFR Corp., and Supelco, Inc. All of the data were acquired by GC–MS using a Hewlett-Packard 5992A hyperbolic quadrupole mass spectrometer in the authors' laboratory. All quadrupole mass spectrometers will, if not used carefully, produce spectra with varying relative abundances of ions throughout the mass range. This can be monitored using decafluorotriphenylphosphine as a reference compound and the tuning of the instrument adjusted accordingly. If these precautions are taken, spectra obtained by others should be similar to those reported here.

Another source of variation between spectra acquired using different instruments is the ease of formation of multiply charged ions. These ions (or the corresponding isotopic species) are easily recognized if they appear at nonintegral $m/e$ values. In such instances, particular attention should be given to the relative abundances of nearby doubly charged ions of integral mass, since they may not be reproducible.

**Selected Bibliography.** Up to five citations of the relevant literature are given for each substance. Both Chemical Abstracts and Gas Chromatography–Mass Spectrometry Abstracts were searched.

Comprehensive indexes follow the data compilations.

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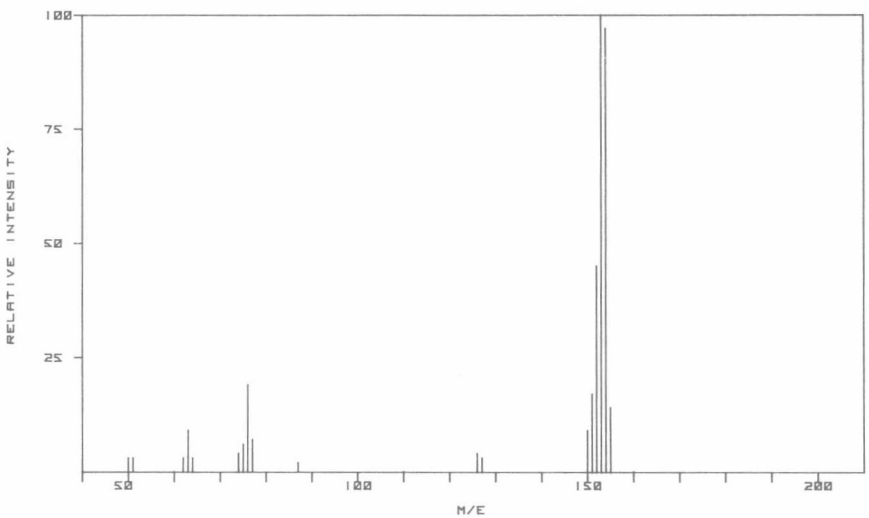
# ACENAPHTHENE

This compound is, strictly, not a polynuclear aromatic hydrocarbon since it is not fully unsaturated, but the comments on these compounds (*q.v.*) are pertinent.

Acenaphthene (derived from coal tar) was once used as an insecticide and fungicide. It has also been used in the manufacture of dyes and plastics.

## ACENAPHTHENE $C_{12}H_{10}$ (154)




### Spectral Data

| Mass | Abundance | Mass | Abundance | Mass | Abundance |
|---|---|---|---|---|---|
| 50 | 2.6 | 75 | 5.9 | 150 | 8.5 |
| 51 | 3.4 | 76 | 19.0 | 151 | 16.7 |
| 62 | 2.9 | 77 | 7.3 | 152 | 44.6 |
| 63 | 8.9 | 87 | 2.3 | 153 | 100.0 |
| 64 | 2.5 | 126 | 4.3 | 154 | 96.5 |
| 74 | 3.9 | 127 | 3.4 | 155 | 14.0 |

## ACENAPHTHENE—*continued*

Base–neutral extractable
CAS Name: Acenaphthene
Synonyms
1,2-Dihydroacenaphthylene
*peri*-Ethylenenaphthalene
1,8-Ethylenenaphthalene
Naphthyleneethylene

CAS Registry No.: 83-32-9
Merck Index Ref.: 19

Major Ions: 153, 154, 152, 76, 151, 155, 63, 150
EPA Ions: 154, 153, 152

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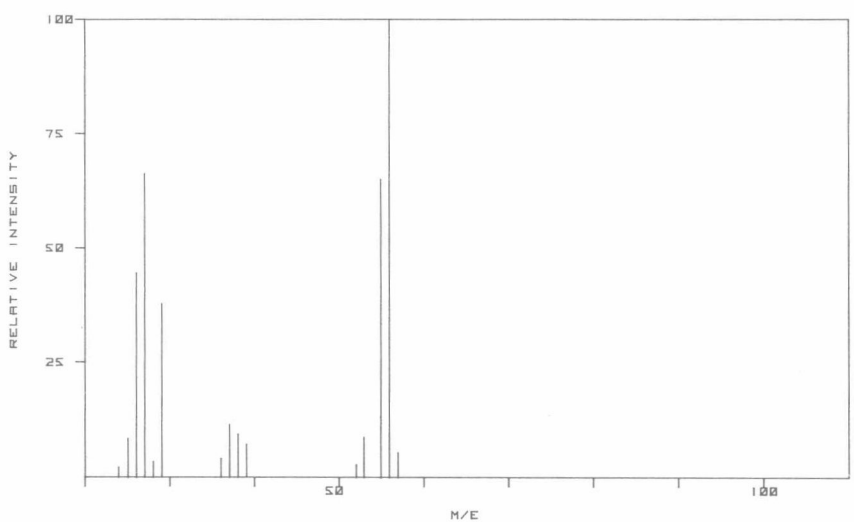
# ACROLEIN

Although listed as a "volatile," acrolein is insufficiently volatile to be purged from aqueous solution at room temperatures. Recovery is enhanced at elevated temperatures. Direct aqueous injection is suggested as an alternative procedure. Phenylhydrazone derivatives are employed for the colorimetric assay of acrolein, and are also amenable to mass spectrometry.

Acrolein is used for aquatic weed control and also for inhibiting the growth of sulfur-bacteria in oil field brines. Among its other uses are in the production of plastics, perfumes, and colloidal forms of metals. It has been used in chemical warfare agents and as a warning agent in methyl chloride refrigerants.

**ACROLEIN** $C_3H_4O$ (56)




**Spectral Data**

| Mass | Abundance | Mass | Abundance | Mass | Abundance |
|---|---|---|---|---|---|
| 24 | 2.1 | 29 | 37.7 | 52 | 2.6 |
| 25 | 8.3 | 36 | 4.0 | 53 | 8.6 |
| 26 | 44.5 | 37 | 11.3 | 55 | 64.9 |
| 27 | 66.2 | 38 | 9.3 | 56 | 100.0 |
| 28 | 3.3 | 39 | 7.1 | 57 | 5.3 |