WHO
International Reference Centre
for
Community Water Supply

The Hague, The Netherlands

Analysis of organic compounds in water to support health effect studies

A consultants report by Dr. A. W. Garrison

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WHO INTERNATIONAL REFERENCE CENTRE
FOR
COMMUNITY WATER SUPPLY

ANALYSIS OF ORGANIC COMPOUNDS IN WATER TO SUPPORT HEALTH EFFECT STUDIES

A CONSULTANTS REPORT
BY DR. A. W. GARRISON

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The importance of research on the health effects of long-term ingestion of chemical substances resulting from the (indirect) re-use of waste water for human consumption has been fully and early recognized by the International Reference Centre for Community Water Supply (IRC). The need to ensure the continuing safety of community water supplies requires improved knowledge of micro-pollutants in drinking water.

In January 1975, the IRC convened in Amsterdam an international group of experts in the field of analytical chemistry, microbiology, toxicology and epidemiology. The working meeting was also attended by representatives from international and national organizations concerned with the health effects relating to the re-use of waste water for potable purposes. The meeting had the object:

- to review the existing knowledge;
- to formulate research projects and studies needed to supplement the knowledge;
- to consider international cooperation and coordination in research;
- the exchange of information on research programmes.

On that occasion the IRC was requested by the meeting to stimulate and coordinate health effects research by assisting cooperative schemes and by facilitating the exchange of information, so that unnecessary duplication of efforts would be prevented and priority allocation of recommended projects achieved. A first step in planning subsequent activities was taken by Professor H.I. Shuval of the Hebrew University, Environmental Health Laboratory, who acted as consultant to the IRC after the meeting.

The evaluation of health effects requires identification and characterization of suspect substances in waters. Organic compounds, in particular, are causing concern and their study is assuming greater significance in the light of recent tentative findings.

The methodology for the analysis of organic compounds in waters needs careful consideration. The IRC was pleased to find Dr. A.W. Garrison of the U.S. Environmental Protection Agency (EPA), Environmental Research Laboratory, Athens, Georgia, prepared to act as consulant on this aspect.

The present consultant's report reflects the work undertaken by Dr. Garrison. The IRC has pleasure in publishing the study, as a contribution to the development of the analytical methodology to support health effects research and epidemiological studies.

While working on his assignment, Dr. Garrison received assistance from Ir. B. C. J. Zoeteman, of the Netherlands National Institute for Water Supply, and his staff. Ir. E. H. A. Hofkes of the IRC, provided technical and administrative support.

During the course of his consultantship, Dr. Garrison visited a number of experts involved in the analysis of organic compounds in water. Gratefully acknowledged is the kind help given by Dr. R. F. Packham, Dr. M. Fielding and Dr. A. Waggott of the Water Research Centre, U. K. Thankfully recorded is the assistance rendered by Dr. H. Ott of the Management Committee for the Analysis of Organic Micropollutants, Environmental Research Programme of the European Communities, and by Dr. O. Hutzinger, Laboratory of Environmental Chemistry, University of Amsterdam.

In the Netherlands, useful visits were paid to the National Institute for Public Health, the Testing and Research Institute of Water Undertakings and the Amsterdam Water Works' Laboratory.

It is hoped that Dr. Garrison's report will serve its purpose to assist those involved in health effects research and epidemiological studies, in developing the methodology for the analysis of organic compounds in water.

I. INTRODUCTION

The general approach to preparation of this report was to first examine and classify the data available on organic compounds thus far identified in water (Appendix 1). Then the current status of analytical methodology for organics in water was summarized (Appendix 2). From this summary, the need for certain improvement in methodology became obvious (Appendix 3) - some of these needs are now being met by research in water pollution laboratories in various parts of the world, others are yet to be investigated. These needs, which constitute the heart of this report, are summarized in Part II, below.

Consideration for protocols for chemical analysis to support epidemiological studies are outlined in Appendix 4.

During the course of this consultantship, several trips were made to facilities and organizations involved in the analysis of organic compounds in water and a colloquium was held on this topic. Meetings with experts during these visits and colloquium were extremely useful in the preparation of this report: a summary of corresponding discussions and observations is given in Appendix 5.

II. NEEDS IN ANALYTICAL METHODOLOGY FOR ORGANIC COMPOUNDS IN WATER

The report addresses only the analysis of specific compounds or groups of compounds. *In situ* monitoring needs can best be addressed by a toxicologist concerned with acute toxicity. The relationship of chronic health effects to organic compounds in water can best be determined by laboratory analyses, of which there are three types:

(1) Survey analysis - use of a broad method, as comprehensive as possible, allowing for the identification and measurement of as many components of the sample as possible.

(2) Chemical class analysis - use of a method designed to "analyze for" specific members of a given chemical class of organic compounds.

(3) Group analysis - use of method or "test" designed to "analyze for" a group of organic compounds, usually with similar chemical characteristics, *in toto*. These are sometimes vaguely called "monitoring" methods.

Each type of analysis may be subdivided into volatile and non-volatile organic methods, since methods for each of these two volatility classes are by nature different; also the development of non-volatile methodology lags considerably behind that for the volatile compounds. In no case should a method be limited to qualitative analysis - quantification is essential for meaningful assessment of the importance of identified compounds or groups. The above catagories of analysis are described in more detail in Appendix 2, A.

A. Health Related Problems to which Chemical Analysis must be Applied

Each situation of re-use, each epidemiological study and water plant laboratories will have specific needs for different types of organic analysis. These cannot be dealt with here in detail. However, some applications of current and future analytical technology include:

1. Epidemiological studies.

   a. Analysis of selected organics by chemical class and/or group to support narrow prospective epidemiological studies. Selection of classes for study will depend upon the health effects association being hypothesized by epidemiologist and toxicologist.

   b. Survey analysis, mostly based on GC-MS techniques, to support broad, prospective epidemiological studies. Survey analysis for non-volatile compounds will also be applicable when methods become available.

2. Planning for Direct Water Re-use.

Planning for re-use requires special knowledge of organics in water that can be gained by:

   a. Survey analysis by GC-MS.

   b. Survey analysis for non-volatile compounds - this is especially important here since non-volatiles can be concentrated during re-cycling of water for re-use.

3. Quality Control of Drinking Water

a. Survey analysis of drinking water by GC-MS in very large water works laboratories or in central laboratories to evaluate water quality relative to specific organic compounds on a regular basis (monthly or bi-monthly).

b. Chemical class or group analyses of organics in a large water works laboratory or, for smaller water works, in a central laboratory. Certain classes of compounds are not amenable to survey analysis by GC-MS (assuming it were available) or need more frequent measurement because of special health significance. Classes or groups to be monitored should be determined by health effects considerations (by toxicologists) and by abundance of classes of organics. This type of monitoring will be more important for directly re-used water in order to maintain public confidence in its quality.

c. Analysis of non-volatile organics, if they are shown to have adverse health effects.

4. Research

a. Enlargement of the data base of volatile and non-volatile organics in water by analyses of effluents, surface water and other raw sources of drinking water, as well as drinking water, by government, industrial and university research laboratories.

b. Analyses to support studies of treatment effectiveness, effects of chlorination, fate of pollutants, effects of pollutants, etc; these require extensive chemical analyses that must be tailored to suit the research need.

B. Specific Needs in Development of Analytical Methodology for Organics in Water

Those needs are arranged in priority groups, but the numbers within groups do not indicate a ranking. Relative importance of the needs for certain applications are indicated by the number of crosses (0-3) in the "Needed For" columns. "Supported by" indicates the Appendix of this report that should be referred to for detailed supporting data.

PRIORITY A

	Needed for:				Supported by:
	Research	Epidemiological Studies	Water Re-use Planning	Water Quality Control	
1. Collation of specific compound data in the following way a. Continual updating of the present COST project 64b/WRC list. b. Establishment of a similar EPA list. c. Computerization and coordination of both lines Abundance Index, designed to allow continual evaluation of the distribution of organic compounds in water relative to analytical methodology needs and health effect studies.	XXX	XX	XXX	X	Appendix 1, including Table.
2. Development of analytical methods for classes of organic compounds that are shown to be "abundant" and of health significance and that are not adequately covered by GC-MS survey analysis because of: - the necessity for more frequent analysis of a particular class, because of special health significance, than is possible in a central GC-MS laboratory system, or - unsuitability of a special class for analysis by the broad GC-MS survey approach; e.g. a class of non-volatile compounds. Possibly important classes needing methods or improvements in methods are: Aromatic amines Chlorinated non-volatiles Chlorinated volatiles Chlorophenols Dyes and optical brighteners of various classes Organobromine Organofluorine compounds Phthalates Polynuclear aromatic hydrocarbons Resin acids Specific odour-intensive com compounds Non-volatile nitrosamines	X	XXX	X	XXX	Appendix 2, Part C, 1 and Appendix 3, Part E, 1.

	Needed for:				
	Research	Epidemiological Studies	Water Re-use Planning	Water Quality Control	Supported by:
3. Development of methods for survey analysis for non-volatile organics in water. Most of the work is needed in these areas: a. Extraction/concentration, especially by accumulator columns. b. Separation, especially for aqueous concentrates. c. More universal and more sensitive detectors. d. On-the-fly identification (analogous to GC-MS).	XXX	XX	XX	X	Appendix 2, Parts B, 1e and B,3 and Appendix 3, Part C
4. A study of the problems associated with analysis of organics adsorbed on suspended or collodial solids in water.	XXX		X		Appendix 3, Part D, 2
5. Streamlined quantification techniques for survey analysis of volatile organics in water. At least three areas need investigation: a. Provision of standard reference materials. b. Establishment of guidelines for optimum use of standards. c. Establishment of guidelines for semi-quantitative analysis by mass spectrometry ion current (GC-MS)	XX	XX		XXX	Appendix 3, Part B, 3
6. Increased availability of less expensive, reproducible capillary GC columns for survey analysis.	XXX	X		XX	Appendix 2, Part B, 3 and Appendix 3, Part B, 1

PRIORITY B	Needed for:				Supported by:
	Research	Epidemiological Studies	Water Re-use Planning	Water Quality Control	
7. Establishment of an analytical protocol to collect specific compound information for broad, prospective epidemiological studies.		XXX			Appendix 4
8. Feasibility study, including an economic evaluation, on the establishment of a system of central laboratories in each country capable of GC-MS survey analysis of samples collected regularly by local water works.			X	XXX	Appendix 2, Part B, 4 and Appendix 3, Part D, 1
9. Development of an automatic sampler for organics in water. One use would be by local water works to collect samples for regular submission to central laboratories for GC-MS survey analysis and/or analysis by chemical class.	X	X	XX	XXX	Appendix 3, Part D, 1
10. Development of analytical methods for monitoring groups of organics expected to be of adverse health effect, particularly in cases where treated re-used water is not stored sufficiently long enough for survey-type analysis before use. Groups to be monitored would be determined by toxicologists (health effect consideration) and analytical chemists (abundance consideration). Possibly important groups needing methods or improvements are: Total organic halogens Volatile organic halogens Total organic sulfur Volatile organic sulfur Volatile organic carbon			XX	XXX	Appendix 2, Part C, 2 and Appendix 3, Part E, 2

	Needed for:				Supported by:
	Research	Epidemiological Studies	Water Re-use Planning	Water Quality Control	
Taste and Odour compounds Organochlorine pesticides Surfactants <u>Total</u> measurements for each of these classes of compounds: Aromatic amines Chlorophenols Heterocyclic nitrogen compounds Nitrosamines Organobromine compounds Organofluorine compounds Polychlorinated biphenyls Polynuclear aromatic hydrocarbons					
11. Improvements in mass spectral matching programmes in at least four ways. a. Arrange a world-wide system for automatic submission of new mass spectra, especially those of water pollutants, to the computer files. b. Create subsets of spectral files of known water pollutants c. Determine statistically the reliance that may be placed on identification of a compound by computer matching only. d. Take other necessary action to lower the cost of spectral matching.	XX	XX	X	XXX	Appendix 2, Part B, 4 and Appendix 3, Part B, 2

	Needed for:				Supported by:
	Research	Epidemiological Studies	Water Re-use Planning	Water Quality Control	
12. Development of a reproducible method for survey analysis of intermediately volatile organics in water based upon accumulation by activated carbon columns. Compare results with those obtained using XAD resin columns.	XX	XX		XXX	Appendix 2, Part B, 1d and Appendix 3, Part B, 1
13. Commercial availability of Grob's purging (headspace analysis) device for extraction/concentration of volatile organics from water for survey analysis	XXX	X		XX	Appendix 2, Part B, 1b and Appendix 3, Part B, 1
14. Characterization of non-specific, high molecular weight compounds in drinking water and source water (not specific identification).	XXX	X			Appendix 3, Part C
15. The development of clear, universal, quality assurance guidelines for qualitative and quantitative analysis.	XX	XX		XXX	Appendix 3, Part B, 3

PRIORITY C

	Needed for:				Supported by:
	Research	Epidemiological Studies	Water Re-use Planning	Water Quality Control	
16. Refinement of analytical methods for survey analysis for volatile organics - this is in progress now in many laboratories and needs for special impetus.	XXX	X		XX	Appendix 2, Part B including Table; and Appendix 3, Part B, 1

APPENDIX 1

DISTRIBUTION AND CLASSIFICIATION OF ORGANICS IN WATER

A. Introduction

Almost 2000 organic compounds have been identified in water of all types. This number is increasing rapidly, as scores of laboratories examine effluents, surface water and drinking water for organic compounds for various reasons. It is speculated that every natural and synthetic organic compound can be found in some water sample if detection limits are lowered sufficiently. Although several lists of compounds found in water have been compiled[1/2/3], the lists are usually limited to certain classes of organics, or to certain types of samples. The most comprehensive list is that compiled by the Water Research Centre for the Commission of the European Communities (CEC) COST Project 64b, entitled "A comprehensive list of polluting substances which have been identified in various fresh waters, effluent discharges, aquatic animals and plants, and bottom sediments".

This mass of data needs to be continually updated, classified and computerized for use in health effects studies, development of analytical methodology and related research.

B. CEC and U. S. EPA Collation Efforts

The CEC/COST Project 64b list gives concentration (if available), type of water sampled, data of sample and reporting laboratory. No claim is made for complete coverage, but an extensive listing is maintained by searching the literature and by regular submission from laboratories participating in the COST Project 64b efforts. Private communications supplement the list. .Although the bulk of the compounds listed are those found in Western European waters, much data from the U. S. EPA is included. Compounds are listed by major chemical class. A computer programme is currently being developed to print out the compound list and associated data, rather than manually type it[5]. There are plans within the CEC to computerize the COST Project 64b list for automatic collation and updating of data and for data retrieval.

The U. S. EPA has no comprehensive listing of organics in water as yet. A list of compound names with number of times found in water of different types is being compiled for computer printout and will soon be published[6]. This list will be more comprehensive and up to date than others, and includes compounds on the COST Project 64b list. Its main purpose is to allow determination of compounds that should be included in a subset of mass spectral data to be used for more efficient computer searching and identification of organics extracted from water.

The EPA has definite plans for development of a comprehensive computerized collation and data retrieval system for organics in water, to be conducted by an extramural contractor over the next year. This system, to be called Water DROP (Distribution Register of Organic Pollutants in Water) will include a means for continual updating and dissemination of new information on organics in water. It will include various chemical, biological and geographical descriptors for each compound, as well as data on concentration, source, etc., and can be accessed by several modes to search for compounds of particular interest to analytical chemists, epidemiologists, enforcement groups and others.

C. Coordination and Dissemination of Specific Compound Information

Communication should be maintained between the CEC and the U. S. EPA relative to the computerization and distribution of data on specific organics in water. The optimum degree of overlap in the EPA and CEC computer libraries should be decided soon. It may be desirable, once each group has developed its initial library, for the CEC to concentrate on data relative to European waters, while the EPA concentrates on U. S. or North American waters. An obvious option would be for each lirabry to contain as much data as possible from world wide sources - this complete overlap may be necessary to allow easy access to all data by user countries in different parts of the world. In any case, it would be highly desirable for both libraries to be based upon a compatible computer language to allow easy exchange of programmes and data.

Some means should be developed for dissimination of data on specific organics in water to interested users throughout the world. Groups in many countries in addition to those in the CEC or U. S. need such data for a variety of reasons. Since the computer libraries discussed above will become the repositories for most of this information, the data contained in them should be available to all potential users. The International Reference Centre for Community Water Supply in The Hague would be a logical clearing house and distribution centre for such information, working between the CEC/U. S. EPA on the one hand and other interested nations on the other. The libraries themselves could be made available on computer tape or in hard copy form, or abstracts of new data coming into the libraries could be generated and distributed periodically.

D. Chemical Classification System

It is essential that the large data base on organic compounds in water be logically organized for efficient use. There is a special need for classification of specific organics into an array useful to those studying health effects and to analytical chemists. Classification by chemical functionality is most logical, since chemically related compounds often have similar health effects and usually are amenable to the same analytical techniques. Chemical classification into classes of the optimum size should allow toxicologists to examine the data bank more efficiently and more effectively prioritize chemical classes for health effects studies. This, in turn, should prioritize the classes according to needs for analytical methods development. In light of these factors, the following classification system for organics in water is proposed. This system is that of an analytical chemist; it is based upon similarities in chemical functionality and broken down into narrow enough groups so that one or two analytical methods will suffice for specific analysis of all members of each class. Health effects considerations are of necessity secondary since so little is known in this area.

The COST Project 64b list is classified into twenty-two chemical or usage groups - this was the starting point for development of this more narrow, hopefully more useful, classification system.

It is hoped that a chemical classification system of this type will be incorporated into the EPA and CEC computerized libraries - it will be useful, both to analytical chemists and those studying health effects, to retrieve data on all compounds within a chemical class. However, the particular system described here is not necessarily the best; other chemical subdivisions may be more appropriate.

CLASSIFICATION SYSTEM FOR ORGANIC COMPOUNDS IN WATER

a. Major classes

All compounds are grouped into the following 28 alphabetically arrayed major classes. All classes are of functional groups except Dyes, Pigments and Optical Brighteners; Miscellaneous Non-Volatile Compounds; Pesticides and Herbicides and Surfactants.

Alcohols
Aldehydes
Alkane Hydrocarbons
Alkene Hydrocarbons
Amides
Amines
Amino Acids
Benzenoid Hydrocarbons
Carbohydrates
Carboxylic Acids
Dyes, Pigments and Optical Brighteners
Esters
Ethers and Heterocyclic Oxygen Compounds
Halogenated Aliphatic Compounds
Halogenated Aromatic Compounds
Ketones
Miscellaneous Non-Volatile Compounds
Nitro-Compounds
Nitrogen Compounds, Miscellaneous
Non-Volatile Compounds, Miscellaneous
Organometallic Compounds
Pesticides and Herbicides
Phenols and Naphthols
Phosphorus Compounds
Polynuclear Aromatic Hydrocarbons
Steroids
Sulfur Compounds
Surfactants

b. Hierarchy of Assignment

In cases of more than one functional group in a compound (usually the case), the hierarchy of assignment of major class is as follows. In all cases, the 4 usage classes take priority and are listed first in alphabetical order.

1. Dyes, Pigments and Optical Brighteners
2. Miscellaneous Non-Volatile Compounds
3. Pesticides and Herbicides
4. Surfactants
5. Halogenated Aliphatic Compounds
6. Halogenated Aromatic Compounds
7. Amino Acids
8. Phosphorus Compounds
9. Sulfur Compounds

10. Carbohydrates
11. Steroids
12. Organometallic Compounds
13. Nitrogen Compounds, Miscellaneous
14. Non-Volatile Compounds, Miscellaneous
15. Carboxylic Acids
16. Phenols and Naphthols
17. Amines
18. Nitro-compounds
19. Ketones
20. Aldehydes
21. Alcohols
22. Esters
23. Amides
24. Ethers and Heterocyclic Oxygen Compounds
25. Polynuclear Aromatic Hydrocarbons
26. Benzenoid Hydrocarbons
27. Alkene Hydrocarbons
28. Alkane Hydrocarbons

c. Sub-Classes

Within most of the 28 major functional group classes, each compound is assigned to a more narrow chemical sub-class. These are listed below with examples.

ALCOHOLS

Aliphatic - butanol
Aromatic - α-methylnezyl alcohol
Terpenoid - α-terpineol
Miscellaneous - 3-methylcyclopentan-1, 2-diol

ALDEHYDES

Aliphatic - iso-butyraldehyde
Aromatic - 2,4,6-trimethyl benzaldehyde
Miscellaneous - crotonaldehyde

ALKANE HYDROCARBONS

Branched - isodecane
Cyclic - cyclopentane

Normal - decane
Miscellaneous - abietane

ALKENE HYDROCARBONS
Regular - cyclopentene
Terpenoid - beta-ocimene

AMIDES
Aliphatic - caprolactam
Aliphatic, substituted - N,N-dimethylolamide
Aromatic - acetanilide

AMINES
Aliphatic - cyclohexylamine
Aliphatic, substituted - 2-amino-2-ethyl-1,3-propanediol
Alkylanilines (including aniline and benzidine) - dimethylaniline
Anilines, other substituted - 4-aminostilbene
Naphthylamines - naphtylamine
Nitroanilines
Miscellaneous - 4,4'-diaminodicyclohexylbenzene

AMINO ACIDS - leucine

BENZENOID HYDROCARBONS
Alkybenzenes, w/saturated substituents - ethylbenzene
Alkybenzenes, w/unsaturated substituents - vinylbenzene
Biphenyls and Polyphenyls - methylbiphenyl
Indan and Tetralin hydrocarbons - ethylindan

CARBOHYDRATES - 4,6-di-o-isopropylidene-L-sorbofuranose

CARBOXYLIC ACIDS
Aromatic (benzoic types) - t-butylbenzoic acid
Aromatic, hydroxy (hydroxy-benzoic type) - 3-hydroxybenzoic acid
Aliphatic, dicarboxylic - succinic acid
Aliphatic,hydroxy- and keto - 2-hydroxybutyric acid
Aliphatic, long-chain (From C-7) - palmitic acid
Aliphatic, short-chain (C-1 to C-6) - isovaleric acid
Aliphatic, unsaturated - oleic acid

Phenylalkanoic - phenylacetic acid
Resin - abietic acid
Miscelleneous - dimethylnitrobenzoic acid

DYES, PIGMENTS AND OPTICAL BRICHTENERS

Dyes and pigments - Disperse Blue 3
Optical Brighteners - "coumarine type optical brightner"

ESTERS

Adipates and azelates - bis(2-ethylhexyl) azelate
Alkyl alkanoates (incld. substituted) - vinyl propionate
Aromatic - methyl dimenthoxybenzoate
Fatty acid methyl esters - methyl linoleate
Phthalates - di-n-butyl phthalate
Miscellaneous - butyl octyl maleate

ETHERS AND HETEROCYCLIC OXYGEN COMPOUNDS

Aliphatic - 4-methyl-1,3-dioxolane
Aliphatic, substituted and/or unsaturated - dimethylfuran
Aromatic - ethyl benzyl ether

HALOGENATED ALIPHATIC COMPOUNDS

Aliphatic bromides and/or iodides - dibromoethane
Aliphatic chlorides - dichloroethane
Aliphatic chlorides with bromine, iodine and/or fluorine - dibromodichloroethane
Aliphatic chlorides, other substituted - ethycloroacetate
Aliphatic fluorides
Ethers, chlorinated aliphatic - 1,2-bis(chloroethoxy)ethane
Paraffins, chlorinated ("chloroparaffins")
Miscellaneous - ethyl fluoroacetate

HALOGENATED AROMATIC COMPOUNDS

Brominated,iodinated and/or fluorinated aromatics - dibromobenzene
Chlorinated aromatic amines - 2-chloroaniline
Chlorinated benzenes and alkylbenzenes - tetrachloroethylstyrene
Chlroinated benzoic acids - 5-chlorosalicylic acid
Chlorinated nitro-aromatics - 1,3-nitrochlorobenzene
Chlorinated phenols and naphthols - methyltetrachlorophenol
Chlorinated heterocyclic aromatics - chloromethylquinoline

Polychlorinated biphenyls (PCB's) and Arochlors - heptachlorobiphenyl

Miscellaneous - chlorophenylethyl sulphone

KETONES

Aliphatic - butyl propyl ketone

Aliphatic, substituted - methyl propenyl ketone

Anthraquinones and Quinones - anthraquinone

Aromatic - acetophenone

NITRO-COMPOUNDS

Aliphatic - nitromethane

Aromatic - nitroethoxybenzene

Miscellaneous

NITROGEN COMPOUNDS, MISCELLANEOUS

Azo Compounds - azobenzene

Carbamates - 3-methyl butanonitrile

Cyanides - benzyl cyanide

Heterocyclic - caffeine

Indoles and Carbazoles - 3-hydroxyindole

Nitrosamines

Pyridines - dimethylpyridine

Quinolines - dimethylquinoline

Xanthines and Uric Acids - 1-methylxanthine

NON-VOLATILE COMPOUNDS, MISCELLANEOUS - guanosine

ORGANOMETALLIC COMPOUNDS - copper phthalocyanine

complexed species- metal + ligand

Organometallic compounds with carbonmetal bonds - tiphenyltin hydroxide

PESTICIDES AND HERBICIDES

Aromatic halogenated pesticides, miscellaneous - dicamba

Atrazine derivatives - atrazine

"Benzenehexacloride" (BHC) isomers - alpha BHC

Carbamates - carbaryl

Chlorinated phenoxy acids - 2,4-D,butyl ester

DDT derivatives - 4,4'-DDE

Organophosphorus pesticides - malathion

Polycylic halogenated pesticides - aldrin
Miscellaneous - alachlor

PHENOLS AND NAPHTHOLS
Alkylphenols (incld. phenol) - 2-nonylphenol
Alkoxyphenols - 2-methoxyphenol
Aminophenols - aminophenol
Hydroxyphenols - resorcinol
Naphthols - alpha-naphthol
Nitrophenols - 2-nitrophenol
Miscellaneous - 2-phenylphenol

PHOSPHORUS COMPOUNDS
Phosphates - tributylphosphate
Miscellaneous - S,S,S-tributylphosphorotrithioate

POLYNUCLEAR AROMATIC HYDROCARBONS
Alkyenaphthalenes (and naphthalene) - 1-methylnaphthalene
Indenes - 3-methylindene
Polynuclear aromatic hydrocarbons, other - 3,4 (a) pyrene

STEROIDS - coprostanol

SULFUR COMPOUNDS
Aromatic - methyl diphenyl sulfide
Compounds w/S-O bonds - dimethyl sulfoxide
Compounds w/S-N bonds - N-ethyl-2-toluenesulfonamide
Heterocyclic - dithiane
Mercaptans - t-butyl mercaptan
Sulfides and Disulfides - diethyl disulfide
Miscellaneous - ethyl isothiocyanate

SURFACTANTS

d. Miscellaneous Rules

1. Halogens - any compound containing a halogen atom except those in one of the 4 usage classes (Part II, major classes 1-4) is assigned under "Halogenated Aliphatic Compounds" or "Halogenated Aromatic Compounds".

2. The various "Aromatic" sub-classes usually include all compounds of the major class concerned with any aromatic function, even if the major functional group is not on the ring. Benzyl alcohol is thus listed under Alcohol, Aromatic instead of Alcohol, Aliphatic. (Phenylalkanoic acids, however, are listed separately.)

3. Anthraquinones and Quinones are a class under Ketones.

4. Alkylnaphthalenes and Indene Derivatives are arranged under Polynuclear Aromatic Hydrocarbons. Indans and Tetralins, Biphenyls and Polyphenyls and all hydrocarbon-substituted benzenes are classified under Benzenoid Hydrocarbons.

5. The order of hierarchy of functional groups for assignment to sub-classes is the same as that for assignment to major classes (see part II), where applicable.

6. "Substituted" aliphatics usually include unsaturated aliphatics.

7. "Non-Volatile Compounds, Miscellaneous" includes chlorophyll, enzymes, fulvic acids, humic acids, complex nitrogen bases, tannic acids, vitamines, xanthophylls, etc.

8. "Pesticides and Herbicides" include associated manufacturing byproducts.

E. Distribution of Organic Compounds in Water

A logical use of such chemical classification system as developed above is in the organization and display of data on the distribution of organic compounds in water. Table 1 illustrates one way in which distribution data may be displayed. The major chemical classes and sub-classes are listed. The number of different compounds found in each class is given, along with the number of times members of each class have been found in various types of samples and the total times found.

This total, together with concentration data, allows the calculation of an Abundance Index, which will be discussed later. The suspected source(s) of each class of compound is given, along with some indication of persistence of the class. Such distribution data should allow a semi-quantitative assessment of the pollution potential of each of the various classes of organics found in water and should be useful in health effects studies, as well as to analytical chemists.

Table 1 is only partially filled out, using data from EPA computer listing, "Frequency of Organic Compounds Identified in Water"[6]. Bias in the data does not allow calculation of a meaningful Abundance Index, even when quantitative data are available and information on compound source and persistance is sparse. However, entries of numbers of compounds found and sample type is the latest available. One exception is the "industrial effluent" sample category - the data that specify whether compounds were found in raw or treated waste waters were not readily available. It was known that most (perhaps three-fourths) of the compounds were found in treated industrial waste waters so all the compounds were entered under this catagory. An update of this table will include a correction of these entries. Another possibily misleading part of the table is that dealing with pesticides. Most of the pesticides identified in various water monitoring programmes conduct throughout the world during the last two decades are not included - most of the listings are of pesticides found recently in survey analyses for all types of organics. However, the number of different pesticides found and their chemical classifications should be nearly correct; the number of times found in different types of water should be only representative. This is true to a lesser extent for the halogenated aliphatic compounds; e.g. some of the recent EPA survey data for selected halogenated organics is not included. Two other comments on specific classes: (1) no specific surfactants were found in the EPA list; some may be included in other classes listed on the table, and (2) no nitrosamines are on the EPA list, but there have been unconfirmed identifications of nitrosamines in water.

The Abundance Index (AI) is a quantitative expression of the extent of distribution of a class of organic compounds in water, being the multiplicand of the average concentration of all members of the class, in appropriate units and the total number of times members of the class have been found.

$$\text{AI} = (\text{total times found}) \times \text{exponent of} \left[\begin{array}{l}\text{average conc. in mg/l to the} \\ \text{nearest power of } 10 \times 10^6\end{array}\right.$$

For example, according to the COST Project 64b list (which includes much quantitative data), aliphatic alcohols have been found in water a total of 26 times. The average concentration in mg/l, to the nearest power of 10, is 10^{-1}. This is multiplied by 10^{6} (to achieve a managable unit) to give 10^{5}. Therefore:

AI (for aliphatic alcohols) = 26 x 5 = 130

Similar calculations using data from the COST Project 64b list give the following AI values for the other three sub-classes of alcohols:

aromatic, 32; terpenoid, 90; miscellaneous 27.

These particular calculations are for illustrative purposes only and may be misleading. There is not enough unbiased quantitative data yet available to allow a meaningful calculation of an Abundance Index, except for a few cases. At least three types of bias exist: (1) Bias by source; e.g., most chlorinated drinking water contains chloroform, most other types of water samples do not. Therefore, concentrated interest in organics in drinking water leads to an unduly large number of chloroform (or other haloform) detections. (2) Intentional bias by analytical method; e.g., again in the case of chloroform, for drinking water many methods have been designed to "analyze for" chloroform or haloforms. (3) Non-intentional bias by analytical method; e.g., recovery of individual organics from a carbon accumulator column is not equally efficient and the percentage is unknown for many compounds. Even more disparaging is the lack of data on non-volatile organics, for which analytical methods are not yet available.

A useful Abundance Index can now be calculated only for a particular type of water, all samples of which have been analyzed by the same method. For example, a survey of many surface waters in the areas of industrial complexes by liquid-liquid extraction followed by GC-MS analysis could give sufficient data to calculate Abundance Indices of semi-quantitative significance. These Indices could be useful to toxicologists and analytical chemists in first-approximation assignments of priorities by chemical class for further studies.

An extension of this concept would be the calculation of Abundance Indices for individual organic compounds. Perhaps this will be feasible in the future when much more distribution data is available from computerized libraries.

F. References

1. R. G. Webb, A. W. Garrison, L. H. Keith and J. M. McGuire, "Current Practise in GC-MS Analysis of Organics in Water", EPA Research Report No. EPA-R 2-73-277, Washington D. C., August 1973, pp. 62-87.

2. G. A. Junk and S. E. Stanley, "Organics in Drinking Water". Part 1 - Listing of Identified Compounds". ERDA Report IS-3671, U. S. Department of Commerce, Springfield, VA. July 1975.

3. World Health Organization, International Reference Centre for Community Water Supply, "Health Effects Relating to Direct and Indirect Re-use of Waste Water for Human Consumption". Report of an International Working Meeting, Amsterdam, the Netherlands, January 13-16, 1975, Technical Paper No. 7, September 1975.

4. Water Research Centre, "A Comprehensive List of Polluting Substances which have been Identified in Various Fresh Waters, Effluent Discharges, Aquatic Animals and Plants and Bottom Sediments", Stevenage Laboratory, Elder Way, Stevenage, Hertfordshire SG1 1TH, England, October 1975.

5. A. Waggott, Water Research Centre, Stevenage Laboratory, Stevenage, England, Private Communication, February 1976.

6. W. Shackelford and L. H. Keith, "Frequency of Organic Compounds Identified in Water" compiled by the Analytical Chemistry Branch, Environmental Research Laboratory, U. S. EPA, Athens, GA. 30601.

TABLE 1. DISTRIBUTION OF ORGANIC COMPOUNDS IN WATER BY CHEMICAL CLASS

CHEMICAL CLASS Subclass	Approximate number of compounds found	Number of Times found per Sample Type						TOTAL TIMES FOUND	Range of Concentration (mg/l)	Average Conc. (mg/l) (to nearest power of 10)	Average Conc. x 10^6 (Exponent)	ABUDANCE INDEX (exponent x total times found)	Suspected Source P = Primary, M = Minor									Persistance
		Indust. Effluent		Municipal Effluent																		
		Raw or Settled	Treated	Raw or Settled	Treated	Surface Water*	Drinking Water						Natural	Industrial Process	Ind. Waste Treat.	Domestic Waste	Dom. Waste Treat.	Agriculture	Air	Environmental Transformation	Drinking Water Treatment	
ALCOHOLS	65		118	6	17	68	46	274														
Aliphatics	26		44	1	11	32	38	135														
Aromatic	10		17			1	1	23														
Terpenoid	12		43	3	4	17	6	76														
Miscellaneous	17		14	2	2	18	1	40														
ALDEHYDES	23		16		8	6	47	92														
Aliphatic	17		2		7	5	37	64														
Aromatic	2		7			1	5	14														
Miscellaneous	4		7		1		5	14														
ALKANE HYDROCARBONS	67		78			33	96	241														
Branched	9		2			3	8	16														
Cyclic	8		0			17	12	17														
Normal	49		76			13	76	207														
Miscellaneous	1		0					1														
ALKENE HYDROCARBONS	36		57			12	14	91														
Regular	20		16			5	12	40														
Terpenoid	16		41			7	2	51														

* Includes subterrainean water and landfill leachates

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CHEMICAL CLASS Subclass	Approximate number of compounds found	Number of Times found per Sample Type						TOTAL TIMES FOUND	Range of Concentration (mg/1)	Average Conc. (mg/1) (to nearest power of 10)	Average Conc. x 10^6 (Exponent)	ABUDANCE INDEX (exponent x total times found)	Suspected Source. P = Primary, M = Minor									Persistance
		Indust. Effluent		Municipal Effluent		Surface Water*	Drinking Water						Natural	Industrial Process	Ind. Waste Treat.	Domestic Waste	Dom. Waste Treat.	Agriculture	Air	Environmental Transformation	Drinking Water Treatment	
		Raw or Settled	Treated	Raw or Settled	Treated																	
AMIDES	9		8	2	2	8	1	23														
Aliphatic	4		2	2		5	1	11														
Aliphatic, substituted	4		4		2	3		10														
Aromatic	1		2					2														
AMINES	35		54	7	3	22	13	101														
Aliphatic	8		16	3	2	2	8	33														
Aliphatic, substituted	2		2	0				2														
Alkylanilines (including aniline and benzidine)	16		26	1	1	19	5	52														
Anailines, other substituted	6		6	3				9														
Naphthylamines	2		2			1		3														
Nitroanilines	0																					
Miscellaneous	1		2					2														
AMINO ACIDS	16		0	17	1			18														
BENZENOID HYDROCARBONS	65		117	8	30	90	99	449														
Alkybenzenes, w/saturated substituents	51		73	5	26	81	77	361														
Alkylbenzenes, w/unsaturated substituents	6		23			3	9	37														

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CHEMICAL CLASS Subclass	Approximate number of compounds found	Number of Times found per Sample Type						TOTAL TIMES FOUND	Range of Concentration (mg/l)	Average Conc. (mg/l) (to nearest power of 10)	Average Conc. x 10^6 (Exponent)	ABUDANCE INDEX (exponent x total times found)	Suspected Source P = Primary, M = Minor									Persistance
		Indust. Effluent		Municipal Effluent																		
		Raw or Settled	Treated	Raw or Settled	Treated	Surface Water*	Drinking Water						Natural	Industrial Process	Ind. Waste Treat.	Domestic Waste	Dom. Waste Treat.	Agriculture	Air	Environmental Transformation	Drinking Water Treatment	
Biphenyls and Polyphenyls	5		16	3	2	4	9	37														
Indan and Tetralin hydrocarbons	3		5		2	2	5	14														
CARBOHYDRATES	13		2	11		1	3	17														
CARBOXYLIC ACIDS	108		141	25	70	142	21	402														
Aromatic (benzoic types)	4		10			3	4	19														
Aromatic, hydroxy (hydroxy-benzoic type)	8		9	1		1	1	12														
Aliphatic, dicarboxylic	3		1	2	1			4														
Aliphatic, hydroxy- and keto-	8		7	3				10														
Aliphatic, long-chain (From C-7)	34		55	4	40	48	10	157														
Aliphatic, short chain (C-1 to C-6)	11		13		10	63	3	91														
Aliphatic, unsaturated	6		13	2	11	5		31														
Phenylakanoic	8		3	4	5	4	2	19														
Resin	7		18			5	1	24														
Miscellaneous	19		12	9	3	13		35														
DYES, PIGMENTS AND OPTICAL BRIGHTENERS	10		8	2				10														
Dyes and pigments	9		8	1				9														
Optical Brighteners	1			1				1														

[*] Includes subterrainean water and landfill leachates.

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		Indust. Effluent		Municipal Effluent		Surface Water*	Drinking Water						Natural	Industrial Process	Ind. Waste Treat.	Domestic Waste	Dom. Waste Treat.	Agriculture	Air	Environmental Transformation	Drinking Water Treatment	
		Raw or Settled	Treated	Raw or Settled	Treated																	
ESTERS	85		69	23	32	115	78	340														
Adipates and azelates	3		2			7	2	13														
Alkyl alkanoates (incld. substituted)	20		12	7	10	19	14	66														
Aromatic	9		10			3	4	18														
Fatty acid methyl esters	9		6	2	8	7	3	30														
Phthalates	25		23	12	14	73	47	178														
Miscellaneous	19		16	2		6	8	35														
ESTERS AND HETEROCYCLIC OXYGEN COMPOUNDS	52		83	10	20	35	40	198														
Aliphatic	33		40	10	20	24	24	124														
Aliphatic, substituted and/or unsaturated	1		1					1														
Aromatic	19		42			11	16	73														
HALOGENATED ALIPHATIC COMPOUNDS	135		168	37	69	118	470	928														
Aliphatic bromides and/or iodides	9		5	1	1	4	29	46														
Aliphatic chlorides	44		89	25	48	68	257	518														
Aliphatic chlorides with bromine, iodine and/or fluorine	16		11	7	13	15	130	188														
Aliphatic chlorides, other substituted	25		21		6	9	25	67														

* Includes subterrainean water and landfill leachates

TABLE 1. DISTRIBUTION OF ORGANIC COMPOUNDS IN WATER BY CHEMICAL CLASS

CHEMICAL CLASS Subclass	Approximate number of compounds found	Number of Times found per Sample Type						TOTAL TIMES FOUND	Range of Concentration (mg/1)	Average Conc. (mg/l) (to nearest power of 10)	Average Conc. x 10^6 (Exponent)	ABUDANCE INDEX (exponent x total times found)	Suspected Source P = Primary, M = Minor									Persistance
		Indust. Effluent		Municipal Effluent																		
		Raw or Settled	Treated	Raw or Settled	Treated	Surface Water*	Drinking Water						Natural	Industrial Process	Ind. Waste Treat.	Domestic Waste	Dom. Waste Treat.	Agriculture	Air	Environmental Transformation	Drinking Water Treatment	
Aliphatic fluorides	0																					
Ethers, chlorinated aliphatic	18		9	3		15	19	52														
Paraffins, chlorinated ("chloroparaffins")	0																					
Miscellaneous	23		33	1	1	7	10	57														
HALOGENATED AROMATIC COMPOUNDS	144		108	21	78	152	125	509														
Brominated, iodinated and/or fluorinated aromatics	3					2	5	10														
Chlorinated aromatic amines	10		16		2	7		25														
Chlorinated benzenes and alkylbenzenes	35		38	8	33	93	82	265														
Chlorinated benzoic acids	11		9	1	3	1		14														
Chlorinated nitro-aromatics	8		5			8	6	20														
Chlorinated phenols and naphthols	28		24	8	14	11	18	80														
Chlorinated heterocyclic aromatics	9		1		6	2	2	12														
Polychlorinated biphenyls (PCB's) and Arochlors	10		4	1	9	8	7	32														
Miscellaneous	30		11	3	11	20	5	51														
KETONES	56		81	5	21	72	98	299														
Aliphatic	24		48	4	17	44	72	201														
Aliphatic, substituted	16		12		1	12	10	39														

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		Indust. Effluent		Municipal Effluent																		
		Raw or Settled	Treated	Raw or Settled	Treated	Surface Water[x]	Drinking Water						Natural	Industrial Process	Ind. Waste Treat.	Domestic Waste	Dom. Waste Treat.	Agriculture	Air	Environmental Transformation	Drinking Water Treatment	
Anthraquinones and Quinones	5		6			10	3	20														
Aromatic	11		15	1	3	6	13	39														
NITRO-COMPOUNDS	20		31	1	1	16	9	61														
Aliphatic	4		6		1	2	4	14														
Aromatic	15		25	1		13	5	46														
Miscellaneous	1					1		1														
NITROGEN COMPOUNDS, MISCELLANEOUS	64		41	19	12	23	27	142														
Azo Compounds	2		1				1	3														
Carbamates	1		2			4		6														
Cyanides	16		6		3	3	12	33														
Heterocyclic	22		9	7	3	9	14	50														
Indoles and Carbazoles	4		6	1	2			9														
Nitrosamines	0																					
Pyridines	9		11		1	7		21														
Quinolines	3		6					6														
Xanthines and Uric Acids	7			11	3			14														
NON-VOLATILE COMPOUNDS, MISCELLANEOUS	16		5	10	2	3	1	21														

[x] Includes subterrainean water and landfill leachates

TABLE 1. DISTRIBUTION OF ORGANIC COMPOUNDS IN WATER BY CHEMICAL CLASS

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		Indust. Effluent		Municipal Effluent		Surface Water*	Drinking Water						Natural	Industrial Process	Ind. Waste Treat.	Domestic Waste	Dom. Waste Treat.	Agriculture	Air	Environmental Transformation	Drinking Water Treatment	
		Raw or Settled	Treated	Raw or Settled	Treated																	
ORGANOMETALLIC COMPOUNDS	2			2				2														
PESTICIDES AND HEBRICIDES	79		111	3	3	91	59	287														
Aromatic halogentated pesticides, misc.	3		2				2	4														
Atrazine derivatives	8		11			4	9	28														
"Benzenehexachloride" (BHC) isomers	4				1	4	4	10														
Carbamates	2		1			1		2														
Chlorinated pehnoxy acids	16		1		1	13		17														
DDT derivatives	8			1		21	7	32														
Organophosphorus pesticides	13		24	1	1	11	4	41														
Polycyclic halogenated pesticides	17		71	1		29	24	133														
Miscellaneous	8		1			8	9	20														
PHENOLS AND NAPHTHOLS	89		155	6	9	50	21	249														
Alkylphenols (incld. pehnol)	41		86	5	8	32	12	147														
Alkoxyphenols	13		29			6	2	39														
Aminophenols	3		4				2	7														
Hydroxyphenols	8		7			2		9														
Naphthols	2		3			1		4														
Nitrophenols	6		11			4	1	16														
Miscellaneous	16		15	1	1	5	4	27														

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CHEMICAL CLASS Subclass	Approximate number of compounds found	Number of Times found per Sample Type						TOTAL TIMES FOUND	Range of Concentration (mg/1)	Average Conc. (mg/1) (to nearest power of 10)	Average Conc. x 10^6 (Exponent)	ABUDANCE INDEX (exponent x total times found)	Suspected Source P = Primary, M = Minor									Persistance
		Indust. Effluent		Municipal Effluent		Surface Water*	Drinking Water						Natural	Industrial Process	Ind. Waste Treat.	Domestic Waste	Dom. Waste Treat.	Agriculture	Air	Environmental Transformation	Drinking Water Treatment	
		Raw or Settled	Treated	Raw or Settled	Treated																	
PHOSPHORUS COMPOUNDS	6		7	2		14	6	32														
Phosphates	5		7	1		14	6	31														
Miscellaneous	1			1				1														
POLYNUCLEAR AROMATIC HYDROCARBONS	46		117	18	16	86	71	315														
Alkylnaphthalenes (and naphthalene)	10		57	4	8	23	25	120														
Indenes	7		14			5	11	32														
Polynuclear aromatic hydrocarbons, others	24		43	11	8	55	34	154														
STEROIDS	5		3	3		3		9														
SULFUR COMPOUNDS	49		63	4	4	40	34	144														
Aromatic	8		9		1	1		11														
Compounds w/S-O bonds	8		5			4	13	16														
Compounds w/S-N bonds	6		3			12	3	19														
Heterocyclic	17		24	4	1	19	11	64														
Mercaptans	1					1		1														
Sulfides and Disulsifdes	5		15			3	2	18														
Miscellaneous	4		7		2		5	15														

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		Indust. Effluent		Municipal Effluent																		
		Raw or Settled	Treated	Raw or Settled	Treated	Surface Water*	Drinking Water						Natural	Industrial Process	Ind. Waste Treat.	Domestic Waste	Dom. Waste Treat.	Agriculture	Air	Environmental Transformation	Drinking Water Treatment	
SURFACTANTS	0																					
TOTALS	1291		1637	239	398	1197	1379	5245														

* Includes subterrainean water and landfill leachates

APPENDIX 2

ANALYSIS OF ORGANIC COMPOUNDS IN WATER - CURRENT STATUS

A. Introduction

Analysis of organic compounds in water falls into two main categories termed by Budde[1] "analysis for" and "survey" analysis. "Analysis for" methods are those used for a specific compound or class of compounds, with no interest in other materials present. For example, one "analyses for" PCB's,designing the extraction, clean-up and concentration processes so as to maximize the recovery of PCB's and designing the GC separation and detection techniques to optimize PCB separation and detection. Such "analyse for" methods are of increasing importance, since in many laboratories monitoring and health effects studies are based on assessment of organics by chemical classes; these methods will be referred to here as chemical class analyses.

Survey analysis cuts broadly across organic chemical classes and is used when one wishes to identify and quantify as many compounds in the sample as possible. This is a functional approach in which the analytical methodology is a function mostly of physical properties of organics found in water, suchas volatility and solubility, which in turn are dependent upon the molecular weight and polarity of the various compounds. Therefore, methods are usually classified according to the extraction/concentration techniques found useful for best recovery of organics of a certain range of water solubility and/or volatility. This is the basis of the arrangement of extraction/concentration techniques in Table 1. For example, purging is a viable technique for any compound in water that is volatile enough to boil below 150°C and is less than 2% water soluble - this includes many materials besides halogenated aliphatic compounds. Various degrees of specificity may be included in the method to narrow the range of compounds detected; e.g., purging is fairly class-specific for halogenated aliphatics if a halogen-specific detector is employed for gas chromatography (GC) peak detection.

After compounds are extracted and concentrated, survey analysis may be further unavoidably narrowed in scope by the separation technique. For example, some compounds that can be extracted from water by liquid extraction or on an accumulator column cannot be separated by GC and cannot be derivitized for GC, so must be separated by liquid chromatography.

B. Survey Analysis

Table 1 indicates the techniques of extraction/concentration and separation that have been shown to be appropriate for various classes of compounds. The classification scheme is the same developed in Appendix 1, Section D, but its application here is not to show the methods used to "analyze for" a certain class of compounds but to show the application of each technique in a broad survey mode that cuts across chemical class division. None or very few members of some of these classes have yet been found in water - in such cases, the techniques expected to be most appropriate for extraction/concentration and separation of these compounds are indicated. The table is not meant to be all inclusive or even to give the ultimate best technique, only suggestions as to appropriate survey methods. Certain extraction/concentration techniques that are valuable in "analysis for" certain classes of compounds, such as polyurethane foam plugs for PCB's, are not included. The same is true for separation techniques, i.e., TLC is a valuable separation tool for certain classes of compounds, such as phenols, in water. Also, the "remarks" are very general and incomplete as far as prescribing limits of each technique.

1. Extraction and Concentration

Available extraction and concentration techniques for organics in water may be broadly classified as shown in Table 1. There are several variations of each technique.

a. Direct Aqueous GC. Water soluble, low molecular weight (less than about 200), non-ionic compounds may be detected by direct injection of the aqueous sample into the gas chromatograph[2]. Since this involves no concentration of the organics, sensitivity is very limited; at least 1 mg/l is required. It is a useful technique for alcohols, glycols, volatile free acids, etc. in industrial effluents. Some concentration of the organics, albeit with some loss, may be effected by direct distillation of the sample; e.g. distill 500 ml and collect the first 25 ml, redistill the 25 ml and collect the first 1 ml for GC analysis.

b. Purging. The most common purging techniques involve sparging of dissolved volatile organic compounds from the aqueous sample with an inert gas into an accumulator column, usually tenax resin or a "chromosorb" type adsorbent. The U. S. Environmental Protection Agency (EPA) uses the acronym

"VOA" (for Volatile Organic Analysis) for all such purging techniques. Variations of the sample size, sample temperature, sparging time and adsorbent are still being tried to optimize   the detection limit may be as low as 0.1 $\mu g/l^3$. In class analysis, the class of compounds being analyzed for will determine the exact conditions. For example, the "Bellar" modification of the purging technique was used to analyze for six volatile halogenated compounds (chloroform, bromoform, bromodichloromethane, chlorodibromomethane, carbon tetrachloride and 1,2-dichloroethane in the EPA National Organics Reconnaissance Survey[4]. An electrolytic conductivity GC detector was used to give class specificity for halogenated compounds. For GC-MS survey analysis, some purging technique needs to be standardized to achieve the best overall volatile organics recovery; it can then be expected to be quantitative or at least reproducible for all volatile organics of relative low boiling point (molecular weight below about 250 and low polarity) that are less than about 2% water soluble.

An important and more comprehensive and sensitive variation of purging is that devised by Grob[5], in Switzerland. This technique uses a large sample, up to 5 l, immersed in a constant temperature water bath (30°C). The water sample is sparged with a recycled inert gas, pumped by an all metal bellows pump, for 0.5 to 16 hours, depending upon the character of the sample. Water is condensed from the headspace vapours, which then pass through 1 mg. of activated carbon in a special holder. The use of such a small amount of carbon allows elution of adsorbed organics with a small amount of solvent (usually 10-15 μl of carbon disulfide or methylene chloride), so that no extract evaporation is necessary; the organics are already quite concentrated. This technique is broader than the VOA technique; organics of higher polarity and higher molecular weight may be recovered by increasing the sparging time. Non-polar compounds up to the boiling points of C-23 alkanes can be recovered quantitatively; polar compounds are recovered less efficiently. Although Grob's method is more complicated than the VOA methods (e.g. the special carbon holder is not widely available) it should be preferred, especially when capillary GC columns are used.

Occassionally the head space gas over a water sample is analyzed for organics that are not water soluble and favour the vapour phase. For example, vinyl chloride may be analyzed to 1μg/l by injection of head space gas[6], obtained after equilibration of a few milliliters of the water sample, perhaps at an elevated temperature, in a closed vial with a milliliter or so of headspace.

All purging techniques depend upon GC for separation of the collected organics - in the VOA techniques, organics are thermally desorbed from the collecting resin directly in the GC. In the Grob technique, the extract from the activated carbon is injected into the GC. For survey analysis, flame ionization devices may be used for detection and quantification while GC-MS is ultimately used for identification, or the organics may be desorbed directly into the GC-MS system for identification and semi-quantitative analysis. In the class analysis approach, where class-specific detectors are used, there is still a need for occasional confirmation of peak identity by GC-MS.

c. Liquid Extraction. Liquid extraction - the common terminology for extraction of an aqueous sample with an organic solvent - is the oldest and widest used technique for extracting organics from water. Most pesticide residue analyses have depended upon this technique for two decades. It is fairly comprehensive in approach, the extraction efficiency being generally acceptable for water insoluble organics of a wide variety of molecular weights. Final analysis is by GC with a flame detector, except when class specificity is desired. Many class-specific techniques are based on liquid extraction, but these usually involve various pH adjustments, back extraction and separate clean-up techniques to optimize recovery of the desired class of compounds, as well as the use of specialized GC detectors; e.g., chlorinated phenol[7] or pesticide analysis using an electron capture detector or organophosphorus pesticide analysis using a flame photometric detector.

There are definite limits to liquid extraction for survey analysis: (a) No one solvent is best for all compounds, chloroform and methylene chloride are popular but to get high recovery of polar compounds more polar solvents may be necessary. (b) Regardless of the solvent used, some pH adjustment is usually required to obtain high recovery of acidic and basic compounds; this may lead to 3 or 4 extracts per sample. (c) Concentration of this extract is required to increase sensitivity for GC analysis; this causes some loss of volatile components and can increase the level of impurities in the solvent to create serious interferences. (d) Extracts of complex environmental samples may be so "dirty" that extra "clean-up" steps are required; also in most cases, non-volatile, non-gas chromatographable materials are present that gradually degrade performance of the chromatograph inlet system, column, or detector. This is particularly true for capillary columns.

(e) The solvent usually gives a relatively broad, early eluting GC peak that masks the more volatile components extracted from the water.

With all these limitations, liquid extraction is still the first technique to be considered in planning a GC-MS survey analysis of organics in water. It is simple and inexpensive and the recovery and concentration factors are such that a detection level of 1 μg/l can be readily realized for hundreds of intermediately volatile organic compounds found in grab samples of 1 to 5 liters.

To take full advantage of the wide variety of compound types extractable using liquid extraction, it is usually necessary to derivitize the acid extracts, e.g. with diazomethane, to make methyl esters of acids and ethers of phenols. This allows these compounds to be gas chromatographed, increasing the number of compounds detected. There can be adverse effects upon derivitization; e.g. incomplete reaction, undesired side reactions and a decrease in overall recovery since a separate analytical step is involved.

Two unusual modes of solvent extraction may be useful for certain problems. A high boiling solvent can be used in an extraction technique[8] designed especially for highly volatile compounds. These solvents leave a "window" for the first few minutes of the chromatographic run through which the volatile compound peaks can be seen. Tetralin was found to be the best solvent for this purpose. None of these high boiling solvents can be concentrated to enhance sensitivity of the technique; the maximum concentration factor is realized with about a 1000/1 water/tetralin extraction ratio and this is not sufficient for organics in drinking water below the 10 μg/l level. Glaze[9] uses pentane extraction of highly volatile organics in an unusual way as a substitute for the VOA technique. He displaced 5 ml of the sample water from a completely filled septum-capped serum vial (normally of 125 ml volume) with 5 ml of pentane, without exposure to the atmosphere, and shakes mechanically for 15 minutes. He analyzes the pentane layer for volatile chlorinated compounds by GC with an electrolytic conductivity detector and claims better recovery then by the VOA sparging technique; however, the concentration factor is too small for GC-MS survey analysis.

Automatic liquid extractors are now available[10] - these systems save manpower, are more efficient and are feasible for the extraction of large volumes of water. They usually involve continuous solvent recycling, which results in less solvent use and limits the need for extraction evaporation. However, some thermal degradation is possible since the solvent must be boiled for recycle.

d. Accumulator Columns. Activated carbon has been used for many years, not only as a means of cleaning water, but conversely to remove and concentrate organic compounds from water for analysis. In the past three years, other solid adsorbent materials, notably the macroreticular XAD resins, have come into use as a means of extracting and concentrating organic compounds from all types of water. Such solid adsorbents are known as accumulator columns. For these accumulators, predetermined amounts of water, usually at a metered flow, are passed through the adsorbent, usually contained in a cyclindrical glass column. The adsorbed organics are dissolved by elution with an organic solvent, usually chloroform for carbon and diethyl ether for the XAD resins; however, the carbon is usually dried first, while the resin is not dried but treated with a water miscible organic solvent to allow more effective wetting by the eluting solvent. The eluant containing the organic pollutants is treated similarly to the extracts obtained during liquid extraction (discussed above) and most of the same problems are involved in preparing the extract for analysis. Analysis is by GC, using a flame detector, with ultimate compound identification by GC-MS.

Both carbon and resin adsorption have been used in recent surveys of organics in drinking water. Carbon adsorption was the main survey-type analytical technique used in the U.S. EPA's National Organic Reconnaissance Survey and in the 1974 examination of New Orleans drinking water[11]. However, XAD resins are becoming more popular and are now used more frequently than carbon.

Junk[12] has studied XAD resin adsorption extensively and developed detailed techniques for its application. His work has been supplemented by that of Webb[13] and others. Most of the experimental parameters, e.g., type of resin, flow rate, ratio of water to resin, elution techniques, have been studied and several organic chemical recovery studies have been made. After consideration of certain variations in techniques, these resins may now be applied routinely. One variation is to make the water sample acidic before adsorption to increase recovery of organic acids. A continual problem in use of resins is their initial contamination; certain stringent cleaning processes are necessary.

Although the carbon adsorption accumulator technique has been in use much longer, its application is considerably less well defined than that of the XAD resins. A definite method has been prescribed by the EPA for the measurement of total CCE (Carbon Chloroform Extractables) in water by use of small carbon columns, but choice of the carbon and other method parameters is not optimized for subsequent analysis of specific compounds in the extract. Undetermined variables in the use of carbon include: the carbon itself (type, source, batch reproducibility), method of cleaning the carbon, water/carbon ratio, water flow rate drying technique, extraction solvent and extraction time, etc. The optimization of experimental parameters for carbon adsorption of organics from water is badly needed.

Both XAD resin and carbon adsorption cover a wide spectrum of organic compounds. Both are limited on the volatile end of the spectrum by the need to evaporate the eluting solvent for maximum concentration - resins are slightly better for volatile compounds because a lesser amount of a more volatile solvent is usually required than for carbon elution; e.g., chloroform in water can be measured by the resin technique, although recovery is not quantitative. At the non-volatile end of the spectrum, evidence indicates that carbon has the advantage since ethyl alcohol extracts of carbon columns which have already been extracted with chloroform contain large amounts of polar compounds, some of which may be chromatographed, especially after derivitization.

For the compounds of intermediate volatility, recovery studies under different experimental conditions using scores of the compounds found in water are needed to determine the best application of each adsorption technique. A considerable amount of this has been done for resins and such a programme is underway in the USA to compare carbon and resin as accumulator materials[14]. Preliminary results show that the resins give better recovery than carbon; carbon is an excellent adsorper but desorption is difficult. Another interesting result is that drying the sample-wet carbon before desorption may not be beneficial.

The real utility of accumulator columns lies in their ability to concentrate organics from hundreds of liters of water, either drinking water under its positive pressure or effluent or surface water pumped through the column. In the EPA's New Orleans study concentration factors of 1,000,000 to 1 were realized using activated carbon; this allowed identification of compounds present to as low as 0.1 μg/l. This great capability makes recovery studies imperative to realize the full potential of accumulator columns as a comprehensive anaytical tool

A third type of accumulator column, a polyamide resin, has been used by Dunlap[15] for extraction and concentration of polar organics from ground water. This material needs to be fully evaluated as to recoveries of compounds for which it is applicable.

Finally, preliminary experiments with tenax resin - the same accumulator material used in the purging technique (b above) - indicate the possibility of direct adsorption of highly volatile ("purgeable") organics from water passed through the column. This would eliminate the sparging step and greatly simplify recovery of highly volatiles.

e. Aqueous Concentration and other Techniques. One of the few approaches to survey analysis of non-volatile compounds, which are generally not amenable to extraction by other methods discussed here, is that advanced by Pitt and Jolley[16/17]. They use a combination of direct vacuum distillation and freeze-concentration of up to 100 liters of water to achieve a concentration factor of up to 3000. This removes all volatile compounds and leaves mostly the water soluble, polar, higher molecular weight (mostly above 200) materials for subsequent analysis by high pressure liquid chromatography (HPLC). There are problems associated with the occlusion of organics in the inorganic salts that precipitate during concentration; this tends to limit the possible degree of concentration and thus effectively limit the current technique to effluent samples. Better concentration methods need to be devised for these water soluble non-volatile organics in drinking water.

Waggott[18] at the Water Research Centre, Stevenage, England, analyzes non-volatiles in sewage effluents by HPLC. He extracts with a series of organic solvents ending with butanol to extract highly polar materials.

Reverse osmosis (RO) has been used for concentration of intermediately volatile and non-volatile organics in water[19]. There are problems with selectivity of the RO membranes and organic impurities in the membranes, and the concentration factor is usually only ten. The main advantage of RO is that organics in the sample are not likely to be decomposed or otherwise changed. This may be a good concentration technique for non-volatile organics to be subsequently analyzed by HPLC, but the concentration factor needs to be greatly increased.

2. Pre-separation (Post-concentration) Clean-up

After extraction and concentration, it is sometimes necessary to "clean-up" the extract for subsequent GC or GC-MS analysis in order to obtain reasonable peak separation for identification of organics. This is not possible for the purging and direct aqueous injection techniques, of course, and, in fact, is often unnecessary for extracts obtained by liquid extraction or from accumulator columns. Computerized GC-MS, which allows for background subtraction and specific ion monitoring for selected compounds, decreases the need for extract clean-up. In addition, it is sometimes possible to deduce the presence of, and sometimes identify, two components in one GC peak by mass spectrometry.

When clean-up is necessary, fairly well established techniques are available. These include: (a) pH adjustment during extraction to separate acids, bases and neutrals; (b) column chromatography on florisil of silica gel[20] with elution by a series of solvents of increasing polarity to separate broad classes of organics; and (c) thin layer chromatography.

Recent research has shown that activated carbon and macroreticular resin columns may be useful for chromatographic pre-separation, in addition to their standard function of extraction of organics from water[21]. Other groups are investigating the use of HPLC as a pre-separation technique for organic extracts[22]; this may be especially useful where sensitive capillary columns are to be used for final separation.

3. Separation and Detection

Survey methods must be as broad as possible to make them economically more feasible than the more traditional class analysis approach. Their power lies in the number of compounds identifiable from one sample extraction, so efficient separation and sensitive, non-selective detection are required.

Gas chromatography is a suitable separation technique for most compounds extracted by purging, liquid extraction and/or accumulator columns and for those not extractable but concentrated enough to analyze directly in the aqueous phase (see Table 1). It is necessary to chemically derivitize some compounds to make them volatile enough for GC. Separation of volatile compounds has been dramatically improved by the commercial advent of capillary columns, allowing more identifications to be made on the same extract. Although the application of capillary columns is by no means routine[23], efficient application can be made by anyone who has suitable GC instrumentation, provided he modifies the instrument appropriately (e.g. by use of the Grob injector) and pays particular attention to details. Flame detectors are still best for survey analysis by GC; the most specific detectors are usually limited to class analysis.

Liquid chromatography (LC) has a rich future since it is the logical complement of gas chromatography for non-volatile compounds that can not be readily and reliably derivitized. However, the converse of this should be emphasized; there is no logic for the use of LC for separation and detection of compounds that can be analyzed directly or after derivitization by GC. GC is an established, reliable technique, generally more efficient and sensitive than LC and GC may be interfaced with MS for spectral fingerprinting. Since LC has the highest potential for compounds that are polar, water soluble and non-volatile, a corresponding problem in its application is how to concentrate the organics in water before analysis (see 1,e, above).

The work by Pitt and Jolley[16] in identifying non-volatile compounds of biological origin in sewage effluents illustrates the potential of LC as a separation technique. Their method was an important first step in the analysis of specific non-volatile organics in water. Fifty-eight compounds were identified in primary and secondary effluents and over 100 were detected[17]. The LC detection limit was about 1-10 μg/l, depending upon the degree of concentration and the molecular structure of the compound being detected. In another phase of this work, over 60 chlorinated compounds were detected by LC (and 17 were tentatively identified) in municipal sewage after laboratory chlorination.

Fine's[24] use of a LC with a nitrosyl-specific chemiluminescense detector to separate and detect possible non-volatile nitrosamines in river and drinking water further illustrates the application of LC to problems involving compounds that are not gas chromatographable.

Waggott's HPLC method[18] (see 1,e, above) involves incremental gradient elution with a series of 12 solvents of increasing polarity, with a moving wire detector for the eluting compounds. Moving wire detectors are less selective than the more widely used and more sensitive (for compounds with appropriate absorption characteristics) UV detectors. Detectors are a problem in HPLC - there is great need for a sensitive, universal detector to parallel the performance of the flame detector in gas chromatography.

4. Identification

Since it is extremely difficult to obtain definitive data from gas chromatography alone ("there is nothing so ambiguous as a GC peak"), especially for complex environmental extracts, separation by GC must be complemented by on-the-fly mass spectrometry to give a truly comprehensive approach. Almost all survey analysis of water pollutants today depends upon gas chromatography-mass spectrometry (GC-MS) for final separation, detection and identification of specific compounds. The application of coupled GC-MS systems is now a routine reality in many government water pollution laboratories, industrial and university laboratories and even in a few municipal laboratories. Furthermore, many GC-MS systems now sold are computerized for mass spectral data accumulation and storage, with programmes available for data reduction. Extensive spectral matching files, one containing spectra of about 40,000 compounds[25], are now available in most parts of the world. Access to these files allows a person inexperienced in the interpretation of mass spectra to narrow the possible number of matching spectra for an unknown compound from many thousand to fewer than five, in most cases, if the compounds of interest is indeed in the file. Finally, mass spectral interpretative programmes are being developed to give structural clues as to the identity of compounds not in the spectral files[26].

It is obvious that although GC-MS computer systems are available, effective and even routine in many laboratories, their initial expense and maintenance costs, coupled with the requirement for highly trained personnel, places them out of reach of most laboratories concerned with water pollution analysis, for example the great majority of water work laboratories. This effectively limits the survey analytical approach to a relatively small number of laboratories. A complicating factor is that now, when it seems that regulations will require the monitoring of certain pollutants in drinking water and already public concern urges the measurement of many hazardous pollutants, confirmatory analysis by GC-MS of a certain percentage of the samples analyzed by simpler but less definitive analytical techniques will be required. This problem has been addressed by Donaldson[27], who proposed a system of central laboratories for confirmatory GC-MS analysis. He further proposes that in most cases it is not necessary for water works laboratories to do specific compound or class monitoring, since central GC-MS laboratories could, by survey analysis of samples submitted on a time-programmed basis, measure most pollutants of special interest and, as a bonus, observe many compounds that were not realized present. This may also be applicable to re-used water - the recommendations[28] for at least a 48 hour retention time prior to the distribution of treated, reclaimed water would allow for survey analysis at a central laboratory, in some cases even before the water is used. This central laboratory concept should be advanced whenever possible; it's realization would limit the number of class analysis techniques required at a local level. However, as new toxicological information is developed, other class-specific techniques would be required, since all compounds are not currently amenable to one or two broad survey-type examination (e.g. non-volatile nitrosamines).

A special problem is the identification of non-volatile compounds separated by LC. In some cases, these can be collected from the LC column, derivitized and analyzed by GC and GC-MS. This is a labourous, time consuming process and derivitization can result in compound structural changes. Research is ongoing to develop LC-MS interfaces; these should be commercially available in the next year or two, but much more development work will be required to make LC-MS as reliable and efficient as GC-MS.

5. Confirmation and Ab Initio Identification

Confirmation of suspected identities, e.g., as obtained from computerized MS data banks (see above), by matching GC retention times and mass spectral fragmentation patterns with those of standards is generally accepted as adequate. Indeed there are cases where reliance on the computer match with visual checking of the spectra is sufficient for identification. Criteria for identification should be determined and stated for each analysis. Confidence limits for accuracy of mass spectral computer matches need to be established. Nevertheless, in cases involving extremely important pollutants or legal actions, confirmation by matching spectral patterns with other instruments after low resolution mass spectrometry may be required.

Fifty percent or more of the compounds detected during many GC-MS analyses do not have corresponding standard spectra in the computerized MS data banks, or even in printed catalogues, or fail to give a definitive match. These compounds must be subjected to _ab initio_ identification techniques using advanced instrumentation.

Applicable instrumentation for the above problem areas includes chemical ionization mass spectrometry, high resolution mass spectrometry and infrared (IR) spectroscopy. The most applicable infrared technique is that of GC - Fourier transform - IRC spectroscopy[29], since the compound of interest does not have to be separated from the extract before subjection to the instrument.

6. Quantification

The total number of organic compounds identified in water will increase in proportion - perhaps almost direct proportion - to the lowering of detection levels as instrumental sensitivities are increased. The mere identification of compounds at such low levels is hardly significant in relation to health effects studies. Toxicologists are overburdened now with the mass of organic identification data available. Quantitative data is imperative.

Once a compounds is identified, the usual technique for quantification is to compare its signal area of height on the GC or LC with that of a standard run under the same conditions. This is so time consuming as to constitute perhaps half the total analysis time for a complex sample. This situation can be improved by, for example, the use of small on-line GC computers, internal standards and other methods to be discussed in Appendix 3.

C. Analysis by Chemical Class or Group

1. Chemical Class Analysis

As defined in the Introduction to this Appendix, chemical class analytical methods are those designed to "analyze for" specific members of a given chemical class of organic compounds. Such methods may be necessary to support narrow prospective epidemiological studies (e.g., analysis of all specific halogenated aliphatics in selected drinking water supplies to determine the relationship of their presence to a disease of the population), certain research investigations (e.g., the effect of activated carbon treatment on halogenated aliphatics in drinking water), or to provide adequate quality control of drinking water, especially for health-related compounds not amenable to survey analysis by GC-MS (e.g., non-volatile nitrosamines).

It should be emphasized that it is more cost-effective to include "chemical class" analyses as part of the GC-MS survey analysis, assuming that GC-MS instrumentation is available either locally or at a central laboratory within a reasonable time frame, and that the members of the chemical class of interest are amenable to GC. This is especially true considering the fact that chemical class analyses by less definitive techniques must occasionally be confirmed by GC-MS or other advanced instrumentation anyway.

The final separation and detection of members of a given chemical class usually depend upon gas chromatography or, in a few cases, liquid chromatography. Fairly expensive and complicated equipment is thus required. Such equipment should be available to and applicable by water works laboratories of most towns above 50,000 population and even some smaller towns. On the other hand, GC-MS equipment will be available only to large towns of over 500,000 population; only a few municipalities have such equipment now (probably less than 10 in the world).

The specificity of a chemical class method is usually dependent upon the extraction and/or pre-separation techniques employed, or, in a few cases, upon the specificity of the GC or LC detector. Appendix 3, Section E, lists some important chemical classes for which methods are now available, or for which new methods or improvements are expected to be needed, along with possible techniques for limiting detection to the desired class of compounds.

2. Group Analysis

"Group Analysis" is defined here as the use of a method or "test" designed to "analyze for" a group of organic compounds, usually of the same chemical family, *in toto*. Such methods are sometimes termed "surrogate" and at other times "monitoring" methods since *in situ* monitoring by necessity depends upon measurement of a total parameter. Group analysis does not involve separation of specific members of the group. The application of group methods may be the same as those described in section 1 above for chemical class methods. However, the measurement of a total group parameter instead of specific compounds within a chemical class will often not provide adequate information for pollution control and health effects studies. Only one or a few members of the group may be responsible for certain effects and the various members may come from several different sources. Also, total group measurements are generally less sensitive than chemical class analysis where sensitive GC or LC detectors are employed. On the other hand, group methods do not usually depend upon expensive or complicated instrumentation such as GC or LC, and can thus be applied by almost all municipalities. They are usually rapid and can sometimes be particularly applicable to the monitoring of water treated for direct re-use, where public pressure requires continuous surveillance.

Section E in Appendix 3 includes some of the important groups of compounds for which group methods are now available or for which new methods or improvements are needed.

D. References

1. W. L. Budde and J. W. Eichelberger, Development of Methods for Organic Analysis for Routine Application in Environmental Monitoring Laboratories, in "Identification and Analysis of Organic Pollutants in Water", L. H. Keith, Ed., Ann Arbor Science Publishers Inc. Ann Arbor, MI, 1976, Chapter 10.

2. L. E. Harris, W. L. Budde and J. W. Eichelberger, "Direct Analysis of Water Samples for Organic Pollutants with Gas Chromatography-Mass Spectrometry", Anal.Chem, 46, 1912-1917, 1974.

3. F. C. Koplfer, R. G. Melton, R. C. Lingg and W. E. Coleman, GC-MS Determination of Volatiles for the National Organics Reconnaissance Survey (NORS) of Drinking Water, in "Identification and Analysis of Organic Pollutants in Water", L. H. Keith, Ed. Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1976, Chapter 6.

4. U. S. Environmental Protection Agency, "Preliminary Assessment of Suspected Carcinogens in Drinking Water". Report to Congress, December 1975.

5. K. Grob and F. Zürcher, "Stripping of Trace Organic Substances from Water, Equipment and Procedure", J. Chromatogr., 117, 285-294, 1976.

6. E. W. Loy, Region IV, U. S. Environmental Protection A-ency, Athens, GA. Personal communication, January 1975.

7. B. C. J. Zoeteman, G. J. Piet, C. F. H. Morra and F. E. de Grunt, "Organic Micropollutants in Drinking Water Derived from Surface Water in the Netherlands". Paper from the National Institute for Water Supply, P. O. Box 150, Leidschendam, the Netherlands.

8. R. G. Webb, "Isolating Organic Water Pollutants: XAD Resins, Urethane Foams, Solvent Extraction", U. S. Environmental Protection Agency Res. Rep. No. EPA-660/4-75-003, June 1975.

9. J. E. Henderson, IV, G. R. Peyton and W. H. Glaze, A Convenient Liquid-Liquid Extraction Method for the Determination of Halomethanes in Water at the Parts-Per-Billion Level, in "Identification and Analysis of Organic Pollutants in Water", L. H. Keith, Ed. Ann Arbor Science Publishers Inc. Ann Arbor, MI., 1976, Chapter 7.

10. (a) G. J. Piet, National Institute for Water Supply, P. O. Box 150, Leidschendam, the Netherlands. Personal Communication, February 1976.

    (b) W. van de Meent, Keuringsinstituut voor Waterleidingartikelen, KIWA, N.V., Rijswijk, the Netherlands, Personal Communication, February 1976.

11. L. H. Keith, A. W. Garrison, F. R. Allen, M. H. Carter, T. L. Floyd, J. D. Pope and A. D. Thruston, Jr., Identification of Organic Compounds in Drinking Water from Thirteen U. S. Cities, in "Identification and Analysis of Organic Pollutants in Water", L. H. Keith, Ed., Ann Arbor Science Publishers Inc. Ann Arbor, MI, 1976, Chapter 22.

12. G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arguillo, R. Vick, H. J. Svec, J. S. Fritz and G. V. Calder, "Use of Macroreticular Resins in the Analysis of Water for Trace Organic Contaminants" J. Chromatogr. 99, 745-762, 1974.

13. R. G. Webb, "Isolating Organic Water Pollutants: XAD Resins, Urethane Foams, Solvent Extraction", U. S. Environmental Protection Agency Report No. EPA-660/4-75-003, June 1975.

14. P. van Rossum and R. G. Webb, "XAD Resins and Carbon for Isolation of Organic Pollutants from Water", in preparation.

15. W. J. Dunlap, D. C. Shew, M. R. Scalf, R. L. Cosby and J. M. Robertson, Isolation and Identification of Organic Contaminants in Ground Water, in "Identification and Analysis of Organic Pollutants in Water", L. H. Keith, Ed., Ann Arbor Science Publishers Inc. Ann Arbor, MI., 1976, Chapter 27.

16. S. Katz, W. W. Pitt, Jr., C. D. Scott and A. A. Rosen, "The Determination of Stable Organic Compounds in Waste Effluents at Microgram per Liter Levels by Automatic High Resolution Ion Exchange Chromatography", Water Res., 6, 1029, 1972.

17. W. W. Pitt, R. L. Jolley and S. Katz, "Automated Anaysis of Individual Refractory Organics in Polluted Water", U. S. Environmental Protection Agency Res. No. EPA 66/2-74-076, August 1974.

18. A. Waggott, Steven Laboratory, Water Research Centre, Stevenage, England, Personnal Communication, February 1976.

19. R. G. Tardiff and M. Deinzer "Toxicity of Organic Compounds in Drinking Water" 15th Water Quality Conf., Organic Matter in Water Supplies, University of Illinois, Urbana, IL, 1973.

20. (a) W. Giger, M. Reinhard, C. Schaffner and F. Zurcher, Analysis of Organic Constituents in Water by High Resolution Gas Chromatography in Combination with Specific Detection and Computer Aassisted Mass Spectrometry, in "Identification and Analysis of Organic Pollutants in Water", L. H. Keith, Ed., Ann Arbor Science Publishers Inc. Ann Arbor, MI., 1976, Chapter 26.

(b) W. van de Meent, Keuringsinstituut voor Waterleidingartikelen, KIWA, N. V., Rijswijk, the Netherlands, Personal Communication, February 1976.

21. R. G. Webbm Environmental Research Laboratory, U. S. Environmental Protection Agency, Athens, GA. Personal Communication, March 1976.

22. G. J. Piet, National Institute for Water Supply, P. O. Box 150, Leidschendam the Netherlands. Personal Communication, February 1976.

23. K. Grob and G. Grob, Class Capillary Gas Chromatography in Water Analyses: How to Initiate Use of the Method, in "Identification and Analysis of Organic Pollutants in Water", L. H. Keith, Ed., Ann Arbor Science Publishers Inc., Ann Arbor, MI., 1976, Chapter 5.

24. (a) D. H. Fine, D. P. Rounbehler, N. M. Belcher and S. S. Epstein, "N-Nitroso Compounds in the Environment", presented at the International Conference on Environmental Sensing and Assessment, Las Vegas, Nevada, September 18, 1975 and at the Fourth IARC Meeting, Tallinn, Estonia, U.S.S.R. October 16, 1975.

(b) D. H. Fine, F. Rufeh and B. Gunther, "A Group Specific Procedure for the Analysis of Both Volatile and Non-volatile N-Nitroso Compounds in Picogram Amounts", Analytical Letters, 6, 731-33, 1973.

25. S. R. Heller, J. M. McGuire and W. L. Budde, "Trace Organics by GC-MS, Environ. Sci. Technol. 9, 210 - 213, 1975.

26. F. W. McLafferty, R. Venkataraghavan, K. S. Kwok and G. Pesyna, "A Self-Training Interpretive and Retrieval System for Mass Spectra", Adv. Mass Spectrom., 6, 999, 1974.

27. W. T. Donaldson, "Alternative Methods of Identifying Organics in Water", Proceedings of the AWWA Water Quality Technology Conference, Atlanta, GA. December 8-9, 1975.

28. World Health Organization, International Reference Centre for Community Water Supply, "Health Effects Relating to Direct and Indirect Re-use of Waste Water for Human Consumption", Report of an International Working Meeting, Amsterdam, The Netherlands, January 13-16, 1975, Technical Paper No. 7, p. 50, September 1975.

29. L. V. Azarraga and A. C. McCall, "Infrared Fourier Transform Spectrometry of Gas Chromatography Effluents", U. S. Environmental Protection Agency, Res. Rep. No. EPA660/2-73-034, January 1974.

TABLE 1. APPROPRIATE METHODS FOR SURVEY ANALYSIS OF ORGANIC COMPOUNDS IN WATER

CHEMICAL CLASS Subclass	Extraction/ Concentration Techniques: Direct GC (not extracted)	Purging (P)[b]	Liquid Extraction (LE)		Accumulator Columns (AC)		Aqueous concentration (ACon)[c]		REMARKS[e]
Separation Techniques:	GC	GC	GC	LC[d]	GC	LC[d]	GC	LC[d]	
ALCOHOLS									DA good for low molecular weigth (MW) alcohols (methanol, ethanol, α-terpineol, etc.) if concentrated enough.
Aliphatic	+	+	+		+				
Aromatic	?	?	+	+	+	+			P good for alcohols of low solubility.
Terpenoid	+	+	+		+				GC-Chemical Ionization-MC (GC-CI-MS) good for identification of many alcohols.
ALDEHYDES									Same remarks apply to aldehydes as to alcohols.
Aliphatic	+	+	+		+				
Aromatic		+	+	+	+	+			
ALKANE HYDROCARBONS									P good for hydrocarbons.
Branched	+	+	+		+				GC-CI-MS is useful for identification of alkane and alkene hydrocarbons.
Cyclic	+	+	+		+				
Normal	+	+	+		+				
ALKENE HYDROCARBONS									
Regular	+	+	+		+				
Terpenoid	+	+	+	?	+				Some terpenoid hydrocarbons may be amenable to LC/UV detector analysis.
AMIDES		?							No data on P for amides.
Aliphatic	+		+		+				
Aliphatic, substituted	+		+	?	+	?			Some substituted amides may be amenable to LC/UV detector analysis.
Aromatic			+	+	+	+			

TABLE 1. APPROPRIATE METHODS FOR SURVEY ANALYSIS OF ORGANIC COMPOUNDS IN WATER

CHEMICAL CLASS Subclass	Extraction/ Concentration Techniques:	Direct GC (not extracted)	Purging (P)[b]	Liquid Extraction (LE)		Accumulator Columns (AC)		Aqueous concentration (ACon)[c]		REMARKS[e]
	Separation Techniques:	GC	GC	GC	LC[d]	GC	LC[d]	GC	LC[d]	
AMINES			?							No data on P for amines - should be good for volatiles.
Aliphatic		+		+		+				
Aliphatic, substituted		+		+	?	+	?			Some substituted aliphatic amines may be amenable to LC/UV detection.
Alkylanilines (including aniline and benzidine)		?		+	+	+	+			Aromatic amines may be amenable to DA if soluble and in high concentration.
Anilines, other substituted		?		+	+	+	+		?	Non-volatile substituted anilines may be amenable to ACon.
Naphthylamines				+	+	+	+			
Nitroanilines		?		+	+	+	+			
AMINO ACIDS						+	+	+	+	Amino acids can be derivitized for GC or LC after extraction or concentration.
BENZENOID HYDROCARBONS										Higher MW benzenoids may not be volatile enough for P.
Alkybenzenes, w/saturated substituents			+	+	+	+	+			
Alkylbenzenes, w/unsaturated substituents			+	+	+	+	+			
Biphenyls and Polyphenyls			?	+	+	+	+			
Indan and Tetralin hydrocarbons			?	+	+	+	+			
CARBOHYDRATES						+	+	+	+	Carbohydrates can be derivitized for GC or LC after extraction or concentration.
CARBOXYLIC ACIDS										GC-CI-MS may be useful for identification of carboxylic acids (after derivitization).
Aromatic (benzoic types)				+	+	+	+	+	+	Many carboxylic acids are non-volatile enough for ACon, but are not amenable to LC/UV detection and must be derivitized for GC.
Aromatic, hydroxy (hydroxy-benzoic type)				+	+	+	+	+	+	
Aliphatic, dicarboxylic				+		+		+		
Aliphatic, long-chain (from C-7)				+		+		+		
Aliphatic, hydroxy- and keto-				+		+		+		

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CHEMICAL CLASS Subclass	Extraction/ Concentration Techniques: Direct GC (not extracted)	Purging (P)[b]	Liquid Extraction (LE)		Accumulator Columns (AC)		Aqueous concentration (ACon)[c]		REMARKS[e]
Separation Techniques:	GC	GC	GC	LC[d]	GC	LC[d]	GC	LC[d]	
Aliphatic, short-chain (C-1 to C-6)	+	+	?		?				Short chain aliphatic acids may be too volatile for LE or AC.
Aliphatic, unsaturated			+		+		+		
Phenylalkanoic			+	+	+	+	+	+	
Resin			+	?	+	?	+	?	Some resin acids may be amenable to LC/UV detection.
DYES, PIGMENTS AND OPTICAL BRIGHTENERS									Some disperse dyes and brighteners may be amenable to LC or AC and GC.
Dyes and pigments			?	?	?	+	?	+	
Optical Brighteners			?	?	?	+	?	+	
ESTERS	?	?							Some esters, in addition to alkyl alkanoates, may be amenable to P or DA.
Alipates and azelates			+		+		+		
Alkyl alkanoates (incld. substituted)	+	+	+		+				High MW esters may be amenable to ACon.
Aromatic			+	+	+	+			
Fatty acid methyl esters			+		+				
Phthalates			+	+	+	+	+	+	
ETHERS AND HETEROCYCLIC OXYGEN COMPOUNDS									GC-CI-MS may be useful for identification.
Aliphatic	+	+	+		+				Some substituted ethers may be amenable to the LC/UV detector.
Aliphatic, substituted and/or unsaturated	+	+	+	?	+	?			
Aromatic	?	?	+	+	+	+			Some aromatic ethers may be amenable to P or DA.

TABLE 1. APPROPRIATE METHODS FOR SURVEY ANALYSIS OF ORGANIC COMPOUNDS IN WATER

CHEMICAL CLASS Subclass	Extraction/ Concentration Techniques:	Direct GC (not extracted)	Purging (P)[b]	Liquid Extraction (LE)		Accumulator Columns (AC)		Aqueous concentration (ACon)[c]		REMARKS[e]
	Separation Techniques:	GC	GC	GC	LC[d]	GC	LC[d]	GC	LC[d]	
HALOGENATED ALIPHATIC COMPOUNDS										P is appropriate for almost all halogenated aliphatics. LC is rarely applicable.
Aliphatic bromides and/or iodines		+	+	+		+				
Aliphatic chlorides		+	+	+		+				
Aliphatic chlorides with bromine, iodine and/or fluorine		+	+	+		+				
Aliphatic chlorides, other substituted		+	+	+	?	+	?			
Aliphatic fluorides		+	+	+		+				
Ethers, chlorinated aliphatic		+	+	+		+				
Paraffins, chlorinated ("chloroparaffins")			?	+		+				Chlorinated parrafins may be too high MW for P and too insoluble for DA.
HALOGENATED AROMATIC COMPOUNDS		?	?							Some halogenated aromatics may be solubles and concentrated enough for DA. Some are volatile enough for P.
Brominated, iodinated and/or fluorinated aromatics			+	+	+	+	+			
Chlorinated aromatic amines				+	+	+	+	+	+	Polar members may be amenable to ACon, but may need derivitization for GC.
Chlorinated benzenes and alkylbenzenes			+	+	+	+	+			
Chlorinated benzoic acids				+	+	+	+	+	+	
Chlorinated nitro-aromatics				+	+	+	+			
Chlorinated phenols and naphthols		+		+	+	+	+	+	+	
Chlorinated heterocyclic aromatics				+	+	+	+	+	+	
Polychlorinated biphenyls (PCB's) (e.g. Arochlors)				+	+	+	+			
KETONES										
Aliphatic		+	+	+		+				
Aliphatic, substituted		+	+	+	?	+	?			
Quinones		?		?	+	?	+	?	?	Some anthraquinones and quinones may not be stable enough for GC and may be too volatile for ACon.

TABLE 1. APPROPRIATE METHODS FOR SURVEY ANALYSIS OF ORGANIC COMPOUNDS IN WATER

CHEMICAL CLASS Subclass Extraction/ Concentration Techniques:	Direct GC (not extracted)	Purging (P)[b]	Liquid Extraction (LE)		Accumulator Columns (AC)		Aqueous concentration (ACon)[c]		REMARKS[e]
Separation Techniques:	GC	GC	GC	LC[d]	GC	LC[d]	GC	LC[d]	
Aromatic	+	?	+	+	+	+			Amenability of aromatic ketones to P depends upon volatility.
NITRO-COMPOUNDS									Amenability to P depends upon volatility
Aliphatic	+	+	+	?	+	?			Some aliphatic nitro compounds may be detected by LC/UV.
Aromatic	?	?	+	+	+	+			
NITROGEN COMPOUNDS, MISCELLANEOUS									Some cyanides and nitrosamines are volatile enough for P.
Azo Compounds			+	+	+	+	+	+	
Carbamates			+	+	+	+			
Cyanides (Nitriles)	+	+	+	+	+	+			Some cyanides are soluble enough for DA.
Heterocyclic			+	+	+	+	+	+	
Indoles and Carbazoles			+	+	+	+	+	+	Most of these materials are amenable to LC/UV detection.
Nitrosamines		+	+	+	+	+		+	
Pyridines			+	+	+	+	?	?	Many of these are non-volatile enough for ACon, but some of these may be derivitized for GC.
Quinolines			+	+	+	+		+	
Xanthines and Uric Acids						+		+	
NON-VOLATILE COMPOUNDS, MISCELLANEOUS						+		+	ACon is most appropriate and LC/UV is probably and adequate detector for most. Some may be concentrated by AC.
ORGANOMETALLIC COMPOUNDS						+		+	Same remarks as for non-volatiles above.

TABLE 1. APPROPRIATE METHODS FOR SURVEY ANALYSIS OF ORGANIC COMPOUNDS IN WATER

CHEMICAL CLASS Subclass	Extraction/ Concentration Techniques:	Direct GC (not extracted)	Purging (P)^b	Liquid Extraction (LE)		Accumulator Columns (AC)		Aqueous concentration (ACon)^c		REMARKS^e
	Separation Techniques:	GC	GC	GC	LC^d	GC	LC^d	GC	LC^d	
PESTICIDES AND HERBICIDES										Pesticides and herbicides are generally too insoluble for DA and not volatile enough for P.
Aromatic halogenated pesticides, miscellaneous			?	+	+	+	+			Some members are probably amenable to ACon.
Atrazine derivatives				+	+	+	+	+	+	Many are detectable by LC/UV.
"Benzenehexachloride" (BHC) isomers				+		+				
Carbamates				+	+	+	+			
Chlorinated phenoxy acids				+	+	+	+	+	+	
DDT derivatives				+	+	+	+	?	?	
Organophosphorus pesticides				+	+	+	+	+	+	Organophosphorus pesticide degradation products may be non-volatile enough for ACon.
Polycyclic halogenated pesticides				+		+				
PHENOLS AND NAPHTHOLS		?	?							Some phenols may be soluble enough for DA.
Alkylphenols (incld. phenol)		+		+	+	+	+	+	+	Some low MW phenols are probably volatile enough for P.
Alkoxyphenols				+	+	+	+	+	+	
Aminophenols				+	+	+	+	+	+	Most phenols are amenable to LC/UV detection.
Hydroxyphenols				+	+	+	+	+	+	Some phenols are non-volatile enough for ACon.
Naphthols				+	+	+	+	+	+	
Nitrophenols				+	+	+	+	+	+	Some may need to be derivitized for GC.
PHOSPHOROUS COMPOUNDS										Some phosphorous compounds may be soluble enough for DA or volatile enough for P.
Phospates		?	?	+		+				Most phosphates are not amenable to LC/UV detection, except those with aromatic groups.
Others				+		+		+	+	Polar organophosphorous compounds may be amenable to ACon.

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CHEMICAL CLASS Subclass Extraction/ Concentration Techniques:	Direct GC (not extracted)	Purging (P)[b]	Liquid Extraction (LE)		Accumulator Columns (AC)		Aqueous concentration (ACon)[c]		REMARKS[e]
Separation Techniques:	GC	GC	GC	LC[d]	GC	LC[d]	GC	LC[d]	
POLYNUCLEAR AROMATIC HYDROCARBONS		?							PAH's are too insoluble for DA.
Alkylnaphthalenes (and naphthalene)			+	+	+	+			Some PAH's may be volatile enough for P.
Indenes			+	+	+	+			PAH's are amenable to LC/UV detection.
Polynuclear aromatic hydrocarbons, other			+	+	+	+			
STERIODS			+	+	+	+	+	+	Steriods may be derivitized for GC.
SULFUR COMPOUNDS									Little is known about recovery of sulfur compounds.
Aromatic	?	?	+	+	+	+	?	?	
Compounds w/S-O bonds			+	+	+	+	+	+	Those with S-O and S-N bonds are probably best analysized by ACon followed by LC, but may be derivitizable for GC.
Compounds w/S-N bonds			+	+	+	+	+	+	
Heterocyclic	?		+	+	+	+	+	+	
Mercaptans (aliphatic)	+	+	+		+				Most mercaptans, sulfides and disulfides are volatile enough for P and some may be soluble enough for DA.
Sulfides and Disulfides (aliphatic)	+	+	+		+				
SURFACTANTS									Most surfactants are ionic and best analyzed by ACon followed by LC/UV. Some are non-ionic and may be amenable to extraction and GC.
Surfactants			+	+	+	+		+	
Surfactants degredation products				+		+		+	

Footnotes

[a] DA method is severly limited by concentration; between 1 and 50 mg/l is required, therefore compounds must be soluble to this extend. They much also be volatile and gas cormatographable.

[b] Purging is limited to organics with medium to low polarity, molecular weight below about 250 and low water solubility.

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	Separation Techniques:	GC	GC	GC	LC[d]	GC	LC[d]	GC	LC[d]	

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[c] "ACon" refers to direct aqueous concentration of the non-volatiles in water by removal of most of the water and the volatile organics.

[d] LC is considered viable here only for classes of compounds with suitable ultraviolet absorption characteristics that make them amenable to the common LC/UV detector.

[e] GC-MS is assumed to be the most standard identification technique for all gas chromatographable compounds.

APPENDIX 3

IMPROVEMENT NEEDED IN ANALYTICAL METHODOLOGY

A. Introduction

The needed improvements discussed in this Appendix are prefaced by Appendix 2, a state-of-the-art description of current analytical methodology for organics in water. There is some overlap; an examination of the current status naturally points up areas where improvements are needed. The two Appendices are organized differently, however; Appendix 2 is organized first according to logical steps in an analytical sequence, while this Appendix is primarily organized into sections dealing with volatile and non-volatile organics so as to emphasize the great need in the area of non-volatiles.

B. Survey Analysis for Volatile Organics

1. Extraction, Concentration and Separation Techniques

Analytical techniques are available to survey for almost all volatile organic compounds expected to be found in water, as indicated in Table 1, Appendix 2. Considerable work is still in order before carbon adsorption can be used routinely (see Appendix 2, Section B, 1, d) and a comparison of XAD resin versus carbon as an organic accumulator needs to be made to determine the best applications of each technique. The U. S. EPA is beginning such a study, as mentioned in Appendix 2, but this study is not expected to provide all the needed information about carbon adsorption.

Refinement of all techniques in Appendix 2 is still important and many laboratories are involved in modifying the various extraction, concentration and separation techniques to achieve optimum conditions for specific applications - most of these modifications and improvements are discussed in Appendix 2. In particular, more research is needed to optimize the VOA technique. Grob's variation of purging needs to be more widely applied and the required equipment needs to be made commercially available. Accumulator columns for polar compounds and for highly volatile compounds should be investigated more thoroughly. There will be a continual requirement for recovery studies as new organic pollutants are found.

Finally, there is a great need for commercially available high quality, durable, glass capillary columns at a lower cost. The greatly improved separation afforded by these columns will justify the research necessary to make their application routine.

2. Qualitative Analysis (Identification)

Most survey analyses depend upon final identification by GC-MS-computer, as discussed in Appendix 2, Section B, 4. Although this technique is routine in many laboratories, the fact that it is actually cost-effective for any laboratory doing more than occasional survey analysis has not been generally understood. Now that this is being realized there is an increasing need for cheaper spectral matching files at central locations accessible via remote terminals. The Cyphernetics system[1], containing 40,000 mass spectra and capable of being searched by several programme modes, is currently the most complete, but use-cost needs to be reduced to make it suitable for routine access. Measures are underway to do this. There is a continual need to update these spectral files and a system should be developed whereby the spectra of newly identified compounds are automatically submitted to the data bank. There is also a need for subsets of mass spectra of the compounds found most frequently in water (perhaps any found more than twice); this would reduce search time and cost and such subsets could probably be made available to individual laboratories with appropriate computer capabilities.

The Cyphernetics system includes an EPA developed sub-routine whereby a person inexperienced in the interpretation of mass spectra can obtain a similarity index (SI), which is an expression of the goodness-of-fit of the unknown spectrum with that in the data bank. This SI becomes more realiable as more mass spectra of higher quality are included in the data bank. However, there needs to be a statistical study of the reliance that one can put on the SI; perhaps in terms of a confidence level. For certain survey applications and in some cases where other qualitative data are available, a 90% confidence level for the spectral match may be adequate. This could lead ultimately to a GC-MS-computer system with a programme to print the most likely compound name on the computer-reconstructed gas chromatogram, with an estimated probability of error (e.g. 90% confidence level).

The various computerized spectral interpretative techniques now being developed will be useful in identifying the many compounds now occuring in organic extracts that can not be identified by spectral matching, computerized or manual. As many as 50% of the peaks in some chromatograms remain unidentified after exhaustion of current mass spectral interpretative approaches.

3. Quantitative Analysis and Quality Control

Appendix 2, Section B, 6 discusses the importance of quantitative analysis of organics in water. Quantitative analytical techniques are available now, but these are so time consuming as to constitute perhaps half of the total analysis time for a complex sample. This situation must be improved. Small dedicated on-line computers are available for efficient collection of raw data and calculation of concentrations for GC runs of complex extracts. Standards are necessary, of course, but guidelines need to be established as to their optimum application. For example, in more cases sufficient quantitative accuracy can be achieved by use of only one standard for each narrow class of chemical compound (such as the sub-classes of Table 1, Appendix 2).

Computer programmes are now available for semiquantitative analysis by comparison of mass spectrometric ion current (GC-MS) with standards. There are certain inherent problems that limit the accuracy of thic technique, but improvements can be made. Guidelines should be established to determine the degree of accuracy required. Reliance on the MS data for quantification of organic compounds could result in 25% time savings on total analysis of complex samples.

Very recently work has been carried out to automate gas chromatographic procedures aimed at analysing the volatile organics in water. This technique involves a direct coupling of an accumulator column with the gas liquid chromatograph so that the concentration, extraction and separation stages are within the scope of one experimental apparatus. The technique would enhance reproducibility, eliminates the inconvenience and loss of time due to the manipulation and breakage of injection port liners and improves chromatographic resolution as a result of expanded temperature programming capabilities. It is standardized to such a degree, that it can be performed routinely in any laboratory. The development of commercially available instrumentation would classify as an important improvement needed in analytical methodology.

As these techniques become more routinely used, there will be greater need for standard reference materials (SRM's), both individual pure compounds and standard mixtures in typical aqueous environmental matrices. The National Bureau of Standards in the U. S. A. has within the last year initiated a comprehensive programme to determine the needs for such SRM's and to make them available. They could, of course, be valuable for qualitative as well as quantitative analysis.

Quality control is necessary for both qualitative and quantitative analyses, but in different forms. For qualitative analysis, one must be assured that operation of gas chromatographs, mass spectrometers, computers, spectral matching systems, etc., are in accordance with predetermined operating standards. Quantitative ayalysis, however, requires a system of quality control to be applied to the entire analytical protocol, including compound identification. The applicability of quality control will vary with routineness of the analysis. For survey analyses involving a changing variety of standards and calibration of instrumentation may be appropriate. On the other hand, for routine runs of similar samples, statistical quality control of precision and accuracy is appropriate - this is certainly the case with routine chemical class or specific compound analysis. Finally, control or blank samples are an inherent part of any good analytical scheme; results are incomplete without analysis of corresponding controls.

C. Survey Analysis for Non-volatile Organics

The biggest gap in knowledge about organic compounds in water is in the area of non-volatile compounds, which constitutes at least 50% and in most cases 75% to 95% of the total organic material.

These non-volatiles are water soluable, polar and of relatively high molecular weight. Most of them have been assumed to be humic or fulvic acids of natural origin. They actually consist of at least three groups; (1) highly polar compounds of intermediate molecular weigth (200 - 700) that are separable into specific compounds; (2) higher molecular weight materials (700 - several thousand) that are probably not separable into specific compounds, but are mostly not polymers (but possible oligomers);and (3) higher molecular weight materials (over several thousand) that are mostly polymers.

Group 1 overlaps in a few cases with extractable materials, e.g. phenols and carboxylic acids, which are polar enough to remain in the water during concentration by vacuum distillation. Much of group 1, however, consists of carbohydrates, xanthines and other nitrogen bases,and amino acids. These are amenable to separation by liquid chromatograph (LC), especially the ion exchange LC used by Pitt and Jolley[2]. As described in Appendix 2, Section B, 1, e and

B, 3 there are two important problems associated with LC analysis of these materials: (a) Vacuum distillation and freeze-concentration are not adequate concentration techniques, especially for drinking water samples. Recently techniques involving accumulator columns to concentrate the organics directly from the water sample, followed by interfacing the accumulator column directly with the LC analytical column for elution and separation, have been proposed. This approach holds considerable promise. (b) LC detectors are not adequately sensitive, nor universal enough. Fair sensitivity (1 μg/l in the original water sample) can be achieved for compounds that have a high absorbtivity for UV light, such as those with aromatic rings, by use of commonly available UV detector and even higher sensitivity can be achieved for compounds that fluoresce, using a fluorescence detector. There is some work being done on more general detectors; e.g. Pitt and Jolley experimented with a cerate oxidative detector[3], good for detection of moderately oxidizable compounds down to 0.1 μg/l based on the original water sample, assuming a 1000-fold concentration. Moving wire/flame ionization, electrolylic and other general detectors are evolving, but few of them are commercially available. There is a definite need for an inexpensive LC system with a sensitive (at least 100 μg/l detection level for organics in the LC column effluent), universal organic detector; this instrument would be the counterpart of flame ionization GC for non-volatile organics.

On-the-fly spectral fingerprinting detectors are also needed for liquid chromatographs, although this involves another magnitude of expense. Even if LC equipment with sensitive, universal detectors were available, the only qualitative information obtainable would be the retention time. Therefore, for confirmation and ultimately for survey analysis analogous to the current application of GC-MS developments of LC-advanced instrumental interfaced systems have begun. Several groups (McLafferty at Cornell University, Horning at Baylor University, McFadden with the Finnigan Corp. and Futrell at the University of Utah) are experimenting with LC-MS interfaces. Other groups are just beginning investigations of LC-Infrared and LC-Raman spectroscopy combinations. LC-MS shows the most promise because of the potential overlaps with extensive knowledge about GC-MS. The U. S. EPA has begun contract support of work in all three of these areas.

Much less work has been done on the other two groups of non-volatile organics in water (groups 2 and 3). These compounds are not amenable to complete separation and identification; they are non-specific high molecular weight materials subject only to characterization. Some characterization, mostly according to physical properties, has been accomplished for these materials in domestic waste waters[4] and in natural waters[5]. Such characterization needs to be more detailed and applied to drinking water. Such a programme has been planned by the EPA; this will involve liquid chromatography of concentrated drinking water into as narrow fractions as possible. The separable individual compounds (group 1, above) would be separated for subsequent identification; the other materials would be separated into molecular weight fractions by gel permeation and other types of LC, with subsequent characterizations of each fraction by physical properties (solubilities, molecular weight range, etc.) and chemical properties (functional groups, chemical reactivities, spectral properties, etc). A material balance by TOC measurement would allow determination of the percentage of each fraction present in typical drinking water.

Although most of the toxic, taste and odour causing and other hazardous organics have generally been assumed to be contained with the 5 to 25% of volatile organics in water, the non-volatiles can no longer be neglected. Evidence already indicates that the chlorination of humic materials is responsible for the formation of haloforms during drinking water treatment and that non-volatile nitrosamines may be present in drinking water. Furthermore, since non-volatiles are likely to be more concentrated in directly re-used water, the development of methods of analysis for non-volatile organics in these water is of particular concern.

D. Miscellaneous Needs

1. Automatic Sampling

Sampling must be carefully controlled and the samples' integrity must be maintained. Considering expected governmental requirements for the monitoring of organics in drinking water and the continuing need for monitoring waste water effluents and surface water, the number of sampling operations will be increasing greatly in the near future. The time is therefore appropriate for development of a new type of automatic sampler, especially designed to collect samples for subsequent organics analysis. Such a sampler would be a necessary part of the central laboratory concept envisioned by Donaldson[6] (see Appendix 2, Section B, 4).

The simplest automatic sampler would fortuitously be based on solid accumulator columns, which are the most comprehensive extraction/concentration media now available. The sampler would contain a series of interchangable XAD resin and/or activated carbon modular columns that would be removed and shipped to the central analytical laboratory, after sample collection, by the water treatment plant operator, or analyzed at the local laboratory of a large water works. These columns could be automatically sealed for sample integrity. Sampling would be time-proportional and several columns in a predetermined sequence would be used to obtain representative samples corresponding to, for example, each day of the week or each week of a month. The sample could be metered from a pressurized system, such as a drinking water distribution line, or pumped from an effluent or surface water by a built-in pump. For full flexibility, the system would need to be capable of line current and battery operation. It would be refrigerated for preservation of collected organics. Finally, the sampler could be designed to automatically collect and seal vials of water for laboratory analysis of very-volatile compounds by a purging method. A prototype of such an automatic sampler will be designed under a U. S. EPA contract.

2. Analysis of Organics Adsorbed on Suspended Solids

Many types of organic compounds are adsorbed on particulate, suspended or collodial matter in water and much of this matter is itself organic. One is always faced with the question of whether to filter the sample before extraction and, if so, whether to attempt to analyze the separated solids for organics. This may be a rare problem in finished drinking water, where suspended solids are reduced to a very low level, but it is a serious question in the analysis of source water, effluents and surface water. Guidelines and procedures need to be established for separation and analysis of such solid materials for adsorbed organics.

E. Improvements Needed in Chemical Class and Group Analyses

1. Chemical Class Analysis

Following is a list of some important chemical classes for which methods of class analysis are now available, or for which new methods or improvements may be needed. (The background discussion of this tabulation is given in Appendix 2, Section C, 1.) Included are brief comments on the method of the need, with suggestions as to new or improved techniques. The classification system is mostly the same as that used in the Table in Appendices 1 and 2, but only the classes and sub-classes of known or expected importance are considered. This is not meant to be a literature survey, so that class listings and comments on methodology are not complete. Other methods could be suggested, or may even be under development. The listing is not prioritized as to need; this would be best done by a toxicologist with extensive knowledge of health effects of organics and data as to their distribution and abundance in water (see Appendix 1).

ANALYSIS OF ORGANIC COMPOUNDS IN WATER BY CHEMICAL CLASS

ALCOHOLS - Terpenoid and other alcohols can cause taste and odour problems. Separation from other classes of compounds is difficult. Ultimate detection is best by GC/FID.

ALDEHYDES - Same analytical problems as with alcohols. May be detected by disappearance upon mild oxidation.

ALKANE HYDROCARBONS - Fractionate into neutral fraction by pH adjustment of sample, separate from polar hydrocarbons by silica gel or florisil column chromatography. Separate and detect by GC/FID.

ALKENE HYDROCARBONS - Same as for alkanes, except may be further separated on a silver nitrate impregnated column.

AMINES - All amines can be extracted and pre-separated by pH adjustment of sample before extraction, but recoveries have not been determined and separation from other classes of basic organic compounds is difficult. Separation of compounds may be by GC, but column conditions are critical. Detection is by GC/FID or nitrogen specific GC detector. Aromatic amines can be detected by LC/UV. Both the KIWA laboratory in the Netherlands[7] and the Netherlands National Institute for Public Health[8] are working on methods specific for aromatic amines, the former by pH adjustment/extraction/GC-MS and the latter involving bromination of the amines followed by electron capture GC.

AMINO ACIDS - Concentrate by direct evaporation or on accumulator columns. Separate by ion exchange LC with colorimetric detection, or freeze dry and derivitize with chemical reagents for GC/FID detection. Aromatic amino acids may be detected by LC/UV without derivitization. Chlorinated amino acids may be produced during chlorination treatment and may be toxic.

BENZENOID HYDROCARBONS - Fractionate into neutral fraction, pre-separate by silica gel or florisil column chromatography, separate and detect by GC/FID. More specificity is needed to analyze for this important class of compounds, which includes benzene and other toxic compounds.

CARBOXYLIC ACIDS - Most acids may be concentrated by direct evaporation, or can be extracted and pre-separated from basic and neutral compounds by pH adjustment of sample before extraction. Final separation and detection is by GC/FID of chemical derivatives. Aromatic (benzoic acid type) and phenylalkanoic acids can be separated and detected by LC/UV. Resin acids may be amenable to LC/UV class analysis. Short chain aliphatic acids can be detected separately from other acids by direct aqueous GC. Unsaturated aliphatic acids can be détected by disappearance upon oxonolysis[9].

DYES, PIGMENTS and OPTICAL BRIGHTENERS - Most are separated as non-volatile compounds and detected by LC/UV, LC/colorimetric or spectrofluorometric methods. TLC is also a separation and detection technique for these coloured compounds. Better methods are needed for separation and detection of dyes.

ESTERS - A method for separation and detection of phthalates is desirable. They can be partially separated now by column chromatography.

ETHERS and HETEROCYCLIC OXYGEN COMPOUNDS - Ozonides and peroxides may be formed during ozonation treatment of water - class analysis methods may be useful for these compounds.

HALOGENATED ALIPHATIC COMPOUNDS - Most of these compounds can be separated from water and many organics by purging techniques; interferences can be further reduced by using a halogen-specific electrolytic conductivity detector on the GC used for final separation. Some higher NW chlorinated paraffins and water soluble polar halogenated aliphatics may be missed. Some purging techniques need to be standardized for this compounds and recovery studies need to be made for a wide variety of sub-classes.

HALOGENATED AROMATIC COMPOUNDS - This class has too wide a polarity range and molecular weight range for purging to be a method common to all members. A common method for the neutral compounds might be based on extraction by solvent or accumulator columns, followed by separation/detection by GC with a halogen specific detector. Chlorinated benzoic acids and chlorinated phenols and naphthols, can be separated from neutrals by pH adjustment during solvent extraction; chlorinated aromatic amines and can also be separated from other sub-classes. Poly-chlorinated biphenyls and the commerical Arachlors can conveniently be extracted by passing the water sample through polyurethane foam plugs in a glass column, after which the plugs are solvent extracted[10]. The Netherlands National Institute of Public Health is developing a method for chlorophenols in water based on acetylation followed by GC/electron capture detection[8].

BROMINATED and FLUORINATED COMPOUNDS - Brominated organics are replacing chlorinated organics for many commerical applications; class analysis methods are needed for these in water. The Netherlands National Institute for Public Health is experimenting with such a method[8]. There may also be a need for a class analysis method for fluorinated organics, since these are now being found in water.

KETONES - Anthraquinones and quinones are possible important classes of organics which require special analytical methods for extraction and separation.

NITRO COMPOUNDS - Some of these compounds may be toxic; no special methods of class analysis are available, although a nitrogen specific GC detector would allow some specificity.

NITROGEN COMPOUNDS, MISCELLANEOUS - Compounds of this major class that are volatile can be separated and detected by GC with nitrogen specific detection. Separation of one subclass from another would be difficult. Some heterocylclics, the xanthines and uric acid derivatives are non-volatile and can be separated from other nitrogen compounds by distillation. Some of the subclasses would be detected by LC/UV, some would not. Special methods are available for carbamates (as for carbamate pesticides). Some of the subclasses are basic and can be separated from others by extraction with aqueous acid. Nitrosamines are the most important subclass of nitrogen compounds due to their carcinogenicity. The Thermal Energy Analyser (TEA) is reported to be a specific detector for nitrosamines in environmental matrices[11]; volatile nitrosamines are first separated by GC while their non-volatile or heat labile counterparts are separated by LC. This TEA detector needs to be evaluated for specificity.

NON-VOLATILE COMPOUNDS, MISCELLANEOUS - This major group includes a wide variety of subclasses, with the only common characteristics being that of non-volatility. They must be separated by LC; some can then be detected by UV, but with little specificity. Methods specific for halogenated non-volatiles are needed since these compounds may be produced during chlorination of water.

ORGANOMETALLIC COMPOUNDS - These are mostly non-volatile and usually detected by spectrophotometry. There are some methods now for separation by GC. The complexed metal ions may be detected by plasma emission spectroscopy after separation, allowing detection of the total compound.

PESTICIDES and HEBRICIDES - There are class analysis methods for every chemical class of pesticide or herbicide, though some need increased specificity and other improvements.

PHENOLS and NAPHTHOLS - These acidic compounds are usually separable from neutral and basic compounds by pH adjustment of the samples before extraction but recoveries are usually low. Separation is by GC with FID detection, although derivitization may be necessary for efficient GC. Separation by LC with UV detection is also feasible. Derivitization with appropriate agents could give added specificity to LC/UV. More work is needed to improve recoveries by phenols and naphthols by liquid extraction and by use of accumulator columns. These compounds are important because of their taste and odour causing potential and their ease of chlorination.

PHOSPHORUS COMPOUNDS - Organophosphorus compounds may be volatile or non-volatile, aliphatic or aromatic and so may be detected with a certain degree of specificity depending upon extraction technique used and amenability to UV detection. Compounds separable by GC may be specifically detected using phosphorus-sensitive flamephotometric detectors. Of course, the importance of organophosphorus compounds lies in their ability to inhibit cholinesterase.

POLYNUCLEAR AROMATIC HYDROCARBONS - Most PAH's are fairly volatile and can be extracted by conventional techniques, separated by GC,and detected by FID. Alternatively, they can be separated by TLC or LC and detected by UV or fluorescense spectrophotometry[12]. Some degree of specificity is attained by column chromatographic pre-separation. More specific extraction, separation and detection techniques are needed for this very important class of environmental pollutants, some members of which are carcinogenic.

STEROIDS - Steroids can be partially separated from other materials by column chromatography, then separated and detected by LC/UV, or then chemically derivitized, separated and detected by GC/FID. Some degree of specificity is attained, but more is desirable. The Water Research Centre laboratory in Medmenham, England has developed LC methods specific for steroids[13].

SULFUR COMPOUNDS - These compounds include several subclasses of varying volatilities and structures. Most mercaptans, sulfides and disulfides can be partially separated from other materials by purging from the sample; GC with a sulfur-specific flame photometric detector then allows considerable specificity. More interferences would be expected for aromatic and other sulfur compounds extracted by solvent or accumulator columns, even when using the sulfur detector. Some heterocyclic sulfur compounds and those with S-O and S-N bonds are non-volatile and would require separation by LC. Use of a microcoulometric detector with the LC would allow a considerable degree of specificity for these compounds.

2. Group Analyses

Following is a list of some groups of compounds, grouped either by chemical class, element, or function, for which group or "surrogate" methods would be valuable. A brief discussion is given of available methodology and improvements needed.

The background discussion is given in Appendix 2, Section C,2.

ANALYSIS OF GROUPS OR ORGANIC COMPOUNDS IN WATER IN TOTO

TOTAL EXTRACTABLE ORGANIC HALOGENS - A method based on liquid extraction, pyrolysis and measurement of evolved hydrogen halides by microcoulometric titration is in use in Europe[14]. This is limited to extractable organic halogens and the highly volatile (purgeable) halogens are not included. Glaze at North Texas State University, Denton, Texas, is developing a similar method that uses esin accumulators in such a way as to include the volatile halogens[15]. This group method should be useful in following the production of halogenated compounds during chlorination and monitoring them in surface water and effluents. E(xtractable) O(rganic) Cl(chlorine).

VOLATILE ORGANIC HALOGENS - This is a modification of the total method (above) in which measurements are made before and after purging of the sample to remove the highly volatile halogenated organics. A knowledge of the concentration of these volatiles is useful in light of their possible carcinogenicity and high concentrations in drinking water relative to the compounds of intermediate volatility.

TOTAL ORGANIC SULFUR - A method based on extraction/pyrolysis/microcoulometry is being developed by the National Institute for Public Health in the

Netherlands[16]. One application would be to quickly survey samples to determine those with high sulfur levels which might need class analysis to determine specific sulfur compounds responsible for taste and odour or toxicity. This method would be more useful if it included highly volatile compounds.

VOLATILE ORGANIC SULFUR - An adaptation of the above total method to measure total sulfur before and after purging of the highly volatiles would be useful to indicate the presence of highly volatile taste and odour causing sulfur compounds.

VOLATILE ORGANIC CARBON - A simple method to measure the total highly volatile (purgeable) organic compounds in water would be a useful complement to the total organic carbon (TOC) methods now widely used. Current TOC methods do not accurately measure highly volatile organics below several parts per million.

TASTE AND ODOUR COMPOUNDS - The only group test for taste and odour causing compounds is the human nose. Methods have been developed for the establishment and use of panels to determine taste and odour thresholds of selected compounds in water and to determine odour numbers as a water quality parameter. The only chemical methods are those that measure the individual compounds causing the taste and odour by conventional analytical methodology. It may be useful to develop groups tests for in toto measurement of certain classes of compounds, such as sulfides, known to cause taste and odour in water.

ORGANOCHLORINE PESTICIDES - No group method is available for total organochlorine pesticides. It is conceivable that such a method could be developed for the members of this group that show a common effect on biota or enzymes, analogous to the cholinesterase inhibition methodfor organophosphorus pesticides. A group test for polycyclic halogenated pesticides such as dieldrin, endrin, kepone, etc., would be very useful for monitoring.

POLYCHLORINATED BIPHENYLS - PCB's can be perchlorinated to a common molecule, decachlorobiphenyl[17]. A simple method for this conversion, plus detection of the product, would be useful for monitoring. A similar method for polybrominated biphenyls might be desirable.

SURFACTANTS - The widely used methylene blue test for surfactants is simple but only good for anionic members. A simple test for total surfactants would be useful.

TOTAL METHODS FOR SELECTED CLASSES OF COMPOUNDS - The following classes of compounds have been shown to be environmentally significant because of either toxic effects, expected toxic effects or wide distribution. Surrogate methods for each class would have some utility. See Section E, 1 for further rationale and methodology.

Aromatic amines (including benzidine)
Aromatic nitro compounds
Atrazine derivitives (mostly herbicides, several of which have been found in drinking water)
Benzenoid hydrocarbons (including benzene)
Carbamates (mostly pesticides)
Chlorinated phenoxy acids (most herbicides)
Chlorinated aromatics (includes many subclasses)
Chlorophenols (taste and odour causing and toxic)
Epoxides (if shown to be formed during ozonation or chlorination)
Heterocyclic nitrogen compounds
Nitrosamines
Organobromine compounds
Organofluorine compounds
Peroxides (if formed during ozonation)
Phthalates
Polychlorinated biphenyls (see discussion above)
Polynuclear aromatic hydrocarbons

F. References

1. S. R. Heller, J. M. McGuire and W. L. Budde, "Trace Organics by GC-MS", Environ. Sci. Technol. 9, 210-213, 1975.

2. S. Katz, W. W. Pitt, Jr., C. D. Scott and A. A. Rosen, "The Determination of Stable Organic Compounds in Waste Effluents at Microgram per Liter Levels by Automatic High Resolution Ion Exchange Chromatography", Water Res., 6, 1029, 1972.

3. W. W. Pitt, R. L. Jolley and S. Katz, "Automated Analysis of Individual Refractory Organics in Polluted Water", U. S. Environmental Protection Agency Res. No. EPA 660/2-74-076, August 1974.

4. J. Manka, M. Rebhun, A. Mandelbaum and A. Bortinger, "Characterization of Organics in Secondary Effluents", Environ. Sci. Technol. 8, 1017-1020, 1974.

5. J. H. Weber and S. A. Wilson, "The Isolation and Characterization of Fulvic Acid and Humic Acid from River Water", Water Research, 9, 1079-1084, 1975.

6. W. T. Donaldson, "Alternative Methods of Identifying Organics in Water", Proceedings of the AWWA Water Quality Technology Conference, Atlanta, Georgia, December 8-9, 1975.

7. W. van de Meent, Keuringsinstituut voor Waterleidingsartikelen KIWA, N.V. Rijswijk, the Netherlands, Personal Communication, February 1976.

8. P. A. Greve, National Institute of Public Health, Utrecht, the Netherlands. Personal Communication, February 1976.

9. A. W. Garrison, J. D. Pope and F. R. Allen, GC-MS Analysis of Organic Compounds in Domestic Wastewater, in "Identification and Analysis of Organic Pollutants in Water", L. H. Keith, Ed. Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1976, Chapter 30.

10. H. D. Gesser, A. Chow, F. C. Davis, J. F. Uthe and J. Reinke, "The Extraction and Recovery of Polychlorinated Biphenyls (PCB) Using Porous Polyurethane Foam", Anal. Lett., 4, 883-886, 1971.

11. D. H. Fine, D. P. Rounbehler, N. M. Belcher and S. S. Epstein, "N-Nitroso Compounds in the Environment", presented at the International Conference on Environmental Sensing and Assessment Las Vegas, Nevada, September 18, 1975 and at the Fourth IARC Meeting, Tallinn, Estonia, U.S.S.R., October 16, 1975.

12. J. Borneff and H. Kunte, "Carcinogenic Substances in Water and Soil, Part XXVI:Routine Method for the Determination of Polycyclic Aromatics in Water", Arch. Hyg., 153, 220-229, 1969.

13. M. Fielding, Medmenham Laboratory, Water Research Centre, Medmenham, England, Personal Communication, February 1976.

14. P.A. Greve and B. J. A. Haring, "Die Mikrocoulometrische Bestimmung von Organisch Gebundenem Halogen in Oberflächen und anderen Gewässern" Schriftenreihe des Vereins für Wasser- Boden- under Lufthygiene, Berlin - Dahlem, 37, 59-64, 1972.

15. W. H. Glaze, J. E. Henderson, IV and G. Smith, Analysis of New Chlorinated Organic Compounds in Municipal Wastewaters after Terminal Chlorination, in "Identification and Analysis of Organic Pollutants in Water", L. H. Keith, Ed. Ann Arbor Science Publishers Inc., Ann Arbor MI, 1976, Chapter 16.

16. G. de Groot and P. A. Greve, "A Microcoulometric Method for the Determination of Nanogram Amounts of Sulphur in Organic Compounds", *Anal. Chim, Acta, 79*, 279-284, 1975.

17. D. T. Williams and B. J. Blanchfield, JAOAC, 55, 93-5, 1972.

APPENDIX 4

CONSIDERATION FOR PROTOCOLS FOR CHEMICAL ANALYSIS TO SUPPORT EPIDEMIOLOGICAL STUDIES

Several factors must be considered when developing protocols for the analysis of organic compounds in water to support epidemiological studies. It is assumed that in such studies epidemiologists will be seeking cause and effect relationships between organic compounds in drinking water and certain diseases. These studies will be broad or narrow in scope, depending upon the extent of knowledge about the suspected relationship. If the history of the case has allowed the chemicals of concern to be narrowed to one or a few classes of compounds, then a narrow study of these classes by "class analysis" methods is probably more cost effective than the broad survey approach using GC-MS for analysis of all volatile compounds in the samples. The latter approach is, of course, the one used where there is no historical data to allow selection of a few chemical classes of concern.

Following is an outline of factors that must be considered when developing protocols for analyses to support either type of epidemiological study. Both highly volatile (purgeable) and intermediately volatile compounds are considered; the paucity of knowledge concerning the analysis of non-volatile organics does not allow protocol development for these compounds at this time.

I. Sampling

  A. Geographical location.

  B. Season of the year and historical water quality pattern relative to season

  C. Sampling sites.

    1. Consider sampling source water (raw water) and water during treatment to help determine origin of compounds in treated water.

    2. Consider sampling in distributions lines and at comsumer taps as well as just after treatment.

D. Background or control and blank.

1. Background or control sampling considerations are the same as those for any sample.

2. The blank should consist of all reagents, solvents, accumulator materials, etc., carried through all the processes used for the samples, using similar equipment. Volumes should be the same as for samples. It is desirable to use ultra-pure water for the blank, but it is better not to use "blank" water at all, or only the minimum amount, if avaialble supply might contain interfering organics. In such a case, the control sample should be devised to serve as the blank.

E. Obtaining a the presentative sample - consider:

1. Specific collection points, including vertical profile.

2. Times, frequencies and volumes required to produce a good composite.

F. Collection technique.

1. Consider the volatility of organics to be analyzed:

a. For highly volatile (purgeable) only - collect samples in serum bottles to provide for VOA analysis[1] or for pentane extraction in the bottle[2]. The VOA technique is preferred.

b. For intermediately (mostly non-purgeable) volatiles - use grab samples for solvent extraction or use XAD accumulator columns[3]. Solvent extraction is preferred when the desired detection limit is 1 μg/1; accumulators are preferred for lower detection levels since they allow compositing of large volumes of sample. Accumulators also have the great advantage of concentrating organics <u>during</u> sample collection.

c. For both purgeable and non-purgeable volatiles - consider using Grob's technique[4], the only method available that allows for extraction and concentration of both volatility classes simultaneously at sub μg/1 levels. However, the equipment is not widely available and is complicated. Grab samples are used for Grob's technique; sample containers must be well sealed to hold purgeables and transfer to Grob's sparging device must be in a closed system.

2. Consider necessity of pH adjustment to allow better recovery of acids and bases - this will increase the number of extracts for analysis.

3. Consider particulate material - should it be filtered and discarded, included in the sample, or filtered and extracted separately?

4. For class analysis, use the collection technique expected to give the highest recoveries for the class or classes of compounds concerned (see Appendix 3, E, 1).

G. Materials and purity.

1. Use inert sampling equipment, materials and containers.

2. Clean or purify all equipment, resins, solvents, etc., by established methods.

H. Quantification.
Measure all volumes and consider the inclusion of internal standards for later quantification of individual compounds.

I. Preservation.

1. Freezing or cooling is usually best.

2. Preliminary extraction in the field by the addition of solvent helps preserve grab samples that are to be solvent extracted.

J. Logistics.
Maintain preservation and minimize the time between collection and analysis.

II. Extraction and Concentration
Extraction of organics from water can be accomplished by adsorption during

sampling if accumulator columns are used (see 1,F); extraction involves sparing coupled with an adsorption process when the various purging techniques are used. Concentration is coincidental to extraction/adsorption. For the purging techniques, a second "extraction" process is that of thermal desorption of organics from the accumulator, except for Grob's method. In the case of liquid extraction of the water sample and extraction of adsorbed organics from accumulators, the extraction/concentration factors in A and B should be considered:

A. Extraction solvent properties.

1. Must be a good solvent or solvent mixture for a wide variety of organic compounds.

2. Must be of high purity to avoid interferences.

3. Should be low boiling for ease of concentration and fast elution from the GC.

4. Must be chemically inert and stable to heat and light.

5. For liquid-liquid extractions, the solvent should be less than 10% water soluble.

6. For solvent-accumulator extractions, the solvent must wet the accumulator resin well.

7. Should be easily obtainable commercially.

B. Concentration.

1. Use minimum amount of extracting solvent to reduce concentration problems.

2. Concentrate slowly, carefully and only as much as is absolutely necessary to obtain desired detection level. Concentration below 0.3 ml results in large losses of volatile organics. Use the techniques and apparatus described by Webb[5].

3. Store this final extract in a sealed vial in a freezer until ready for GC analysis.

C. Sparging and thermal desorption.

These "extraction" processes are part of the VOA purging technique and procedures have been established to obtain reasonable recoveries for most highly volatile compounds[1]. However, these procedures are still undergoing optimization. Factors to consider for sparging and thermal desorption include:

1. Transfer of sample from serum bottle to sparging chamber without loss of highly volatiles.

2. Flow of sparging gas.

3. Time of sparging

4. Temperature of sample during sparging (increases in flow, time and temperature result in removal of more organics form the aqueous phase, but may also cause loss of some adsorbed organics from the resin).

5. Type of resin accumulator.

6. Amount of resin.

7. Interface of accumulator column containing adsorbed organics to the gas chromatograph inlet system.

8. Desorption temperature.

9. Transfer of organics in a "slug" to the GC column.

III. Separation and Detection

A. For <u>survey</u> analysis, gas chromatography with flame ionization detection (FID) is best for both highly volatile and intermediate by volatile compounds. The following factors should be considered:

1. Injection - is the extract in solution or adsorbed on a solid phase (as in the VOA method)?

2. Column size - capillary colums give the best separation but are more expensive and complicated.

3. Column active phase - polar, non-polar or more specialized (e.g., special columns for bases).

4. Chromatographic conditions; temperature, programme rate, carrier gas flow, etc.

5. Quantitative accuracy - it may be that these initial GC runs can be re-used for quantification of peaks after identification.

6. The need for analyses by more than one column to improve certain separations.

7. Detection by specific detectors; e.g., flame photometric for phosphorus or sulfur, or electrolytic conductivity for halogen compounds, in addition to the FID, to increase sensitivity for certain compounds.

8. Computerization of the GC for retention time and peak area measurements.

B. For class analysis, the separation and detection is often still by GC, but the column conditions and type of detector are dependent upon the chemical nature of the class members. This dependence also exists in the case of TLC and LC separation and detection (see Appendix 3, E, 1).

IV. Identification

A. For survey analysis, identification will be by mass spectrometer (GC-MS). These factors should be considered:

1. GC-MS interface - transfer of as much of each compound as possible to the MS ion source without chemical change. For capillary GC-MS, direct coupling without a separator is the best technique.

2. GC, MS and computer operation conditions; adjustment to allow production of reconstructed gas chromatograms (MS detection) that can be visually matched peak for peak with gas chromatograms (FID).

3. MS operating conditions, to obtain accurate spectra.

4. MS background - minimize. Also minimize GC column bleed into the MS.

5. MS computerization - necessary for efficient spectral acquisition, data handling and spectral matching. Programmes should be available for spectral background subtract, spectral plotting and spectral matching.

6. Spectral matching- use of the Mass Spectral Search System[6] saves much time over manual catalogue spectral matching and the appropriate output devices allow visual comparison of total spectra.

7. Criteria for identification, with confidence limits, should be established; these could be based on similarity indices, using the MSSS search system.

B. For class analysis, identification will often be by GC, LC or TLC retention time. Consideration must be given to the specificity of the detector (e.g., a specific type GC detector of a TLC colour indicator) when establishing criteria for identification.

V. Confirmation

For survey analysis, where separation and detection are not class specific, confirmation of many identifications will be required; more so than in class analysis where more specificity exists. The following factors must be considered;

A. What compounds are to be confirmed, based on selection criteria such as apparent concentration, expected health effects (based on tentative MS identification), repetition of occurrance, etc.

B. Method of confirmation - matching complete mass spectra with that of a literature or computer data bank standard, matching GC retention time and/or mass spectra with that of a standard run in the same laboratory,etc.

C. Overkill - in special cases with important compounds, it may be necessary to obtain additional confirmation by matching other spectra, e.g., high resolution MS or infrared, with those of a standard.

D. Class analysis - confirmation of class analysis identification will be required occasionally in cases of doubtful identifications or as a means of routine quality control. This should be done by GC-MS analysis, if possible.

VI. Ab Initio Identification

In cases of compounds not identified or confirmed but giving some indication of special importance based on predetermined criteria (e.g., large GC peak size or tentative MS identification as a member of a toxic class of chemicals) advanced instrumental techniques must be used to establish identity. These may include high resulution MS, chemical ionization MS, infrared spectrophotometry, etc.

VII. Quantification

For meaningful assessment of health risks, all compounds identified and actually some only partially identified as to parent chemical class, must be quantified. The following should be considered:

A. Degree of accuracy required - e.g., within a factor of 2 of a factor of 10?

B. Use of standards (determined to some extent by the degree of accuracy required):

1. Comparison with internal standards. These can be mixed with the original water sample to allow calculation of semi-quantitative recovery factors, or mixed with the extract just before chromatography. There can be one standard per GC run or one standard for each major chemical class expected to be in each extract. The latter method includes some correction for differences in detector response to different classes of compounds.

2. Comparison with external standards - this is necessary if more accuracy is required for individual compound quantification; it involves the use of standard for each compound measured and is very

time consuming. However, no recovery correction is possible.

3. Recovery studies - standards of compounds of special importance should be dosed into the original sample matrix and the analysis repeated to allow the most accurate degree of quantification.

C. Peak measurement/detector response - a detector with response independent of chemical properties of the compounds detected would be ideal; this is not available, but the flame ionization detector is less dependent than the mass spectrometer. However, in cases where differences in detector response is not the limiting factor in quantitative accuracy, computer comparison of mass spectrometer total ion current measurements obtained during the GC-MS run with those of internal standards is considerably less expensive than re-running the sample by GC-FID for quantification.

VIII. Quality Control[7]

A. Qualitative analysis - quality control here involves programmes to assure correct calibration of instrumentation used to measure mass spectra, GC retention times, etc.

B. Controls and blanks - use of background or control samples helps confirm the unique characteristics of the sample (i.e. identify and quantity of organics present) and helps account for artifacts. Blanks are essential to the determination of the presence and source of artifacts. (see I. D.)

C. Quantitative analysis - a statistical quality control programme is necessary to assure precision and accuracy of quantitative measurements for samples of a repetitive nature. For non-repetitive samples, quality control is still necessary to assure quality of standards and quantitative measurements of volumes and areas.

REFERENCES

1. (a) F. C. Kopfler, R. G. Melton, R. D. Lingg and W. E. Coleman, GS/MS Determination of Volatiles for the National Organics Reconnaissance Survey (NORS) of Drinking Water in "Identification and Analysis of Organic Pollutants in Water", L. H. Keith, Ed., Aan Arbor Science Publishers Inc., Ann Arbor, MI., 1976, Chapter 6.

   (b) W. E. Coleman, R. D. Lingg, R. G. Melton and F. C. Kopfler, The Occurrance Volatile Organics in Five Drinking Water Supplies Using GC/MS in "Identification and Analysis of Organic Pollutants in Water", L. H. Keith, Ed., Ann Arbor Science Publishers Inc., Ann Arbor, MI, 1976, Chapter 21.

2. J. E.Henderson, IV, G. R. Peyton and W. H. Glaze, A Convenient Liquid-Liquid Extraction Method for the Determination of Halomethanes in Water at the Parts-Per-Billion Level, in "Identification and Analysis of Organic Pollutants in Water", L. H. Keith, Ed. Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 1976, Chapter 7.

3. (a) G.A. Junk, J. J. Richard, M. D. Grieser, D. Witaik, J. L. Witiak, M. D. Arguillo, R. Vick, H. J. Svec, J. S. Fritz and G. V. Calder, "Use of Macroreticular Resins in the Analysis of Water for Trace Organic Contaminants" J. Chromatogr. 99, 745-762, 1974.

   (b) R. G. Webb, "Isolating Organic Water Pollutants: XAD Resins, Urethane Foams, Solvent Extraction", U.S. Environmental Protection Agency Report No. 660/4-75-003, June 1975.

4. K. Grob and F. Zürcher, "Stripping of Trace Organic Substances from Water, Equipment and Procedures", J. Chromatogr., 117, 285-294, 1976.

5. R. G. Webb, "Isolating Organic Water Pollutants: XAD Resins, Urethane Foams, Solvent Extraction", U. S. Environmental Protection Agency Report No. EPA-660/4-75-003, June 1975.

6. S. R. Heller, J. M. McGuire and W. L. Budde, "Trace Organics by GC-MS", Environ. Sci. Technol. 9, 210-213, 1975.

7. (a) U. S. Environmental Protection Agency, "Handbook of Analytical Quality Control in Water and Wastewater Laboratories", Analytical Quality Control Laboratory, Cincinnati, Ohio, June 1972.

   (b) J. W. Eichelberger, W. M. Middleton and W. L. Budde, "Analytical Quality Assurance for Trace Organics Analysis by GC-MS", U. S. Environmental Protection Agency Research Report No. EPA-600/4-75-007, September, 1975.