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Project Summary

Master Analytical Scheme for Organic Compounds in Water

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A Master Analytical Scheme (MAS) has been developed for the analysis of volatile (gas chromatographable) organic compounds in water. In developing the MAS, it was necessary to evaluate and modify existing analysis procedures and develop new techniques to produce protocols that provide for the comprehensive qualitative-quantitative analysis of almost all volatile organics in many types of water. The MAS provides for analysis of purgeable and extractable, as well a neutral and ionic water soluble organics in surface and drinking waters and in leachates and various effluents. Nominal lower quantifiable limits range from 0.1 μg/L to 100 μg/L, depending on the chemical and physical class of the analyte and the complexity of the aqueous matrix. Recoveries are reported for about 260 model compounds of a wide variety of chemical classes and physical properties dosed into representative samples of several types of water.

This Project Summary was developed by EPA's Environmental Research Laboratory, Athens, GA, to announce key findings of the research project that is fully documented in five separate reports (see Project Report ordering information at back).

Introduction

The MAS represents the first effort to develop a comprehensive qualitative-quantitative scheme for the analysis of organic compounds in water. It is a set of analytical protocols for a broad range of organics with a wide variety of functional groups and physical properties. These protocols provide for the gas chromatography-mass spectrometry-computer (GC-MS-COMP) analysis of the usual purgeable and extractable compounds, with the addition of various neutral and ionic water soluble compounds. In fact, any compounds that can pass unchanged through a gas chromatograph, or can be derivatized to do so, are amenable to analysis by the procedures. Recoveries have been determined from distilled and drinking water, industrial and municipal effluents, and, in some cases, surface water and energy effluents, so the protocols are expected to be applicable to most water types. One unique feature of the MAS is its comprehensiveness. Another is its quantitative aspect: an extensive data base of mass spectrometer detector responses and recovery factors for model compounds allows computer estimation of concentration without recourse to standards for each compound.

Tables 1-3 of this summary provide summarized recovery data for the chemical classes applicable to each protocol. During MAS development, recovery data were generated for approximately 260 different model compounds of a wide variety of chemical classes and physical properties dosed into representative samples of several major types of water. Complete recovery data for the individual analytes are given in the MAS protocols (Volume I, Part 1).

Although designed to span the complexity encountered in a variety of water types, procedures are included in the MAS protocols that define the water quality and allow for optimal detection limits for that water sample. If the nominal detection limit for qualitative GC-MS analysis is assumed to be 10 ng for an organic compound, then the limits for the MAS range from 0.1 μg/L (e.g., volatile organics in drinking water) to 100 μg/L (e.g., nonvolatile strong acids in energy

effluents) depending upon the physical/chemical class of the analyte and complexity of the matrix.

The prospective user has the latitude of applying all the protocols or just those that cover organic group types of interest. Thus, each protocol stands alone, containing the elements for determining water quality, collecting the sample, adding internal standards and processing the sample with subsequent analysis according to prescribed GC-MS-COMP conditions.

In developing the MAS, existing analytical techniques were evaluated and modified and new techniques were developed to produce the comprehensive protocols. Development was in two stages. An interim set of protocols was developed by October 1980; analysis of environmental samples by these protocols revealed several important deficiencies that were subsequently corrected by additional experimental work. The final result is this edition of MAS protocols: Master Analytical Scheme for Organic Compounds in Water; Part 1, Protocols, and Part 2, Appendices.

Two companion reports resulted from MAS development: (1) *Experimental Development of the Master Analytical Scheme for Organic Compounds in Water* and (2) *Literature Review for Development of the Master Analytical Scheme for Organic Compounds in Water*. The user can refer to the experimental report for information on techniques considered and studied for MAS incorporation, and on experiments dealing with technique optimization and recovery studies. The other report is essentially a literature review through June 1982 on techniques for analysis of organics in water; in an earlier version, it was the starting point for experimental development and will also be of interest to many users. Neither report is essential to MAS use, however; the protocols report stands alone as the handbook for implementation. Part 2 of the protocols report ("Appendices to Protocols") includes: Appendix A – specific instructions on fabrication of the purge and trap apparatus and ancillary devices for purgeable organics; Appendix B – hard copy of computerized relative molar response and recovery data for standards and analytes; and Appendix C – documentation of MASQUANT computer program for quantification of MAS data.

MAS Overview

Figure 1 depicts a flow diagram of the procedures for implementation of the MAS. Each step is summarized below.

Sample Handling

Seven sub-samples (one for each protocol class) are required for a comprehensive sample analysis. Procedures are prescribed in the protocols for sample collection, storage, and preservation. Volatile organic (VO fraction) samples are collected in septum-capped bottles with no headspace. Methylene chloride is added to all extractable and ionic compound samples as a bacteriocide; hexane is used as "keeper" solvent layer for extractable compounds. Chlorine determination indicates the level of sodium thiosulfate necessary to stoichiometrically reduce any residual chlorine left from water treatment. All samples are stored at ~4°C in the dark.

Various water quality scouting measurements help in the selection of appropriate analytical procedures, which are optimized according to water quality rather than sample "type" (e.g., drinking water or municipal effluent). Headspace gas analysis by GC of a separate small sample is employed to determine the dilution necessary for VO purge and trap analysis. A trial shake-out with methylene chloride of a small aliquot of the extractable (WABN) sample shows whether emulsion formation is a problem, and thus whether the flow-under extractor must be used. Conductivity measurements indicate maximum sample volume allowable for isolation of ionic compounds by ion-exchange resin without exceeding resin capacity.

Internal Standards

Prescribed deuterated internal standards (included in Table 1) are added to each sub-sample, preferably in the field, before processing or storage. Selection of packaging assures that from one to nine standards of the total of 20 will appear in each extract for GC-MS analysis; retention times are such that the standards span the chromatographic window in most cases. These standards are used for monitoring recovery during analysis, for quantifying sample components, and for calculating relative retention times.

The initial sets of MAS standards were prepared by the National Bureau of Standards. Purgeable standards, in methanol, are packaged in glass capillary ampoules that are placed in an empty sample bottle, then crushed with a magnetic stirbar after the water sample has been collected. For other sample aliquots, internal standards are packaged in vials in methanol or water solution such that emptying the entire content of the vial into the prescribed sample volume produces the optimum concentrations of standards.

Isolation of Organics

After addition of internal standards, the seven subsamples are processed as follows. (Protocol symbols are in parenthesis.)

Volatile Organics (VO)—Highly volatile (purgeable) organics (Table 1) are analyzed by a modification of the Bellar-Lichtenberg method (EPA's Method 624), using a custom built purge and trap system designed especially for capillary GC columns. (Fabrication of this system is described in Appendix A to the protocols.) Sodium sulfate is used to "salt out" the organics in a 200 mL sample, which is purged at 30°C. More concentrated samples are first diluted to 200 mL in accordance with the total concentration of purgeable organics as indicated by GC scouting of the separate headspace sample. Dilution prevents saturation of the GC-MS-COMP and decreases foaming potential. Purged organic vapors are collected on a Tenax GC sorbent trap, from which they are thermally desorbed into a liquid nitrogen cold trap. An "external" standard, perfluorotoluene, is added to the cold trap from an injection port system, which is installed between the sorbent trap and the cold trap, before desorption of the purged sample components into the cold trap. The total condensate is then flash evaporated into a fused silica capillary for analysis by GC-MS-COMP. Comparison of MAS signals for the external standard with those for the internal standards purged from the sample allows calculation of recoveries of the internal standards, thus monitoring performance of the entire analytical operation.

Neutral Water Soluble Compounds (NEWS)—Low molecular weight, water soluble, non-extractable compounds (Table 1) are purged from a 10-mL water sample containing 20% sodium chloride at 80°C and trapped on Tenax, using the same equipment as for the VO fraction. To achieve lower limits of detection for drinking water, a 200-mL sample is concentrated by azeotropic distillation to produce a 3-mL aqueous condensate enriched in neutral organics. This condensate is then purged as above.

Organics Extracted at pH 8 (WABN)—Compounds of intermediate volatility, most of which are water insoluble (Table 1), are analyzed by batch liquid-liquid extraction of 1 L of water sample with

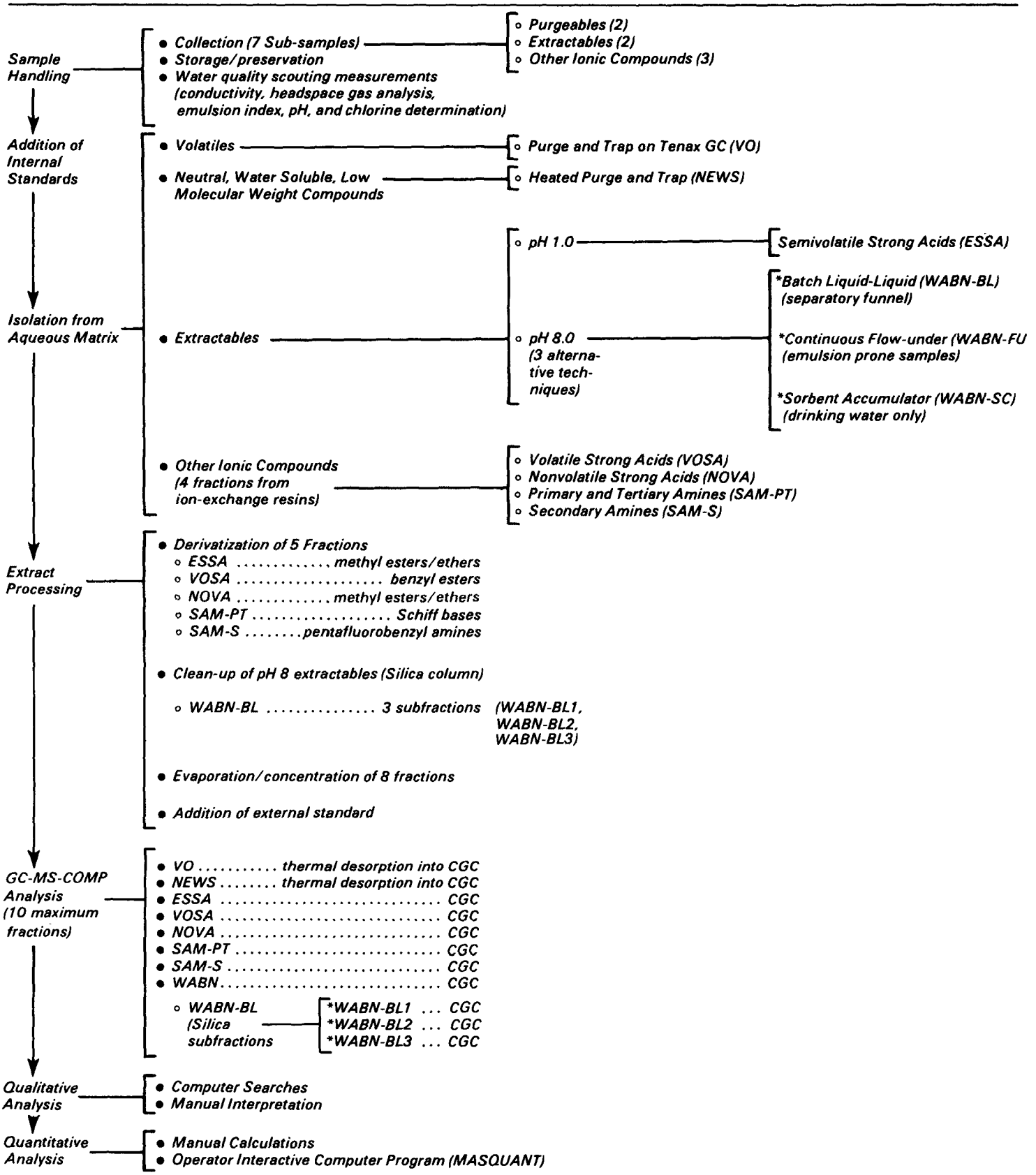

Figure 1. *Master analytical scheme flow diagram.*

Table 1. *Summary of Master Analytical Scheme Recovery Data (Including Deuterated Internal Standards)*

Protocol Class Chemical Class (Examples)	Compounds Studied	Recovery Range, %	Mean Recovery, %	CV Range, %	Mean CV, %	Footnotes
Volatile (Purgeable) Organics (VO)						
Aromatic Hydrocarbons (benzene, naphthalene)	9	59-113	85	3-35	11	a
Halogenated Aromatics (chlorobenzene; 1,2,4-tri-chlorobenzene)	7	91-106	100	2-30	15	a
Misc. Aromatic Compounds (anisole)	1	-	68	-	12	a
Aliphatic and Alicyclic Hydrocarbons (cyclohexane; n-tridecane)	11	44-120	82	1-40	16	a
Halogenated Aliphatic Hydrocarbons (chloroform; 1,4-dibromobutane)	7	77-118	90	4-16	9	a
Miscellaneous Oxygen & Sulfur Compounds (diethyl ether; hexyl ether)	5	70-115	93	3-26	11	a
Deuterated Standards (d_5-bromoethane; 2,4,6-d_3-anisole; d_5-chlorobenzene; d_8-naphthalene)	4	57-120	90	10-25	18	a
Neutral Water Soluble Organics (NEWS)						
Alcohols (1-propanol; 1-heptanol)	4	106-131	115	18-25	22	b
Aldehydes (n-butyraldehyde; crotonaldehyde)	3	72-83	79	25-32	29	b
Esters (methyl formate; ethyl butyrate)	7	45-93	74	4-17	7	c
Ethers (tetrahydrofuran; dioxane)	2	50-79	65	14-31	23	b
Ketones (methyl ethyl ketone; cyclohexanone)	2	65-69	67	2-32	17	b
Nitriles (acrylonitrile; benzonitrile)	4	57-95	83	6-14	9	b
Nitro Compounds (nitromethane; nitrobenzene)	3	70-96	86	5-13	9	b
Deuterated Standards (d_9-t-butanol; d_5-nitrobenzene)	2	93-98	96	7-10	9	b
Weak Acids, Bases, and Neutrals (WABN-SC and WABN-BL)						
Weak Acids (phenol, 2,4-dichlorophenol)						
accumulator column	6	55-95	77	5-23	11	d
batch liquid-liquid	12	49-118	71	5-27	13	e
Weak Bases (aniline; carbazole)						
accumulator column	16	53-59	82	0-16	7	d
batch liquid-liquid	15	40-86	64	6-40	24	e
Alkanes (n-decane; n-tridecane)						
accumulator column	8	42-66	52	6-20	15	d
batch liquid-liquid	11	45-82	62	13-31	21	f
Aliphatic Ketones, Alcohols, and Esters (fenchone; methyl stearate)						
accumulator column	7	49-94	75	1-22	10	d
batch liquid-liquid	9	49-111	71	10-43	25	e
Misc. Aliphatic Compounds (di-t-butyldisulfide; tributylphosphate)						
accumulator column	6	40-92	72	2-36	18	d
batch liquid-liquid	4	57-104	75	9-36	21	e

Table 1. *(Continued)*

Protocol Class Chemical Class (Examples)	Compounds Studied	Recovery Range, %	Mean Recovery, %	CV Range, %	Mean CV, %	Footnotes
Aromatic Hydrocarbons (2-methylnaphthalene, pyrene)						
accumulator column	10	60-87	74	1-27	16	d
batch liquid-liquid	7	48-118	79	13-41	24	e
Halogenated Aromatics (o-chloroanisole; hexachlorobenzene)						
accumulator column	10	56-100	73	1-42	16	d
batch liquid-liquid	9	43-107	68	13-33	20	e
Aromatic Aldehydes and Ketones (o-tolualdehyde; acetophenone)						
accumulator column	3	88-96	92	2-17	12	d
batch liquid-liquid	4	43-105	69	6-19	13	e
Aromatic Esters and Sulfonates (benzylacetate, ethyl-p-toluene-sulfonate)						
accumulator column	6	46-87	69	7-17	12	d
batch liquid-liquid	7	55-138	84	3-19	11	e
Misc. Aromatic Compounds (nitrobenzene; tetraphenyltin)						
accumulator column	6	47-89	74	6-24	13	d
batch liquid-liquid	10	48-105	68	8-33	17	e
Deuterated Standards (d_{10}-xylene; d_5-phenol; d_5-acetophenone; d_5-phenylethanol; d_5-nitrobenzene; d_5-propiophenone; d_8-naphthalene; d_9-acridine; d_{12}-perylene)						
accumulator column	9	55-93	78	4-21	10	d
batch liquid-liquid	8	40-78	58	11-40	26	e
Extractable Semivolatile Strong Acids (ESSA)						
Carboxylic Acids (benzoic acid; palmitic acid)	17	63-110	89	2-20	9	g
Phenols (2-nitro-p-cresol; pentachlorophenol)	5	88-100	94		4-19	8
Deuterated Standards (d_{13}-heptanoic acid; d_5-benzoic acid)	2	65-92	79	6-12	9	g
Volatile Strong Acids (VOSA)						
Volatile Carboxylic Acids (acrylic acid; n-octanoic acid)	16	46-90	65	4-34	19	h
Deuterated Standards (d_7-butyric acid)	1	-	85	-	14	h
Nonvolatile Acids (NOVA)						
Carboxylic Acids (succinic acid; 2,4,5-trichloro-phenoxyacetic acid)	6	42-87	64	2-45	18	i
Sulfonic Acids (benzenesulfonic acid; 2-naphthalene-sulfonic acid)	4	84-110	96	7-45	23	i
Misc. Nonvolatile Acids (benzenephosphoric acid; pentachlorophenol)	3	62-140	102	11-50	25	i
Deuterated Standards (2-naphthalenesulfonic acid-d_7-H_2O)	1	-	110	-	14	i
Strong Amines (SAM-PT and SAM-S)						
Primary and Tertiary Amines (n-butylamine; tri-n-butylamine)	11	58-86	72	12-41	24	j

Table 1. (Continued)

Protocol Class Chemical Class (Examples)	Compounds Studied	Recovery Range, %	Mean Recovery, %	CV Range, %	Mean CV, %	Footnotes
Secondary Amines (diallylamine; 2-methylpiperidine)	6	40-98	63	20-53	36	j
Deuterated Standards (d_9-butylamine; d_4-phenylethylamine; N-ethyl-2-fluorobenzylamine)	1	-	75	-	27	j,k

[a]*Mean recoveries are for triplicate determinations from drinking water, spiked at 0.2 to 1.8 ppb (nominally 1 ppb), plus triplicate determinations from a 60/40 industrial/municipal wastewater, spiked at 30 to 87 ppb (nominally 50 ppb).*
[b]*Mean recoveries are for triplicate determinations from drinking water, spiked at 0.8 to 1.2 ppb (nominally 1 ppb), plus triplicate determinations from a 60/40 industrial/municipal wastewater, spiked at 40 to 63 ppb (nominally 50 ppb).*
[c]*Mean recoveries are for triplicate determinations from 60/40 industrial/municipal wastewater only, spiked at 40 to 63 ppb (nominally 50 ppb).*
[d]*Mean recoveries are for triplicate determinations from drinking water, spiked at 0.5 to 5 ppb (nominally 1 ppb), using XAD-4 resin sorbent columns.*
[e]*Mean recoveries are for triplicate determinations from a 60/40 industrial/municipal wastewater or, for about 1/4 of the total compounds, from reagent water spiked at 15 to 50 ppb (nominally 25 ppb), using batch liquid-liquid extraction, with clean-up included.*
[f]*Mean recoveries are for triplicate determinations from reagent water only, with clean-up step included. (Interferences prevented recovery determinations from wastewater.)*
[g]*Mean recoveries are from triplicate deteminations from drinking water only, spiked at 50-100 ppb (nominally 55 ppb). Recoveries were not determined from more complex waters.*
[h]*Mean recoveries are for triplicate determinations from drinking water, spiked at 0.3 ppb, plus triplicate determinations from a 60/40 industrial/municipal wastewater, spiked at 120 ppb.*
[i]*Mean recoveries are for triplicate determinations from several industrial and municipal effluents.*
[j]*Mean recoveries are for triplicate determinations from three industrial and two municipal effluents spiked at 110 ppb, and including, in some cases, triplicate determinations from drinking water spiked at 35 ppb.*
[k]*Recoveries determined for only one (d_9-butylamine) of the three internal standards.*

methylene chloride in a separatory funnel. Adjustment of sample to pH 8.0 allows reproducible extraction of the weak acids, (e.g., most phenols) and weak bases (e.g., most anilines) as well as neutral compounds.

For some samples, however, batch liquid-liquid extraction is not suitable. Initial trial solvent extraction in a stoppered graduated cylinder indicates whether emulsion formation is likely to be a problem. For emulsion-prone samples, continuous liquid-liquid extraction with methylene chloride in a flow-under extractor should be used. For samples in which the extractable organic concentration is expected to be low, such as drinking water and some surface waters, XAD-4 resin sorbent accumulator columns are used for sorption/concentration from 10-15 L of water. The organics are desorbed using methanol followed by methylene chloride.

Organics Extracted at pH 1 (ESSA)—Extraction at pH 8 does not efficiently recover strong acids or bases. Strong bases are extracted on ion-exchange resins, but a new procedure has been developed for semivolatile strong acids (Table 1). This involves batch liquid-liquid extraction of a 1-L sample with methylene chloride at pH 10 to remove most neutrals and bases (discarded), after which the sample is made to pH 1.0 with HCl and the semivolatile strong acids are extracted with methyl-*t*-butyl ether. This procedure includes most carboxylic acids and strongly acidic phenols. The lower molecule weight carboxylic acids, however, are included in a separate volatile acids protocol (VOSA); they are too volatile to be efficiently recovered during liquid-liquid extraction and subsequent extract processing. In addition, some acids, e.g., sulfonic acids, are too ionic to be extracted under these conditions and are included in the nonvolatile strong acid analytical protocol (NOVA).

Semivolatile strong acids are derivatized with diazomethane to form the corresponding methyl esters or ethers before GC/MS analysis.

Other Ionic Compounds (VOSA, NOVA, SAM)—Compounds that are easily dissociated in water have not previously been included in analytical schemes because of difficulties with extraction and chromatography. New techniques, however, were developed to allow inclusion of most of these compounds in the MAS. Ion-exchange resins are used to separate four classes of ionic compounds from the sample matrix using three separate aliquots of the sample.

"Volatile" strong acids (VOSA), such as acrylic acid, octanoic acid, and other volatile carboxylic acids (Table 1) are separated from the water on Biorad AG 1-X8 anion exchange resin, then eluted with sodium bisulfate in an acetone:water solution. The volatile acids are distilled from the eluate, converted to nonvolatile salts, then derivatized with benzylbromide to form benzyl esters.

"Nonvolatile" strong acids (NOVA), e.g., naphthalene sulfonic acids, (Table 1) are also separated from water on Biorad AG 1-X8 resin. They are eluted with HCl in methanol, the solvent is evaporated, and the acids are methylated with diazomethane.

Strong amines (SAM), such as butylamine and diallylamine (Table 1) are isolated from the water sample on Biorad AG 50W-X8 cation exchange resin, then eluted with sodium hydroxide in acetonitrile:water solution. The eluate is acidified, the solution is evaporated to dryness, and the amine hydrochloride salts are dissolved in base and extracted with methyl-*t*-butyl ether. The extract is split, half is derivatized with pentafluorobenzyl bromide to make the pentafluorobenzyl tertiary amines from the secondary amines (SAM-S), and half is derivatized with pentafluorobenzaldehyde to make Schiff bases of the primary amines (SAM-PT).

Tertiary amines are also separated by this protocol and quantified (underivatized) in the primary amine function. Certain other weak bases may also be detected in these fractions, but are measured in the pH 8 extractable fraction (WABN), where they are extracted more

efficiently. (Quarternary amines are not addressed by the MAS.)

Extract Processing

Extractable and ionic fractions require further processing before GC/MS. The necessary derivatization steps, for example, are mentioned above and summarized in Figure 1.

The pH 8 extractable fraction (WABN-BL) of many industrial effluents will require clean-up and sub-fractionation before effective separation can be achieved, even on capillary columns. First, however, a scouting procedure is implemented to determine whether clean-up is necessary. The crude extract is analyzed by GC using a packed column and flame ionization detection; baseline rise relative to a separately run standard is the evaluation criterion. Clean-up, if necessary, is on a silica gel column from which three fractions (WABN-BL1, -BL2, and -BL3) are eluted using pentane, methylene chloride, methanol, and their mixtures.

Concentration of extracts for GC-MS analysis is by Kuderna-Danish evaporation down to 4 mL, followed by nitrogen blowdown to 0.5 mL or 1.0 mL using a modified Snyder column. "External" standards are added to each final extract just before GC-MS analysis to monitor recovery of the deuterated internal standards that were added to the original water samples. The external standard for the purgeable fractions (VO and NEWS) is perfluorotoluene. External standards for all the other fractions are 2-fluorobiphenyl and/or 4-fluoro-2-iodotoluene.

Gas Chromatography

As shown in Figure 1, as many as 10 extracts or fractions may be obtained from one sample if the entire MAS protocol is applied (this may be reduced to 7 if cleanup of the pH 8 (WABN) extract is not necessary, and if the primary and secondary amine fractions can be mixed for a single GC-MS analysis). Glass or fused silica capillaries are prescribed. Bonded phase (e.g., Durabond DB-1 or DB-5), wide-bore, thick film (1.0 μm), 30- or 60-m fused silica columns are recommended for inertness, stability, and sample capacity. In all cases performance standards (see Quality Assurance) rather than specific columns are specified in the analytical protocol. No more than four different GC columns should be necessary for the entire MAS. The analytical protocol for each fraction prescribes optimum GC conditions for the GC-MS-COMP system.

Qualitative Analysis

Sample components are identified by established GC-MS-COMP techniques. No research was conducted on MAS identification procedures. GC-MS data are stored on tape or disk. Internal standards in each extract are used as reference points for retention time measurements as well as for quantification. Compounds are identified by computer searching of mass spectra data banks or by manual interpretation.

Quantitative Analysis

Extensive recovery studies were conducted during development of the MAS. Approximately 260 different model compounds from a wide variety of chemical classes and physical property groups were dosed into representative samples of several major types of water (distilled and drinking water, and municipal and/or industrial effluents). Recoveries were determined and average recovery factors were stored in a computer data bank. Relative molar response (RMR) factors (relative to the deuterated internal standards), based on MAS selected ion peak areas, were also determined and stored in the data bank. (Appendix B to the protocols is a hard copy of these data.) The MAS user can use these data banks and a computer program developed for the MAS (MASQUANT, which is documented in Appendix C to the protocols) to calculate the concentration in the original water sample for these model compounds as they are identified.

If the identified sample component is not a model compound, RMR and recovery factors of a structurally similar compound in the data bank may be used for an estimate of concentration. In addition to this obvious source of error, an additional error is involved in using any recovery factors from the data bank. Because sample matrices used for recovery studies were only representative of the various water types, and because all recovery values for all matrices studied were averaged to give the factor in the data bank, errors will occur in applying these factors to other samples. This error is dependent on the matrix differences between the sample being analyzed and the representative recovery samples. On the other hand, separate recovery values are given for drinking water for all MAS fractions except nonvolatile acids. These are more accurate than MASQUANT data for drinking water analysis because the MASQUANT data bank (Appendix B) values are averages over all water types studied. Recoveries using the WABN-FU protocols (for industrial effluents) are so matrix dependent that there is no representative sample matrix for recovery studies. The user must generate his own recoveries for his own sample matrix in this case.

Quality Assurance/ Quality Control

Complete quality control steps are prescribed for the user in each MAS protocol. Some of these steps are outlined below.

System Performance Solution—Standard performance solutions are used to check performance of the GC-MS-COMP each day. The MAS prescribes a standard performance solution and corresponding criteria of acceptance for each analytical protocol. Solutions include compounds to measure GC peak asymmetry, separation number, resolution, polarity, and column acidity and basicity; capacity of the capillary column; inertness of the GC to MS transfer line; limits of detection of the MS-COMP system; and tune of the MS. These solutions also contain deuterated internal standards and the external standard appropriate to each protocol for periodic RMR verification and, if necessary, determination of the RMR correction factor by linear regression.

Internal and External Standards—Comparison of the recovered quantity of deuterated internal standards to the quantity of external standard added to the extract just before GC/MS analysis reveals recovery deficiencies, thus serving as a check to indicate malfunctions of the MAS analytical procedure. The primary use of deuterated internal standards is for quantification; reference to an internal standard is generally accepted as the most accurate quantitation technique available for the broad spectrum GC-MS analysis of organics in water. Internal standards may also be used as retention time indices to aid in compound identification.

Sample Scouting—As described earlier, several sample scouting measurements are prescribed to characterize water quality and in turn allow selection of the appropriate and optimal analytical techniques for a particular water sample. Scouting measurements also help in determining optimum sample sizes and dilution factors for certain protocols.

Blanks, Controls, Duplicates, and Surrogate Samples—Requirements and procedures for field and laboratory blanks, spiked field and laboratory controls, and

duplicate and surrogate samples are specified in each sampling protocol. Procedures for cleaning glassware and apparatus and other steps to assure quality of measurement are also specified throughout the MAS.

MAS Test Samples—For each MAS protocol, instructions are given for preparing control samples (for quality assurance) by dosing known amounts of analytes into reagent water. Test samples for practicing and checking MAS procedures may be prepared in the same way.

Resource Requirements for the MAS

A very preliminary estimate of time per comprehensive MAS sample, or a corresponding quality assurance sample, is 80 hours. This is for a laboratory analyzing only a few, say 10 to 50, samples per year, using personnel who are experienced in trace organic analysis of water and set up with the equipment and techniques used for the MAS.

It should be remembered that the MAS protocols were developed and designed as separate entities so that a laboratory could analyze only the fractions appropriate to its mission. The cost for analyzing pH 8 extractables, for example, might be only 10% of that for a comprehensive MAS analysis.

Recovery and Precision

Tables 1-3 provide summarized recovery data for the chemical classes corresponding to each MAS protocol. Footnotes to Table 1 give informaiton on sample matrices and spiking levels used for recovery studies. Several observations can be made regarding these data (see Table 2): (1) recoveries for volatile (purgeable) organics are highest (these purgeables data are for a wide variety of compound classes from several types of water); (2) neutral water soluble organics, a new class of organic analytes, are recovered adequately with adequate precision; and (3) two classes of ionic compounds, volatile strong acids and strong amines, are characterized by relatively low recoveries and poor precision. It is also seen from Table 2 that recovery of organics using accumulator columns is better than with batch liquid-liquid extraction in a separatory funnel, and that precision is also better. Matrix effects may be more important than the extraction technique, however; only drinking water was extracted by accumulator column, whereas more complex matrices were extracted by the batch technique.

Table 2. *Summary of All MAS Recovery Data by Protocol Class*

Protocol Class	No. Compounds	Mean Recovery,[a] %	Mean CV,[a] %
Volatile (Purgeable) Organics (VO)	44	89	13
Neutral Water Soluble Organics (NEWS)	27	84	14
Weak Acids, Bases, and Neutrals (WABN)			
accumulator column (WABN-SC)	87[b,c]	74[c]	12[c]
batch liquid-liquid (WABN-BL)	96[b]	69	20
Extractable Semivolatile Strong Acids (ESSA)	24[c]	89[c]	9[c]
Volatile Strong Acids (VOSA)	17	66	19
Nonvolatile Acids (NOVA)	14[d]	85[d]	20[d]
Strong Amines (SAM-PT and SAM-S)	18	69	28
	327[b]	76[e]	16[e]

[a] *Unweighted means are given, i.e., the n value for each chemical class within a protocol was not included in the calculations.*
[b] *Sixty-nine compounds were used for both accumulator column and batch liquid-liquid recovery studies; the total number of different compounds in this table is therefore 258.*
[c] *ESSA and WABN-SC recovery data are for drinking water only.*
[d] *NOVA recovery data are for industrial and municipal effluents only.*
[e] *Overall mean recoveries and mean CVs were calculated from values for the 327 individual compounds.*

Table 3. *Summary of MAS Recovery Data for Organics in Drinking Water by Protocol Class*[a]

Protocol Class	No. Compounds	Spiking Range (ppb)[b]	Nominal Spiking Level (ppb)[b]	Mean Recovery[c] %	Mean CV[c] %
Volatile (Purgeable) Organics (VO)	52	0.2-1.8	1	90	10
Neutral Water Soluble Organics (NEWS)	25	0.8-1.2	1	84	16
Weak Acids, Bases, and Neutrals (WABN-SC, accumulator column)	87	0.5-5	1	74	12
Extractable Semivolatile Strong Acids (ESSA)	24	50-100	55	89	9
Volatile Strong Acids (VOSA)	18	-	0.3	82	10
Strong Amines (SAM-PT and SAM-S)	11	-	35	81	16
	217			82[d]	12[d]

[a] *For triplicate determinations from drinking water. Nonvolatile Acids (NOVA) were not determined in drinking water.*
[b] *Level spiked into water sample*
[c] *Unweighted means are given, i.e., the n value for each chemical class within a protocol was not included in the calculations.*
[d] *Overall mean recoveries and mean CVs were calculated from values for the 217 individual compounds.*

Table 3 shows summarized recovery data for organics in drinking water only, by MAS protocol. (These data were integrated into the total recovery data of Tables 1 and 2.) Spiking ranges and nominal spiking levels are significantly lower than those used for recoveries from industrial and municipal effluents (see footnotes to Table 1). Recoveries for VO and NEWS compounds are practically the same as those given in Table 2; i.e., matrix effects or spiking levels did not make a significant difference in the summarized data. Extractable semivolatile strong acids were recovered well from drinking water, with good precision, but

the spiking level was relatively high. The other ionic classes of organics (VOSA and SAM) were recovered at significantly higher levels and with better precision from drinking water than from other matrices (cf. Table 2).

Mean recoveries over all protocols for water types studied (Table 2) for 327 determinations (258 different compounds) was 76% with a mean relative standard deviation (for 3 or more measurements) of 16%. For drinking water (Table 3), the mean recovery for 217 spiked compounds was 82%, with a mean RSD of 12%.

Chapter 1 of the MAS protocols includes much more recovery data than is given in Tables 1-3. Recovery values are given for each individual analyte, and separate recovery values are given for drinking water for all MAS fractions except non-volatile acids. As mentioned above, recoveries using the WABN-FU protocols (for industrial effluents) are so matrix dependent that there is no representative sampling matrix for recovery studies, and no recovery data are provided.

Conclusions

The Master Analytical Scheme protocols for analysis of volatile organic compounds in water have been developed and recoveries have been established. The MAS is unique in its comprehensive scope—no other collection of protocols exists that includes such a broad spectrum of organic compounds. This complete set of protocols may be applied for a survey analysis, or each protocol may be used as a separate entity for analysis of organic fractions of particular interest. The main application of the MAS will be for the analysis of carefully selected samples to answer the question, "What compounds are present above detection limits and approximately how much of each is present?" Applying the MAS should be cost effective in areas such as:

- Drinking Water—In epidemiological studies and as early warning for toxic pollutants below acutely toxic levels.
- Industrial/Municipal Wastewaters—In wasteload allocations, permit application evaluation and long-range projections for the state of the environment.
- Surface Waters—In trends analysis, assessments of abatement program effectiveness, watershed management (including exposure assessment), and incident investigation.
- Landfill Leachates—In exposure assessment, evaluation of landfill performance, and diagnosis of problems.
- Environmental Processes—In chemical characterization of aqueous sources and discharges from natural processes and treatment systems.

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***A. W. Garrison** is the EPA Project Officer (see below).*
This Project Summary covers the following reports:
- *"Master Analytical Scheme for Organic Compounds in Water: Part 1. Protocols," (Order No. PB 85-154 367/AS; Cost: $28.00, subject to change).*
- *"Master Analytical Scheme for Organic Compounds in Water: Part 2. Appendices to Protocols," (Order No. PB 85-204 360/AS; Cost: $20.50, subject to change).*
- *"Literature Review for Development of the Master Analytical Scheme for Organic Compounds in Water," (Order No. PB 85-152 874/AS; Cost: $26.50, subject to change).*
- *"Experimental Development of the Master Analytical Scheme for Organic Compounds in Water: Part 1," (Order No. PB 85-153 096/AS; Cost: $56.50, subject to change).*
- *"Experimental Development of the Master Analytical Scheme for Organic Compounds in Water: Part 2," (Order No. PB 85-153 088/AS; Cost: 53.50, subject to change).*

The above reports will be available only from:
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