Water Quality Measurement

THE MODERN ANALYTICAL TECHNIQUES

edited by
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PREFACE

In the past few years more and more chemists have turned their attention to the analytical chemistry of water--with emphasis on water quality and the effects of man and technology on the natural water environment. This interest on the part of chemists has arisen mainly from a real concern about changes in the ecology and the tremendous health problems already found and/or predicted to be caused by trace constituents in water. In the past decade or so, huge sums of money have been invested by the federal, state, and local government agencies as well as private funds in an effort to clean up sources of pollution and to understand the ecological and health effects of these chemicals.

One of the first conclusions that came out of these efforts was that much of the previous analytical data concerning the concentrations of trace constituents in water systems was not valid. Interlaboratory comparisons showed that a number of the usual analytical methods of analysis were neither accurate nor reproducible. Furthermore, it quickly became evident that for a great many suspected species, there were no methods at all with the sensitivity necessary for analysis at the levels at which they were thought to exist in water systems. Another problem soon became evident. A great many trace elements and compounds exist in different chemical forms (such as the mercury and arsenic compounds), and the toxicity is dependent on the chemical nature of those compounds. Thus, methods of analysis which yield only to concentration for an element such as mercury, even if accurate and precise, are not sufficient to determine the nature and composition of a water sample. Analytical methods must determine the concentrations of each chemical species as it exists naturally. Thus, it has become obvious that no effective effort to clean up water

systems, regulate quality, determine the health hazard effect of trace constituents, correlate ecological changes to trace constituents, etc., can be made until reliable analytical methods and data are available. To try to do these things without an accurate knowledge of the composition of the water systems follows the old cart before the horse principle and could lead to more harm than good, not to mention the waste of billions of dollars, both directly and indirectly.

Because of the great importance of the analytical problems outlined above, it was felt that a book covering the modern developments in instrumentation and techniques in analytical chemistry applicable to water analysis would be appropriate and useful at this time. This volume presents comprehensive and critical reviews of the modern techniques, written by experts at the forefront of their development and use in trace analysis. Each chapter will acquaint the reader with one of these techniques. Discussions of the fundamental principles involved will enable analytical chemists, chemical and civil engineers, and water quality management personnel to determine the usefulness, advantages, and limitations of each method for their respective needs. Wherever possible, illustrative examples of the uses of the new techniques for water analysis are provided, and potential future applications suggested.

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Chapter 1

ORGANIC WATER POLLUTANT ANALYSIS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Integral to setting and enforcing water-quality criteria, determining the fate and effects of water pollutants, and developing optimum control measures is the ability to identify specific organic compounds. The contribution of the chemical analyst to environmental pollution control is further emphasized by the results of an analysis of industrial wastes illustrated in Table 1. As the table shows, twice as many compounds were identified by chemical analysis in the plant effluent as were predicted by the discharger based on knowledge of products, raw materials, and processes.

The identification technique selected by the analyst must be highly specific, because thousands of compounds must be considered, and highly sensitive, because organic compounds can cause problems at very low concentrations [for example, some are toxic to aquatic organisms at concentrations below 10 micrograms per liter (µg/l)]. Currently, the method that best meets these requirements for organic

*Dr. Webb is deceased.

Table 1. Comparison of Compounds Reported by Discharger with Compounds Identified by EPA in an Industrial Effluent

Products or raw materials reported	Compounds identified	
Propylene	All xylenes[a]	1,5-Cyclooctadiene
Ethylene	Isopropylbenzene	Styrene[a]
Butadiene	*o*-Ethyltoluene	*o*-Methylstyrene[a]
Butane	Diacetone alcohol	Indan[a]
Octane	2-Butoxyethanol	β-Methylstyrene
Ethylene glycol	Indene[a]	Dimethylfuran isomer
Ethylene oxide	*n*-Pentadecane	1-Methyl indene[a]
Polyglycols	3-Methylindene	Acetophenone
Ammonia	*n*-Hexadecane	α-Terpineol
Raw gas	Naphthalene[a]	Both methyl naphthalene isomers[a]
Ethane	Benzyl alcohol	Both methyl naphthalene isomers[a]
Refinery gases	Ethylnapthalene	α-Methylbenzyl alcohol
Refinery C_2 Stream	2,6-Dimethylnaphthalene[a]	Phenol[a]
	2,6-Dimethylnaphthalene[a]	Methylethylnaphthalene
Refinery C_3 Stream	Cresol isomer	Acenaphthene
	Acenaphthalene	Methylbiphenyl isomer
Propane	Fluorene	Two phthalate diesters
Hydroformer gas	3,3-Diphenylpropanol	
Platformer gas	3,3-Diphenylpropanol	

[a]Identification confirmed with a standard.

pollutants in water is gas chromatography-mass spectrometry (GC-MS). Any compound that can be gas chromatographed without decomposition can be analyzed by GC-MS.

The earliest applications of GC-MS analysis in water pollution studies dealt with industrial effluents containing milligram-per-liter (part per million) amounts of materials [1]. With recent improvements in sample concentration techniques, the application of direct GC interfacing to a mass spectrometer, and the use of a compute for machine control and data processing, however, materials present at only a few micrograms per liter (part per billion) can be readily identified. Analyses at part-per-trillion concentrations are often made as well. Along with advancements in sensitivity, GC-MS has undergone a marked improvement in identifying components of an environmental sample. As a consequence of improved sensitivities, better chromatographic columns, and computerized spectral matching, today's systems can identify many more compounds in water samples in 1 day than could have been identified in 6 months by early systems.

One reason for the widespread use of GC-MS in water pollution analysis is its ability to do two jobs well. It is unsurpassed as a method for surveying and identifying a broad range of organics in water with moderate sensitivity. Moreover, it can be used to find minute traces of specific individual compounds through the use of specialized techniques such as single-ion monitoring (SIM).

The most common type of water pollution analysis in the Environmental Protection Agency GC-MS laboratories is the general organic survey of industrial effluents, although increased emphasis has been placed recently on the survey of organics in drinking waters. In addition, GC-MS is applied to the analysis of taste and odor problems; the confirmation of pesticide residues; the identification of "volatile" organics such as chloroform, vinyl chloride, and bromoform; the analysis of sewage and landfall leachate; the preparation of baseline studies before major construction; and the analysis of water and tissue samples from fish kills.

The first use of MS in a water-pollution study involved the identification by John Teasley of the Athens Federal Water Pollution

Control Administration (now EPA) Laboratory of a pesticide derivative causing a fish kill in Charleston Harbor in 1966 [2]. The next year the laboratory purchased a GC-MS instrument exclusively for analysis of water samples. Each succeeding year has seen more laboratories, both here and abroad, begin to use GC-MS for pollutant analysis. Within the U.S. Environmental Protection Agency alone, for example, there are now 50 GC-MS systems.

Each year has also seen the number of compounds identified increase in direct correlation with the amount of effort devoted to this research. Recently, several international efforts have been initiated to prepare complete lists, accessible by computer, of all compounds identified in air, water, and biota. For each compound, information would be given on concentrations, geographical locations, frequency of occurrence, and toxicity.

As an example of typical materials identified by GC-MS, the following compounds were found three to five times in different industrial effluent surveys in the Southeastern United States from 1971 to 1973:

Acenapthene	Palmitic acid
Dehydroabietic acid	Pentachlorophenol
Dibenzofuran	Pentadecane
Dodecane	Phenol
2-Ethyl-1-hexanol	α-Terpineol
1-Methyl naphthalene	Tridecane
Naphthalene	Undecane
o-Nitrotoluene	

Among the materials commonly found in various waters are normal hydrocarbons containing up to 26 carbons, aromatic hydrocarbons, haloforms and chlorinated solvents, phthalate plasticizers, chlorinated ethers, phenols, pesticides, and various fatty acids.

I. GC-MS OPERATION

The gas chromatograph may be thought of as a specialized inlet for the mass spectrometer. In the most common mode of operation, a

compound enters the mass spectrometer and is exposed to an electron beam. This high-energy electron beam dislodges one or more electrons from the neutral molecule and leaves a charged, often unstable, molecular ion that usually fragments into several charged species of lower atomic weights. By electrical or magnetic methods, the MS then scans or "filters" all the ions so that they arrive at the detector in reasonably discrete groups. The groups consist of all the ions having the same atomic mass-to-charge ratio, that is, all singly charged ions of mass 43, all singly charged ions of mass 44, etc. The detector measures the current produced by the ions of each group and sends the signal to an appropriate recording and storage device, which in modern mass spectrometers is a computer. The computer can be instructed to operate a plotter or cathode-ray tube and display the MS scan in graphical form, such as Fig. 1. The x axis lists mass-to-charge values (m/e) rather than mass values. Usually the two are the same,

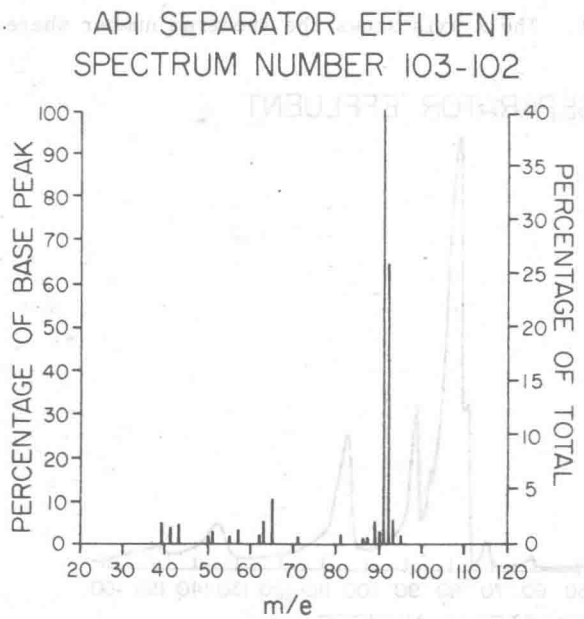

Figure 1. Typical bar graph representation of the mass spectrum of toluene.

but some molecules form ions of double charge and give a m/e signal that is half their actual mass. The most intense mass peak in a spectrum, called the *base peak*, is arbitrarily assigned an amplitude of 100. All the other fragment peaks are normalized to the base peak and their intensities are plotted as percentages of the base peak. This method of presenting the data helps make the spectra of identical compounds taken on different mass spectrometers directly comparable. This comparability feature, coupled with the fact that most individual organic compounds have unique fragmentation patterns, and hence unique spectra, makes MS a powerful identification tool.

In GC-MS, the mass spectrometer, usually under computer control, measures and stores a complete mass spectrum every 1 to 5 sec. As the run proceeds, the total ion current produced during each scan can be continuously plotted to provide a chromatogram like any other GC detector. At the end of the run, a reconstructed gas chromatogram (Fig. 2) is plotted. In this plot, the largest total ion current observed in the run is given a value of 100 and the other values are plotted relative to it. The x axis shows the spectrum number where

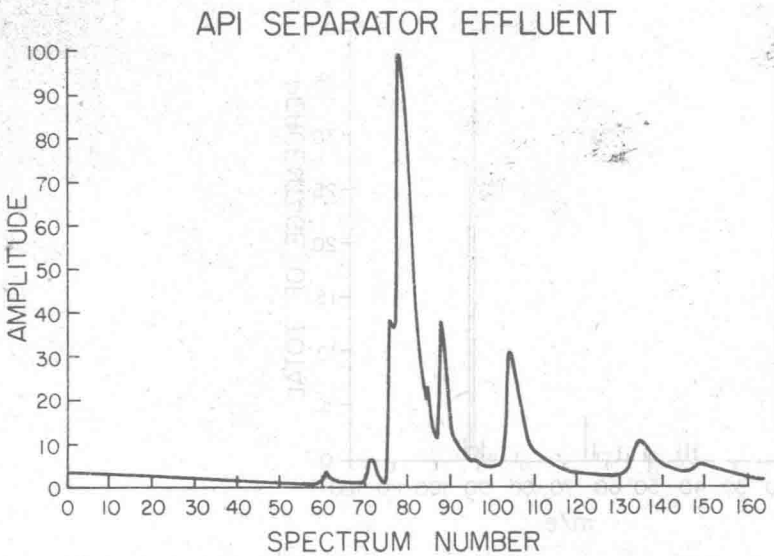

Figure 2. Reconstructed gas chromatogram.

each current was observed. Figure 1 is the spectrum representing the difference between spectrum 103 of Fig. 2 and the baseline spectrum 102.

II. SAMPLE PREPARATION

Before any GC-MS identification can be made, the sample must be obtained from the environment and processed so that it is suitable for gas chromatography and thus for GC-MS.

Occasionally, sample preparation is not required. Direct aqueous injection of 1 or 2 µl is sometimes used with samples suspected of having one or more components present at part-per-million levels [3].

The more common course, however, is to remove and concentrate the organics from the water by some form of extraction or sorption. The three most useful methods have been solvent extraction, sorption on solids (accumulators), and the most recent addition to the sampling arsenal, volatile organics analysis (VOA). Each of these methods has its limitations, and each month's technical literature contains papers describing improvements, criticisms, and modifications of sampling methods and devices.

The application of the VOA technique, developed largely by Bellar and Lichtenberg [4,5], was the key to the discovery of the widespread presence of chloroform, bromoform, and other bromine-chlorine-containing species in our drinking waters. Traces of these materials have probably been present in drinking waters since water-treatment systems adopted chlorination for bacterial disinfection. They had not been detected previously because the common extraction methods involve solvents (often chloroform itself) whose elution period in GC analysis overwhelms the area of the chromatogram where these materials usually occur.

With VOA, a small (5-500 ml) sample of water is placed in a closed system and a stream of inert gas is passed through the water and then led through a trop of porous polymer before venting to the room. The volatile organics that are stripped from the water are absorbed on the polymer. The unique feature of the polymers used as

traps is that they do not absorb water vapor. The trap is then placed in the heated inlet of a GC and the hot carrier gas desorbs the organics into the GC column.

The VOA technique has allowed quantitative detection of microgram-per-liter (ppb) amounts of materials that are less than 2% soluble in water and boil below about 150°C. A large number of aromatic and aliphatic hydrocarbons and their chlorine, bromine, and iodine derivatives fit these criteria. Although VOA is not quantitative for highly water soluble materials at low concentrations, enough of these materials can be isolated prior to analysis to allow qualitative identification by using a 500-ml or larger sample and heating it during the gas-purging step.

An alternate method for isolating low-molecular-weight alcohols, simple ketones, amines, volatile acids, ethers, and other similar materials is to collect the first 25-30 ml of distillate from a 500-ml sample, redistill the 25-ml portion, and collect the first milliliter. The analysis is by direct aqueous injection.

Many of the gas-chromatographable materials present in water are also solvent extractable, a factor that is a key to their isolation. Obtaining a representative sample is one of the major problems in extraction, as well as other preparation techniques, however. Lake and river waters are not homogeneous, and industrial effluents change with time. To solve this problem, some investigators prefer to take subsamples from various locations and at different times and to combine them for analysis. Moreover, many chemists avoid filtering the sample because the colloidal and suspended particulates frequently have organics sorbed on their surfaces.

The volume of the sample collected is usually 1 to 4 liters. Compounds present in a 1-liter sample at concentrations of 2 µg/l or greater will generally give good quality spectra when processed by extraction, concentration, and GC-MS techniques. Larger samples are required, however, if the analysis is for compounds present at lower concentrations. For example, 20-liter samples of municipal sewage have been processed with an apparent detection limit of 0.1 µg/l based

on an internal standard added to the extract before concentration. As a practical matter, however, multiple samples larger than about 4 liters are usually not processed by extraction because of the excessive labor and handling involved.

Because samples may have to be transported or stored for a considerable time before analysis, cooling or freezing is usually used to stop biological action and prevent chemical changes. The addition of strong acid as a preservative is not recommended because it degrades sensitive compounds such as geosmin and 2-methyl isoborneol (taste- and odor-causing compounds). Glass sample containers are usually packed in ice at the collection site and are refrigerated in the laboratory at about 4°C.

A typical isolation procedure is to extract a liter sample of water with two or three 50- to 100-ml portions of solvent. The combined extracts are evaporated to 1 ml or less for GC analysis.

The two most popular solvents are methylene chloride and chloroform. Methylene chloride has a much lower inhalation toxicity than chloroform and thus is safer to use. Other solvents in common use are petroleum ether, hexane (also 15% diethyl ether in hexane), diethyl ether, and carbon tetrachloride. Petroleum ether and hexane are so nonpolar that they do not effectively extract polar materials such as fatty acids and phenols. Therefore, some investigators prefer to do a first extraction with one of these solvents and then isolate the more polar materials with a second extraction using chloroform or methylene chloride. We do not recommend ether (except in very small quantities for diazomethane methylations) because of its flammability, the danger of explosion from peroxide impurities, and the presence of additives. Various preservatives are added to ether to inhibit peroxide formation but are not usually listed on the container label. For example, one peroxide inhibitor identified by GC-MS and later confirmed by the manufacturer was 2,6-ditertiarybutyl-p-cresol. This compound was recognized as an artifact because it also occurred in the blank. Finally, in solvent comparison studies, ether was found to be only half as effective as chloroform in extracting a paper-mill