

Development of Analytical Techniques for the Determination of Trace Organic Materials in Water

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FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

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ABSTRACT

A study dealing with the development of analytical chemical techniques for the determination and characterization of trace organics in water has been conducted.

Development of analytical techniques was conducted in conjunction with the definition of quality requirements and criteria for acceptance of desalinated water by the general consumer. A technique for the determination of total organic content of potable water has been applied to assessment of the water quality in municipalities of the western United States. The feasibility of determining major classes of organics present in natural water has been demonstrated. The method for differentiation between natural organics and chemicals introduced into product water by desalination processes is discussed.

INTRODUCTION

Chemical parameters affecting the efficiency and operation of a desalination process include the nature and concentration of the organic constituents present in water. Most studies in the field of desalination have been concerned with removal of the inorganic constituents, and minimal attention has been directed toward the organic matter present in the water. As a result, the effect of organics on the efficiencies of the desalination processes and the quality of the product waters are not known.

The concentration level of organic matter in surface sea water is of the order of 2 milligrams of carbon per liter. Of this, the amount of carbon per liter is 0.15 milligram for the biomass, 0.30 to 0.40 milligram for detritus, and 1.50 milligrams for the dissolved organics. The latter are arbitrarily defined as organic compounds in true solution and particulates less than approximately 0.5 micron in diameter. Many bays and coastal waters contain much more organic matter because of abundant aquatic life, proximity to rivers and harbors, pollution, circulation patterns, and other factors. The concentration level in these localities may approach 20 or more milligrams of carbon per liter.

Although the organic content of sea water may appear insignificant, its influence is manifested in several ways. The nature and concentration of organic matter in the feed water have a pronounced effect on the efficiencies of desalination processes. This is indicated by many of the engineering problems encountered in plant operations.

Periodic foaming problems in the distillation processes may originate in variations occurring in the biological-organic cycle of the sea. The foaming behavior of sea water has been shown to be related to the presence of organic matter as well as being influenced by salinity and temperature. The organic matter also appears to be a factor in the corrosion occurring in distillation plants. Corrosion rates can be increased by chelation of dissolved metal ions or solubilization of corrosion products by the dissolved organics present in the water.

The freezing and hydrate processes are affected by the organic materials present in the source water. Ice nucleation and crystal growth are extremely sensitive to interfacial tension changes caused by organics, and low temperatures tend to precipitate suspended matter. Studies have shown that the addition of organic matter increases the nucleation rate of ice in sea water, and that the nucleation rate can be decreased by aging or passing the sea water through absorbent charcoal¹. Furthermore, the hydrogen-bonding organics and amino acids which have been isolated from sea water are excellent ice nucleating agents²⁻⁵.

There is evidence that membrane processes are adversely affected by the presence of trace contaminants in the source water. Organic matter, either

dissolved or particulate, appears to be directly or indirectly responsible for the clogging of membranes observed in plants operating on some brackish waters⁶.

To deal with these operational problems on a sound engineering basis, the role of organics in the desalination processes must be clarified. The nature and seasonal variations of the organic matter in the source waters must be established. Characterization and determination of distribution of the classes of organics in the feed water, in the process stages within the desalination plant, and in the potable water must be carried out to effectively cope with many problems. Advancements and improvements in analytical methodology will be required to determine the roles of organic matter in the desalination processes.

The quality of desalinated waters must meet the requirements established for domestic water supplies if the water is to be acceptable to the consumer. These standards⁷ cover the presence and concentration of bacterial, organic, and inorganic species. The potability of water in regard to organic content has been defined at 0.2 ppm as determined by the carbon chloroform extract (CCE) procedure. This stringent requirement is the result of the U.S. Public Health Service policy⁷ which states:

"The most desirable condition is one in which the water supply delivered to the consumer contains no organic residues. In view of a general inability to clearly define the chemical and toxicological nature of this material, it is most desirable to limit it to the lowest obtainable level. Analysis of data available indicates that water supplies containing over 200 micrograms CCE/liter of water represent an exceptional and unwarranted dosage of the water consumer with ill-defined chemicals....."

In addition to the total residual organic matter, the presence of organic materials which impart taste or odor to the finished potable water will be objectionable to the consumer. Chlorination of processed waters, while destroying bacterial life, does not remove organic matter and may produce chlorinated organic compounds which are objectionable from either taste, odor, or toxicological considerations. A limit of 1 microgram/liter of phenol in water has been established because of the undesirable taste often resulting from chlorination of waters containing extremely low concentrations of phenolic materials⁷.

For potable water to meet established standards on water quality, the degree of organic removal and the fate of the organic materials in the desalination processes must be known. It is expected that distillation will remove a large portion of the organic materials together with the inorganic salts. However, heat ruptures biological cells which results in release of organic compounds into the water, and many organic compounds are known to readily steam distill. The efficiency of freezing processes in the removal of

organics during production of potable water will be dependent on the organic materials concentrating in the brine and on effective separation of brine from the ice. Membrane processes will afford a certain amount of mechanical exclusion of the organic matter from the desalinated water.

It is apparent that either the organic matter must be completely removed or the organics must be characterized and classified to determine if toxic or objectionable materials are present in the processed water. Because total organic removal is not economically practical, the advancement of analytical methodology to institute capabilities for characterizing the trace organics present in water is necessary. The product water must at least meet the quality standards of municipally distributed potable water. Therefore, this research program had as its objective method development for characterization of organics in naturally occurring water providing the criteria to which desalinated water should conform.

PROGRAM OBJECTIVES

This program was directed toward the development of the advanced analytical methodology and instrumentation necessary for process and quality control in the desalination technologies. The effort was concentrated in areas where the state-of-the-art methods and instrumentation cannot fulfill the requirements for data acquisition and process control in desalting plants. This includes methods and techniques for the monitoring of product water quality and the characterization of nonpotable water sources.

The research studies conducted under this contract were concentrated in two general areas.

DETERMINATION OF TOTAL ORGANIC CONTENT OF NATURAL WATER SOURCES

This area included refinement of the instrumentation developed for the determination of total organic content under O.S.W. Contract No. 14-01-0001-332. Demonstration of the utility of developed instrumentation in the field of chemical hydrology has been combined with the accumulation of data on the organic content of municipal water supplies in the western United States. These data can provide a guide in setting public acceptance standards for potable water produced by desalination processes.

CHEMICAL CHARACTERIZATION OF ORGANIC COMPOSITION OF NATURAL WATER SOURCES

This characterization was accomplished by means of selective separation of the organic matter into gross particulate matter, bacteria, and dissolved organics. The separation was achieved by cascade filtration, and the characterization of the resulting fractions was carried out by pyrographic means.

The developed methodology can be used for the differentiation between the natural organic background of water and the process chemicals introduced by desalination processes, and will provide information vital to acceptance of desalinated water by the customer.

The organic composition of any natural water body is the overall result of its history since its precipitation as rain or snow. Almost all of the organic substances in sea water are derived from the activity of living organisms. The physical state of the organic impurities is determined by either the biological activities occurring in the water or from solution of suspended particulate organic materials over a period of time.

The processes of solution of particulate matter are complex and the resulting fragments can range from small molecules present in true solution to minute particles having the composition of the parent substance. Subsequent contact of the fragments with other organic materials may alter the amounts present through equilibria changes or various processes such as adsorption, coagulation, or reaction to form other compounds.

The more important changes in the organic composition occur because of the biological activities in the water. These processes continuously both consume organic matter present in the water, and contribute dissolved and particulate organics to the water through mechanisms of excretion and decay of organisms. By far, most of the decomposition of organic matter in water is performed by bacteria and other microorganisms using the organic matter as food. The process of degradation is carried out mainly by the saprophytic bacteria which subsist upon dead organic matter by breaking it down into simpler compounds. When the bacteria feed on an organic compound, only a small portion of the compound is assimilated for cell building and the remainder is dissimilated as waste products. This degradation of organic matter is accomplished through the action of enzymes secreted by the bacterial cells. The multicellular fauna such as plankton have the ability to ingest particles of organic matter.

In comparison to the particulate and biological organics, there are approximately three times more dissolved organics in sea water. The fragmentary data available⁸ indicate that the dissolved organics in water can be classed into three major categories which are carbohydrates, proteins, and lipids.

The carbohydrate category includes polysaccharides, disaccharides, monosaccharides, intermediate degradation products, and the final simple molecule end-products. The later include glyceric acid, pyruvic acid, lactic acid, ethanol, formic acid, acetic acid, and others. The protein, or nitrogen-containing organics, category includes proteins, proteoses, and polypeptides together with decomposition products such as amino acids, amines, and amides. The lipids, or fats, are esters of the fatty acids with alcohols. This category includes the degradation products of the lipids.

Analytical methodology for the rapid measurement of the total organic content of water must possess both high sensitivity to organics in the presence of water and also the capability for measuring the totality of organic matter. To meet these requirements, the pyrographic concept for the direct summation of the organic matter in aqueous media was developed under O.S.W. Contract No. 14-01-0001-332⁹. The concept is based on the pyrolysis of the organic matter in the presence of water followed by the hydrogen flame ionization detection of the volatile organic fragments. During the current phase of the investigation, design of the instrumental system was further refined and its utility was demonstrated in the study of the organic content of waters used by Southwest and Pacific Coast municipalities. The information obtained in this study provides data on the actual organic content of waters received by the consumer, and consequently can be used as a guide for the establishment of realistic quality standards for desalinated water produced by processes developed under Office of Saline Water sponsorship.

INSTRUMENTATION

The instrumentation was assembled from commercially available equipment to specifically meet the requirements of the problem. The components of the instrumentation consisted of an Aerograph Model 600-C gas chromatograph equipped with a flame ionization detector, a tubular pyrolysis chamber heated by a microcombustion furnace, a custom-built sample injector, and a 1-millivolt recorder.

The hydrogen source for the flame ionization detector was either a hydrogen generator or a cylinder of hydrogen. With the latter source, the hydrogen flow was stabilized by sequential passage through a flow controller, a needle valve, and a flowmeter. The source of carrier gas was a steam generator. A 3/16-inch-OD by 10-foot stainless-steel column packed with 60 to 80 mesh glass beads was installed in the gas chromatograph.

The gas chromatograph was modified by removing the injector tube from its mounting block and heater. To connect the gas chromatographic column to the pyrolysis chamber, a stainless-steel adaptor (Fig. 1) was installed in the mounting block with the external tubing in a horizontal position. A septum closure was also provided on the adaptor.

The pyrolysis chamber was constructed from stainless-steel components and a nickel tube as shown in Fig. 1. A Nupro check valve (No. 2C) was connected to the carrier gas inlet of the chamber to prevent pressure surges into the steam generator. The chamber was filled with short lengths of nickel wire (1/16-inch OD by 3/16 inch long) retained by a small plug of quartz wool at each end of the nickel tube. The pyrolysis chamber was installed in the

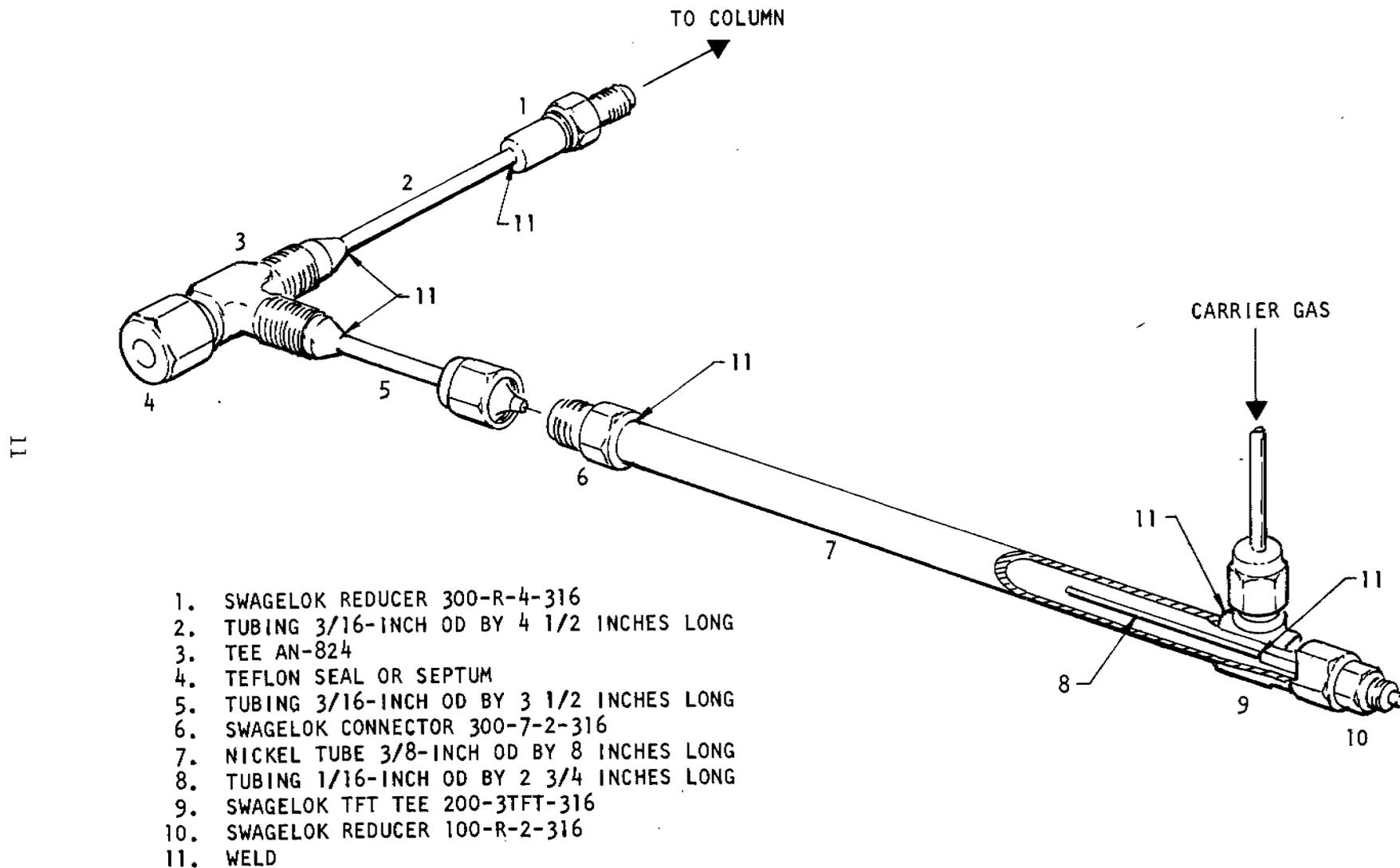


Figure 1. Adaptor and Pyrolysis Chamber

microcombustion furnace, connected to the adaptor, and then the carrier gas line was connected to the check valve. The external tubing of the adaptor, the check valve, and the portions of the pyrolysis chamber outside the furnace were maintained above 100°C with heating tapes to prevent condensation of steam.

The sample injector, constructed as shown in Fig. 2, was mounted horizontally and was connected to the Swagelok reducer on the pyrolysis chamber. The intake tubing dipped downward into the water sample.

ORGANIC CONTENT OF SOUTHWEST AND PACIFIC COAST MUNICIPAL WATERS

During the development of the pyrographic technique for measurement of the total organic content of desalinated waters, knowledge concerning the amounts of organic matter present in municipal water supplies was desired. The only information derived from a search of the literature was that a concentration of 200 micrograms/liter of carbon chloroform extract (CCE) should not be exceeded in municipal waters⁷. Also, clean surface and ground waters usually contain only 25 to 50 micrograms/liter of CCE although highly colored waters may exceed this level.

The carbon chloroform extract procedure is a standard method¹⁰ for measuring the organic content of potable waters. In practice, the organics are adsorbed on activated carbon in a cylinder placed in a waterline for 2 weeks. Then the activated carbon is extracted with chloroform which is subsequently evaporated to yield a weighable residue. It is realized that the method does not determine the total organic content of water. The carbon does not adsorb all the organics and the chloroform solvent does not recover all of the adsorbed materials. It is stated that recoveries of selected, easily adsorbed materials may range from 50 to 90 percent. Recoveries of the organic matter existing in natural and municipal waters are not known.

Because the literature yielded no information on actual organic content, a study was initiated to accumulate data on the water supplies available to consumers through municipal distribution systems. Such information would be used as a guide in establishing acceptance criteria for desalinated water. For this investigation, municipal supplies from communities in the Southwest and Pacific Coast regions of the United States were utilized. This permitted assessment of three of the parameters which could affect the organic content of municipal waters. These parameters are source, climate, and treatment. In the regions considered, the sources are both surface and ground waters, and the climate ranges from desert to rain forest with the accompanying change in vegetation. Treatment ranged from simple chlorination to processes involving coagulation, filtration, and chlorination.

Samples of water as delivered to the consumer from each municipal distribution system were collected in clean 4-ounce bottles which were immediately sealed with foil-lined screw caps. The bottles had been previously cleaned with

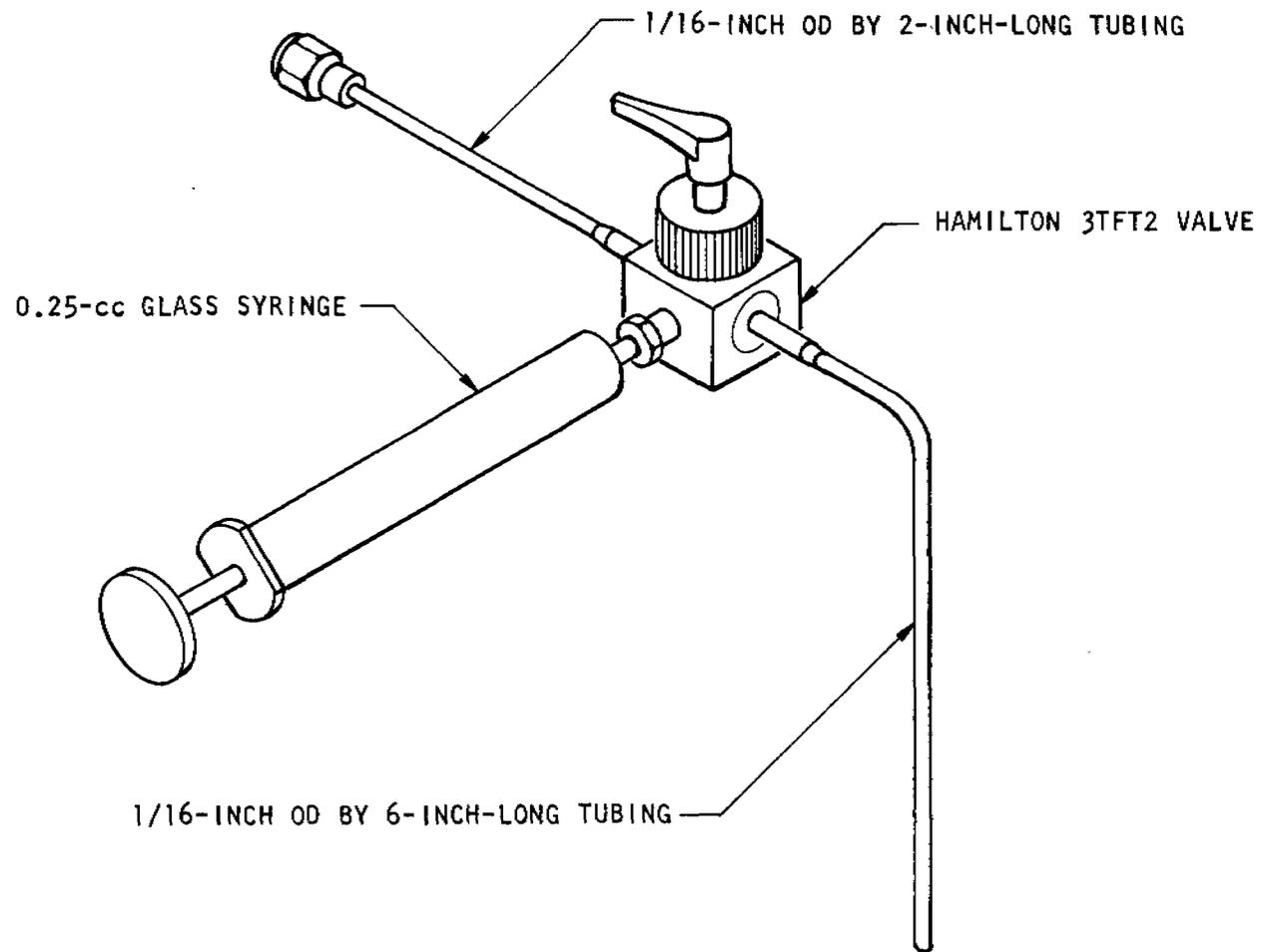


Figure 2. Sample Injector

hot nitric acid containing 10-percent sulfuric acid, thoroughly rinsed with triply distilled water, dried in a protective environment, and sealed. At the time of sample collection, the bottle was first rinsed several times with the water being sampled. All analyses were conducted as soon as possible after sample collection.

In the procedure, steam serves as the carrier gas and 0.25-cc portions of a water sample are injected at 6-minute intervals into the pyrolysis chamber. The fragments, which are produced in the pyrolysis of the organic matter present in the water, are transported by the steam through the flow stabilization column to the detector. Because no separation is achieved on the stabilization column, these organic fragments are measured as a sum by the flame ionization detector. After the average peak area for the set of peaks is obtained by planimetry, the organic content of the water sample is calculated. Calibration is performed with materials representative of the major organic classes present in water.

The source of each municipal water supply was ascertained through reference to a Public Health Service compilation¹¹, and in some cases, by direct inquiry. The treatment given the water before delivery to the consumer and other data are also tabulated in the same publication.

The organic content of the municipal water supplies originating from ground waters are presented in Table 1. These municipalities are located in Southern California and in the Southwest, and all use wells as the source of water with the exception of Grand Canyon which uses an infiltration gallery. In general, these waters are either not given any treatment or are only chlorinated before use. An examination of Table 1 shows these municipal water supplies averaged 0.9 mg C/liter with a range of 0.7 to 1.6 mg C/liter. From these results, it appears that a water supply obtained from ground sources in a region with a low annual rainfall and sparse vegetation would have an organic content of approximately 1 mg C/liter. No data on organic contents are available for well waters from Northern California or Oregon where the precipitation is greater and the lands are heavily forested.

In Table 2, organic contents are presented for the water supplies in municipalities utilizing surface waters as a source. The treatment of these waters before distribution to the consumer varies from only chlorination to a complete purification treatment including coagulation and filtration. There was no correlation between the amount of organic matter and the treatment given the water.

According to the data in Table 2, municipal supplies obtained from surface sources generally have much higher organic contents than those procured from ground sources. Furthermore, the effects of climate, and vegetation, on the organic content of the waters can be seen. Because the climate in the northern Pacific Coast region has a high rainfall, the drainage basins

of the streams are heavily forested. This vegetation must contribute very significantly to the organic content of the water. The municipalities in Oregon and northern California have waters with high organic contents. The values range from 3.7 mg C/liter for Santa Rosa, California to 7.7 mg C/liter for Portland and Eugene in Oregon. The source of water for Portland is a protected, uninhabited mountain watershed on the western side of the Cascade Mountains. This watershed, which is closed to public entry, is densely covered with trees and other vegetation. Consequently, the organic matter in this municipal water is derived solely from vegetation and none originates from man-made pollution.

TABLE 1

ORGANIC CONTENT OF MUNICIPAL WATERS FROM GROUND SOURCES

<u>Municipality</u>	<u>Organic Content, mg C/liter</u>
Arizona:	
Flagstaff	0.7
Grand Canyon	0.8
Kingman	1.6
California:	
Carlsbad	0.8
Paso Robles	0.9
Salinas	0.9
San Juan Capistrano	1.5
Santa Ana	0.7
Santa Barbara	1.0
Thousand Oaks	0.9
New Mexico:	
Albuquerque	0.9
Grants	0.7

In contrast, waters procured from streams in desert or semi-arid Southwest region with sparse vegetation have a much lower organic content. It appears the level of organics in the streams approaches that of the ground waters in the area. This may be seen by comparing the two nearby municipalities of Santa Fe and Albuquerque. The organic content of Santa Fe water obtained from the Santa Fe River was 1.3 mg C/liter and that of Albuquerque water from wells was 0.9 mg C/liter. Similarly, waters distributed in the adjacent communities of Flagstaff and Williams originate in ground and surface sources and had organic contents of 0.7 and 1.3 mg C/liter, respectively.

TABLE 2

ORGANIC MATTER IN WATERS DISTRIBUTED BY MUNICIPALITIES
UTILIZING SURFACE SOURCES

<u>Municipality</u>	<u>Source</u>	<u>Organic Content, mg C/liter</u>
Arizona:		
Williams	Surface	1.3
California:		
Alameda	Reservoir	2.1
Del Mar	Cottonwood Creek and Otay River	1.1
Los Angeles	Owens River	2.7
Redding	Sacramento River	4.8
San Diego	Cottonwood Creek and Otay River	1.4
San Luis Obispo	Salinas River and Creek	1.3
San Mateo	Lakes and Streams	1.1
Santa Rosa	Russian River	3.7
Santee	Cuyamaca Lake	1.6
Ventura	Ventura River	2.5
Nevada:		
Las Vegas	Lake Mead	1.3
Reno	Truckee River and Hunter Creek	1.6
New Mexico:		
Santa Fe	Santa Fe River	1.3
Oregon:		
Eugene	McKenzie River	7.7
Gold Beach	Rogue River	6.3
Medford	Big Butte Springs and Bear Creek	4.7
Portland	Bull Run Lake and Bull Run River	7.7
Seal Rock	Deer Creek	3.9
Tillamook	Killiam and Fawcett Creeks	6.4

ANALYTICAL APPROACH

The organic content of natural waters consists essentially of gross particulate matter, dissolved organics, and biomass. The analytical approach to the characterization of the organic composition of natural waters investigated as part of this program consisted of:

1. Study of the methods for separation of the principal physical forms of organic matter in water
2. Development of pyrographic methodology for the characterization of the principal chemical classes of organic matter found in water
3. Development of mathematical means for interpretation of the complex pyrograms

Methods of Separation

In conjunction with the development of means for characterizing organic materials, the classification of organic and biological matter in water into particulate, bacteria, and dissolved organics was undertaken. The approach was based on the concept of selective separation through cascade filtration followed by characterization.

In this concept, the organic and biological content of water is separated by filtration through a series of metal membrane filters. A simple two-stage cascade filtration apparatus designed and built under this program is shown in Fig. 3. This filtration assemblage consists of a reservoir connected to two filter holders in series terminating in a collection container. In operation, 5- and 0.2-micron metal membrane filters are placed in the first and second filter holders, respectively. The water sample placed in the reservoir is pressurized with gaseous nitrogen to drive the water through the filters. The 5-micron filter retains gross particulate matter and the 0.2-micron filter collects the bacteria. The filtered water containing the dissolved organics accumulates in the collection container. The two metal membrane filters and the filtered water are then ready for analysis by pyrographic techniques.

The dissolved organics in the filtered water are then analyzed using the characterization apparatus. The residue on the metal membrane filter is pyrolyzed in a special pyrolysis chamber designed to permit rapid introduction of the filter into the hot zone.

A schematic of a proposed, more complex multistage cascade filtration assemblage is shown in Fig. 4. This will yield a more detailed classification of the organic matter in water. The application of pyrolysis-gas chromatographic techniques to each stage will yield information both on the total organic material in the class and on the compositional character of that class.

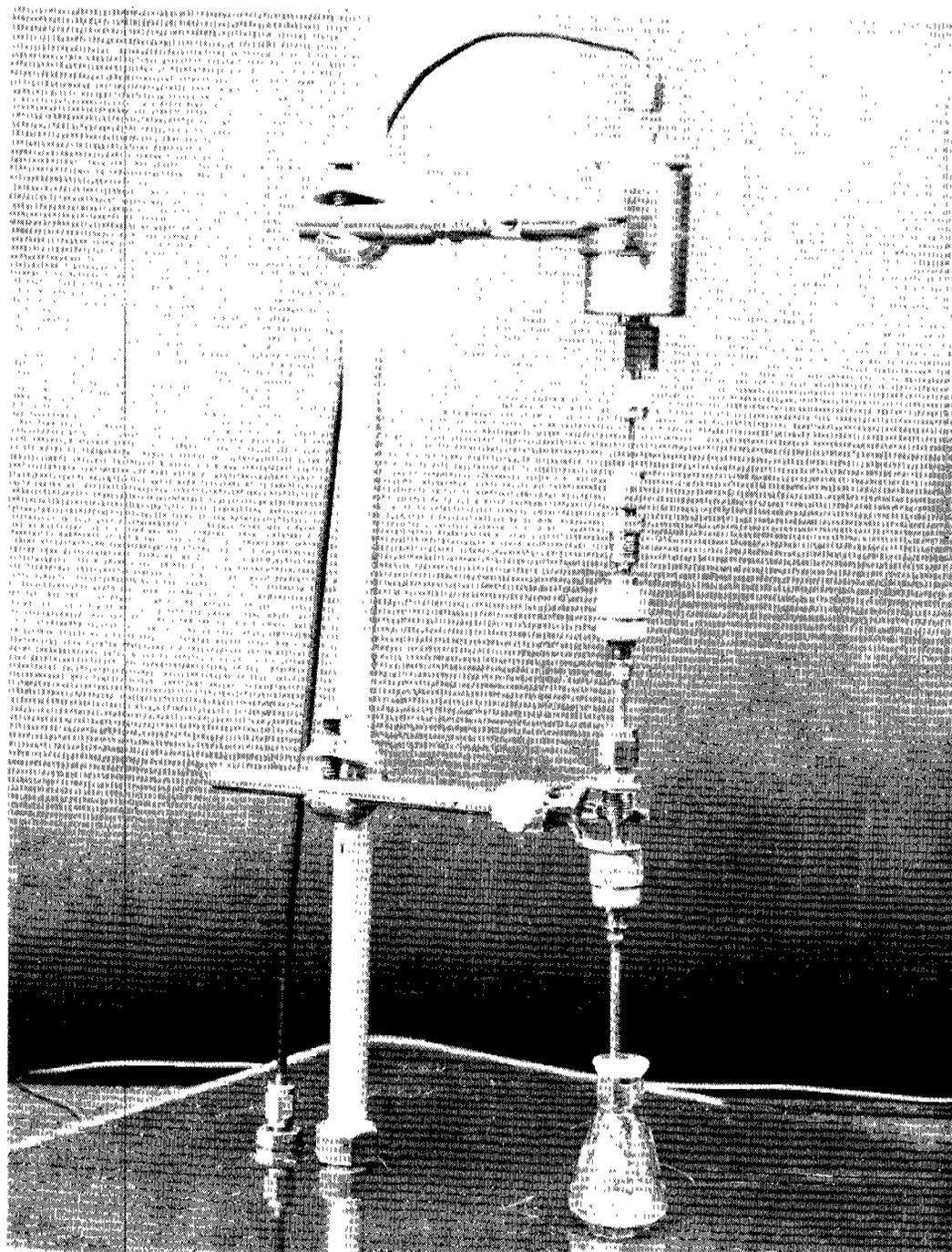


Figure 3. Two-Stage Cascade Filtration Apparatus

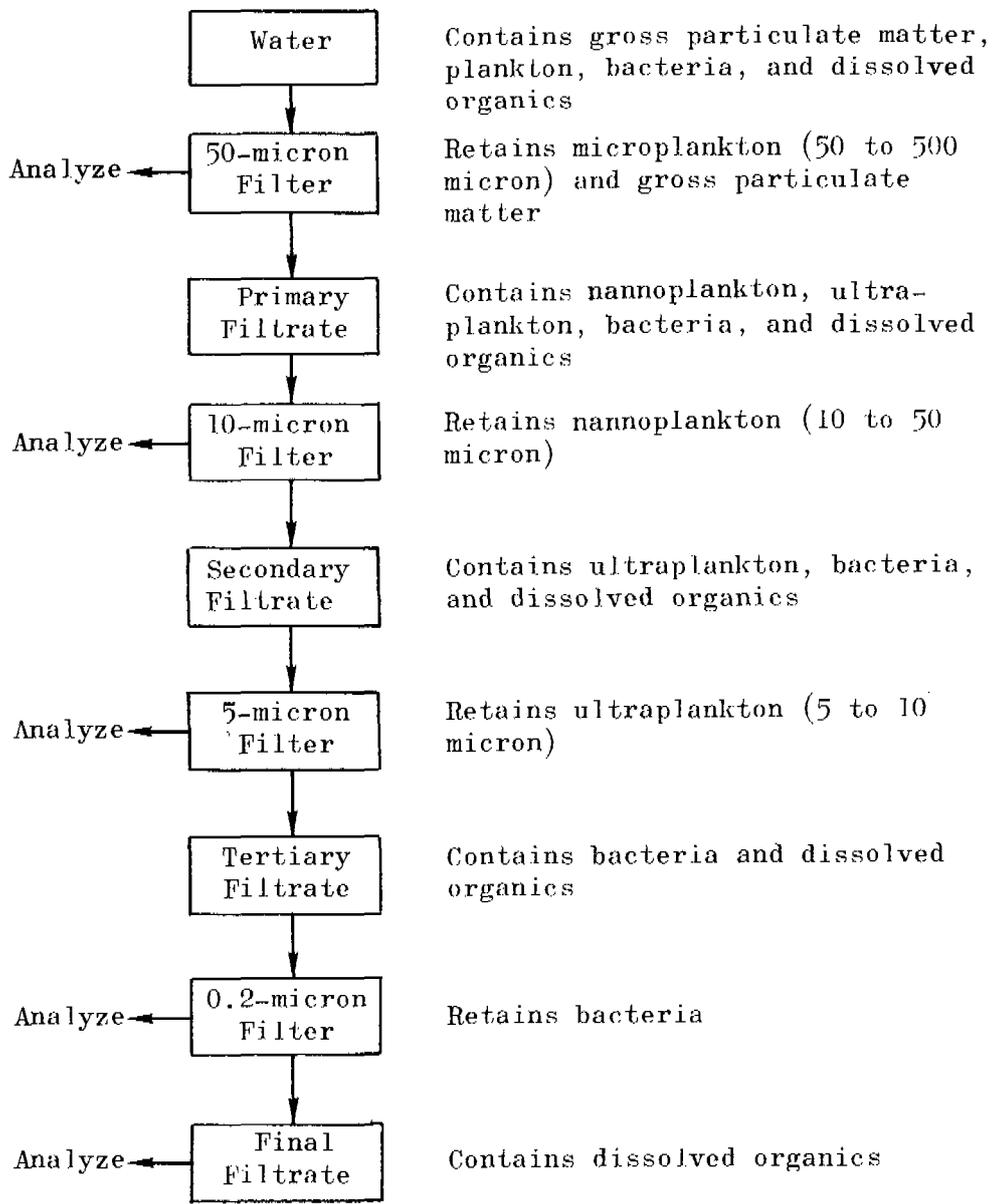


Figure 4. Schematic of Multistage Cascade Filtration

Pyrolytic Characterization

In pyrolysis, an organic molecule subjected to an elevated temperature will decompose into several preferential fragments. At high temperatures, the organic compound will fragment mainly into methane, hydrogen, carbon monoxide, and a few other small molecules. When the pyrolysis is conducted at lower temperatures, short-chain organic fragments are obtained with a corresponding decrease in methane, hydrogen, and other simple molecules.

The bulk of pyrolytic investigations have been conducted at temperatures below 600°C. The reported data are useful because they indicate the fragments formed, the stability of molecular bonds, and the reaction trends with temperature. A considerable number of organic materials, including some natural substances, have been pyrolyzed with their fragmentation products examined in some detail. Starch, cellulose, maltose, and sucrose pyrolyzed at 300°C formed carbon dioxide, acetaldehyde, furan, propionaldehyde, acetone, acrolein, 2-methylfuran, water, and some unidentified light gases¹². There were some differences in the magnitude of peaks in the patterns for the different materials. Under the same conditions, alginic acid gave the same products except only a negligible amount of propionaldehyde was formed. Hemicellulose fragmented at this temperature into carbon dioxide, acetaldehyde, methyl formate, furan, methanol, 2-methylfuran, ethanol, and water. In another study on starch at 400°C, the additional products 2-butanone, 2,3-butadiene, and methyl-1-buten-3-one were formed¹³.

At 300°C, the major products from the pyrolysis of proteins and amino acids were ammonia and methyl-, ethyl-, diethyl-, diisopropyl-, and other amines¹⁴. The amino acids gave various proportions of the amines which correlated to some extent with molecular structures.

There is evidence that lipids and fats cleave first into the corresponding fatty acids and other fragments in a manner analogous to ester degradation¹⁵. The fatty acids then can decarboxylate to form hydrocarbons which can fragment to methane and other hydrocarbon molecules.

In addition to these natural products, the degradation of specific organic compounds has been studied under various conditions and temperatures. These studies provide information of use in the interpretation of the pyrograms obtained with complex materials.

Bacteria can be differentiated on the basis of chemical compounds which are unique to the microorganisms. Extension of this concept has led to both qualitative and quantitative differentiation between individual species. The feasibility of utilizing gas chromatography as a sensitive and rapid method for the analysis of lipids as a basis for the classification of microorganisms by chemical composition has been investigated¹⁶. The lipids were extracted and transesterified to carboxylic acid methyl esters which were resolved to provide distinctive chromatographic patterns. Similarities

in the lipid composition were found among selected species but differences were also noted. A more direct approach to the characterization of bacteria has been gas chromatographic examinations of their pyrolyzates^{17,18}. Under the experimental conditions, the patterns were quite similar for many species but there were also distinct differences in the number of peaks, the magnitude of peaks, and the absence of peaks. The pattern from a species contained sufficient data to constitute a unique fingerprint for the species. These techniques have yet to be applied to water samples containing a mixture of bacterial species.

The organic fragments obtained during pyrolysis are related to the molecular structure of the parent material. In many cases, certain fragments are obtained only from particular organic materials. Thus, the organics in a homologous series or class of compounds can have pyrolytic patterns with one or more peaks characteristic of the class or series. The chromatograms of the pyrolytic fragments from such materials, including bacteria, will possess magnitude differences in the common peaks as well as some characteristic peaks. All of the characteristic fragments may not be resolved on the pattern obtained with one column substrate. However, by using two parallel columns with different substrates, the two different patterns obtained will make it possible to differentiate the peaks of the characteristic fragments. In this manner, the complete qualitative and quantitative characterization of the organic classes in a mixture can be carried out.

Mathematical Treatment of Pyrograms

The mathematical treatment of pyrograms is limited in this presentation to the discussion concerning three major classes of organics present in natural waters: carbohydrates, polypeptides, and lipids. The organics present in water will behave similarly but not necessarily exactly like the compounds selected to represent the naturally occurring compounds. Therefore, the most desirable treatment of the pyrographic data is one which allows extraction of maximum information from all the available data. This is best accomplished by using least squares analysis techniques.

In the treatment of the pyrographic data, three basic assumptions will be made:

1. The peak heights (or areas) are proportional to concentration of the class of compounds.
2. The three classes of compounds, when pyrolyzed, will produce fragments affording many peaks at identical retention times, but the ratio of fragments produced by a given class is unique to that class. In addition, there may be specific peaks for a given class of compounds.
3. The differences in specific peak heights among compounds within a class are small compared with the differences between classes.

The total peak height at retention time t can be represented by the linear equation:

$$\sum_{j=1}^3 a_j x_j = b \quad (1)$$

where

a_j = peak height per unit concentration for the j th known class of compounds

x_j = concentration of the j th class of compounds in the unknown

b = total observed peak height at retention time t

The same form of Eq. 1 is valid for all other peaks. The constants a_j and b will differ for each peak but the x_j is the same. Because the equations have the x_j in common, they can be solved simultaneously. The system of simultaneous equations is represented by:

$$\sum_{j=1}^3 a_{ij} x_j = b_i \quad (2)$$

where i identifies the peak and ranges from 1 to n . Because i is greater than j , there are more equations than unknowns, and the system is overdetermined.

In practice, the solution to the system of Eq. 2 is not exact. That is, there are no values of x_1 , x_2 , and x_3 which will satisfy all of the n equations. A stepwise regression program can be used to obtain the best solution in the least squares sense. Because the equations are not exact, they may be expressed as follows:

$$\sum_{j=1}^3 a_{ij} x_j - b_i = r_i \quad (i = 1, 2, \dots, n) \quad (3)$$

where r_i , the residuals, are measures of the inexactness. The best solution in the least squares sense is the one which makes the sum of the squares of the residuals a minimum. The condition for this requirement is that:

$$\frac{\partial}{\partial x_j} \left(\sum_{i=1}^n r_i^2 \right) = 0 \quad (4)$$

where $j = 1, 2, 3$. Equation 4 is a system of three linear equations in three unknowns. The solution to this set of equations is represented by the following matrix equation:

$$\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = (A^T A)^{-1} A^T \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{pmatrix} \quad (5)$$

where

$$A = \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{13} \\ a_{21} & a_{22} & \cdots & a_{23} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n,1} & a_{n,2} & \cdots & a_{n,3} \end{pmatrix}$$

A^T = Transpose of A

$(A^T A)^{-1}$ = Inverse of $(A^T A)$

The solution to Eq. 5 is unique and is the solution which results in the best fit of the experimental data in the least squares sense.

EXPERIMENTAL

The experimental effort of this phase of the program was centered principally in four areas of activity:

1. Design of improved instrumentation for the pyrolytic characterization of organics in water
2. Evaluation of gas chromatographic columns for separation of the pyrolytic fragments
3. Optimization of the pyrolytic temperature regime
4. Demonstration of the feasibility of the developed technique by developing specific pyrograms for three principal classes of natural organics found in water--carbohydrates, polypeptides, and lipids.

Instrumentation

The instrumentation for the pyrographic characterization of organics in water was based on the principles, operations, and knowledge gained during

the development of methodology for the determination of total organic content in water. A number of modifications and improvements were incorporated into the design of the instrumentation used in this phase of the study. The pyrograph consists of several subsystems: sample injector, pyrolytic unit, carrier gas source, fragment separator, detector, and readout.

Sample Injector. The sample injector for the pyrograph must permit injection of optimum size samples without alteration of sample composition or introduction of contaminants. Prior experience in pyrolytic water analysis has shown that introduction of water samples by conventional injection through the gas chromatographic septums yields pyrolytic patterns with large non-reproducible peaks. It was found that these peaks originate from the minute septum particles which adhere to the syringe needle and are carried into the pyrolysis zone. A three-way injection valve, similar to the one described in the instrumentation for total organic content of water was incorporated in the pyrograph for sample injection.

Carrier Gas Generator. The commercial steam generator used in initial investigations was found to be performing poorly in terms of control of temperature and steam flow, and consequently, a custom built generator was designed. This consisted of a 1.7-liter stainless-steel sphere which was heated with a heating tape. The thermal conditions were regulated by a thermocouple sensor. The generator was equipped with a pressure gage and was connected by 1/8-inch-OD heated tubing through a check valve to the pyrolysis subsystem.

Pyrolysis Unit. The pyrolysis unit consisted of a heavy-duty Lindberg furnace containing a 5-foot-long, 3/8-inch-OD coiled nickel tube. The tube was filled with granular nickel.

Fragment Separation Unit. The fragment separation unit consisted of a Wilkens HyFi Model 600C gas chromatograph equipped with suitable columns.

Detector. The detector was a hydrogen flame ionization sensor manufactured by Wilkens Instrument Co.

Readout. The readout consisted of Sargent Model "SR" 1-millivolt full-scale deflection recorder with multispeed capability.

Column Evaluation

Characterization of the dissolved water organics places stringent requirements on the operating parameters. Steam must be used as the carrier gas to minimize the effects of injected samples on the hydrogen flame ionization detector. In addition, the column must be stable at temperatures above 100°C.

A concentrated effort was made to evaluate all potentially promising gas chromatographic columns. The evaluation was based on several important criteria: (1) the resolution of the pyrolytic fragments from each organic class, (2) the stability of the column in the temperature range from 100 to 200°C, and (3) the extent of column bleeding at elevated temperatures.

In the evaluation, three materials were selected to represent the three major classes of compounds found in natural waters. These were soluble potato starch, gelatin, and heptanoic acid which represent the carbohydrates, polypeptides, and lipids, respectively. One-tenth milliliter aliquots of individual aqueous solutions of each compound were pyrolyzed at 600 and 800°C. The pyrolytic fragments were transported by the steam carrier gas through the 3/16-inch-OD by 6-foot-long gas chromatographic columns to the detector.

The column substrates were selected for investigation on the basis of reported stability at high temperatures and their resolution of different classes of compounds. These substrates included SE-30, Carbowax 20M, silicone oil 710, and m-phenylether (five ring). Porous glass was used as the support for SE-30. The other substrates were coated on 60 to 80 mesh Chromosorb W which had been acid washed and treated with dimethyldichlorosilane to minimize peak tailing.

The pyrograms obtained with SE-30 on porous glass afforded poor sensitivity and reproducibility. The silicone oil column exhibited only moderate temperature stability. Although this column resolved gelatin fragments fairly well, neither heptanoic acid nor starch fragments were notably separated. Both Carbowax 20M and m-phenylether (five ring) substrates exhibit very good temperature stability and separation of pyrolytic fragments. Measurements of retention times show that a total of 14 peaks would be obtained in the pyrolysis of a mixture of the three components on the Carbowax 20M column. The pyrograms indicated that sufficient separation of fragments from natural organics can be developed for application of the mathematical techniques discussed previously.

To complete the column evaluation, three additional substrates were investigated: ethylene glycol adipate, diethylene glycol malonate, and Apiezon L. Examination of the pyrograms obtained at 600 and 800°C for starch, gelatin, and heptanoic acid did not show these substrates to be superior to the Carbowax 20M. As with the substrates investigated previously, these three substrates were deficient in either stability or in resolution of the fragments from the three materials used. Because the Carbowax 20M substrate provided reasonable separation of pyrolytic fragments and was temperature stable, it was further investigated.

Temperature conditions for pyrolysis were also studied. The pyrograms for aqueous solutions of gelatin, starch, and heptanoic acid were obtained at 500, 600 and 700°C. More complex spectra were obtained in all cases at higher pyrolysis temperatures. This would provide better means for subsequent mathematical treatment of the data.

Demonstration of Feasibility of the Pyrographic Technique

The three major classes of organic materials found in natural waters are carbohydrates, polypeptides, and lipids. To illustrate the differences in the pyrolytic patterns, pyrograms were obtained at 700°C for aqueous solutions of starch, gelatin, and heptanoic acid, which can be considered as representatives of the major classes of organics found in water. The pyrograms presented in Fig. 5 through 7 show the similarities and differences obtained for materials of different molecular structure.

Examination of the pyrograms revealed a total of 14 peaks which would be discernible in the pyrolysis of a water sample containing all three materials. The retention times and heights of these peaks are presented in Table 3 for ease of comparison.

TABLE 3
PYROGRAPHIC DATA FOR THREE ORGANIC MATERIALS

Peak No.	Retention Time, minutes	Peak Height		
		Starch	Gelatin	Heptanoic Acid
1	0.22	66	100+	100+
2	0.29	5.5	74.5	46
3	0.34		11.5	18
4	0.38	61.5		
5	0.41		26.5	1.5
6	0.46	2	13	
7	0.49			24
8	0.54	1		
9	0.59		5	
10	0.70		21	
11	0.89		16.5	
12	1.24		8	
13	4.10	2.5		1
14	5.34		2	

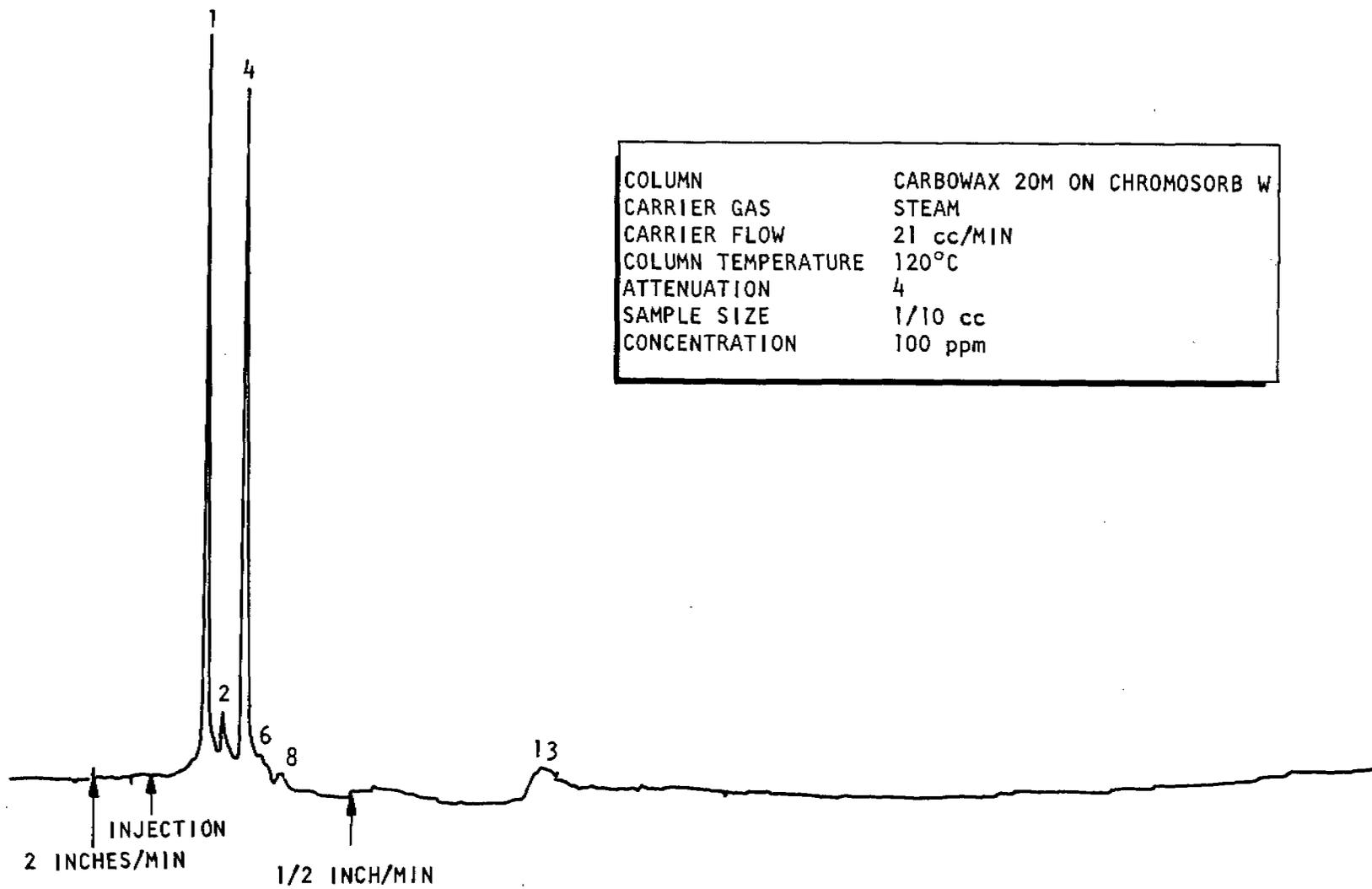


Figure 5. Pyrogram of Aqueous Starch Solution

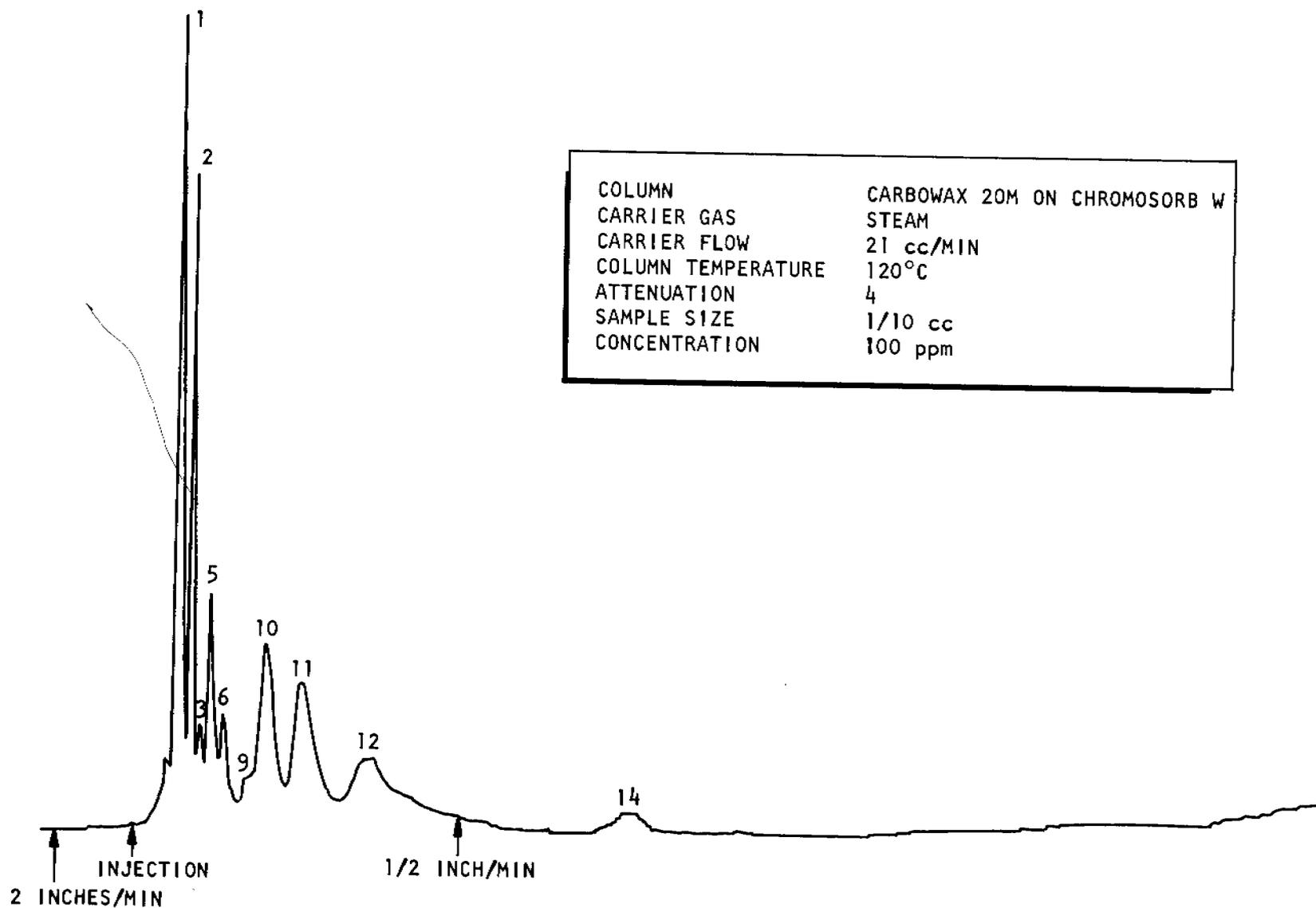


Figure 6. Pyrogram of Aqueous Gelatin Solution

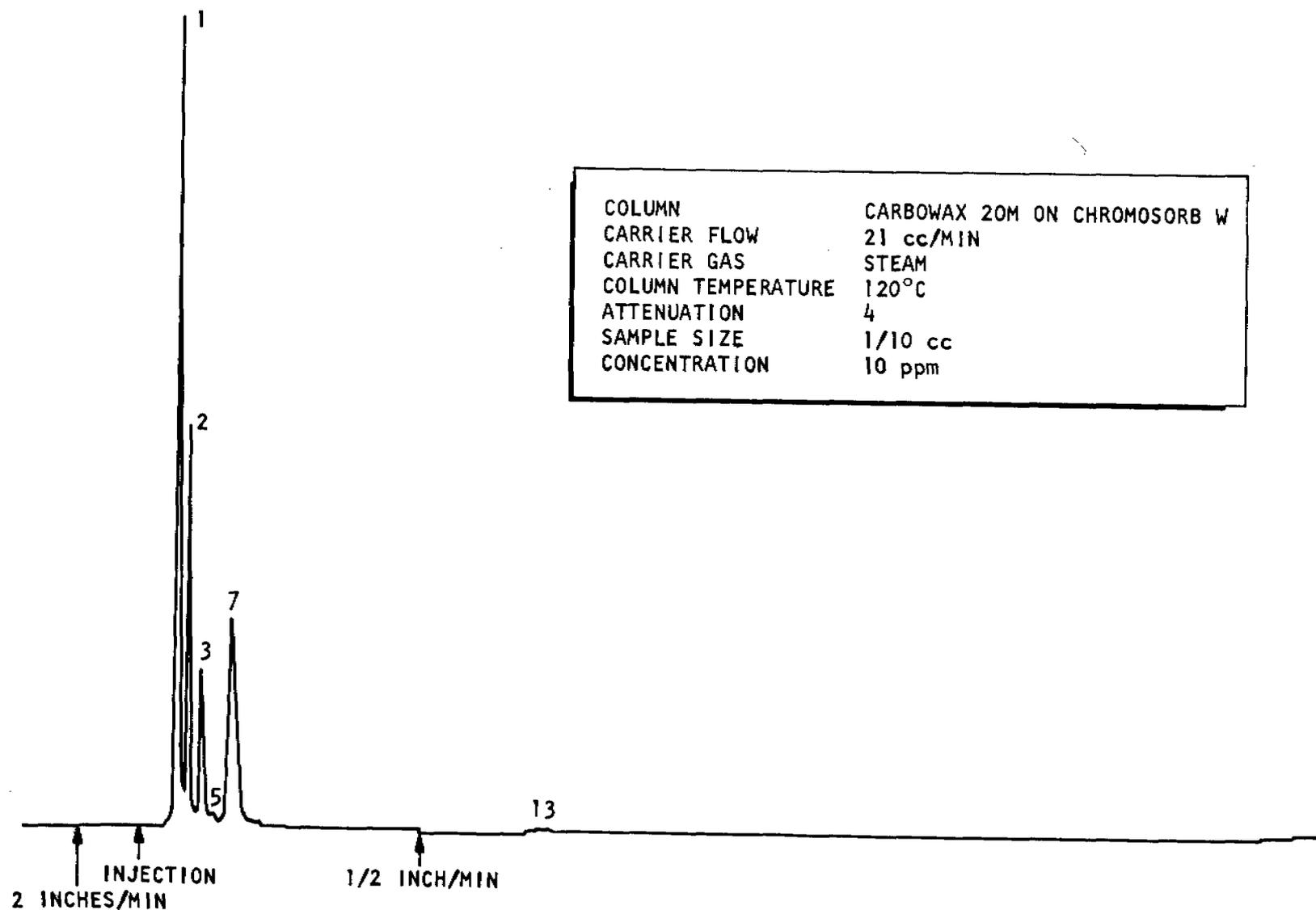


Figure 7. Pyrogram of Aqueous Heptanoic Acid Solution

In a water sample containing a mixture of these organics, all three materials would contribute to most of the major peaks. However, there would also be some distinctive peaks which would originate from only one of the materials (blocked numbers in Table 3). As examination of Table 3 indicates, starch produces the fully distinctive peak 4 at a retention time of 0.38 minute and peak 8 at a retention time of 0.54 minute. Gelatin is fully characterized by a group of distinctive peaks 9 through 12 with retention times of 0.59, 0.70, 0.89, and 1.24 minutes, respectively, and peak 14 at a retention time of 5.39 minutes. Heptanoic acid produced one fully distinctive peak 24 at a retention time of 0.49 minute. While specific and distinctive peaks provide means for identification of certain organic groups, the totality of the pyrogram represents a considerably larger amount of information. Such information can be extracted mathematically. Instead of attempting to use distinctive peaks in interpreting the analytical data, it is better to treat the entire pyrogram by mathematical techniques to develop expressions relating all peaks to the amount of each component.

Characterization of Natural Water Sources

The pyrographic instrumentation and technique were applied to the pyrolytic characterization of natural water sources. In the initial experiment, the instrumentation and procedure was used as described previously. The separation column was 6 feet long, and was filled with a packing of 20-percent Carbowax 20M on Chromosorb W.

A sample of water from Lake Eleanor gave the pyrograms shown in Fig. 8 and 9 when pyrolyzed at 650 and 800°C, respectively. Lake Eleanor is located in the Santa Monica mountains in Ventura County, California. It is a small lake constructed in a stream bed for the purpose of storing runoff water for use in the summer months. The lake is filled by the winter rains, and very little water flows into or out of the lake during the remainder of the year. The shallow portions of the shoreline abound in reeds and marshy plants, and numerous masses of algae float at various points on the water surface. As a result, the organic content of the water can be expected to be high.

At a pyrolysis temperature of 650°C, there appears to be a number of low molecular fragments produced (Fig. 8). The pyrogram shows seven distinct peaks and one shoulder during the first few minutes after injection of the sample. Considerable quantities of unresolved organic fragments are also evident. When pyrolyzed at 800°C, the lake water (Fig. 9) gives three peaks immediately after injection which are followed by a large broad peak with some small superimposed peaks. This pyrogram indicates that some of the organic matter present in the sample is degraded at the higher temperature into fragments with longer retention times on the column.

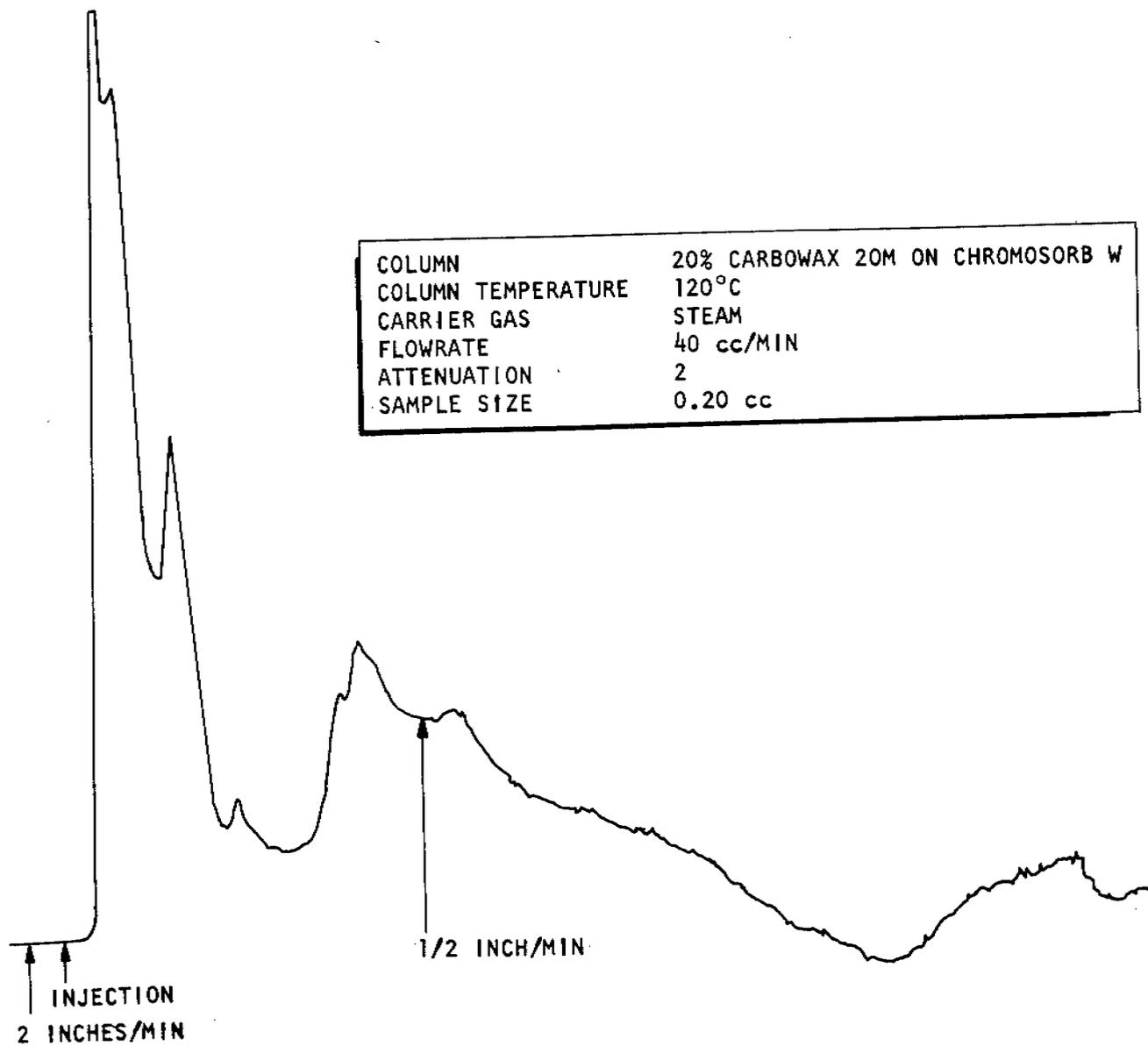


Figure 8. Water From Lake Eleanor Pyrolyzed at 650°C

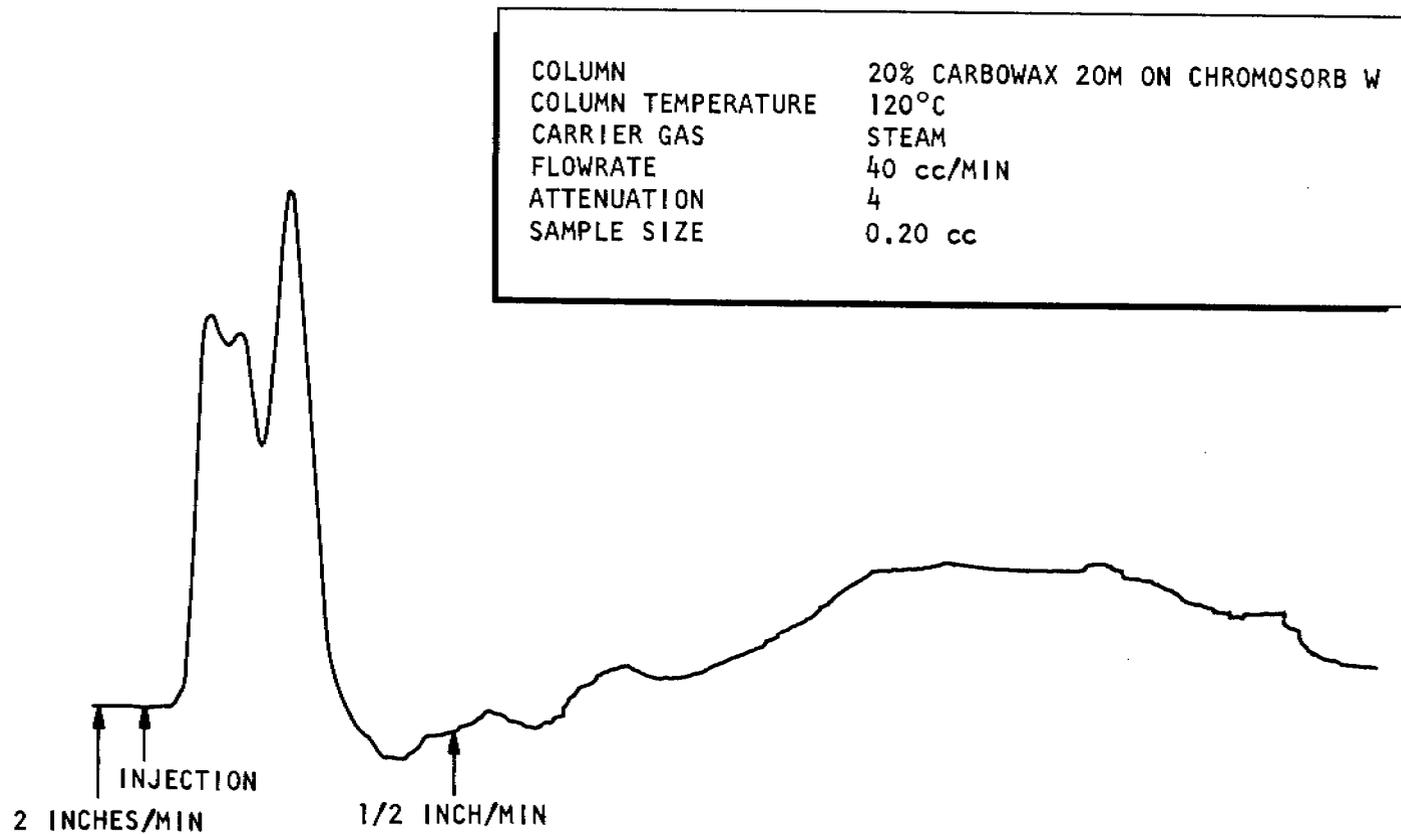


Figure 9. Pyrogram of Water from Lake Eleanor at 800°C

Although it was possible to pyrolytically characterize this natural water source, the peak resolution was of a low order. Therefore, a Poropak column was used for subsequent analysis of natural water sources. The Poropak substrate does not contain a liquid phase, and was found to be superior to the Carbowax 20M in resolving the organic fragments obtained from natural water sources.

The instrumental conditions used with the Poropak column were as follows:

Column	7-1/2 foot by 3/16-inch OD filled with 50 to 80 mesh Poropak Q preceded by a 2-1/2-foot by 3/16-inch OD column filled with 60 to 80 mesh glass beads
Column Temperature	120°C
Pyrolysis Temperature	700°C
Carrier Gas	Steam
Carrier Flowrate	22 cc/min
Detector	Hydrogen Flame Ionization
Hydrogen Flowrate	40 cc/min
Air Flowrate	250 cc/min
Chart Speed	1/2 inch/min
Sample Size	0.20 cc

The water samples of natural origin were procured from streams in localities removed from habitation and other sources of contamination. These localities also differed in geographic and climatic aspects. The pyrographic spectrum of each water sample was obtained with the Poropak column at an attenuation of 2 and the preceding instrumental conditions. These pyrograms are shown in Fig. 10 through 16 and the data are presented in Table 4.

A comparison of Fig. 10 through 16 reveals that there are differences as well as similarities in the pyrograms.

In Fig. 10 through 13 (Virgin River, Utah; Soleduck River, Washington; Hoh River, Washington; Salmon River, Idaho; respectively), the pyrograms are very similar in that they are composed of four main peaks. The relative magnitudes of these peaks differ but the retention volumes are the same. Some minor peaks are discernible in the pyrograms of the waters from the Virgin and Salmon rivers. There are also some quantitative differences, i.e., the Virgin River in Utah (semi-arid wilderness area), appears to have the lowest organic content. Mathematical treatment and detailed analysis would probably show that these pyrograms differ in detail.

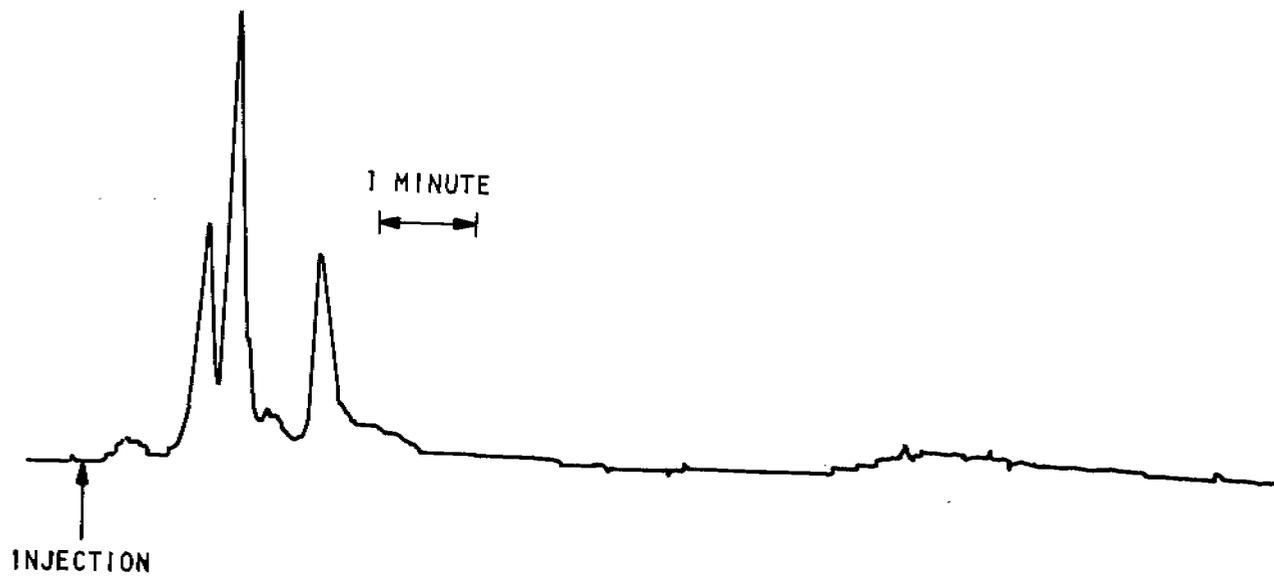


Figure 10. Pyrogram of Water From the Virgin River in Utah

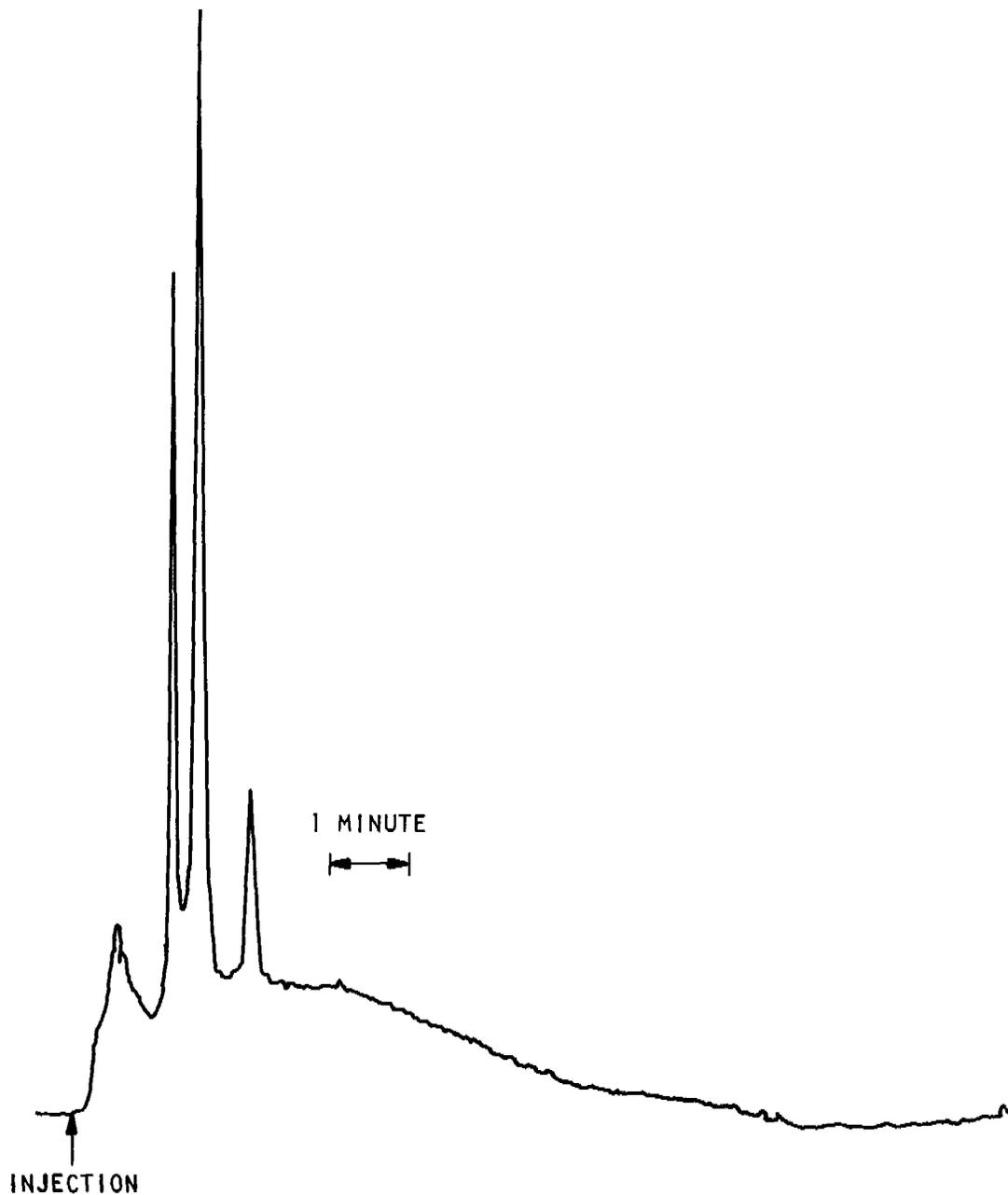


Figure 11. Pyrogram of Soleduck River Water from Washington

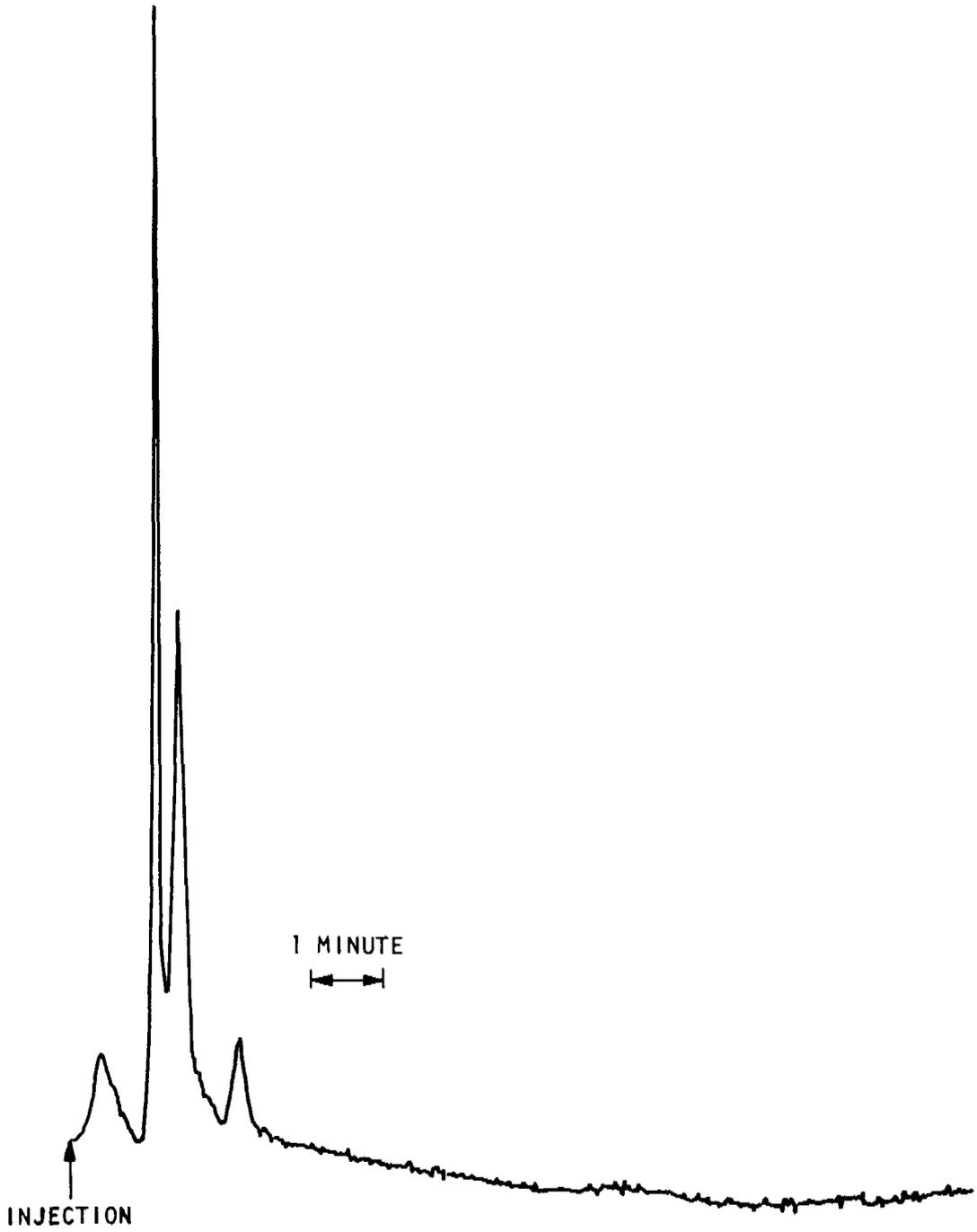


Figure 12. Pyrogram of Water From the Hoh River in Washington

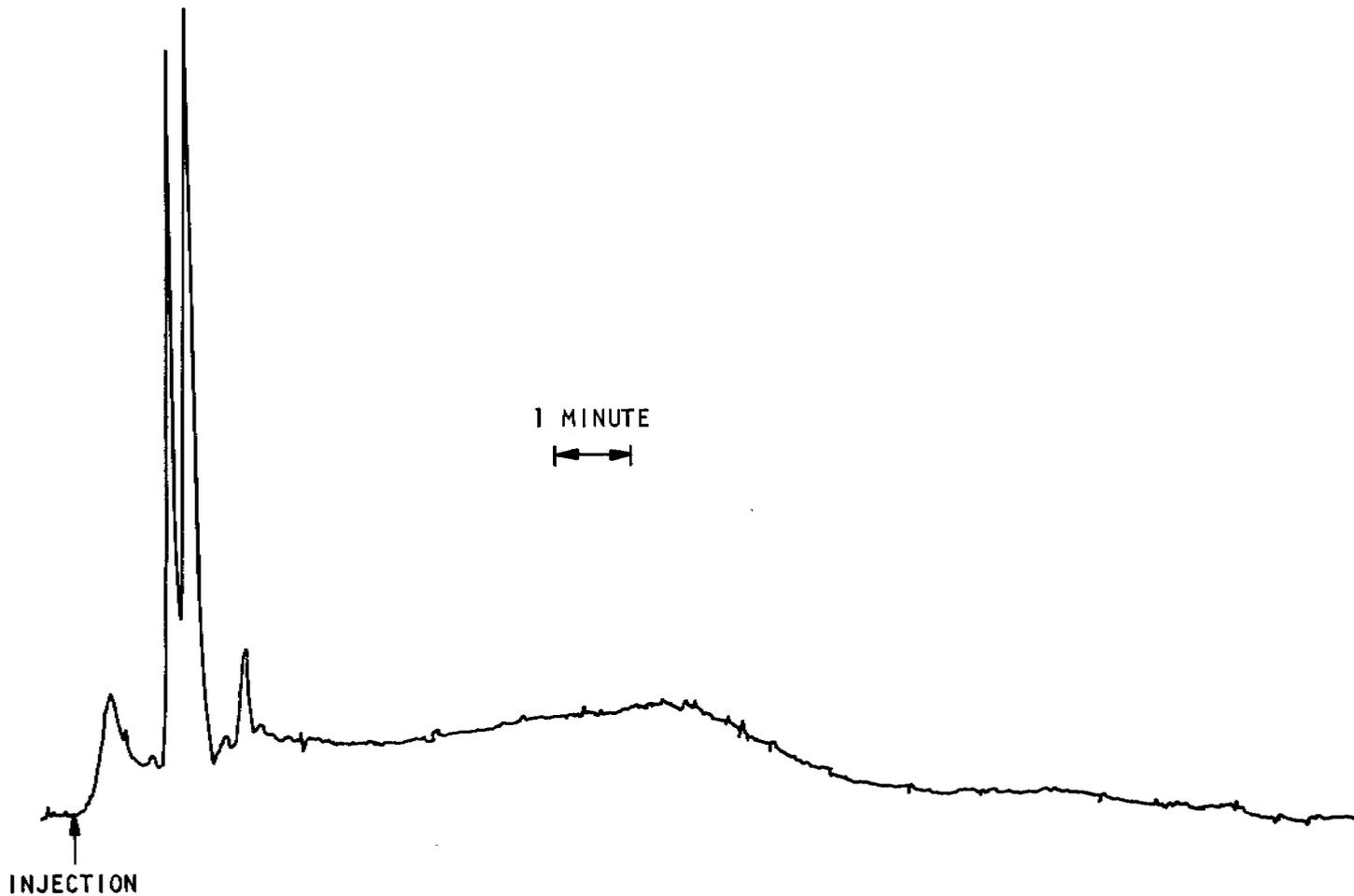


Figure 13. Pyrogram of Salmon River Water From Idaho

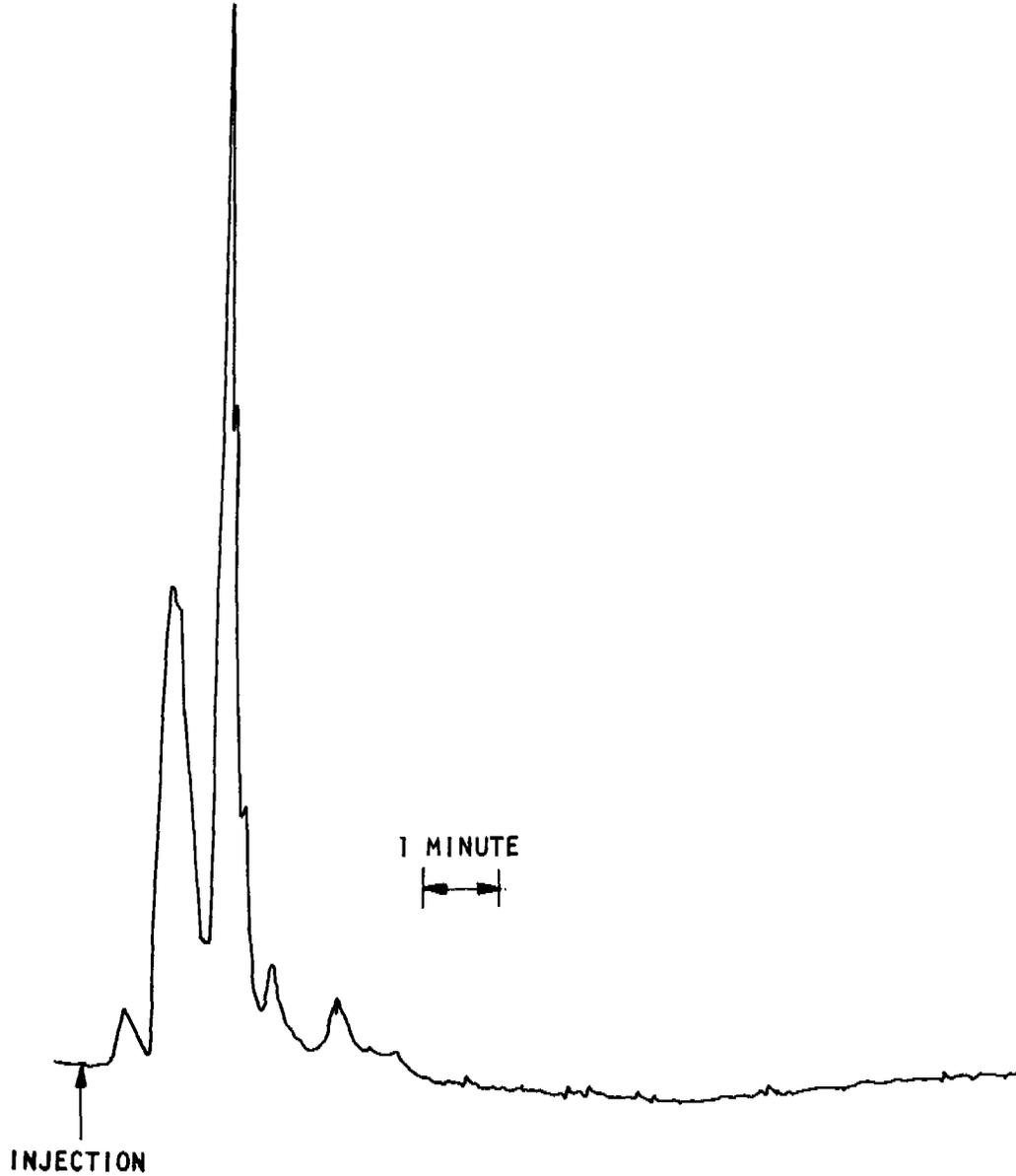


Figure 14. Pyrogram of Water From the Payette River in Idaho

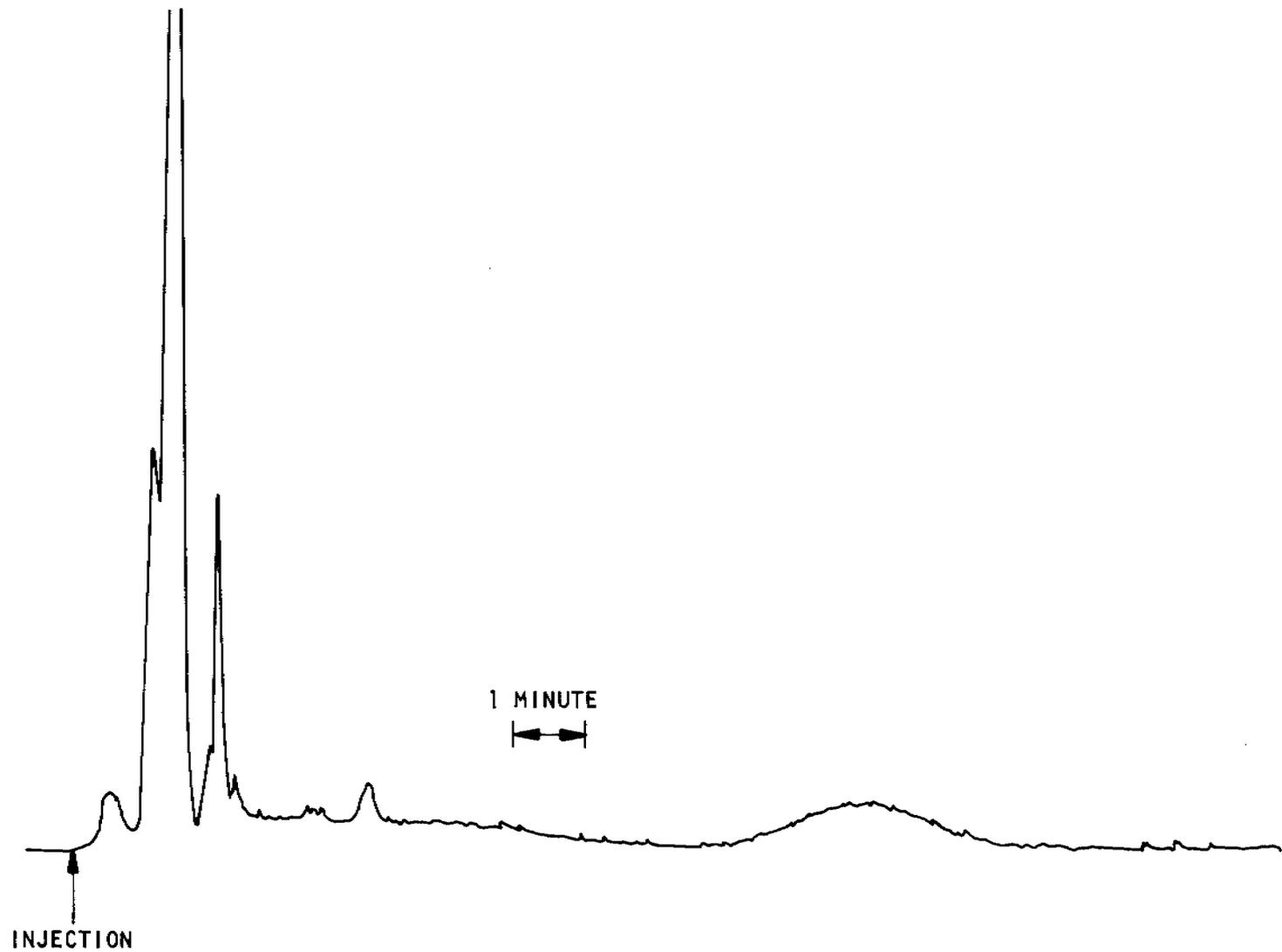


Figure 15. Pyrogram of Water From the Naches River in Washington

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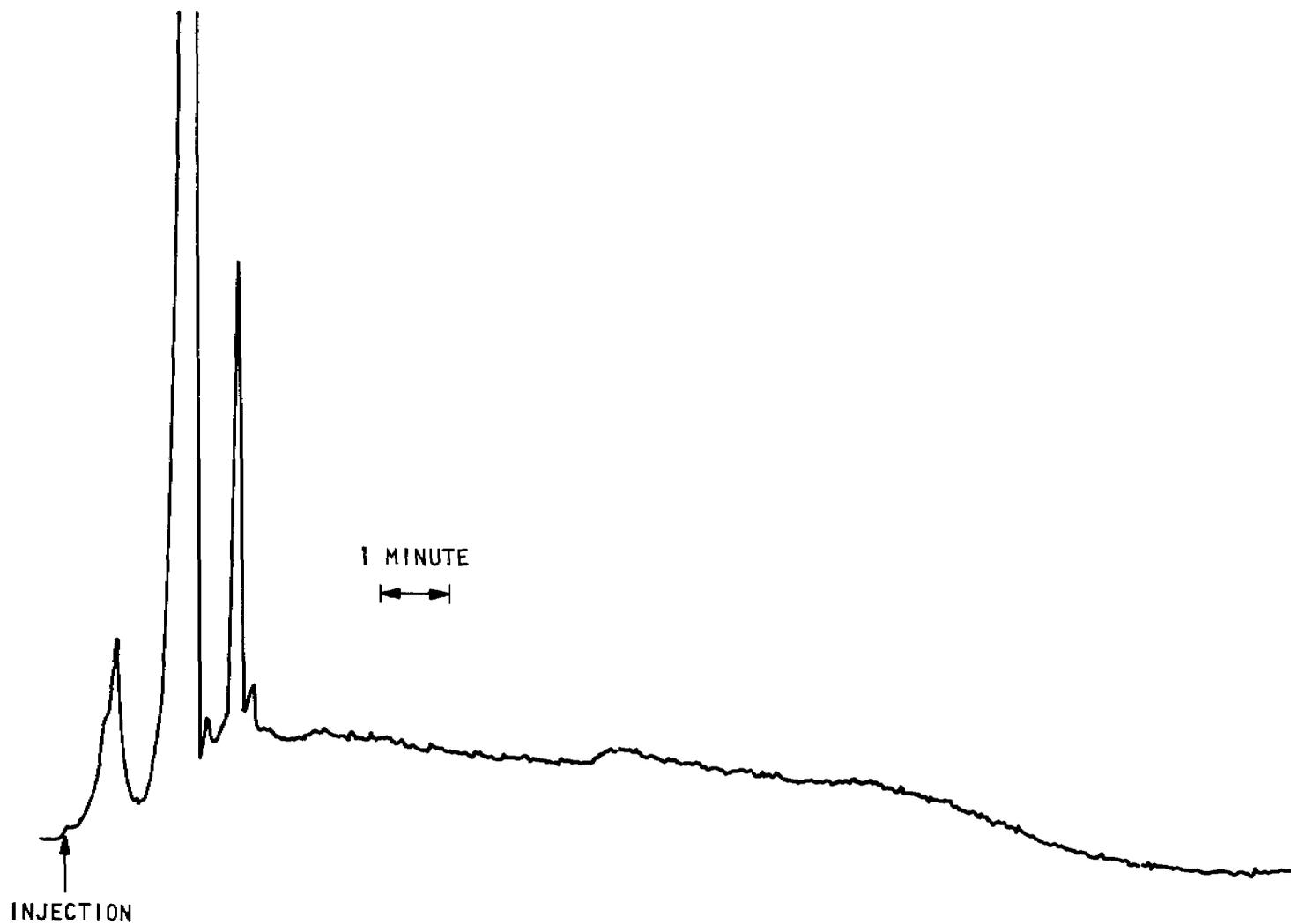


Figure 16. Pyrogram of Provo River Water From Utah

TABLE 4

PYROGRAPHIC DATA FOR WATERS OF NATURAL ORIGIN

Retention Volume, milliliters	Peak Heights (Arbitrary Units)						
	Virgin River	Salmon River	Soleduck River	Hoh River	Provo River	Payette River	Naches River
11	1	9	13	7		4	5
15					15		
26						32	31
28	13	55	59	84			
32				39			100+
33	25	59					
35			74		100+		
40						72	*
42	3					*	
44		6			9		
46			22			*	37
51		12		8			6
53	12				43		
55						7	
57					11		
68	2						
73						5	
92							5
176		8					
198	2						
249							4

*Shoulder

The other three pyrograms of natural waters (Fig. 14 through 16) differ among themselves and from the other four pyrograms. In general, these three pyrolytic spectra consist of one large peak, a second peak of smaller magnitude, and several small peaks. The pyrogram of the water from the Provo River also shows a considerable background after the first peaks. For the Naches River water, a broad peak at a retention volume of 249 exists in the pyrogram.

Although differences in the pyrograms of natural waters are visually apparent and mathematical treatment would be expected to show other variations, the pyrograms are of the same magnitude and show many similarities. Because the organic composition of a natural water body is a steady-state system, the pyrogram for a water obtained by desalination technologies operating on a particular source should be constant with respect to the natural organics present in the source water. The pyrogram would change only if organic materials were introduced into the water by the processing technique. Such organic materials will give distinctive pyrolytic spectra which would be superimposed on the spectrum derived from the natural organics. This addition to the pyrogram would be visually discernible in many cases and would be quantitatively derived by mathematical treatment of the pyrogram.

To show the differences between the pyrograms of organic compounds and the natural organic background of waters, three aqueous solutions of organic compounds were pyrolyzed under the same instrumental conditions as listed previously and at an attenuation of 10. The pyrograms of each compound, at a concentration of 25 ppm, are shown in Fig. 17 through 19 and the pyrographic data are presented in Table 5. Comparison of these pyrograms with those for natural waters shows the pyrograms for the organic compounds are distinctly different. This would enable the qualitative and quantitative identification of the organics in the presence of the natural organic background. Because pyrograms of the same magnitude as in Fig. 17 through 19 would be obtained at an attenuation of 2 for solutions containing 5 ppm of the compounds, the sensitivity would be at least of this order for visual detection and would be considerably less with the application of mathematical techniques. Further investigation should be undertaken in this area.

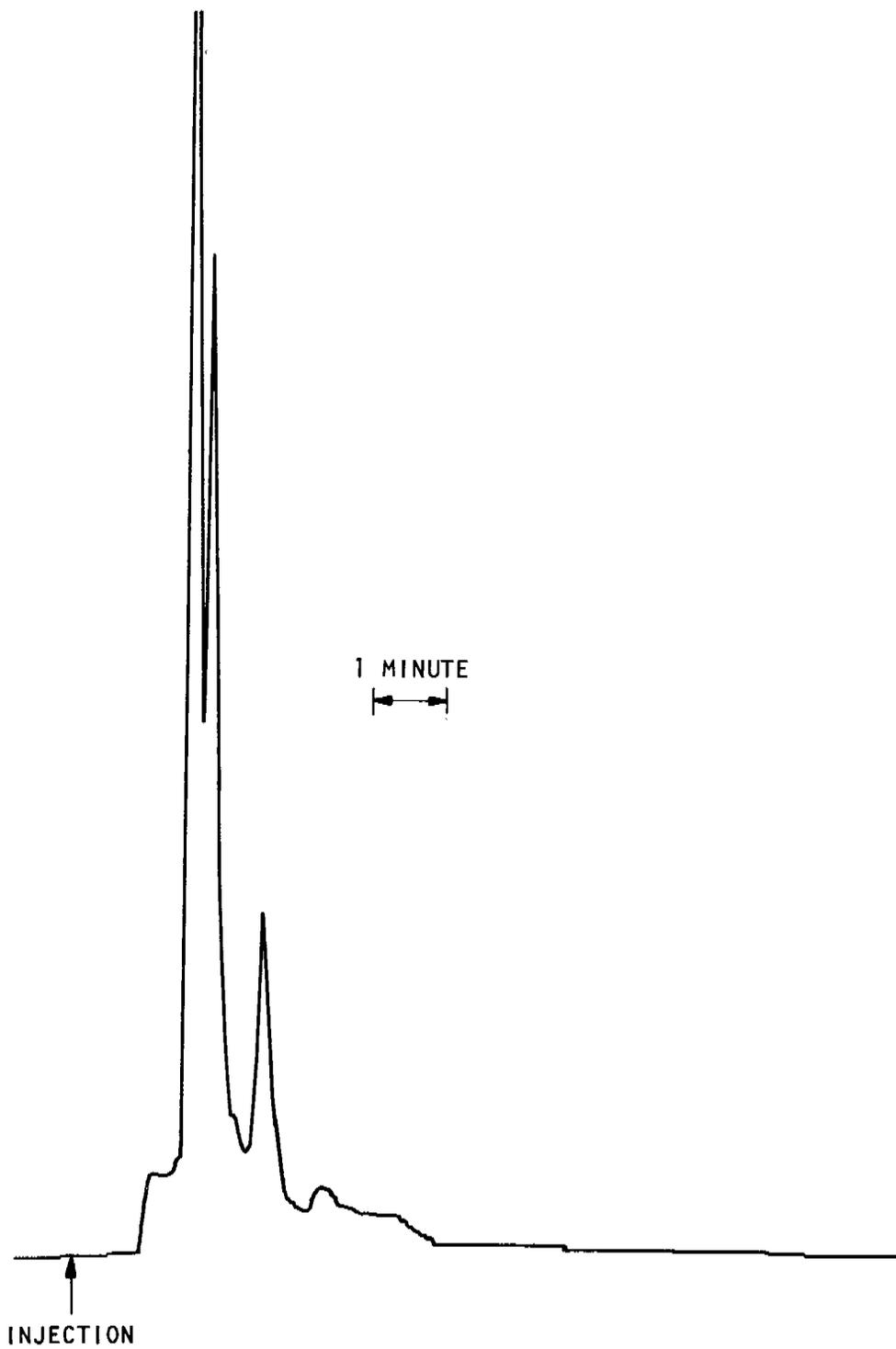


Figure 17. Pyrogram of 25 ppm Aqueous Solution of Ethyl Acetate

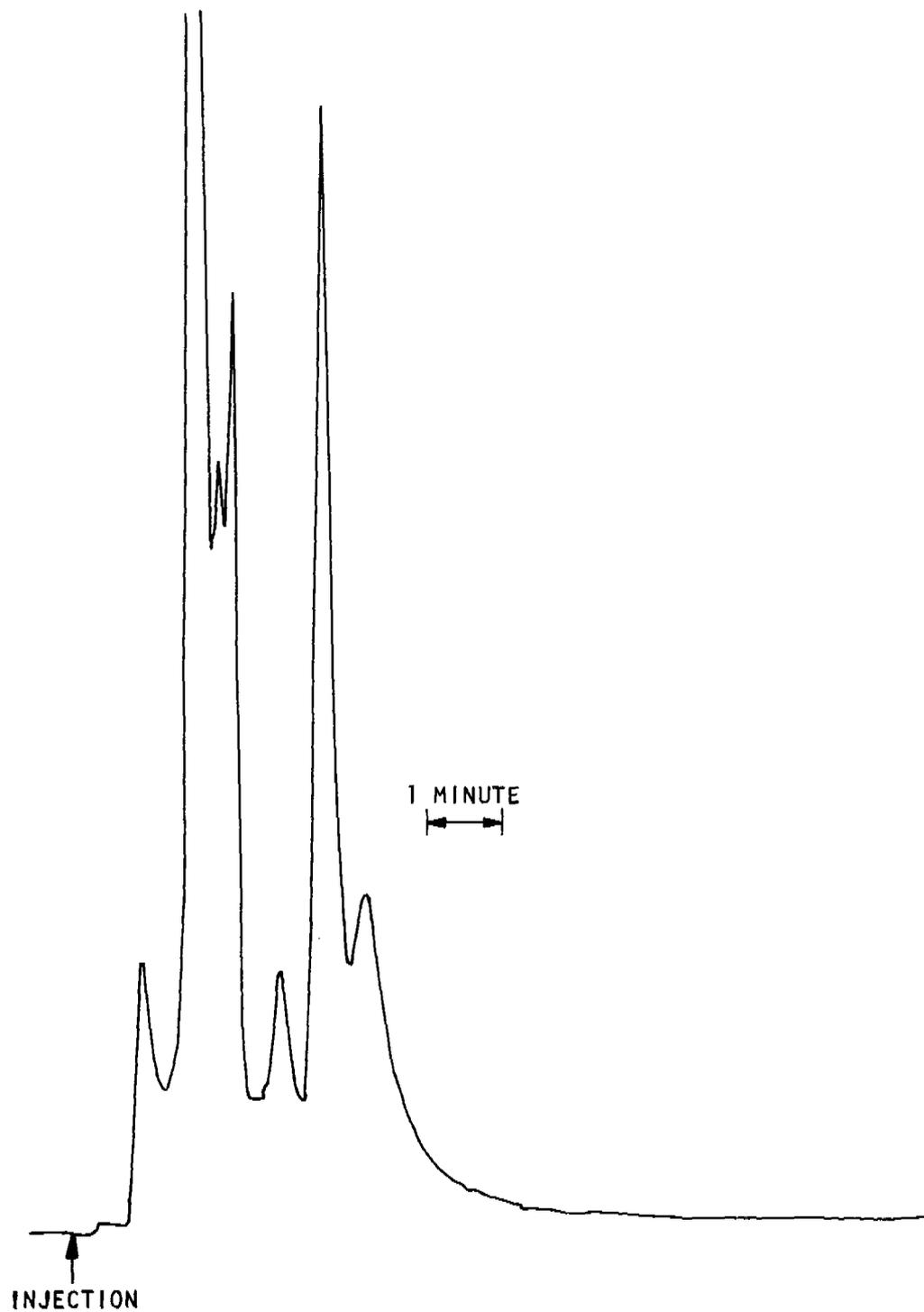


Figure 18. Pyrogram of 25 ppm Propionaldehyde in Water

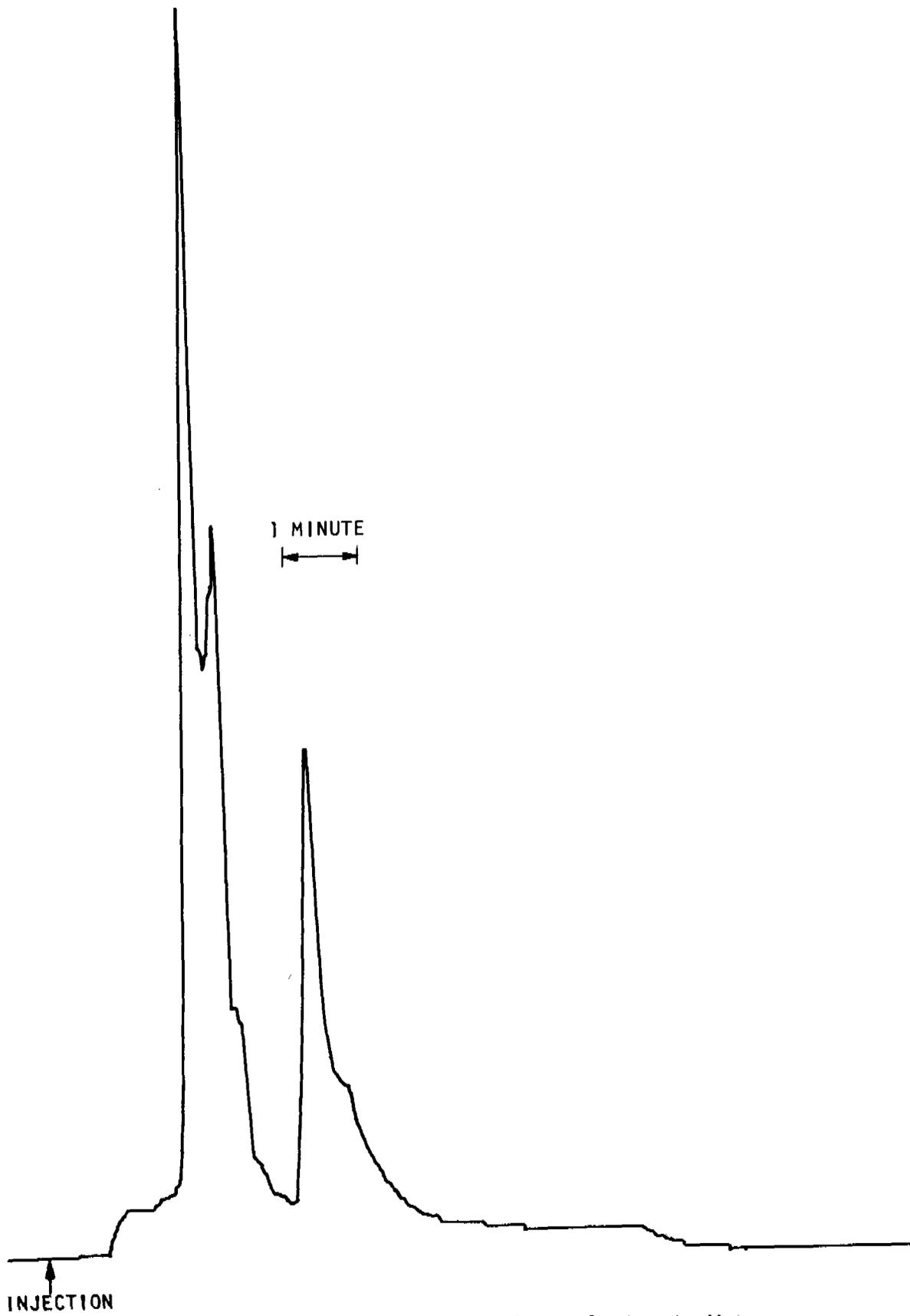


Figure 19. Pyrogram of 25 ppm Diethylamine in Water

TABLE 5

PYROGRAPHIC DATA FOR CHEMICAL COMPOUNDS

Retention Volume, milliliters	Peak Heights		
	Ethyl Acetate	Propionaldehyde	Diethylamine
22		20	
26	6		*
37	100+		
40		100+	
44	73		90
46		66	
51	*	69	
53			53
57			*
59	25		
64		19	
77	5	83	
79			36
90		25	
99	3		

*Shoulder

Since all desalination processes introduce or produce new organic species in the product water, the stringent requirement of the U.S. Public Health Service will be fully applicable to all water supplies produced by desalination processes. In order to deal with this problem, the capability for clear characterization of the chemical nature of desalinated water must be established. The pyrographic class characterization might provide a means of differentiation between the natural organic background of water and the organic species derived from desalination processing. It can then become a useful tool for compliance with the Public Health Service requirements.

CONCLUSIONS

To gain wider public acceptance and approval by responsible Public Health agencies, industrially processed (desalinated) potable water must show quality compatibility with natural potable waters.

The chemical nature of desalinated and natural potable waters differ in a number of ways. The water originating from natural sources, which is distributed to the consumer through municipal water supplies, contains a varied composition of inorganic salts and organic compounds. This composition is regulated by a steady-state ecological cycle existing in any given water body. The water, which is desalinated by an industrial process, could contain some inorganic residue and organic components which are mainly carryovers from the initial composition of a nonpotable water source. In addition, industrial chemicals used in the processing will also be found in the product water.

Current analytical and water quality control methodology is oriented principally towards the problems of natural water supplies. For example, the carbon chloroform extract (CCE) method is widely used for the characterization of the total organic content of water. It is generally recognized that CCE values represent only a fraction of the organic matter present in natural waters. Examination of total organic values obtained on samples of natural waters indicate that CCE represents only 10 to 20 percent of the total organics present. However, when CCE measurement is made on samples having a relatively constant chemical composition, as is the case with waters obtained from an ecologically stable environment, it does have certain informative value. It is possible from this determination of a fraction of the organic matter to deduce the magnitude of the organic content in a given source of natural water. This useful tool for the characterization of natural potable water loses all meaning if applied to the characterization of water with a varied and generally unknown organic composition such as is the case with desalinated water.

The studies conducted under this contract were concerned primarily with the quality parameters of desalinated water. To do this, it has been necessary to characterize the organic composition of naturally occurring potable water. This provides the yardstick for comparing the product water from desalination processes. As part of this research, a pyrographic method for the assessment of the total organic content of water has been applied to study the organic content of municipal water supplies derived from sources varying climatically and geographically. It was found that water obtained from surface sources in the desert and semiarid regions contains organic matter in the 1 to 3 mg C/liter range. Water samples from forested areas with abundant rainfall generally range between 3.7 and 7.7 mg C/liter. It is believed that the majority of municipal water supplies in the United States contain organic matter within the range of these two extremes. The developed analytical methodology and the results of the conducted survey provide a factual basis from which quality standards for desalinated water can be set. This is a more realistic approach to such a task than utilization of data and information derived mainly from analytical methodology currently used for the characterization of natural water sources.

RECOMMENDATIONS

It is recognized that the source of water for desalination is nonpotable. Consequently, assurances must be made to the consumer that the product water meets all quality requirements for potable water, including the organic composition.

To be able to make such assurances, this investigation indicates the need for the following additional studies:

1. Apply the developed analytical methodology for the assessment of the total organic content of desalinated waters. This is of prime importance in the case of distillation processes where no information is currently available on the nature, quantities, and character of the organic materials transferred from a non-potable water source into the product water by steam distillation.
2. Continue research in the area of development and reduction to practice of the techniques for class characterization of organics in water. Apply the developed methodology to differentiate between the organics derived from natural sources and the chemicals introduced or produced by desalination processes.

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OFFICE OF SALINE WATER, U.S. DEPARTMENT OF INTERIOR

1. Kurt H. Nelson and Ihor Lysyj, "Organic Content of Southwest and Pacific Coast Municipal Waters."

Water samples from municipal supplies in some Southwest and Pacific Coast communities were analyzed for organic content by a pyrographic technique. The organic content averaged 0.9 mg C/liter for the supplies from underground sources. Municipal supplies obtained from surface sources in desert and semiarid regions had organic contents from 1.1 to 2.7 mg C/liter. Those procured from surface waters in the northern Pacific Coast had organic contents from 3.7 to 7.7 mg C/liter.

2. Ihor Lysyj and Kurt H. Nelson, "Pyrolytic Characterization of Natural Waters."

Paper in preparation. The organic matter is pyrolyzed in the presence of the matrix water and the fragments are measured with a flame ionization detector after separation on a gas chromatographic column.

3. Kurt H. Nelson and Ihor Lysyj, "Instrument for Pyrolysis of Organics in Water."

Paper in preparation. An instrument is described for the pyrolysis of organic materials in water. The pyrolytic fragments from the organics are transported by steam through selected gas chromatographic columns. The separated fragments are measured with a flame ionization detector and recorded as a pyrogram.

4. Ihor Lysyj and Kurt H. Nelson, "Identification of Aqueous Organic Compounds Through Pyrography."

Paper in preparation. A technique for the identification of organic compounds present in water is described. After the compounds are pyrolyzed in the presence of the water, the fragments are separated by gas chromatography prior to measurement. Characteristic pyrograms, which permit identification, are obtained for the organic compounds.

5. Upon review of the work called for, or required hereunder, to the best of the contractor's knowledge and belief, no subject inventions have resulted from performance under this contract.