

Methods for the Determination of Trace Organic Materials in Water

By I. Lysyj, K. H. Nelson, P. R. Newton, Rocketdyne, A Division of North American Aviation, Inc., for Office of Saline Water, J. A. Hunter, Acting Director; W. Sherman Gillam, Assistant Director, Research; H. E. Podall, Chief, Biosciences Division

UNITED STATES DEPARTMENT OF THE INTERIOR • Stewart L. Udall, Secretary
Frank C. Di Luzio, Assistant Secretary for Water Pollution Control

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FOREWORD

This is the two hundred and thirty-ninth of a series of reports designed to present accounts of progress in saline water conversion with the expectation that the exchange of such data will contribute to the long-range development of economical processes applicable to large-scale, low-cost demineralization of sea or other saline water.

Except for minor editing, the data herein are as contained in the reports submitted by Rocketdyne, A Division of North American Aviation, Inc., under Contract No. 14-01-0001-332 covering research carried out from June 1, 1965 through November 24, 1966. Previous work on this contract is described in the Office of Saline Water Research and Development Progress Report No. 152. 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

The purpose of this research program was the development of analytical methodology for the determination of organics in water as it relates to the problem of water desalination. The principal objective of the research effort was the development of instrumental means for the rapid determination of the total organic content in water matrices. The applicability of this effort includes the quality control of product water, the chemical characterization of source waters, and the effect of natural organic materials on the efficiency of the desalination processes.

Gas chromatographic separation and hydrogen flame ionization detection have been combined with pyrolysis for the rapid direct measurement of the total organic content of water at the parts per million concentration level. Following the pyrolysis of the organics in the presence of the water at 800° C, the methane produced is separated from the water and other pyrolytic fragments on a porous glass column for measurement with a hydrogen flame ionization detector.

A modification of this procedure, which provides higher sensitivity and more uniform response for a greater number of organic compounds, employs steam as a carrier gas, and a glass bead column. In this method, no separation is achieved and all pyrolytic fragments of organic materials are detected as a single peak.

The methods and instrumentation developed during this program have been utilized for a number of hydrologic surveys and field studies. These include (1) the study of the efficiency of the advanced wastewater reclamation processes at the Pomona and Santee projects, (2) the chemical characterization of some surface waters in Los Angeles county, and (3) the survey of the organic content of selected municipal water supplies in Southwest and Pacific Coast regions of the United States.

INTRODUCTION

A program to develop analytical methods for the chemical characterization of trace organic materials in natural and desalinated waters has been conducted under the auspices of the Office of Saline Water, U.S. Department of Interior.

Previous studies culminated in the development of analytical methodologies for the specific and sensitive measurement of volatile nonpolar organics present at extremely low levels in water, and for the determination of ¹ organic materials introduced into potable water by desalination processes.

The organics found in natural water sources are of a complex nature and are present only in extremely low concentrations. The task of identification and quantitative determination of individual species is very difficult, and until the present time, no direct method was available for determination even of the total organic content of water. No data on actual organic content of potable waters received by American consumers are available at this time. The chemical oxygen demand (COD) and carbon chloroform extract (CCF) methods are most commonly used as indirect methods for the estimation of the organic level in water, but have many deficiencies.

The chemical oxygen demand procedure² provides a measure of oxygen equivalent to the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. Only a part of the organic matter is included with the portion depending on the chemical oxidant used, the structure of the organic compounds, and the manipulative technique. This method is used principally for wastewaters because it is designed for waters with an organic content of more than 10 parts per million. As the organic content decreases below this value, accuracy decreases but the procedure may still be used to indicate an order of magnitude.

A procedure² for determining the organic content of potable water appeared for the first time in Standard Methods for the Examination of Water and Wastewater published in 1965. This procedure is called "Carbon Chloroform Extract Method" and does not determine the total organic content of water. The adsorbent (activated carbon) does not adsorb all the organics and the solvent (chloroform) does not recover all the adsorbed materials. It is stated that recoveries of selected easily adsorbed materials may range from 50 to 90 percent. In addition, an analysis requires a 5000-gallon water sample which is extracted with the adsorbent over a period of approximately 14 days. This is followed by the actual analysis of the activated carbon by extraction with the solvent, and finally evaporation of the extract to obtain a residue for weighing. It is obvious that this method, in addition to being not sufficiently accurate, is time consuming and can provide only average results over a period of approximately 1/2 month. Indications of fluctuations in organic content, even in day-to-day composition changes, of water are not possible.

Recently, a method for determining the total carbon in aqueous media has been applied during wastewater treatment programs³. This method first oxidizes the organic components in an oxygen stream and then passes the gas stream through a nondispersive-type infrared analyzer for measurement of the resultant carbon dioxide. The method is most accurate at 100 parts per million total carbon but is sensitive to approximately 2 parts per

million. This sensitivity is equivalent to the maximum organic content found in many potable waters. In addition to the sensitivity limitation, there are conditions under which the method may not be entirely satisfactory for organic carbon. During initial treatment of a sample to remove the carbon dioxide originally present, the volatile organic components are partially lost. Also, particulate organic matter may cause difficulties because the method is designed primarily for analysis of true solutions.

To meet the requirements of desalination programs, a new concept for summation of trace organic materials in water has been developed to an applicable state-of-the-art technique. The analytical methodology advanced for the determination of total organics in water is based on pyrolysis of the organic matter in the presence of the matrix water followed by gas chromatographic analysis of the resulting fragments. With this technique, it is possible to measure the total organics found in various waters even though the organics are of a complex nature and are present only in low trace concentrations. The technique has been implemented with instrumentation designed and constructed specifically to meet the requirements and imposed constraints.

The organic composition of any natural water body is the overall result of its history and use since its precipitation as rain or snow. All the organic impurities present in water result either from the biological activities occurring in the water or from the solution and suspension of organic materials during a period of contact with the water.

The processes of solution and suspension of an organic material proceed while the water is in contact with the material or, under some circumstances, until equilibrium is reached. The composition of the resulting organic matter in the water is complex. These impurities can span the range from small molecules present in true solution through large molecules exhibiting all the characteristics of colloidal particles and up to minute particles having the composition of the original organic materials. Subsequent contact of the water with other organic materials may alter the amounts of previously dissolved organic matter through equilibria changes or through 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 both continuously consume organic matter present in the water, and contribute dissolved and particulate organics to the water through mechanisms of excretion and decay of organisms.

The organic composition of any water body must be considered as a dynamic system. A wide variation in total organic content may exist among large bodies of water, but the relative composition of the organic content changes only within rather narrow limits. The ratio between components does not vary significantly unless cataclysmic conditions occur. Consequently, the organic composition of large water bodies approximates steady-state conditions

This was shown in a study of 529 lakes of the Highland Lake District by Birge and Juday⁴. These lakes ranged from those with an organic content derived mainly from biological activity to those having a very significant contribution from vegetation sources. The organic content of the waters was fractionated by centrifuging into two fractions: plankton and uncentrifugible, dissolved organics. The latter was analyzed for the three primary classes of constituents: carbohydrates, proteins, and ether extractables. The term ether extract was employed rather than lipides or fats because ether may extract small quantities of other materials such as chlorophyll.

In all the waters, the carbohydrates represented the major fraction of the organic content while the ether extract, or fats, was a minor component. The uncentrifugible, dissolved organics fractions had a mean composition of 83.7 percent carbohydrates, 15.6 percent protein, and 0.7 percent ether extract. If the plankton was included, the values changed to 81.9 percent carbohydrates, 17.1 percent protein, and 1.0 percent ether extract.

The effect of factors such as physical size was negligible as shown by two lakes with outlets to the stream network of the region. One of the lakes had an area 16 times larger and an organic content approximately 40 percent higher, but the overall compositions of the organic contents in the two lakes were nearly identical. The organic composition of the small lake was 81.3 percent carbohydrates, 17.2 percent protein, and 1.5 percent ether extract while that of the large lake was 82.6 percent carbohydrates, 16.7 percent protein, and 0.74 percent ether extract. A comparison of other lakes showed similar compositions although organic contents varied sixfold or more.

Extensive surveys conducted on 11 typical lakes showed that the organic matter was distributed throughout the lakes in a generally uniform manner. The primary source of the organic content in the lake waters was the plankton which generates five to six times its own weight of organic solutes. In respect to source and composition, the organic content of the small lakes is believed to be the same as that of all bodies of fresh water. The large inland lakes such as the Great Lakes, tropical lakes, and those near the Arctic circle all yielded similar results.

This consistency of the ratios of the major organic classes present in water is utilized as the basis of the analytical method for total organic content described in this presentation. The utilization involves the pyrolysis of the organic content in the presence of the water and measurement of the pyrolytic fragments. It is not necessary to measure all the carbons but only a proportional amount because of the consistency of the class ratios and the fact that carbohydrates and proteins average 45 and 53 percent carbon, respectively. To better understand this consistency and the calibration concept selected, the mode of decomposition and utilization of the organics present in water bodies by the biological species must be considered. This is discussed in Appendix A.

INSTRUMENTATION

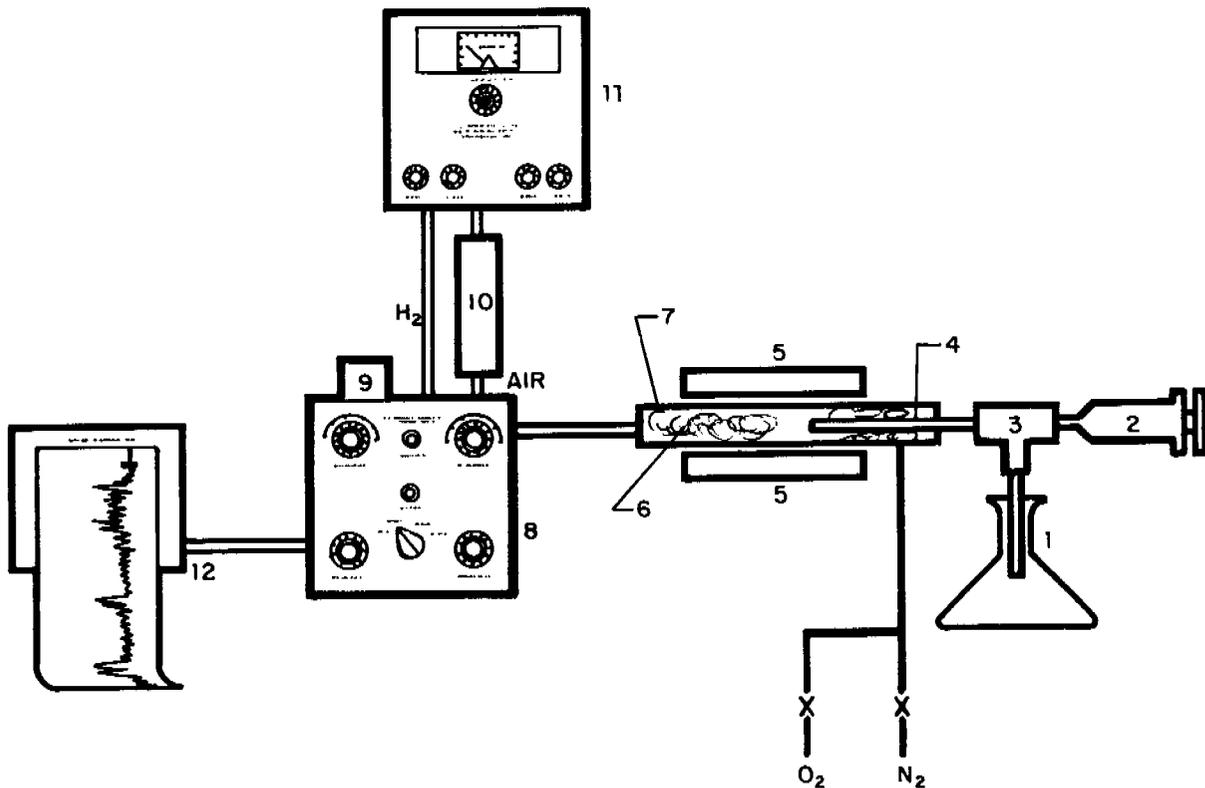
Analytical methodology for the rapid measurement of the organic matter in water must meet certain requirements and imposed constraints:

1. The use of a small sample in the analysis is preferable especially in field work and in control applications.
2. Separation of the organic matter from the water matrix prior to measurement is not attractive because of the trace level concentration of the organic matter and the larger number of organic species present in waters. Incomplete isolation of a desired species and contamination are two major problems ordinarily encountered whenever separation techniques are employed.
3. The methodology must possess both high sensitivity to organics in the presence of water and also the capability for rapidly measuring the totality of organic matter.

To meet these requirements, the concept of a combination pyrolytic-gas chromatographic approach for the direct summation of the organic matter in a water matrix was advanced. This concept is based on the pyrolysis of the organic matter in the presence of the matrix water followed by measurement of the resulting organic fragments with gas chromatography technology. A discussion of the pyrolysis of organics is presented in Appendix B.

Although pyrolysis has been widely used as an analytical technique, the applications have been identification of matrix materials rather than measurement of minor components. These applications have employed commercially available pyrolytic instruments which may be classified into two general types according to their mode of pyrolysis. In the first type, the material to be pyrolyzed is placed on a cool metallic coil or ribbon which is then electrically heated very rapidly to a high temperature. In the second type, the sample is placed in a small boat which is introduced into a pyrolysis tube maintained at a preset elevated temperature. Both types of instruments will readily pyrolyze solid materials and in some cases have been utilized for liquids through the use of techniques such as sealed capillaries. However, for various reasons, none of these instruments were readily adaptable to the rapid analysis of trace organics in a water matrix.

The lack of a suitable commercial pyrolysis instrument necessitated the design and construction of an instrument to specifically meet the requirements of the problem. This instrument, shown in Fig. 1, consisted of an Aerograph Model 600C gas chromatograph equipped with a flame ionization detector, a Sargent 1-millivolt recorder, a sample injector, and a pyrolysis chamber heated by a Sargent microcombustion furnace. The source of hydrogen for the flame ionization detector was either a hydrogen generator (Wilkins Instrument and Research, Inc.) or a cylinder of hydrogen. When the latter was used, the flow of hydrogen was stabilized by sequential passage through a flow controller (Moore Products Co.), a needle valve, and a flowmeter.



- | | |
|----------------------|------------------------------|
| 1. SAMPLE FLASK | 9. FLAME IONIZATION DETECTOR |
| 2. SYRINGE | 10. CHARCOAL FILTER |
| 3. THREE-WAY VALVE | 11. HYDROGEN GENERATOR |
| 4. CAPILLARY TUBE | 12. RECORDER (1 MILLIVOLT) |
| 5. FURNACE | |
| 6. QUARTZ WOOL | |
| 7. PYROLYSIS CHAMBER | |
| 8. GAS CHROMATOGRAPH | |

Figure 1. Schematic of Pyrolytic-Gas Chromatographic Instrument

The gas chromatograph was modified by removing the injector tube from the mounting block and heater. An adaptor for connecting the gas chromatographic column to the pyrolysis chamber was constructed from stainless steel in the following manner. For connection to the column, a Swagelok reducer (No. 300-R-4-316) was welded to one end of 3/16-inch-OD by 4-1/2-inch-long tubing. The other end of this tubing was welded to one tubing port of an AN824 tee. For connection to the pyrolysis chamber, a 3-1/2-inch length of 3/16-inch-OD tubing was welded to the side port of the tee. The third port of the tee was machined flat for a septum closure. This adaptor was installed in the mounting block and heater with the external tubing in a horizontal position.

The pyrolysis chamber was constructed from a 3/8-inch-OD by 8-inch-long nickel tube. For connection to the adaptor, one end of the chamber was mated and welded to the pipe thread port of a Swagelok female connector (No. 300-7-2-316). The other end of the chamber was mated and welded to the pipe thread port of a Swagelok TFT tee (No. 200-3TFT-316). To the side tubing port of this tee, 1-1/2-inch-long by 1/8-inch-OD tubing was welded and then connected with Swagelok fittings to a Nupro check valve (No. 2C). The carrier gas line was connected to the check valve. The pyrolysis chamber was installed in the microcombustion furnace and connected to the adaptor with Swagelok fittings. 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 the water vapor.

The injector was constructed from a Hamilton three-way valve (No. 3TFT2) consisting of 1/16-inch-OD tubing attached to opposite ports, a female luer hub on the intermediate port, and a 90-degree two-way plug. The valve was mounted horizontally with a 0.25-cc glass syringe installed in the female hub. The tubing attached to one port was 6 inches long and bent downward to dip into the water sample. The other tubing was 2 inches long and was fastened with Swagelok fittings to a Swagelok reducer (No. 100-R-2-316). To the tube end of this reducer, 4-inch-long by 1/16-inch-OD tubing was welded. The tube end of the reducer was connected with Swagelok fittings to the tee on the pyrolysis chamber so that the 1/16-inch-OD tubing was positioned coaxially within the chamber. This tubing served to carry the water sample into the heated pyrolysis chamber.

The present injector was developed after initial work with sample injection into the pyrolysis chamber through various gas chromatographic septums yielded pyrolytic patterns with large nonreproducible peaks. The source of these peaks was traced to minute septum particles which adhered to the syringe needle and were carried into the pyrolysis zone. This problem was eliminated by installation of the present injector which permits repetitive sample injection without contamination.

An investigation of some materials of construction for the pyrolysis chamber was conducted to ascertain the best choice to meet the requirements of a low blank and thermal corrosion resistance. Pyrolysis chambers were fabricated from stainless steel, nickel, and Monel and then installed in the instrument for testing. Each chamber was tested for a period of 1 week with repeated injections of redistilled water and organic-containing waters. The magnitude of the blank with redistilled water and the extent

of thermal corrosion were noted for each material during the course of the tests.

When the redistilled water was injected, the size of the blank obtained with the Monel and nickel chambers was smaller by several orders of magnitude than that for the stainless-steel chamber. The high blank for the stainless-steel chamber did not decrease significantly during 1 week of operation. In contrast, the blanks obtained with the nickel and Monel chambers decreased rapidly to a low level and remained low during the test period.

The resistance to corrosion at the elevated temperature of 800° C for 1 week was very good for the Monel and nickel chambers. In contrast, the stainless-steel chamber oxidized and flaked very severely during the week of continuous high-temperature operation.

Because of the low blanks and the good resistance to oxidation, the pyrolysis chamber should be constructed of nickel or Monel rather than stainless steel. Of the two materials, nickel appeared to be somewhat superior.

Some tests with a quartz pyrolysis chamber indicated it would offer definite advantages of a very low blank and no corrosion. A chamber can be easily fabricated from this material, but the problem of a simple, leak-proof, durable connection to the metal system must be solved. The connection must withstand temperatures in the range of 100 to 150° C without leaking or introducing contamination. This requirement eliminated from consideration any connections utilizing organic components.

METHANE METHOD

The conventional analytical procedures for the determination of organic materials in the presence of water involve separation and preconcentration of the organic matter. The separation and preconcentration can be accomplished by adsorption on activated charcoal, extraction with solvents, or gas stripping. The object of this investigation was to devise analytical methodology which would permit measurement of organic matter in water without a separation and preconcentration step.

To facilitate such methodology, gas chromatographic separation of the pyrolysis products from the water matrix was combined with hydrogen flame ionization detection. The necessity for separation has been shown during previous studies. The mechanism of operation of the flame ionization detector involves the combustion of organic matter in a hydrogen-oxygen flame. Although water is always present in the flame as a combustion product, the introduction of additional water vapor into the flame affects the response of the detector when operating at high instrumental sensitivities. The mechanism of this effect is not clear at the present time but may be caused by changes in density and flow characteristics of the carrier gas at the time when the water vapor reaches the detector head.

The separation of the pyrolytic products from the water vapor can be best accomplished by gas-solid chromatography. With this technique, there is no stationary liquid phase present in the column and therefore no column bleeding effects will be detected by the detector.

Porous glass was an excellent substrate for retaining the water vapor to permit detection of the pyrolytic product methane. Although the polarity of porous glass precludes efficient use of this substrate for the separation of polar materials, this same property permits the fast and efficient separation of polar and nonpolar species. Because water has a high polarity and boiling point, it is retained on a porous glass column at ambient temperatures but can be readily eluted by increasing the column temperature. Therefore a porous glass column can be used for analyses until it is saturated with water and then be regenerated to its original retention capacity.

PROCEDURE

To measure the organic matter in an aqueous matrix by detection of the methane produced during pyrolysis, the following operational procedure is used.

A 10-foot by 3/16-inch OD stainless-steel column packed with 50 to 80 mesh porous glass is installed in the gas chromatograph Model 600C (Wilkins Instrument and Research, Inc.), and the hydrogen source is disconnected from the instrumentation. To remove any organic materials as well as adsorbed water vapor on the substrate, the column is initially conditioned by passing oxygen gas through the column and the pyrolysis chamber for several hours. During this conditioning treatment, the column and pyrolysis chamber are maintained at 350 and 600° C, respectively. At the termination

of the treatment, gaseous nitrogen is used to purge the system of oxygen. Then the temperature of the column is reduced to the operating temperature and the hydrogen source is reconnected.

During analysis, the instrumentation is operated under the following conditions:

Column Temperature, °C	50
Hydrogen, cc/min	25
Nitrogen, cc/min	20
Air, cc/min	250
Attenuation	10 x 1, or as required
Injector Setting	50
Heating Tapes, °C	125
Pyrolysis Temperature, °C	800
Chart Speed, in./min	0.5
Sample Size, cc	0.25

As the operating conditions are being established, the injector is cleaned in a two-step operation. First, distilled water is drawn from a foil-closed 25-cc flask through the intake tubing of the injector into the 0.25-cc syringe. Then the flask is removed and the water is expelled from the syringe through the intake tubing. This sequence of steps is repeated several times to thoroughly flush the injector. The same technique is used whenever samples and solutions are changed during the analyses.

The blank is first determined by injecting distilled water into the pyrolysis chamber. A measured volume of distilled water is drawn from a foil-closed flask into the injector syringe, then the three-way valve is turned, and the measured volume of water is expelled from the syringe into the pyrolysis chamber. The resulting water vapor and any pyrolysis products are transported by the carrier gas into the gas chromatograph for separation and detection. Repeated injections of distilled water are made at 5- to 10-minute intervals until four or five pyrograms show identical peak areas for methane.

During the next step, a standard 10-ppm methyl isobutyl ketone solution prepared with distilled water is analyzed. The standard ketone solution is used to establish the response of the instrumentation and to ascertain any day-to-day variations in response. After the injector is flushed with the standard ketone solution, a measured volume (0.25 cc) is injected into the pyrolysis chamber. The results of the first two injections are discarded because they serve to flush the tubing from the three-way valve into the pyrolysis chamber. A series of four or five injections at 5- to 10-minute intervals is carried out with the ketone solution to obtain pyrograms which have methane peaks of nearly identical areas.

Then the injector is flushed with the first water sample. A measured volume (0.25 cc) of this sample is injected into the pyrolysis chamber. Again the results of the first two injections are discarded and a series of four or five injections are made at 5- to 10-minute intervals to obtain pyrograms with approximately equal methane peak areas. Then the injector is flushed and the analysis of the next sample is conducted.

A minimum of three areal measurements of the methane peak on a pyrogram are made with a planimeter. Then the average of these measurements for each peak is multiplied by the attenuation to convert all areas to a common attenuation basis of 1 x 1. The resultant areas of the peaks for each sample are then averaged. After correcting for the blank and any instrumental variation, the organic content of a sample is calculated by multiplying the corrected area by the calibration factor to obtain the organic content in terms of milligrams of organic carbon per liter (mg C/liter).

The 10-foot porous glass chromatographic column has a retention capacity of somewhat more than 10 cc of water. After cumulative injections totaling this amount, the flame is extinguished and fails to relight. Then the column must be purged to remove the retained water from the porous glass by increasing the oven temperature to approximately 250° C for a minimum of 1 hour with the detector turned off. After the column has cooled to the operating temperature, the analyses can be resumed.

At approximately 2-week intervals, any trace residues on the porous glass are removed by passing oxygen at 350° C through the column in place of the nitrogen carrier gas. The interval between treatments is dependent on the number of samples analyzed as well as the organic content of the samples. The oxygen also removes through oxidation any pyrolytic residues that may have deposited either within, or in the vicinity of, the pyrolysis chamber. This precautionary measure is taken to prevent any possible interference by such deposits during subsequent analyses.

CALIBRATION

The calibration of the method was carried out in two steps. As the initial step, the response of the instrumentation to methane was determined. Known volumes of methane were measured with a gas flush microliter syringe (Hamilton Co.) and then injected through an injection port at the head of the porous glass column. The instrumental conditions were identical to those used during pyrolysis. The peak areas per microliter of methane obtained for these injections are shown in Table 1 together with the average of 678 sq cm/microliter. From the average peak area, a response factor was calculated in terms of milligrams of methane per liter per sq cm.

Then a number of waters, with organic carbon contents from 3 to 70 mg C/liter, were analyzed by the pyrolytic-gas chromatographic technique and the areas of the methane peaks were calculated in the described manner. With the response factor and the sample peak areas, the quantity of methane for each sample was calculated as milligrams of methane per liter of water.

From this and data obtained by the carbon oxidation method at the Pomona Reclamation Plant, as subsequently reported, the average ratio of milligrams of organic carbon per liter to milligrams of methane per liter was calculated. Then a calibration factor was obtained by multiplying this ratio by the response factor. This calibration factor then permitted the direct calculation of the organic carbon content of a water sample from the area of the methane peak.

TABLE 1

RESPONSE OF THE DETECTOR TO METHANE

Sample, microliters	Attenuation	Peak Area, sq cm/microliter
40	100 x 128	690
40	100 x 64	640
40	100 x 64	638
30	100 x 32	643
30	100 x 32	673
10	100 x 16	730
10	100 x 16	701
10	10 x 128	696
10	10 x 128	627
5	10 x 64	692
5	10 x 64	702
2	10 x 32	695
2	10 x 32	685

NOTE: The average peak area was 678 sq cm/microliter.

ANALYSIS OF WATERS

The analytical methodology developed for determining the organics in a water matrix has been applied in studies of the organic content of waters from various sources. These applications include analyses of municipal, waste, and natural waters as well as samples procured from industrial sources. In all studies, the water samples were analyzed immediately after collection in 4-ounce bottles which were sealed with foil-lined caps. The bottles had been previously cleaned with 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.

Municipal Waters

Because no data are available on the actual organic content of potable waters received by United States consumers, a study was initiated to accumulate data on the organic content of water supplies available to consumers

through the municipal distribution systems of a number of communities. These data permit accurate ascertainment of the water purity level that must be met by reclaimed water supplies.

The data from analyzing various municipal waters for organics by the developed technique are presented in Table 2. The organic content of these waters is expressed as mg C/liter. An examination of the analytical results for these municipal waters reveals that the organic content ranged from 0.70 to 3.94 mg C/liter. The pyrograms, which were obtained at an attenuation of 10 x 1, for some of the municipal waters are shown in Fig. 2.

TABLE 2
ORGANIC CONTENT OF VARIOUS MUNICIPAL WATERS

<u>Source</u>	<u>Organic Content, mg C/liter</u>
California	
Alameda	2.07
Carlsbad	0.76
Del Mar	1.06
Gilroy	3.94
Los Angeles	2.65
Paso Robles	0.86
Salinas	0.90
San Clemente	2.55
San Diego	1.37
San Juan Capistrano	1.48
San Luis Obispo	1.26
San Mateo	1.11
Santa Ana	0.74
Santa Barbara	0.97
Santee	1.55
Thousand Oaks	0.86
Arizona	
Flagstaff	0.70
Grand Canyon	0.78
Kingman	1.60
Williams	1.26
New Mexico	
Albuquerque	0.90
Grand Lo	0.66
Sante Fe	1.27
Nevada	
Las Vegas	1.34
Reno	1.60
Other	
Washington, D.C.	1.48
Wilmington, N. C.	0.74

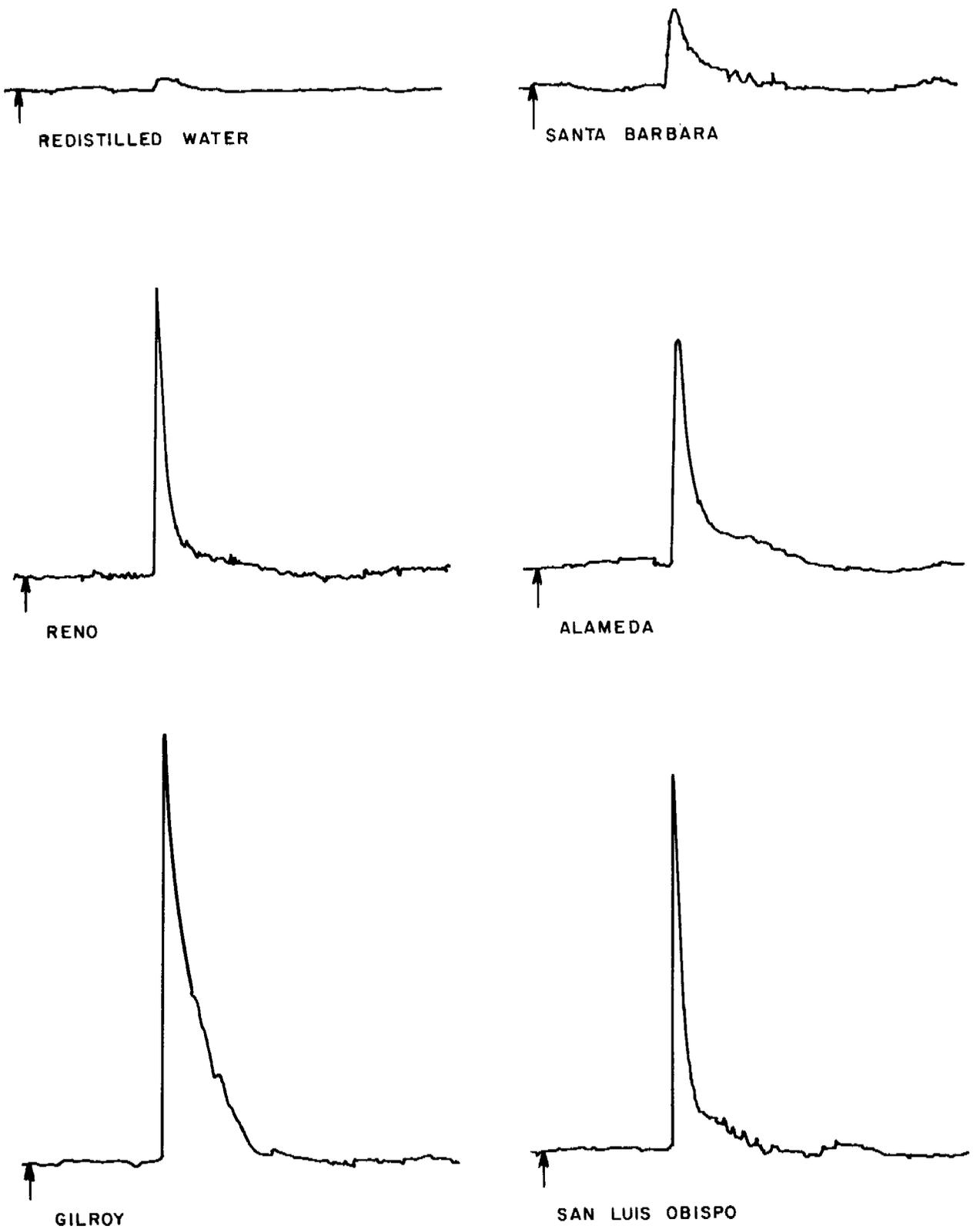


Figure 2. Pyrograms of Various Municipal Waters

Natural Waters

As a part of the study to accumulate data on the amounts of organics present in municipal water supplies, a number of waters from natural sources have also been examined for organic content. These sources include streams in a mountainous drainage area northwest of Los Angeles, saline waters, precipitation, and other sources. The water samples from these sources were analyzed by the developed methodology and the data are presented in Table 3.

TABLE 3
ORGANIC CONTENT OF VARIOUS NATURAL WATERS

<u>Source</u>	<u>Organic Content, mg C/liter</u>
Stream:	
North Fork Matilija Creek	0.45
Santa Paula Creek	1.21
Sespe Creek	1.97
Santa Clara River	1.15
Lake:	
Lake Tahoe (Emerald Cove)	0.43
Lake Tahoe (Sand Harbor)	0.97
Well:	
Brackish Desert Well (near Reno, Nevada)	1.13
Rain:	
Los Angeles, California	
14 November 1965	0.89
16 November 1965	1.12
28 December 1965	0.46
Saline Water:	
Sea Water, Sequit Point	2.41
Salton Sea	8.19

The four streams represent only a fraction of the stream network in a rugged, uninhabited mountainous area. Sespe Creek is the largest and longest creek in the area and has many small tributaries. The water sample from this creek was obtained from a section which had a moderate flowrate and considerable contact of vegetation with the water, both from overhang into the water and growth of moss, weeds, brush, and trees in the water along the sides of the channel. As may be seen in Table 3, this stream had the highest organic content of the streams sampled. At the present time, this portion of the area is being considered as a source of water for Ventura County, California by construction of a dam on Sespe Creek.

The sample from North Fork Matilija Creek was secured near the origin of the creek. In this area, the stream was fast flowing and relatively free of vegetation. This stream had the lowest organic content, 0.45 mg C/liter, of the four streams.

Santa Paula Creek was sampled in a rocky channel where the flow was rapid. Moderate amounts of vegetation exist on the banks along the length of the creek. This water had an organic content of 1.21 mg C/liter.

The Santa Clara River drains Sespe Creek and other streams, but the volume of flow is low, except during heavy rains, because of underground flow. Sampling of the river was upstream from the junction with Sespe Creek. The water was heavily laden with silt which was allowed to settle before the water was analyzed.

The organic content of two samples of water from Lake Tahoe was 0.43 and 0.97 mg C/liter. These samples were procured from two sources: Sand Harbor on the Nevada side and Emerald Cove on the California side. The brackish water from the desert well near Reno, Nevada had an organic content of 1.13 mg C/liter. In respect to total organic content, this water compares favorably to the municipal waters.

For a comparison with the other waters, two samples of rain water were procured during a period of heavy rains in the Los Angeles area during November 1965. Another sample was obtained during a rainstorm in December 1965. Analysis of these samples by the developed technique showed they had an organic content from 0.46 to 1.12 mg C/liter. These organic values are of the same order of magnitude as the waters from the desert well and Lake Tahoe.

Two saline water samples secured from Pacific coastal water and the Salton Sea were analyzed for organics. The water from the Salton Sea was fairly turbid and had a very high organic content. The organic content of this sample was 8.19 mg C/liter but after allowing most of the particulate matter to settle, it was 7.49 mg C/liter. The sea water sample was obtained at Sequit Point, a relatively undeveloped portion of the shoreline north of Los Angeles. Analysis showed the water to have an organic content of 2.41 mg C/liter.

Santee Wastewater Reclamation Program

The Santee wastewater reclamation program was undertaken by the Santee County Water District to (1) meet the waste disposal needs of the Santee community and (2) reclaim the water for recreational, industrial, commercial, agricultural, and other uses. At the present, the reclaimed water is used principally for recreational purposes (swimming, boating, and fishing) and to a limited extent for commercial uses such as watering golf course greens and fairways. The project will eventually culminate in a recycle water management program in which the reclaimed water, after recreational use, will be deposited in the underground storage basin through agricultural, industrial, and other uses. Then the water will be pumped from the aquifer, demineralized, and returned to the municipal water system and the secondary distribution system. A small amount of purchased water will be added to this closed cycle to compensate for transpiration and evaporation losses ^{25,26}.

The unincorporated community of Santee lies along the San Diego River Valley for a distance of 6 miles, beginning approximately 15 miles above the river mouth. It is located just north of the City of El Cajon and approximately 20 miles from downtown San Diego. The community is largely residential with only a few commercial establishments. There is no waste-producing industry.

Sycamore Creek, location of the reclamation project, extends generally northward from the San Diego River channel and forms a canyon containing both the treatment plant for the community and the recreational lakes. There is subsurface flow in Sycamore Canyon but only occasional surface flow. The floor of the canyon slopes upward to the north and narrows from approximately 2000 feet in width at its mouth to about 1000 feet in width above the recreational lakes. The canyon contains an alluvial fill 12 to 15 feet deep, deposited over sedimentary bedrock composed of siltstone and clayey sandstone, which serves to confine the underground stream. Immediately upcanyon from the sewage treatment plant, the area has been extensively worked by a gravel-processing industry to a depth of from 10 to 12 feet. The remaining borrow pits have been reworked into level areas with earthen berms to provide oxidation ponds or lakes to receive the sewage treatment plant effluent.

The Santee technique for water purification begins with primary and secondary (activated sludge) treatment of the sewage at the treatment plant. Effluent from the plant flows into Lake 1 which has a surface area of 16.3 acres and a capacity of 24.7 million gallons. Here the effluent receives tertiary treatment in the lake which serves as an oxidation pond. Next, the water is pumped upcanyon to the percolation beds above the recreational lakes. After percolation through the sand and gravel, the water flows into Lake 5 which has an area of 7.9 acres and a capacity of 14.0 million gallons. Separate swimming facilities are adjacent to this recreational lake. Next, the water flow through three additional recreational lakes (4, 3, and 2). These lakes have areas of 11.0, 7.5, and 6.8 acres, respectively, and capacities of 17.5, 15.9, and 12.1 million gallons, respectively. From Lake 2, the flow is down Sycamore Canyon Creek from which water is pumped for watering the golf course and for other commercial uses.

The Santee project is unique in water reclamation because of public acceptance and use of the water, which is reclaimed from sewage, for swimming, boating, and fishing. The water has been approved for these recreational uses by the Public Health Service as well as by the county and state public health departments after bacterial and viral studies.

This reclaimed water was analyzed for organics as a comparison with waters from municipal and natural sources. Samples of water were obtained from each of the five lakes in the Santee Reclamation Project. These were analyzed for organic content by the analytical methodology developed under this contract and the results are presented in Table 4.

TABLE 4
ORGANIC CONTENT OF WATER SAMPLES FROM THE
SANTEE WASTEWATER RECLAMATION PROJECT

<u>Sample</u>	<u>Organic Matter, mg C/liter</u>
Lake 1	10.44
Lake 2	3.46
Lake 3	2.50
Lake 4	2.37
Lake 5	1.61

Immediately following the treatment in the sewage plant, the water runs into Lake 1 which is the oxidation pond or tertiary treatment of the effluent. This lake had an organic content of 10.44 mg C/liter. From Lake 1, the water is pumped upcanyon to the percolation beds and is collected in Lake 5 after passage through the sand and gravel beds. This lake, which had the lowest organic content of the entire system, is the first recreational use of the purified water. The water then flows into Lake 4 where the water is used for boating and fishing. The organic content of the water in this lake was somewhat higher than in the previous lake. From Lake 4, the water passes into Lake 3 which had nearly the same concentration of organic matter but is used only for fishing. The last lake in the system before the water flows into Sycamore Creek is Lake 2 which is reserved for fish hatchery studies. The water in this lake had an organic content of 3.46 mg C/liter.

These results show that the changes in organic content follow two expected trends in the project. First, the organic content of the water decreases during the purification by percolation. And second, the concentration of organic matter in the water increases as use is made of the water for recreational and fishery purposes.

Pomona Water Reclamation Plant

The Los Angeles County Sanitary District and the U.S. Public Health Service are conducting a joint study to obtain experimental and cost data on the reclamation of water from sewage. This study is being conducted in an experimental purification pilot plant located adjacent to the sewage processing station in Pomona, California.

The effluent from the main sewage plant serves as the feed water for the experimental purification plant. As the first step in the process, this effluent is subjected to another activated sludge treatment. The effluent is then passed through a series of four activated charcoal bed columns which remove impurities remaining after the activated sludge treatment. Following the charcoal treatment, the product water is returned to the sewage plant. A fifth charcoal bed column has been incorporated into the system to allow periodic backflushing or reactivation of individual columns.

Samples were obtained of the main sewage plant effluent and the water after each stage of treatment in the experimental purification plant. These samples were analyzed for organics content by the pyrolytic-gas chromatographic procedure and the data are presented in Table 5. For comparison, the analytical results obtained by the oxygen combustion-infrared technique are also presented.

TABLE 5

ORGANIC CONTENT OF WATER SAMPLES FROM THE POMONA WATER RECLAMATION PROJECT

Sample Number	Sampling Location	Organic Matter, mg C/liter	
		Pyrolytic	Combustion-Infrared
1	Main Sewage Plant Effluent	77.1	70
2	Effluent From Second Activated Sludge Treatment	12.4	10.1
3	Effluent From First Charcoal Column	6.2	8.0
4	Effluent From Second Charcoal Column	6.3	6.2
5	Effluent From Third Charcoal Column	6.8	4.0
6	Effluent From Fourth Charcoal Column	5.0	3.0

The pyrolysis of organic substances at high temperatures converts the organics principally into methane, hydrogen, carbon monoxide, and water. In addition to methane in the exit gases from a dynamic pyrolysis system, incompletely pyrolyzed organic fragments and small-molecule organics such as ethane, ethylene, and formaldehyde may also be present in small amounts. The object of this investigation was to devise methodology capable of measuring both methane and any other small organics formed during pyrolysis of organic matter in water.

To facilitate this methodology, direct coupling of the pyrolysis chamber and a flame ionization detector would allow measurement of all organic substances. However, the carrier gas flow to the detector must be controlled within certain limits at all times for proper detector performance. To achieve this control, a restrictive device must be incorporated between the pyrolysis chamber and the detector to smooth out pressure surges. The necessity for a restrictive device becomes clear when the events occurring during the pyrolysis of a water sample are considered. When a 0.25-cc water sample is injected into a pyrolysis chamber maintained at 800° C, over 1200 cc of water vapor is produced almost instantaneously. Although this vapor will cool rapidly as it exits from the pyrolysis chamber, the flowrate of the vapor and carrier gas to the detector will be suddenly increased between 15 and 60 times the original value. This rapid flow increase will be more than sufficient to extinguish the flame.

A suitable restrictive device to prevent pressure surges from injection of water samples is a column packed with fine glass beads. This type of column will (1) sufficiently restrict the flow between the pyrolysis chamber and detector for continuous operation of the detector, and (2) permit passage of all organic compounds to the detector for measurement. However, the water vapor will also pass through the column and when it enters the flame, the response of the detector will be depressed sufficiently to drive a recorder off scale. This effect can be largely nullified by substituting steam for the usual nitrogen carrier gas and making any necessary instrumental adjustments. The addition of water vapor from the sample to the steam carrier gas will depress the baseline slightly for several minutes beginning almost immediately after sample injection. However, this depression is not sufficient to drive the recorder off scale. The depression results from flame equilibria changes caused by the increased quantity of water vapor introduced into the flame.

PROCEDURE

The procedure used to measure the organic matter in water by detection of methane and any other organic fragments from the pyrolysis is similar to the procedure for measuring only the methane.

A 10-foot by 3/16-inch-OD stainless-steel column packed with 60 to 80 mesh glass beads is installed in the gas chromatograph Model 600C (Wilkins Instrument and Research, Inc.), and a steam generator (Wilkins Instrument and Research, Inc.) is substituted for the nitrogen source. The injector

is disconnected and the fitting on the pyrolysis chamber is capped. Then the column is cleaned by passing steam through the column and pyrolysis chamber overnight at a pressure of 10 psig. During the cleaning, the column and pyrolysis chamber are maintained at 300 and 800° C, respectively. After cleaning, the column is cooled to the operating temperature and the flow of steam is interrupted momentarily for connection of the injector to the pyrolysis chamber. The injector is cleaned in the manner described previously.

During analyses, the instrumentation is operated under the following conditions:

Column Temperature, °C	135
Hydrogen, cc/min	25
Air, cc/min	250
Steam, psig	5.5
Injector Setting	50
Heating Tapes, °C	125
Pyrolysis Temperature, °C	800
Attenuation	10 x 1, or as required
Chart Speed, in./min	2
Sample Size, cc	0.25

The procedures for the determination of the blank and analyses has been described in the Methane Method section of this report.

CALIBRATION

In order that the pyrolytic fragmentation and the detector response will be identical during both calibration and analysis, the calibration is conducted with organic materials similar to those existing in the waters under analysis.

The organic matter in natural waters has been shown by Birge and Juday⁴ to be 81.9 percent carbohydrates, 17.1 percent protein, and 1.0 percent lipides. Other investigators have reported similar findings. This organic matter, including both the parent materials and the series of degradation products, is extensively hydroxylated and aminated, and contains only small amounts of methyl and methylene groups. The fragmentation of this type of organics differs from those composed predominantly of methylene groups.

For natural and municipal waters, the calibration is accomplished through analysis of aqueous solutions containing organics representative of the natural substances and their degradation products normally found in water. The calibration materials used during this work were carbohydrates,

proteins, and some decomposition products. Specifically, these included sugar, agar, gelatin, acetic acid, lactic acid, dl-valine, dl-alanine, and starches from three sources.

In the calibration, the glassware used for solution preparation was cleaned with hot nitric acid containing 10-percent sulfuric acid, rinsed with triply distilled water, drained, and used immediately. Aqueous solutions of each calibration material were prepared by the successive dilution technique to obtain concentrations of 1, 10, or 100 ppm in triply distilled water. The agar and gelatin solutions were prepared by dissolving these materials in a small quantity of hot, triply distilled water and then diluting to volume. Because of slight turbidity, the starch solutions were stirred constantly during preparation and analysis. A standard solution of 10-ppm methyl isobutyl ketone was also prepared.

Each solution was analyzed according to the described procedure by six or more injections into the pyrolytic-gas chromatographic instrument. The area of each peak was measured in the usual manner with a planimeter. The average peak area, on an attenuation basis of 1 x 1, was calculated for each solution. These areas were then corrected for any changes in instrument response as determined with the standard solution and for any area contributed by the distilled water. The average peak area and the concentration of each solution are presented in Table 6. From these data, the response for each solution was calculated as sq cm/mg C/liter and averaged as shown in Table 6. This average response was then used in the analyses of the natural and municipal waters.

TABLE 6

RESPONSE OF INSTRUMENTATION TO CALIBRATION SOLUTIONS

Material	Concentration, mg C/liter	Peak Area, sq cm	Response, sq cm/mg C/liter
Corn Starch	0.45	1.5	3.3
Corn Starch	4.45	19.1	4.3
Corn Starch	44.45	205.3	4.6
Potato Starch	4.45	11.5	2.6
Soluble Starch	44.45	90.8	2.0
Agar	4.45	46.2	10.4
Sugar	4.21	27.0	5.1
Sugar	42.11	131.0	4.5
Acetic Acid	0.40	3.0	7.5
Lactic Acid	40.00	212.1	5.3
Gelatin	0.43	2.1	4.9
Gelatin	42.64	229.4	5.4
dl-Valine	51.26	237.1	4.6

NOTE: The average response was 5.0 sq cm/mg C/liter

The calibration values obtained with different instruments can be expected to vary somewhat because of differences in detectors, injection, and instrumental conditions. The preparation and analysis of dilute solutions of natural materials, such as those used in calibration, present problems because of adsorption, contamination, insoluble phases, and other factors. The linearity of results is illustrated with the corn starch which gave peak areas of 1.5, 19.1, and 205.3 sq cm for 1-, 10-, and 100-ppm solutions, respectively.

ANALYSIS OF WATERS

The procedure developed for determining the organics in a water medium by measuring all pyrolytic fragments was applied to a number of municipal and natural waters.

The water samples were collected in clean 4-ounce bottles which were sealed with foil-lined caps. The collection bottles had been previously subjected to a cleaning treatment consisting of washing in hot nitric acid containing 10-percent sulfuric acid, thorough rinsing with triply distilled water, and drying in a protective environment before sealing. Immediately prior to sample collection, the bottle was rinsed several times with the water being sampled. All analyses were conducted as soon as possible after sample collection.

The data for the various municipal and natural waters are shown in Table 7. An examination of the results for the municipal waters shows that the organic carbon content ranges from 2.5 to 7.7 mg C/liter. These municipal waters originate from both wells and watersheds. As one example, the source of water for Portland, Oregon 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. Therefore, the organic matter in this water is derived solely from vegetation and none is derived from man-made pollution.

TABLE 7
ORGANIC CONTENT OF VARIOUS MUNICIPAL
AND NATURAL WATERS

<u>Source</u>	<u>Organic Content, mg C/liter</u>
Municipal Waters:	
California:	
Redding	4.8
Santa Rosa	3.7
Ventura	2.5

TABLE 7
(Concluded)

<u>Source</u>	<u>Organic Content, mg C/liter</u>
Oregon:	
Eugene	7.7
Gold Beach	6.3
Medford	4.7
Portland	7.7
Seal Rock	3.9
Tillamook	6.4
Natural Waters:	
Eel River	3.7
Lake Elsinore	113.1

The two waters from natural sources, Eel River and Lake Elsinore, had 3.7 and 113.1 mg C/liter, respectively. The Eel River is a large river in northern California but summer flow is curtailed because of absence of precipitation in the region. This river water is clear and flows mainly over rocks and gravel beds for most of its length. Lake Elsinore is a large man-made recreational lake southeast of Los Angeles. This lake is fairly shallow, and at the time of sampling, the water was greenish-colored because of intense algae growth. The particulate matter was allowed to settle before the sample was analyzed. The intense aquatic growth explains the very high organic carbon content found in this water.

All values obtained for these municipal and natural waters are similar to those reported by other investigators. During a study of 529 lakes, Birge and Juday⁴ found the organic carbon content ranged from 1.2 to 28.5 mg C/liter with the mean for all lakes being 7.7 mg C/liter. Of these lakes, 327 had an organic carbon content between 3 and 10 mg C/liter. According to Krylova and others^{27, 28}, Russian lakes contain from 1.7 to 15.2 mg C/liter. In one reservoir, the average content of organic matter in the water was 13.0 mg C/liter with about 20 percent of this being in the form of amino acids and reducing sugars²⁹. The Russian rivers contain from 2.0 to 34.8 mg C/liter depending on the season^{27, 30, 31, 32}. An extensive study³³ of more than 500 subsurface waters showed the organic carbon content varied from 0.2 to 212.5 mg C/liter with an average of 10.5 mg C/liter. In these waters, the organic content depended on the strata, proximity of oil fields, and other factors.

CONCLUSIONS

This study has demonstrated that summation of the organics in a water matrix based on a pyrolytic-gas chromatographic principle is feasible and practical.

Specific analytical techniques utilizing pyrolysis of the organics in the presence of the water followed by gas chromatographic separation and flame ionization detection of the pyrolytic fragments have been developed into state-of-the-art methodologies.

The developed methodologies are applicable to the chemical characterization of source waters, the quality control of product waters, and the study of the effect of natural organic materials on the efficiencies of desalination processes.

The next phase of this program deals with the development of methodology for the complete characterization of the naturally occurring organics in water. An analytical approach based on selective separation by cascade filtration followed by pyrolytic characterization appears to be feasible and more extensive evaluation of this technique will be undertaken.

APPENDIX A

DECOMPOSITION OF ORGANIC MATTER IN WATER

The decomposition of the organic matter in water is the result of the bacteria and other microorganisms using it as a food source. The degradation processes are carried out principally by the saprophytic bacteria which subsist upon dead organic matter. Protozoa and plankton are also present in water, but their direct influence on the decomposition rate of organic matter is minor. However they have an indirect influence through their depredation of the bacterial population.

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. The organic matter is degraded through the action of enzymes secreted by the bacterial cells. Although little is known of the nature of the mechanism by which enzymes act, each enzyme is specific in the reactions which it promotes.

The enzymes active in bacterial decomposition processes can be classed as desmolases, which are intracellular enzymes, and hydrolases, which are extracellular. The latter group is the most important in the decomposition of organic matter in water because they degrade the organic matter outside the cell. These enzymes disintegrate complex organic molecules by hydrolytic mechanisms independently of the presence of bacterial cells. Among these enzymes are the carbohydrases, lipases, esterases, proteases, and amidases.

Many classes of organic compounds may serve as a source of carbon and energy for the bacteria. These include carbohydrates, proteins, saturated and unsaturated fatty acids, amino acids, keto acids, alcohols, hydroxy acids, amines, amides, aromatic compounds, and numerous others. However, to understand the decomposition of organic matter in water, it is best to consider the degradation processes according to the parent materials which are the carbohydrates, proteins, and lipides. Because oxygen is generally available in natural waters, only processes occurring under aerobic conditions need be considered here.

The carbohydrates are usually classified according to the number of simple carbohydrate groups that they contain into polysaccharides, disaccharides, and monosaccharides. The polysaccharides are divided into starch, cellulose, and hemicelluloses.

The degradation of cellulose occurs in two stages as shown in Fig. 3. The first stage involves hydrolysis to a disaccharide cellobiose by means of the enzyme cellulase which is secreted by many bacteria. In the second stage, the cellobiose is further hydrolyzed to glucose through the action of the enzyme cellobiase in a reaction similar to the breakdown of maltose. Both enzymes occur together in the same bacteria.

A large variety of bacteria can degrade starch through secretion of an exocellular hydrolase, diastase, which reacts independently of the presence of living cells. The decomposition of starches can be generalized as shown in Fig. 4. In this degradation, the first products are a variety of high molecular weight materials. These are further decomposed into products such as maltose, which is a disaccharide produced through the action of the diastase. The enzyme maltase then hydrolyzes the maltose into glucose. All disaccharides are hydrolyzed in a similar manner to form two molecules of monosaccharides called hexoses.

The monosaccharides are decomposed both aerobically and anaerobically with the products depending on the molecular structure of the hexose, the organisms, and the environmental conditions. Although knowledge concerning the bacterial degradation of hexoses is incomplete, the mechanism is believed to follow the path shown in Fig. 5. The first step is the splitting of the hexose into two molecules of triose. Then an enzyme converts the triose to glyceric acid which readily forms the enol of pyruvic acid. This enol, in turn, rearranges to the very unstable pyruvic acid. By an alternate mechanism, the enzyme can accept two hydrogen atoms to convert the triose to pyruvic acid. Depending on whether conditions are aerobic or anerobic and on the species of bacteria present, the pyruvic acid is converted to various other organic compounds such as lactic acid, acetaldehyde, ethanol, formic acid, and acetic acid. As with all bacterial decomposition of organic matter, the eventual final products are carbon dioxide and water.

The proteins, proteoses, and higher polypeptides together with their decomposition products such as amino acids, amines, and amides comprise the nitrogenous compounds in water. These parent compounds are broken down sufficiently by bacterial exocellular proteolytic enzymes so that the decomposition fragments can enter cell walls for utilization by the bacteria. The proteins are easily hydrolyzed into their approximately 20 component amino acids. Under aerobic conditions, these are oxidized by bacteria into substituted pyruvic acids. These initial products from bacterial attack undergo further degradation. Unsaturated acids are oxidized and hydrolyzed into smaller acids. The α -keto acids are bacterially oxidized to substituted acetic acids.

The lipides, or fats, are markedly resistant to bacterial attack. Some of the fatty acids present in natural fats are long-chain unsaturated fatty acids and saturated acids such as acetic, butyric, caproic, caprylic, capric, and stearic. These fatty acids undergo bacterial decomposition to ultimately yield carbon dioxide and water. The reaction mechanisms and degradation routes have not been sufficiently studied to determine all the intermediate products.

From the preceding discussion, it is apparent that the organic matter in water is of a highly complex nature. It encompasses many substances ranging from soluble compounds to colloids, particulate materials, and organisms. This very complex composition is a dynamic system subject to alteration by biological activity. However, large natural water bodies have steady-state organic compositions averaging 82 percent carbohydrates, 17 percent protein, and 1 percent lipides.

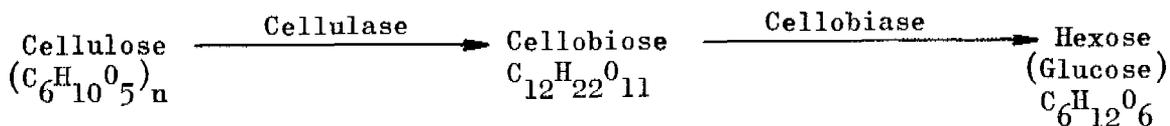


Figure 3. Degradation of Cellulose

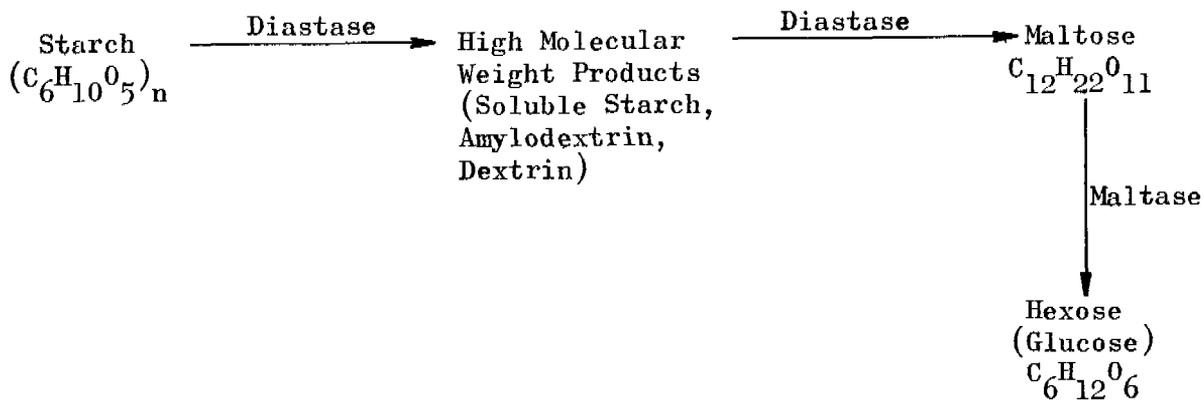


Figure 4. Decomposition of Starches

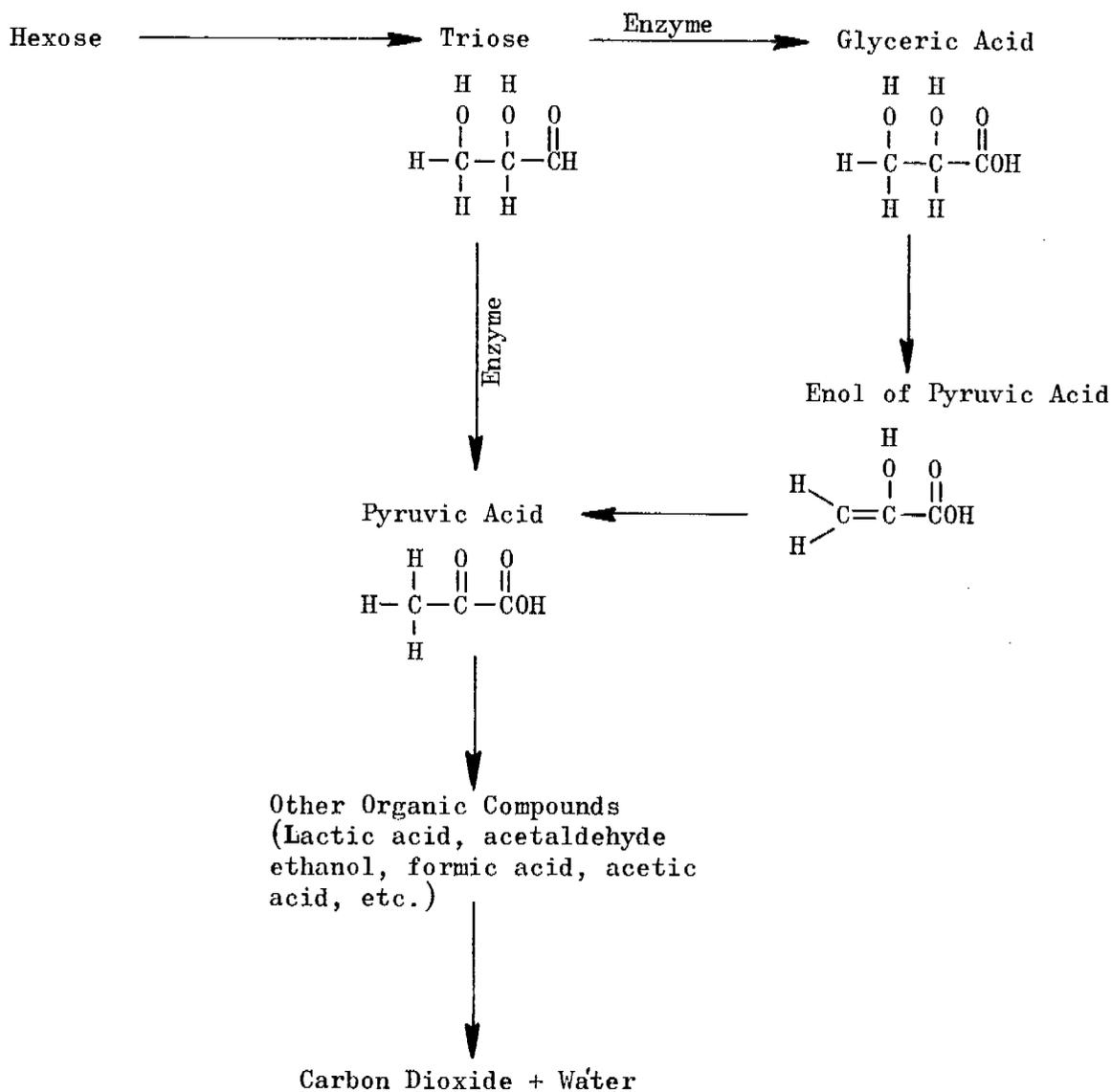


Figure 5. Degradation of Hexoses

PYROLYSIS OF ORGANICS

For more than a century, pyrolysis has been used as a preparative method in the synthesis of organic compounds. The best known application is the thermal cleavage of esters to form an olefin and a carboxylic acid⁵.

During recent years, pyrolysis has come into widespread use as an analytical tool for the qualitative identification of polymers and similar organic materials. The procedure has consisted of rapidly heating the unknown material either on a platinum filament, in a sealed ampoule, or in a quartz-tube furnace. Then the products from the pyrolytic cleavage have been either examined by infrared techniques or separated by gas chromatography for identification. In addition to yielding pyrograms of the material, the latter technique has in many instances enabled unequivocal differentiation of materials.

Very few quantitative procedures using pyrolysis in conjunction with gas chromatography have been reported. One of these is a method for measuring the hydroxyethyl group in modified starch⁶. Pyrolysis of the starch at 400°C produced a number of organic fragments including acetaldehyde which was proportional to the amount of hydroxyethyl group in the starch.

The completeness of pyrolysis and the quantity of pyrolytic products from a sample can be qualitatively related to several interrelated factors. These are (1) the volatility of the organic matter, (2) the geometry and volume of the pyrolysis chamber, (3) the manner of heating the chamber, (4) the area of the heated surface, and (5) the means of sample introduction. Little attention has been focused on these factors in the design of pyrolytic analytical equipment.

The effect of sample volatility is more pronounced when the material is heated on a platinum coil or ribbon. This method of pyrolysis is rather inefficient in comparison to heating the sample in an ampoule or quartz tube. The reason for this inefficiency is that the majority of the sample is volatilized unfragmented onto the cooler chamber walls. Pyrolysis in an ampoule or quartz tube ensures a longer exposure of the sample to elevated temperatures.

The geometry, volume, and manner of heating the pyrolysis chamber affect the extent of cleavage because these factors influence the length of time the sample will reside in a hot zone. Similarly, the area of the heated surface affects the amount of thermal cleavage of a sample. This is readily apparent in a comparison of pyrolysis with a coil filament and a hot quartz tube.

The means of sample introduction is important because false or unsatisfactory pyrolytic patterns can result from contamination or compositional changes in the sample. An example of this is the penetration of a syringe needle through a septum. The needle carries minute septum particles into the pyrolysis zone and this superimposes a spurious pattern on the pattern for the organic material. The use of boats to place a sample in the quartz tube is suitable only for solid materials or very nonvolatile liquids. Volatile liquid solutions such as water cannot be satisfactorily introduced into the pyrolysis zone of any commercially available instrumentation.

The reactions occurring during pyrolysis of organic materials have been studied only to a very limited degree. In general, most investigations have been conducted at a single temperature or over a limited range. Furthermore, complete identification and concentration measurements of all pyrolytic products have been reported for only a few organic compounds. This lack of information makes the prediction of pyrolytic patterns or the selection of an optimum pyrolytic temperature for a particular purpose difficult.

However, some generalizations concerning pyrolysis can be made from the information available in the literature. For identification purposes, the pyrolysis temperature must be as low as possible to produce a distinctive pattern or pyrogram. As the temperature is increased, a greater variety of fragments will be obtained as a result of further cleavage of larger fragments. The extent of fragmentation is governed also by the length of time the organic material is exposed to the elevated temperature. The yield of a particular fragment from an organic material can be maximized by proper temperature selection.

The fragment maximization as a function of temperature is shown in the pyrolysis of polymeric materials reported by Ettre and Varadi⁷. These materials were pyrolyzed in a quartz tube at temperatures from 300 to 950° C. Separation and measurement of the fragments by gas chromatography showed the main products from high-temperature pyrolysis of poly(vinylalcohol) and poly(n-butylmethacrylate) were methane, carbon dioxide, carbon monoxide, and water. As the temperature was increased, the yield of these products rose and the amounts of other organic fragments such as acetaldehyde, methanol, ethanol, and acetic acid decreased rapidly from their values at low temperatures. The amount of methane produced from the poly(vinylalcohol) stabilized after increasing markedly between 700 and 800° C. For poly(n-butylmethacrylate), the methane rapidly increased to a near maximum value between 600 and 700° C.

Although the bulk of pyrolytic investigations have been conducted at temperatures below 600° C, the data are useful because they indicate the compounds formed, the stability of molecular bonds, and the reaction trends with temperature. These data show that characteristic patterns are obtained at low temperatures while the major products for any organic material at sufficiently high temperatures are predominantly methane, hydrogen, carbon monoxide, and water.

A considerable number of organic materials have been pyrolyzed and their products have been examined in some detail. These include natural substances such as carbohydrates^{6,8}, proteins⁹, oils¹⁰, humic acids in soil¹¹, and specific organic compounds which can be classed into amino acids⁹, amines^{12,13}, alcohols^{7,12,14} through 17, ethers¹⁸, esters¹⁹, aromatic compounds²⁰ through 23, aldehydes¹², ketones¹², and hydrocarbons²⁴.

Carbohydrates have been pyrolyzed at 300° C to determine the products formed at low temperatures⁸. Starch, cellulose, maltose, and sucrose all decomposed at this temperature into carbon dioxide, acetaldehyde, furan, propionaldehyde, acetone, acrolein, 2-methylfuran, water, and some unidentified light gases. However, the pyrogram for cellulose differed considerably from the others in respect to the magnitude of the peaks. Under

the same conditions, alginic acid gave the same products except only a negligible amount of propionaldehyde was formed. At 300° C, hemicellulose fragmented into carbon dioxide, acetaldehyde, methyl formate, furan, methanol, 2-methylfuran, ethanol, and water. During a more detailed pyrolytic study on corn starch, Tai et al.⁶ reported that light gases, acetaldehyde, furan, propionaldehyde, acetone, 2-methylfuran, 2-butanone, 2,3-butadione, and methyl-1-buten-3-one were formed at 400° C. Although no appreciable volatile products formed below 350° C, well defined patterns only slightly affected by temperature changes were obtained at 380 to 450° C. As the temperature exceeded 500° C, the products decomposed further.

In the vicinity of 300° C, the principal products from the pyrolysis of proteins and amino acids are ammonia and methyl-, ethyl-, diethyl-, di-propyl-, tripropyl-, butyl-, and tributylamines with the smaller molecules predominating⁹. A study¹³ of the pyrolysis kinetics for mono-, di-, and triethylamines in the temperature range 800 to 1100° C showed that the products were ammonia, methane, hydrogen cyanide, ethylene, and traces of other compounds. Another investigator¹² reported that pentylamine is completely disintegrated into small fragments at 600° C. According to these studies, proteins and amino acids present in water will fragment at high temperatures into methane and ammonia together with small amounts of hydrogen cyanide, ethylene, and other trace products.

There is evidence that at high temperatures, lipides and fats cleave first into the corresponding fatty acids and other fragments in a manner analogous to ester degradation at low temperatures¹⁹. These fatty acids will immediately further degradate through decarboxylation to hydrocarbons. This is the principal reaction¹² in the pyrolysis of pentanoic acid at 600° C. Then the hydrocarbons fragment into methane and other low molecular weight hydrocarbons²⁴.

The degradation of specific organics has been studied under various conditions and temperatures. At 600° C, aldehydes and ketones completely disintegrate into smaller fragments according to an investigation of C₅ aldehydes and ketones¹². Acetaldehyde at 500° C cleaves into methane and carbon monoxide¹⁵ while formaldehyde decomposes to give hydrogen and carbon monoxide^{14,15}. Acetone disintegrates into methane and ketene which forms C₂ and C₃ hydrocarbons through a series of reactions¹⁶. At temperatures in the vicinity of 500° C, dimethyl ether decomposes to form methane, hydrogen, and carbon monoxide as the primary products. Traces of ethylene, formaldehyde, methanol, and other substances are also formed¹⁸.

During pyrolysis at 600° C, the main reaction of alcohols, such as pentanol-1 and pentanol-2, is dehydration with formation of an olefin¹². Similarly, in the degradation of tert-butanol, this reaction is the initial step which produces water and isobutene¹⁷. The olefins decompose quite rapidly to give the main products methane, hydrogen, and water.

The pyrolysis of short-chain alcohols differs. In the pyrolysis on n-propanol and isopropanol, the initiating step is the scission of the C-C bond adjacent to the hydroxyl group. n-Propanol decomposes at 600° C to give methane as the major product together with the intermediates, acetaldehyde and formaldehyde, which pyrolyze to methane, hydrogen, and carbon

monoxide. Only traces of ethane, ethylene, and other products are found¹⁵. At this temperature, isopropanol gives as the primary products hydrogen and acetone. The latter then decomposes to methane and ketene which reacts to form C₂ and C₃ hydrocarbons¹⁶. The dehydration of isopropanol to form propylene also occurs as a secondary reaction. Rather than dehydration being the initial step, ethanol forms mainly methane, hydrogen, and carbon monoxide through a mechanism yielding hydrogen and acetaldehyde which decomposes to methane and carbon monoxide¹⁴.

In addition to methane, the only organic structure which is relatively stable at high temperatures is the aromatic ring. Badger and Novotny²¹ reported that benzene remained 76 percent intact after passage through a tube heated to 700° C. Alkyl groups attached to an aromatic ring decompose similarly to the saturated hydrocarbons. When ethylbenzene was passed through a hot tube, the exit gases contained in addition to aromatics approximately equal amounts of methane and hydrogen with only small amounts of ethane and ethylene²². Because scission of a C-C bond is a process of lower energy than C-H scission, ethylbenzene should break down to give methyl, ethyl, benzyl, and phenyl radicals. Evidence indicates ethyl radicals react more readily than methyl radicals or undergo scission, and finally form the more stable compound methane. Scission to a two-carbon unit appears to be preferred in pyrolysis because propylbenzene gives a large yield of toluene while both ethyl- and butylbenzene give larger yields of benzene than toluene. During pyrolysis, the toluene configuration²³ remained essentially intact at temperatures from 640 to 870° C. It yielded small amounts of methane and hydrogen, and only minute traces of ethane, ethylene, and other products.

Although sparse, literature data show the fragmentation patterns vary for different classes of organic matter when pyrolysis is conducted at low temperatures. At sufficiently high temperatures, however, the majority of organic materials are pyrolyzed to methane, hydrogen, carbon monoxide, and other simple molecular fragments. To determine the total organics present in a water matrix, pyrolysis must be at a high temperature to produce the same fragmentation products from all organics. According to the literature and experimental data, a temperature of 800° C will provide a nearly maximum yield of methane from the organics for measurement.

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