# ORGANIC CHEMICAL COMPOUNDS IN KEYSTONE RESERVOIR

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## PREFACE

The objectives of the present study of organic chemical compounds in Keystone Reservoir were to: (1) determine the comparative semi-quantitative concentration of dissolved organic compounds at different locations within the reservoir and (2) determine if trace aqueous organic compounds could be identified with gas chromatography-mass spectrometry.

Dr. Troy C. Dorris served as major adviser. Drs. Ernest M. Hodnett, Rudolph J. Miller, Dale W. Toetz, and George R. Waller served on the advisory committee and criticized the manuscript. Dr. David E. Bee assisted with statistical analysis of data. Mr. Keith Kenniberg assisted with analysis of organic compounds on the gas chromatograph-mass spectrometer. David Smith, Gene Dorris, and Steve Hensley helped in collection and distillation of carbon adsorption samples. Permission to locate portable samplers on their property was granted by Vernon Stillwell, Tulsa, Oklahoma; Bill Kulchinsky, Manford, Oklahoma; Carl Davis, Cleveland, Oklahoma; and Bill Bishop, Resident Engineer, Keystone Reservoir, U. S. Army Corps of Engineers. The assistance of all these people is appreciated. Special thanks is due my wife, for encouragement and understanding, enabling me to complete this study.

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# CHAPTER I

## INTRODUCTION

The identification of organic chemical compounds in the aquatic environment has been the objective of many investigations (Vallentyne 1957). Knowledge of the organic compounds in different types of aquatic environments is necessary to fully understand interactions between organisms and the surrounding aqueous medium. The number of natural and synthetic organic compounds positively identified in natural waters is less than 50 whereas the number of unknown compounds probably is very much greater. Analytical research is needed to identify the unknown aqueous organic compounds.

Analytical studies of organic compounds have been deterred by the low concentration of aqueous organic compounds and by the complexity of the mixture. Most analytical techniques require several milligrams of a single compound for positive identification. Advances in concentration, isolation, and analytical techniques may soon overcome these obstacles (Ettinger 1965).

The present project was initiated to investigate the organic chemical composition of the water in Keystone Reservoir in Oklahoma. A major objective of the study was to adapt present advanced analytical techniques to analyses of trace aqueous organic compounds.

## Concentration Techniques

The techniques that have been developed to concentrate organic chemical compounds from aqueous solutions can be categorized as solvent extraction, distillation, adsorption, and freeze concentration. All of the techniques will effectively concentrate organic compounds from an aqueous solution but all have certain limitations.

Solvent extraction is an efficient technique for extracting and concentrating organic compounds from small volumes of water. Large volumes of water, however, require large volumes of solvent for extraction of organic solutes. The large volume of solvent is difficult to evaporate and may leave a residue of organic impurities in the final sample (Hoak 1962).

Vacuum, steam, and fractional distillation techniques are useful for separating and concentrating relatively volatile organic compounds from an aqueous solution. Distillation is usually performed on small volumes of water, and is therefore limited as a technique for concentrating trace organic compounds from large volumes of water.

Freeze concentration of organic solutes has been investigated as a technique for concentrating organic compounds from water (Shapiro 1961, Baker 1965). The technique apparently did not alter the chemical structure of the compounds, inhibited bacterial degradation, and reduced the loss of volatile compounds. Quantitative recovery might be achieved if the operating conditions were carefully controlled. This technique should be valuable to future research on trace organic compounds in water.

Adsorption of dissolved organic compounds by activated carbon has been used to concentrate organic compounds which cause tastes and

odors in water supplies (Braus, Middleton, and Graham 1951). The carbon adsorption method (CAM) has been accepted as a tentative standard method by the American Water Works Association Subcommittee on Standard Methods of Organic Analysis (1962). The CAM has been used to collect several trace aqueous organic compounds which were identified (Rosen, Skeel, and Ettinger 1963) and has given impetus to qualitative investigations of aqueous organic compounds (Ettinger 1965).

The main component of the CAM is a glass column filled with granular activated carbon which adsorbs dissolved organic compounds from water passed through the column. The adsorbed organic compounds are extracted from the activated carbon by reflux distillation with chloroform and ethanol. Chloroform, a relatively non-polar solvent, dissolved non-polar organic compounds and ethanol, a relatively polar solvent, dissolves polar compounds. The ratio of the two extracts can be used as a somewhat subjective index to the type of organic matter involved, i.e., the polar compounds result from biological processes whereas the non-polar compounds are derived from petrochemical processes.

The CAM is reproducible at $\pm$ 10 per cent (Anon. 1962, Booth 1965). The rate of organic adsorption by activated carbon varies inversely with the flow rate of water through the carbon column (Booth 1965). Hoak (1962) reported quantitative adsorption of phenol from a prepared solution, but solvent desorption recovered only 70 to 80 per cent of the carbon-adsorbed phenol. Ultra violet spectra of the desorbed phenol indicated changes in the chemical structure. Golden, et al. (1956) reported 72.7 per cent recovery of adsorbed $^{14}C$-labeled phenol from activated carbon.

Activated carbon may differentially adsorb certain organic compounds. Baker (1964) used a gas chromatograph to quantify the carbon column influent and effluent of a prepared organic solution. 14 Grams of activated carbon (Nuchar C-190) removed 99.8 per cent of n-butanol from 590 ml of prepared solution (3,240 mg/liter). Adsorption efficiency dropped rapidly when larger volumes of solution were passed through the carbon column. Nuchar C-190 adsorbed 99.9 per cent of both solutes from a binary solution of n-butanol and n-amyl acetate before breakthrough of the n-butanol. The carbon continued to adsorb all of the n-amyl acetate but n-butanol was partially desorbed.

Daniels, et al. (1963) utilized the CAM to quantify dissolved organic compounds in Lake Michigan and Lake Huron. The ratio of the alcohol extract to the chloroform extract fluctuated seasonally with changes in water level and temperature of the lake.

The mean annual concentration of aqueous organic compounds collected from Lake Mandota by carbon adsorption was 614 µg/liter (Lee, Kumke, and Becker 1965). This is only five per cent of the quantity collected from Lake Mendota by Birge and Juday (1926) using centrifugation, evaporation, and combustion. Lake Mendota does not receive many organic effluents and was considered to be relatively low in organic contant, yet the CCE concentration in Lake Mendota exceeded the CCE concentration in the Ohio River (Lee, et al., 1965).

Rock, et al., (1966) concluded that turbidity at natural pH did not affect the qualitative recovery of organic chemical compounds from water, but removal of turbidity by sand prefilters improved the reproducibility of the quantitative results.

Weber and Morris (1963) reported that the rate-limiting factor in

the carbon adsorption process was intraparticle diffusion of the solute molecules within the micropore structure of the granular activated carbon. The rate of adsorption of various organic compounds indicated than an inverse relationship existed between the rate of equilibrium attainment and size of the molecule. Hassler (1951) concluded that larger molecules were adsorbed more completely than smaller molecules of a homologous series of compounds.

The adsorption process appears to be related not only to molecular size which affects the intraparticle diffusion rate but also to solubility of the compound in water which affects the initial surface adsorption of the compound by the activated carbon. A slightly soluble organic compound with a structurally large molecule will be rapidly adsorbed from aqueous solution but will diffuse slowly within the micropore structure of the carbon. Thus the compound will rapidly saturate the carbon surface and the adsorption rate will decline rapidly.

Coughlin and Ezra (1968) reported that the surface acidity of activated carbon exerted a major influence upon the capacity of carbon to adsorb organic compounds. The authors reduced the adsorption capacity of activated carbon by a factor of eight by oxidizing the carbon. Subsequent reduction of the oxidized carbon restored only seven per cent of the original adsorptive capacity. The results were interpreted as confirming that organic solutes are adsorbed as a multimolecular layer on the surface of activated carbon.

In summary, the main limitation of the CAM is the variable recovery efficiency, which is affected by temperature, pH, turbidity, composition and concentration of organic solutes, contact time (flow rate), volume of water filtered, and surface acidity of the activated

carbon. The CAM data may be interpreted as providing only semi-quantitative indices to the concentration of organic compounds.

Despite its limitations the CAM was selected as a concentration method in the present study, since it is readily adapted to continuous field monitoring of dissolved organics and can concentrate dissolved organic compounds from a large volume of water.

## Analytical Techniques

The complexity of the mixture of trace aqueous organic compounds has been a major obstacle to identification of individual compounds. Classical solubility separations (Cheronis and Entrikin 1963) are time consuming, and usually are not adequate for separating complex mixtures such as exist in natural waters. Solubility separations are useful for separating the complex mixture into smaller, less comples fractions which can then be separated into individual compounds. The final separations can be performed by column, paper, thin-layer, or gas chromatography. Of these methods, gas chromatography and thin-layer chromatography have the greatest resolution capacity. Quantitative and qualitative analyses of micro-quantities of organic compounds have been aided in recent years by gas-liquid chromatography, and many successful applications to water pollution investigation have been reported (Baker 1962, Cochran and Bess 1966, Collins 1966, Hindin, May, and Dunstan 1965).

Compounds resolved by gas liquid chromatography can be positively identified with infrared, nuclear magnetic resonance, mass spectrometry, or other analytical techniques. Infrared spectrometry has been used to identify compounds collected by the carbon adsorption method

(Rosen, Skeel, and Ettinger 1963). The list of compounds identified illustrates the complexity of aqueous organic chemical compounds; naphthalene, tetralin, styrene, acetophenone, ethyl-benzene, bis(2-chloroisopropyl) ether, 2-ethylhexanol, bis(2-chloroethyl) ether, di-isobutylcarbinol, phenylmethylcarbinol, and 2-methyl-5-pyridine. A combination of GLC, infrared, nuclear magnetic resonance, and mass spectrometry was used by Medsker, Jenkins, and Thomas (1968) to identify geosmin from blue-green algae and actinomycetes.

Gas liquid chromatography retention time has been used to "fingerprint" volatile organic compounds which caused malflavors in drinking water (Caruso, Bramer, and Hoak 1966). The suspected compounds had the same GLC retention times as phenol and naphthalene. Swinnerton and Linnenbom (1967) used GLC to compare retention times of $C_1$ to $C_4$ standard hydrocarbons with retention times of hydrocarbons collected from Chesapeake Bay and identified ethane, ethylene, propane, propylene, isobutane, butene, n-butane, isopentane, and n-pentane. All of these compounds except butene were also identified in water collected from the Bahamas.

Sugar and Conway (1968) used GLC retention times on columns of different polarity to identify organic compounds in petrochemical wastes, both before and after biological treatment. The most positive information was obtained by mass spectral analysis of the GLC resolved peaks. 1-Hexanol was identified in the petrochemical waste by this procedure.

The utility of GLC in analyses of aqueous organic compounds has been demonstrated. However, complete elucidation of the complex mixture of organic compounds will require much additional research. New

techniques and modifications of existing techniques must be developed before the organic composition of aquatic environments can be determined. The present study of aqueous organic compounds in Keystone Reservoir, in Oklahoma, utilized the carbon adsorption method for collection and gas chromatograph-mass spectrometry for qualitative analysis.

# CHAPTER II

## DESCRIPTION OF STUDY AREA

Keystone Reservoir dam is located 19.5 kilometers west of Tulsa, Oklahoma, on the Arkansas River 3.3 kilometers below the confluence of the Cimarron River. The reservoir was constructed in 1964-1965 by the U. S. Army Corps of Engineers for flood control, recreation, and hydroelectric power generation. It has a surface area of 10,643 hectares at power pool level (elevation 220 meters mean sea level).

The Arkansas River receives effluents from urban areas and oil refineries in Oklahoma and Kansas. The Cimarron River receives effluents from a smaller number of urban areas and oil refineries in Oklahoma. High dissolved solids in the Cimarron River are derived from salt deposits in northwestern Oklahoma.

Keystone Reservoir was continuously stratified throughout 1965 and part of 1966 because of a chemical density gradient (Eley 1967). Cimarron River water contained higher dissolved solids and was denser than the Arkansas River water. The dense Cimarron River water underflowed the lighter Arkansas River water, forming a stable "hypolimnion."

Sampling sites were located at the upper and lower ends of the Arkansas and Cimarron arms of the reservoir (Fig. 1). A fifth sampling site was located on the Arkansas River approximately 27 kilometers below Tulsa, Oklahoma, 47 kilometers downstream from the reservoir.


Figure 1. Keystone Reservoir, Oklahoma. A through F Sampling Stations.

Samples collected at the lower end of the Cimarron arm were from a depth of 10 meters to insure collection from the Cimarron River water. All other samples were collected from surface waters.

# CHAPTER III

## METHODS

Portable samplers based on the design used by the Robert A. Taft Sanitary Engineering Center were installed at each sampling station (Fig. 2). Malfunction of the constant head tank (D) and metering pump (E) necessitated installation of a direct line from the column effluent end (C) to the volumetric measuring tank (G). A flow valve was installed on the carbon column effluent line to control flow rate. This modification permitted continuous operation without daily attention. Water normally was pumped continuously through the carbon column for a week before the column was recharged with fresh carbon. Most samples were collected without prefiltration since there appeared to be no appreciable effect on qualitative recoveries and only a minor effect on quantitative reproducibility (Kumke 1965, Booth 1965).

Pyrex glass tubes 7.6 cm by 45.7 cm served as containers for the activated carbon. A 40-mesh stainless steel screen in a neoprene gasket prevented the granular carbon from being washed from the column. The end plates were constructed from 0.64 cm brass or plexiglass. Teflon tape was used to seal all joints and polyethylene tubing was used for water supply lines.

The pyres tubes were filled with Nuchar C-190* (30 mesh)

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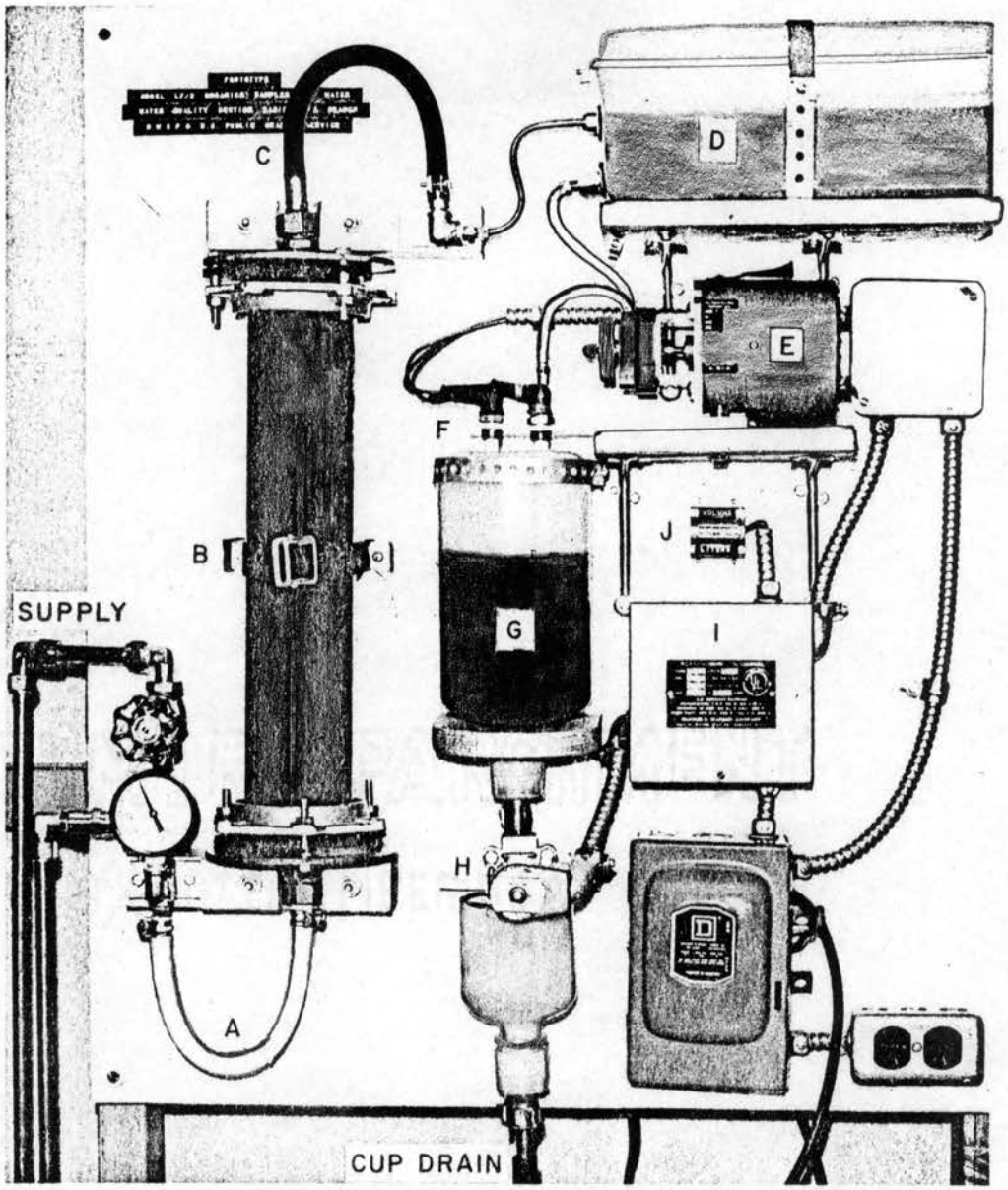
*West Virginia Pulp & Paper Co., New York, N. Y.




MODEL LF-2 ORGANICS SAMPLER FOR WATER

A- TEFLON HOSE
B- WEB STRAP
C- RUBBER HOSE
D- CONSTANT HEAD TANK
E- METERING PUMP
F- PROBE HOLDER BRACKET
G- VOLUMETRIC MEASURING TANK
H- SOLENOID VALVE
I- LIQUID LEVEL CONTROL
J DIGITAL COUNTER

Figure 2. Low Flow Rate Organic Sampler. Source: Specifications Manual. USPHS. Water Quality Section, 1964.

activated carbon without tamping. Water flow rate was normally adjusted to 1 liter/minute or less. The liquid level control was calibrated to dump the volumetric measuring tank at 1000 ml (± 5 ml) and actuate a digital counter.

The adsorbed organic compounds were sequentially extracted in a large-capacity Soxhlet extractor (Corning # 3885) for 48 hours with distilled chloroform and 95 per cent ethanol. The carbon chloroform (CCE) and carbon alcohol extract (CAE) were concentrated to approximately 250 ml by distillation and filtered through a 0.45-micron membrant filter* to remove particulate carbon from the sample. All of the chloroform and ethanol was removed by evaporation at 48 and 65° C, respectively. The quantity of organic compounds contributed by activated carbon blanks was determined by chloroform and ethanol extraction, and subtracted from the gross CCE and CAE. Net weight of CCE and CAE was converted to concentration by the equation:

$$\mu g/\text{liter of CCE or CAE} = \frac{\text{net grams of CCE or CAE} \times 10^6}{\text{liters of water filtered}}$$

The CCE and CAE concentrates were stored at 2 to 4° C until subsequent analytical tests could be performed.

## Analytical Techniques

Initially, a separation based on solubility differences was used to separate the complex mixture of chloroform extractable compounds (USPHS 1965). The neutral fraction was then chromatographed on a silica gel (Davidson code-950) column and eluted successively with

*Millipore Filter Corp., Bedford, Mass.

80 ml each of iso-octane, benzene, and chloroform:methanol (1:1).

Neither the solubility nor the column chromatography fractions could be completely resolved by GLC since the fractions contained many compounds with similar GLC characteristics and most of the compounds were not volatile enough to elute from the GLC at a maximum temperature of 300° C for several hours.

Steam distillation with continuous ether extraction of the steam distillate was investigated as an alternative procedure to separate a simple group of volatile organic compounds from the complex mixture. This procedure proved to be successful and was faster than solubility separation.

Two gas chromatographs, F & M Model 810 equipped with hydrogen flame ionization detector and F & M Model 700 equipped with a thermal conductivity detector, were used to resolve the volatile compounds. Various columns were used to resolve the mixture (Table I). The maximum operating temperature of a GLC column is determined by the stability of the liquid phase. The maximum temperature used in this study was 300° C. All GLC columns were pre-conditioned at 25 to 50° C above the anticipated maximum operating temperature. The percentage of liquid phase was reduced by "bleed-off", thus the actual percentage of liquid phase was less than reported.

Compounds resolved by GLC were collected by insertion of a capillary glass tube into the exit port of the gas chromatographic column (Kabot 1967). Condensation of the gaseous vapors generally occurred upon contact with the air-cooled capillary tube, but in some cases the capillary tube had to be cooled with an acetone-dry ice bath. The collected compound was transferred to a 1.5 mm KBr disc for

TABLE I

GAS LIQUID CHROMATOGRAPHY COLUMNS UTILIZED IN THIS INVESTIGATION

| Material | Dimensions | Per Cent Liquid Phase | Stationary Solid Support |
|---|---|---|---|
| **Cu | 1/8" x 6' | 10% Se 30 | 80-100 mesh Diatoport S |
| *Glass | 1/4" x 6' | 5% Se 30 | 60-80 mesh Chrom W-AW-DMCS |
| *Glass | 1/4" x 6' | 5% OV-1 | 60-80 mesh Chrom W-AW-DMCS |
| *Glass | 1/4" x 8' | 5% OV-1 | 60-80 mesh Chrom W-AW-DMCS |
| **Cu | 1/4" x 6' | 20% Apiezon L | 60-80 mesh Chrom W-AW |
| *Glass | 1/4" x 6' | 5% Apiezon L | 60-80 mesh Chrom W-AW-DMCS |
| *Glass | 1/4" x 8' | 5% Polymethphenyl ether (6 ring) | " " |
| *Cu | 1/8" x 12' | 5% Carbowax 20M | " " |
| **Stainless Steel | 1/4" x 20' | 1% Carbowax 20M | 60-80 mesh Diatoport S |

* Prepared on a weight liquid phase/weight of support percentage, but column conditioning probably reduced the percentage of the liquid phase.

** Purchased prepacked from F & M Scientific Division of Hewlett Packard.

subsequent infrared analysis.

Infrared spectra were obtained with a Perkin-Elmer Model 137 infrared spectrophotometer. The instrument was equipped with a beam condensing unit which permitted spectra to be obtained from micro-quantities of organic compounds pressed into a 1.5 mm KBr disc. Liquid NaCl cells with a 0.1 mm path length were used when sufficient quantity of sample was available.

A combination gas chromatograph-mass spectrometer (GC-MS) instrument (Waller 1967) was utilized to supplement the infrared spectra. The combination GC-MS used the resolving capacity of the GLC to separate mixtures of organic chemical compounds and determines the mass spectra of the separated compounds as they elute from the GLC. The mass spectrum of a compound can be used to determine the molecular weight (M+). The fragmentation pattern produced upon electron impact can be utilized to aid in elucidating the structure of the compound. The GC-MS instrument allows positive identification of a trace compound without the necessity of purifying several milligrams of the unknown compound. If a sufficient quantity of the unknown is available, the GC-MS identification can be supplemented by infrared and nuclear magnetic resonance spectrometry.

# CHAPTER IV

## RESULTS AND DISCUSSION

The concentration of CCE and CAE in the Arkansas River below Tulsa, Oklahoma, and also in Keystone Reservoir varied sporadically during this study (Fig. 3,4,5,6, and 7). Apparently, organic wastes of varying concentration and volume were occasionally discharged into the receiving streams above and below the reservoir. The temporal variation in concentration in the river was reflected by changes in the reservoir water despite quenching factors such as dilution, sedimentation, etc. The Cimarron River arm had less variation in organic concentration than the Arkansas River arm of Keystone Reservoir. Greatest variation occurred in the Arkansas River below Tulsa, Oklahoma. Variation in concentration of organic compounds apparently was indicative of the quantity and quality of organic effluents to receiving streams.

A multiple linear regression analysis was made of the CCE and CAE values, treating water flow rate and quantity filtered as covariables. A month x station interaction was detected for the CCE variable but not for CAE. CCE compounds must have entered the reservoir from point sources, since there was low correlation in rate of change in concentration among stations from month to month. The month x station interaction prevented a meaningful test for differences among annual station CCE means by multiple linear regression. A linear regression

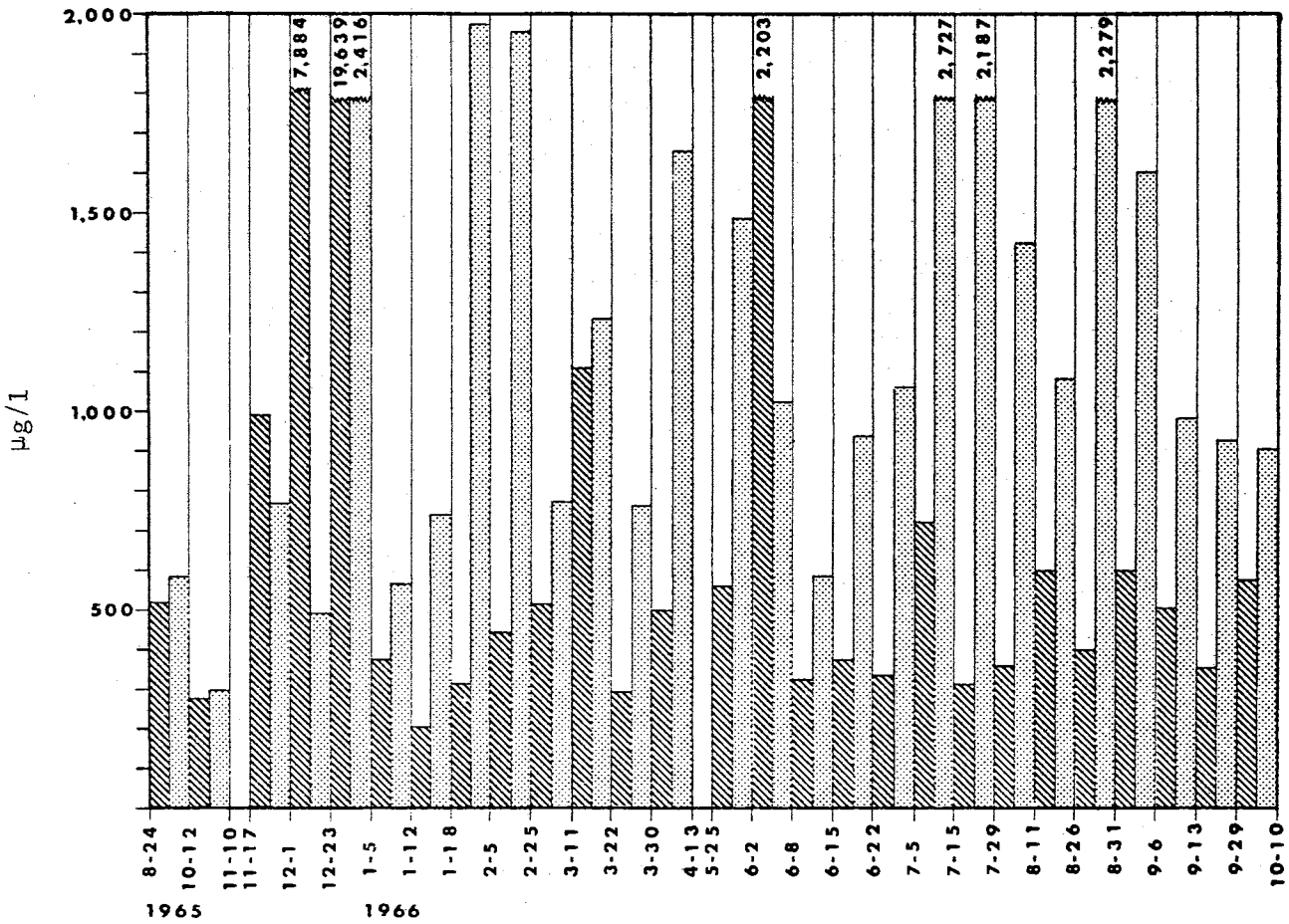



Figure 3. Concentration of Carbon Chloroform Extract (Diagonal) and Carbon Alcohol Extract (Stippled) Collected from (A) Arkansas River below Tulsa, Oklahoma.

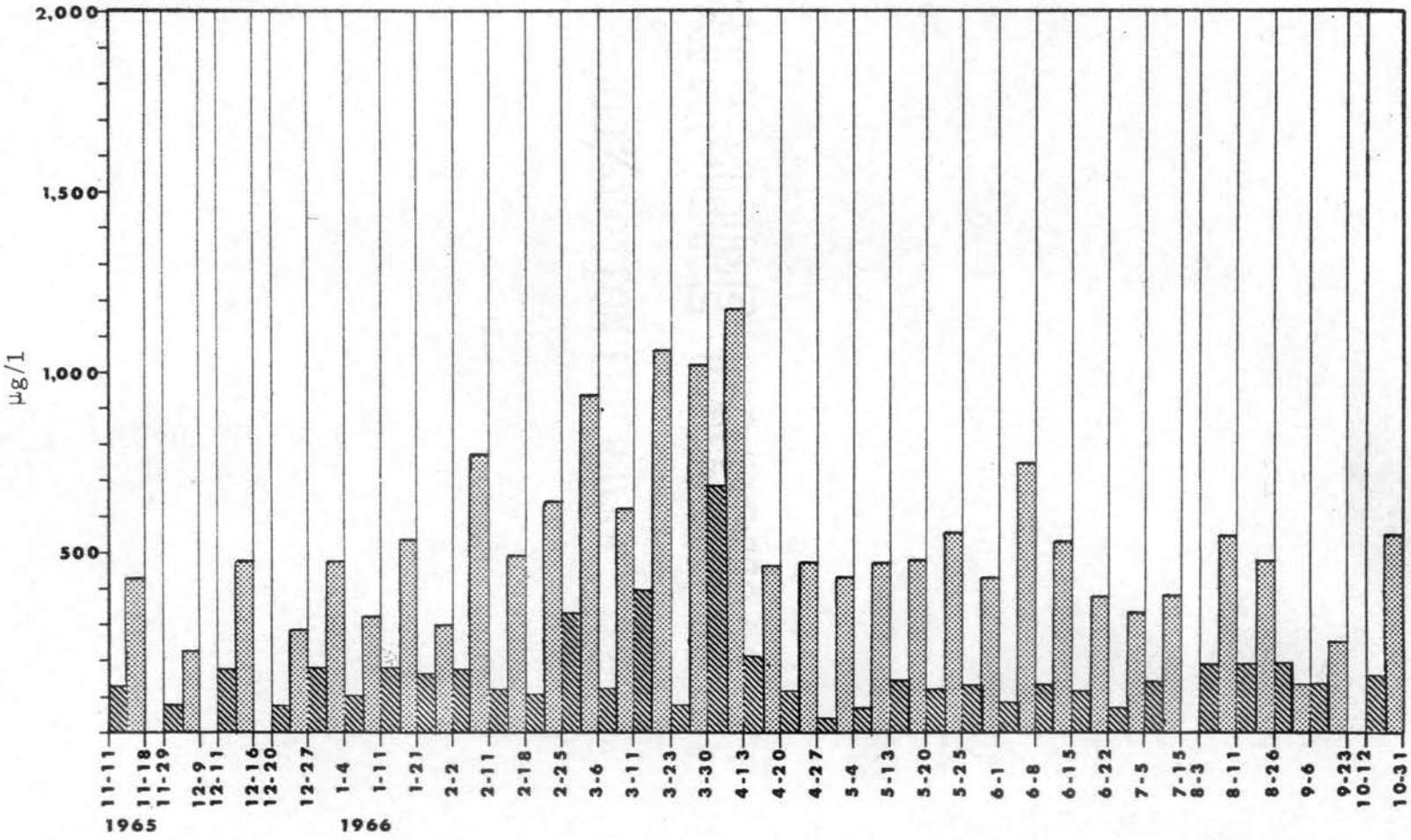



Figure 4. Concentration of Carbon Chloroform Extract (Diagonal) and Carbon Alcohol Extract (Stippled) Collected from (C) Lower End of Cimarron River Arm of Keystone Reservoir.

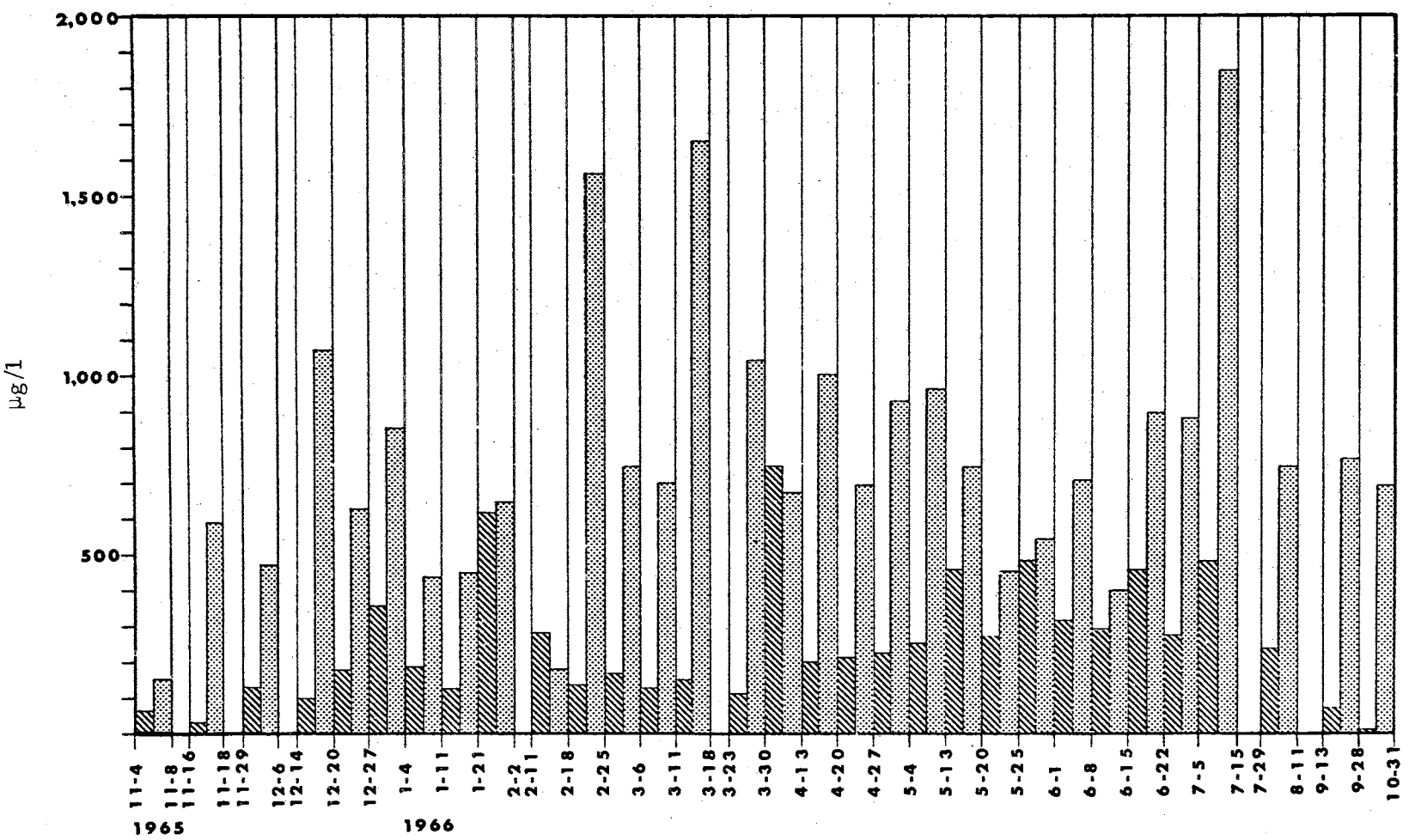



Figure 5. Concentration of Carbon Chloroform Extract (Diagonal) and Carbon Alcohol Extract (Stippled) Collected from (D) Upper End of Cimarron River Arm of Keystone Reservoir.

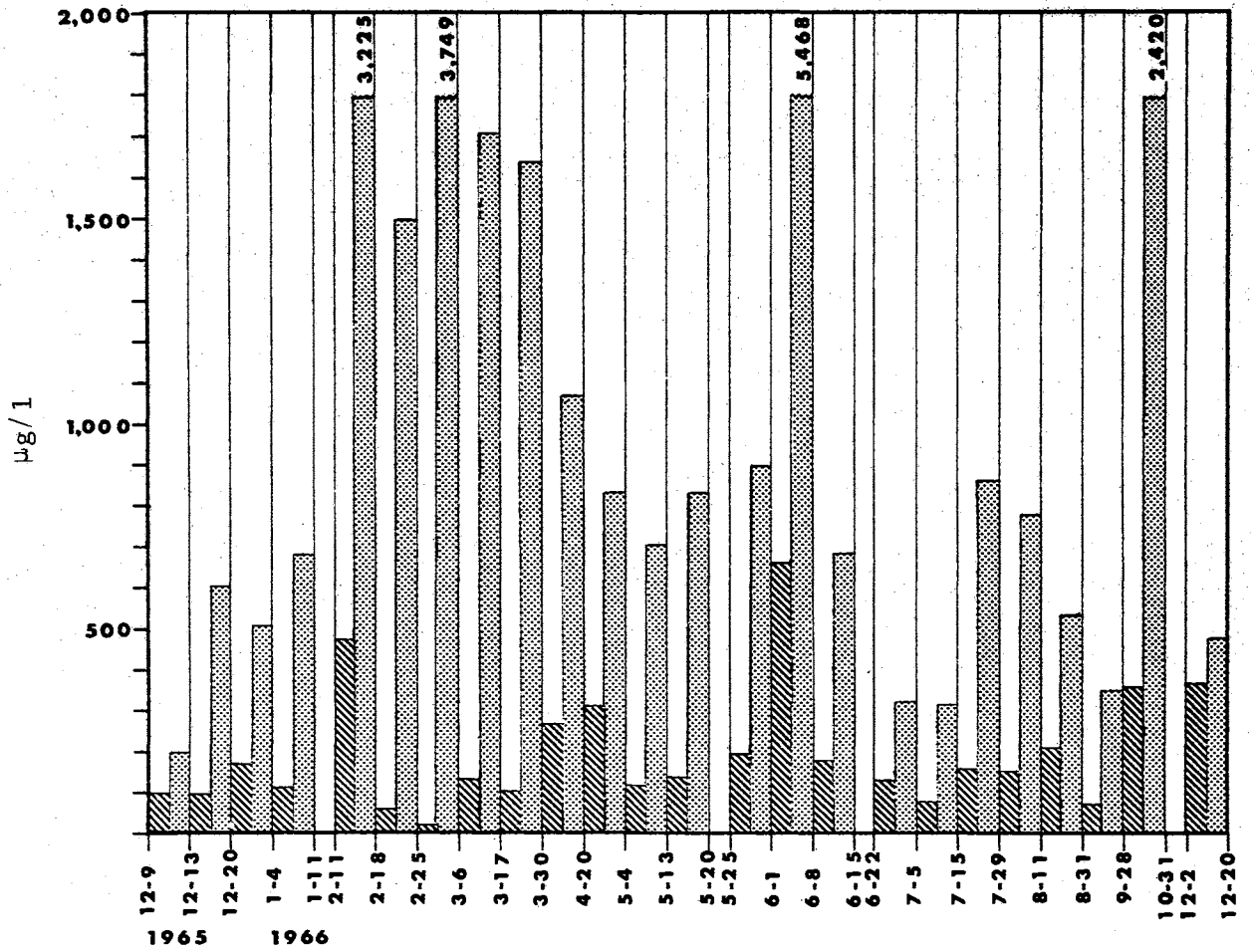



Figure 6. Concentration of Carbon Chloroform Extract (Diagonal) and Carbon Alcohol Extract (Stippled) Collected from (E) Lower End of Arkansas River Arm of Keystone Reservoir.

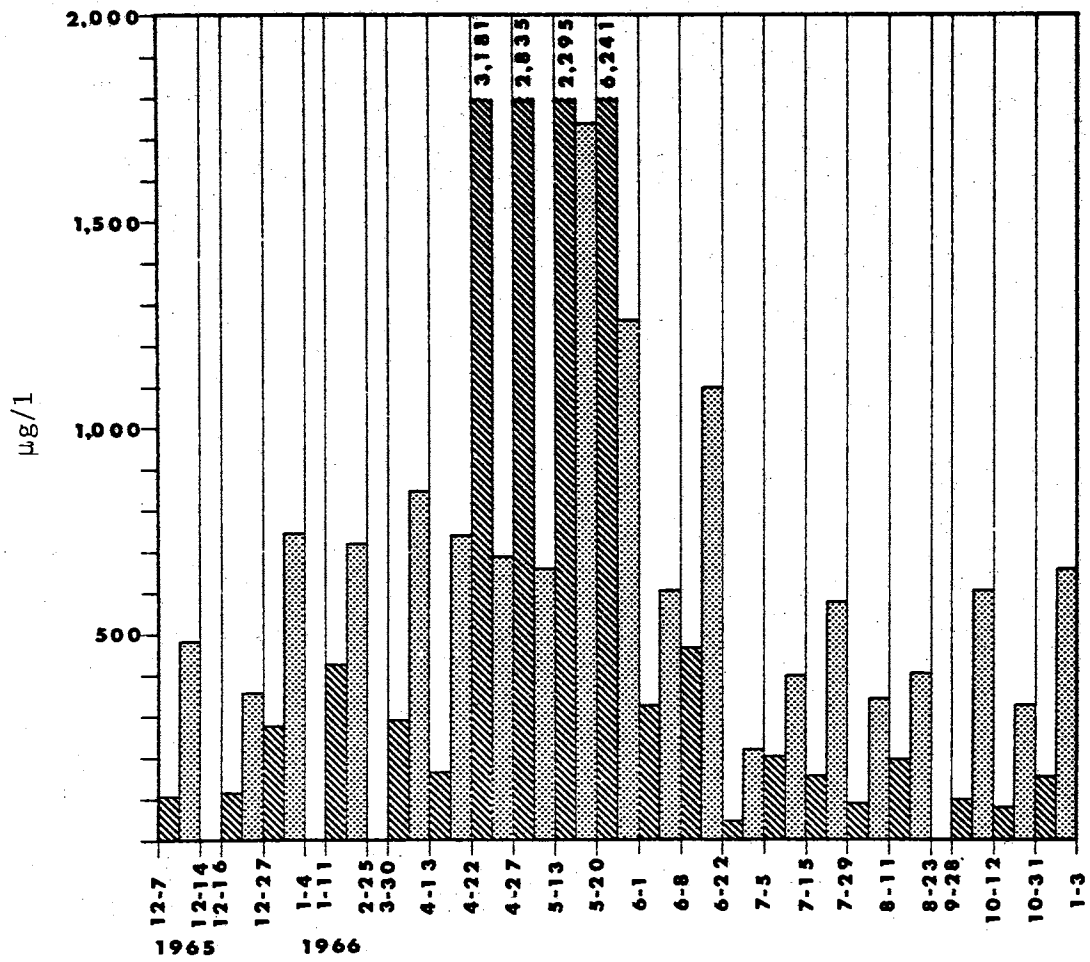



Figure 7. Concentration of Carbon Chloroform Extract (Diagonal) and Carbon Alcohol Extract (Stippled) Collected from (F) Upper End of Arkansas River Arm of Keystone Reservoir.

analysis within months and among stations was performed to detect the nature of the interaction (Table II).

TABLE II

MEAN CCE ADJUSTED FOR COVARIANCE OF FLOW RATE AND VOLUME OF WATER FILTERED

| Months | Station Monthly Mean (grams) A | C | D | E | F | $F^{*}_{cal.}$ | Probability of larger $F_{cal.}$ |
|---|---|---|---|---|---|---|---|
| 12 | 64.6461 | 0.5100 | 0.7107 | 0.0547 | 1.1804 | 2622.69 | (P<.0005) |
| 1 | 1.3137 | 0.1402 | 2.6598 | 1.7761 | 0.7048 | 2.02 | (.50>P<.25) |
| 2 | 0.6857 | 0.4393 | 1.1953 | 0.7567 | 0.7483 | 0.14 | high |
| 3 | 1.8994 | 0.7623 | 0.4613 | 0.4583 | | 3.62 | (.25>P<.1) |
| 4 | 2.0092 | 1.2989 | 1.8483 | 0.1942 | 1.3849 | 0.40 | high |
| 5 | 2.1283 | 0.0207 | 1.5572 | 0.8161 | 3.0305 | 5.10 | (.10>P<.05) |
| 6 | 2.5087 | 1.1110 | 1.6049 | 0.5498 | 0.4148 | 1.58 | (.50>P<.25) |
| 7 | 2.2613 | -0.9752 | 0.0970 | 0.8422 | 0.8183 | 7.34 | (.10>P<.05) |
| 8 | 1.5190 | 0.6862 | 1.9675 | 0.8055 | 0.8733 | 1.05 | (.50>P<.25) |
| 9 | 1.4577 | 1.5125 | 0.5298 | 0.2986 | | 1.25 | (.50>P<.25) |

* $F_{cal.}$ = Adjusted treatment mean square divided by error mean square.

Null Hypothesis: No difference among treatments after adjusting for covariance.

The mean weights of CCE were directly comparable, since adjustments for flow rate and volume of water filtered had been made in the analysis.

The concentration of CAE varied dependently among stations. CAE compounds must have entered the reservoir from many sources, causing a

corresponding relative change in concentration at all stations from month to month. The multiple linear regression analysis of annual CAE means showed that there was a difference among stations ($.05>P<.025$). The deviation of station adjusted means from the total adjusted mean (Table III) was used to detect specific differences between stations (Table IV).

TABLE III

DEVIATION OF STATION CAE MEANS FROM ADJUSTED TOTAL MEAN

| Station | Deviation from Total Mean (grams) |
|---|---|
| A | 0.98258 |
| C | -0.69317 |
| D | 0.56277 |
| E | 0.02479 |
| F | -0.87697 |

TABLE IV

SPECIFIC DIFFERENCES BETWEEN ADJUSTED CAE MEANS

| Contrast | Students' T | Probability of Larger T |
|---|---|---|
| A vs C,D,E, and F | 3.863 | ($P<.001$) |
| C and D vs E and F | 1.1814 | ($.2>P<.3$) |
| E vs F | 2.2019 | ($P<.001$) |
| C vs D | -3.6384 | ($.02>P<.05$) |

Null Hypothesis: No difference among treatments after adjusting for covariance.

An aggregate annual mean concentration of CCE and CAE was determined by dividing the total quantity of organic compounds collected by the total volume of water filtered (Table V). The aggregate was useful for visualizing the differences among the stations and permits the investigator to interpret differences shown by multiple linear regression analysis. Also, the aggregate mean can be compared with published values.

TABLE V

AGGREGATE MEAN CCE AND CAE

| Station | CCE (µg/liter) Mean | CCE (µg/liter) Range | CAE (µg/liter) Mean | CAE (µg/liter) Range |
|---|---|---|---|---|
| Ark. below Tulsa | 2,325 | 202 - 19,639 | 1,133 | 299 - 2,416 |
| Reservoir Stations | | | | |
| Upper Cimarron | 262 | 6 - 752 | 734 | 153 - 3,087 |
| Lower Cimarron | 142 | 39 - 686 | 456 | 139 - 1,176 |
| Upper Arkansas | 302 | 44 - 6,241 | 538 | 221 - 1,732 |
| Lower Arkansas | 167 | 13 - 661 | 834 | 205 - 5,468 |

The CCE compounds are considered to be more detrimental to water quality than the CAE compounds (Middleton, Grant, and Rosen 1956). Station A located on the Arkansas River below Tulsa, Oklahoma, contained

higher concentrations of CCE than the other stations (Table V). The CCE concentration of 19,639 µg/liter was the highest concentration collected and was higher than any published values.

The highest mean CCE concentration among reservoir stations occurred at the upper end of the Arkansas arm. The mean CCE concentration from the Arkansas River arm exceeded that from the Cimarron River arm of the reservoir. The lowest mean concentration of CCE was from the lower part of the Cimarron arm. There was a reduction in mean CCE concentration from the upper to the lower end of both arms in Keystone Reservoir. The reduction was 54 and 55 per cent in the Cimarron and Arkansas arms, respectively.

The highest aggregate mean concentration of CAE occurred in the Arkansas River below Tulsa, Oklahoma. However, the maximum CAE sample value was collected from the lower Arkansas River arm of the reservoir.

Within the reservoir, the lowest mean CAE concentration occurred at the lower end of the Cimarron River arm. The mean concentration of CAE decreased from the upper to the lower end of the Cimarron River arm. In contrast, the mean concentration of CAE increased from the upper to the lower end of the Arkansas River arm of the reservoir. The aggregate mean CAE concentration from the Arkansas River exceeded that from the Cimarron River arm of the reservoir.

There was no apparent correlation between visible evidence such as oil slicks and high concentration of either CCE or CAE. On two occasions, the surface of the Arkansas River below Tulsa was partially covered by an oil slick. There was a two-fold increase in CCE concentration on one occasion but not on the second occasion (see Appendix Tables I, II, III, IV, and V for sample values from each station).

Anoxic conditions developed in the stable hypolimnion in the Cimarron arm of the reservoir during the summer, 1966 (Eley 1967). Hydrogen sulfide and ammonia were produced during this period and were suspected to be the cause of a fish kill in the Arkansas River below Tulsa, Oklahoma. Although water from 10 meters depth from the lower end of the Cimarron River arm of the reservoir had a characteristic hydrogen sulfide odor, and some yellow crystals were obtained in the CCE, there were no radical fluctuations in either CCE or CAE concentration in this arm of the reservoir during the anoxic period. No apparent correlation existed between the fish kill and organic concentration.

The reduction in CCE concentration during passage through the reservoir indicates that some degradation of industrial wastes occurs in the reservoir. The amount of degradation is unknown, since the effects of dilution and sedimentation upon the concentration of CCE was not determined.

The increase in CAE concentration from the upper end to the lower end of the Arkansas River arm of Keystone Reservoir was probably due to the addition of municipal effluent at Cleveland, Oklahoma, and organic compounds from natural sources.

The aggregate mean concentration of CCE from Keystone Reservoir was relatively high compared to published values from other locations (Table VI). The drainage basin of Keystone Reservoir is dominated primarily by an agricultural economy. In contrast, the Ohio, Kanawha, and Missouri Rivers are in highly industrialized regions.

Five CAM samples were collected from an oil refinery effluent located on the Arkansas River above Keystone Reservoir (Table VII). The aggregate mean CCE concentration from the oil refinery effluent

TABLE VI

CONCENTRATION OF CARBON-ADSORBED ORGANIC COMPOUNDS FROM KEYSTONE RESERVOIR, ARKANSAS RIVER, AND OTHER LOCATIONS

| Water Body | Reference | | CCE µg/liter | CAE µg/liter |
|---|---|---|---|---|
| Arkansas River (below Tulsa) | Present Study | $\bar{X}$ | 2,325 | 1,133 |
| Keystone Reservoir Upper Cimarron | " " | $\bar{X}$ | 262 | 734 |
| Keystone Reservoir Lower Cimarron | " " | $\bar{X}$ | 142 | 456 |
| Keystone Reservoir Upper Arkansas | " " | $\bar{X}$ | 302 | 538 |
| Keystone Reservoir Lower Arkansas | " " | $\bar{X}$ | 167 | 834 |
| Arkansas River Ponca City, Okla. | Nat. Water Qual Net. 1958-1959 | $X_i$ | 108 | 135 |
| " " | " 1962 " | $X_i$ | 58 | 76 |
| Ohio River | " 1961 " | $X_i$ | 144 | 198 |
| Columbia River | " " | $X_i$ | 28 | 68 |
| Lake Mendota | Kumke 1963 | $\bar{X}$ | 197 | 424 |
| Kanawha River | Middleton & Lichtenberg 1960 | $X_i$ | 1,800 | 311 |
| Missouri River | Myrick & Ryckman 1963 | $\bar{X}$ | 58 | 100 |
| Sewage Effluent | Myrick & Ryckman 1962 | $X_i$ | 7,000 | 22,000 |
| Sacramento River | Greenberg 1965 | $\bar{X}$ | 81 | 150 |

$X_i$ = Single sample value

$\bar{X}$ = Mean value

TABLE VII

CARBON-ADSORBED ORGANIC COMPOUNDS FROM
AN OIL REFINERY EFFLUENT

| Date 1967 | Water filtered Liters | CCE Concentration µg/liter | CAE Concentration µg/liter |
|---|---|---|---|
| 6/23-6/29 | 3,653 | 6,735 | 1,728 |
| 6/29-7/6 | 3,850 | 7,396 | 1,509 |
| 7/6-7/13 | 814 | 6,369 | 3,656 |
| 7/13-7/27 | 4,942 | 6,557 | 1,326 |
| 7/27-8/3 | 3,297 | 7,566 | 1,733 |

was 6,983 µg/liter and the mean CAE concentration was 1,653 µg/liter. Petrochemical wastes have been considered to be mostly non-polar hydrocarbon type compounds with large CCE/CAE ratios. However, the CCE concentration from the refinery effluent was only about four times the CAE concentration. Bio-oxidation treatment of petrochemical wastes will result in formation of some metabolically oxidized compounds, which would be soluble in the alcohol extract.

The effluent had been treated in an API oil separator, bio-oxidation system, and held in oxidation lagoons before being discharged to the receiving stream. The aggregate mean CCE concentration was less than that reported for a municipal waste treatment plant (7,000 µg/liter) (Myrick and Ryckman 1962). The effluent had apparently been thoroughly treated but bio-oxidation cannot remove all of the organic compounds since many are refractory (Ludzack and Ettinger 1960). Dilution and some degradation of the oil refinery waste occurred before it reached the upper end of the reservoir.

Adsorption Efficiency

Two carbon columns were installed in series to determine the amount of organic compounds not adsorbed by the first column (Table VIII). The range of CCE and CAE compounds adsorbed by the second column was 1.3 to 60.8 and 3.8 to 83.2 per cent respectively of the compounds adsorbed by the first column in the series. These results indicate that a significant amount of organic compounds may not be adsorbed by a single column and that the semi-quantitative data might be low by a factor of as much as two in some cases.

TABLE VIII

CARBON ADSORPTION DATA FOR COLUMNS IN SERIES

| Date 1966 | Flow rate l/min. | Liters filtered | CCE | | CAE | |
|---|---|---|---|---|---|---|
| | | | 1st. column | 2nd. column | 1st. column | 2nd. column |
| 8/26-8/31 | 0.31 | 1,046 | 401 | 244 | 2,279 | 1,228 |
| 8/31-9/6 | 0.66 | 2,151 | 599 | 55 | 1,601 | 178 |
| 9/6-9/13 | 0.63 | 1,433 | 502 | 7 | 981 | 38 |
| 9/13-9/29 | 0.80 | 2,745 | 354 | 19 | 927 | 772 |
| 9/29-10/10 | 0.75 | 3,776 | 576 | 25 | 903 | 270 |

In order to determine the effect of flow rate on adsorption of organic compounds, carbon columns were operated in parallel at different flow rates (Table IX). The effect of sampling continuously for two weeks as compared to collecting weekly samples was also

TABLE IX

CARBON ADSORPTION DATA FOR COLUMNS IN PARALLEL

| Date 1966 | Flow rate l/min | Liters filtered | CCE | CAE | Flow rate l/min | Liters filtered | CCE | CAE |
|---|---|---|---|---|---|---|---|---|
| | Column A | | | | Column B | | | |
| 4/20-4/27 | 0.80 | 4,395 | 219 | 700 | 0.46 | 3,676 | 202 | 776 |
| 4/27-5/4 | 0.51 | 2,776 | 229 | 931 | * | | | |
| 5/4-5/13 | 0.20 | 5,362 | 254 | 962 | 1.07 | 7,866 | 247 | 788 |
| 5/13-5/20 | 1.00 | 1,264 | 458 | 744 | * | | | |
| 5/20-5/25 | 0.95 | 6,975 | 275 | 451 | 0.97 | 6,859 | 322 | 418 |
| 5/25-6/1 | 1.07 | 5,610 | 484 | 543 | 0.42 | 138 | 361 | 806 |
| 6/1-6/8 | 1.01 | 5,463 | 318 | 706 | 0.68 | 4,153 | 279 | 754 |
| 6/8-6/15 | 1.07 | 3,789 | 293 | 400 | * | | | |
| 6/15-6/22 | 0.83 | 3,909 | 457 | 890 | 0.63 | 3,334 | 302 | 564 |
| 6/22-7/5 | 0.95 | 5,837 | 274 | 879 | 0.50 | 4,492 | 270 | lost |
| 7/5-7/15 | 0.97 | 1,615 | 481 | 1,838 | 0.50 | 501 | 242 | 3,087 |
| 9/13-9/28 | 0.53 | 3,769 | 68 | 760 | 0.83 | 6,671 | 66 | 584 |

* A single column B was used to continuously sample for two weeks, while column A was replaced with a fresh column weekly.

determined. A reduction in flow rate increased the CAE concentration but appeared to have a slight, negative effect on the CCE concentration. The maximum amount of leakage of chloroform soluble compounds occurred at a very slow flow rate of 0.80 liters/min. Booth (1965) and Kumke (1963) showed that a slower flow rate increased the adsorption

efficiency of a single column for both CCE and CAE compounds. The maximum leakage of CCE compounds at low flow rates found in the present study may be an anomoly.

## Analytical Results

Five chloroform extracts were subjected to solubility separation to resolve the complex mixture of organic compounds (Table X). The neutral fraction was the largest in each separation. Gas chromatography analysis on a column containing 20 per cent Apiezon L on

TABLE X

SOLUBILITY SEPARATION OF CARBON CHLOROFORM EXTRACTS FROM KEYSTONE RESERVOIR, ARKANSAS RIVER, AND AN OIL REFINERY

| Sample | Weight of Solubility Fractions in Grams | | | | | |
|---|---|---|---|---|---|---|
| | Water Solubles | Ether Insol. | Strong Acids | Weak Acids | Bases | Neutrals |
| *A-11 | 0.0636 | 0.0380 | 0.0318 | 0.1578 | 0.0072 | 0.8273 |
| *A-27 | Lost | 0.0293 | 0.1610 | 0.2655 | 0.0199 | 0.7571 |
| **F-13 | 0.1095 | 0.0879 | 0.0432 | 0.1229 | 0.0019 | 0.2534 |
| **F-22 | 0.0648 | 0.0333 | 0.0301 | 0.0785 | 0.0124 | 0.3225 |
| ***G-5 | 0.5412 | 0.0695 | 0.5415 | 1.7686 | 0.2819 | 11.4254 |

* Samples A from the Arkansas River below Tulsa, Okla. A-11 collected March 11-22, 1966, and A-27 collected September 29 - October 10, 1966.

** Samples F from the Arkansas River above Keystone Reservoir. F-13 collected June 8-22, 1966, and F-22 collected October 31, 1966 - January 3, 1967.

*** Sample G from an oil refinery on the Arkansas River above Keystone Reservoir, collected July 27 - August 3, 1967.

Chrom W-AW failed to resolve the mixtures into individual components. To further subdivide the organic mixture, the neutral solubility fractions of A-11 and A-27 were separated into aliphatics, aromatics, and oxygenated fractions by column chromatography on a Silica Gel G column. Sample A-11 contained 0.3724 g of aliphatics, 0.0997 g of aromatics, and 0.1301 g of oxygenated compounds. 72.79 Per cent of the neutral fraction was recovered from the column. Sample A-27 was collected as 120 two milliliter fractions and was not weighted. The mixtures were still too complex to resolve by GLC.

The mixture of organic compounds contained many compounds that were difficult to elute from the gas chromatographic column. A maximum operating temperature of 300° C, determined by the stability of the stationary liquid phase, would not elute all of the compounds in several hours. An alternative separation procedure was thus selected to separate volatile compounds from the non-volatile compounds.

The activated carbon was treated by steam distillation-ether extraction to remove the volatile compounds from the carbon. The quantity of organic compounds removed by this technique was approximately 10 to 100 mg. Twenty-seven samples were treated and 21 samples yeilded volatile compounds that could be resolved by GLC (Appendix, Fig. 1, 2, 3, and 4).

The GLC retention times of the steam-volatile compounds resolved at nearly identical operating conditions were used to compare composition of the samples (Table XI). Column A contained a highly polar Carbowax 20M liquid phase. Column B contained a non-polar liquid phase, silicon gum rubber (GE Se-30).

GLC peak # 2 (Column A) occurred in the samples collected from

TABLE XI

COMPARISON OF POLARITY (RETENTION TIME) OF COMPOUNDS COLLECTED FROM KEYSTONE RESERVOIR, ARKANSAS RIVER, AND AN OIL REFINERY

Column A

1/8 in. x 12 ft. Cu; 5% Carbowax 20M on 60-80 mesh Chrom W-AW-DMCS
Temp. Prog. $50^{\circ} \rightarrow 250^{\circ}$ @ $10^{\circ}$/min.

| Station and date | Peak Number | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| A-Jan., 1966 | | 13.2 | 14.0 | | | 18.7 | | 23.1 | | 24.9 | |
| A-Mar., 1966 | | 13.1 | | 14.5 | | 18.9 | | | 24.2 | | 26.3 |
| C-Oct., 1966 | | | 13.5 | 14.7 | | | | | 24.3 | | 26.2 |
| D-Oct., 1966 | | | | 15.0 | 16.0 | 18.9 | 20.8 | 23.4 | | 25.5 | |
| E-June, 1967 | | 12.7 | | 14.6 | 16.1 | | | | | | |
| F-May, 1966 | | | 13.9 | 14.7 | | 19.0 | | | 24.1 | | 26.1 |
| F-June, 1966 | | 12.8 | | 14.8 | 15.9 | | | | 24.3 | | 26.3 |
| F-July, 1966 | | | 14.0 | | 16.3 | | | | 24.4 | | 26.5 |
| F-Jan., 1967 | 10.6 | 12.8 | | 14.4 | 16.4 | 18.9 | 20.9 | 23.2 | | | 26.9 |
| Reagent BHT | | 12.2 | | | | | | | | | |

Column B

1/8 in x 6 ft. Cu; 10% Se-30 on 80-100 mesh Diatoport S.
Temp. Prog. $100^{\circ} \rightarrow 250^{\circ}$ C @ $10^{\circ}$/min.

| Station and Date | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| A-Jan., 1966 | | | 11.1 | | 14.1 | | 17.3 | 18.3 | | 23.2 | |
| A-Mar., 1966 | | | | 11.6 | 14.6 | | 17.7 | 18.6 | | | 24.0 |
| A-Oct., 1966 | | | | 11.7 | | | | 18.0 | | | 24.7 |
| C-Dec., 1965 | | | | | 14.1 | | 17.4 | 18.4 | | 23.3 | |
| C-Jan., 1966 | | | | | 14.0 | | 17.1 | 18.1 | | 23.1 | |
| D-Oct., 1966 | | 10.3 | 11.0 | 11.6 | 14.1 | | 17.6 | | 21.0 | 23.0 | |
| E-June, 1967 | 8.6 | | | 11.6 | | | 17.5 | 18.5 | | | 23.8 |
| E-June, 1967 | | | | 11.5 | | 16.7 | 17.6 | | 21.5 | | |
| F-Apr., 1966 | | | | | | | 17.3 | 18.2 | | 23.4 | |
| F-May , 1966 | | | | 11.4 | | | 17.5 | | | | |
| F-June, 1966 | | | | 11.6 | 14.3 | | 17.5 | | 20.5 | 23.5 | |
| F-June, 1966 | 8.7 | 10.2 | | | | 16.3 | | | 21.0 | | |
| F-July, 1966 | | | | 11.6 | 14.1 | | 17.8 | 18.7 | | | 24.1 |
| F-July, 1966 | | 10.5 | | | | 16.5 | 17.1 | | 20.9 | | |
| F-Sep., 1966 | | 10.6 | | | | 16.4 | | | 21.2 | | |
| F-Oct., 1966 | | | | | | 16.5 | 17.2 | | 20.9 | | |
| F-Jan., 1967 | 8.8 | | | | | 16.3 | | | 21.9 | | |
| Reagent BHT | 8.6 | | | | | | | | | | |
| G-4 | 8.5 | 10.1 | 10.9 | 11.4 | | | | | | | |

the Arkansas arm but not detected in samples from the Cimarron arm of Keystone Reservoir. The source of the compound was probably on the Arkansas River above Keystone Reservoir. The persistence of the compounds in samples from the lower portion of the reservoir and below the reservoir indicate that these compounds were refractory or were contributed to the reservoir from many different sources.

GLC peak # 4 (Columns A & B) was present at all stations at various times of the year. It was not detected in carbon blanks which had been steam distilled-ether extracted.

The chromatogram of a sample collected from an oil refinery effluent located on the Arkansas River above Keystone Reservoir contained 26 major peaks (Fig. 4, appendix). The retention times of several peaks (Table XI, Column B, Sample G) were nearly identical with peaks in samples collected from the Arkansas River arm of the Keystone Reservoir. Oil refinery wastes have been shown to be refractory (Myrick and Ryckman 1963), and since several refineries discharge wastes into the Arkansas River above Keystone, some of the compounds could have persisted in waters passing through the Reservoir.

The quantity of organic compounds removed by the steam distillation technique was too small to permit separation and isolation by conventional methods. An attempt to collect the resolved compounds as they were eluted from the gas chromatographic column by using a glass capillary tube for condensor was only partially successful. The major problem encountered was contamination of the isolated compound with liquid phase "bleed-off" from the gas chromatograph column.

## Identification of a Trace Aqueous Organic Compound

Two steam-volatile samples from Keystone Reservoir were analyzed on the combination gas chromatograph-mass spectrometer (GC-MS). The steam volatile samples from the upper and lower ends of the Arkansas arm of the reservoir contained six peaks separable by GLC (Figs. 8 and 9). Only peaks 1, 2, and 3 were analyzed by GC-MS, since column conditions on this instrument were restricted to isothermal temperatures and it was observed that peaks 4, 5, and 6 were not cleanly resolved (Figs. 10 and 11).

Mass spectra of the first GLC peak from both samples indicated that each peak was a mixture of two compounds, one with molecular weight ($M^+$) 218 and the other with molecular weight ($M^+$) 220 (Figs. 12 and 13). Either two compounds were present or two hydrogen atoms were lost due to catalytic decomposition in the sample prior to reaching the ion source (Waller and Kinneberg 1968).

The second GLC peak from both samples had a molecular weight ($M^+$) of 220 (Figs. 14 and 15). The base peak was 205 and the fragmentation pattern was similar to that of 2,6-ditertiary-butyl-4-methylphenol (BHT) (API uncertified Mass Spectrum # 595). The GLC retention time of standard BHT (Fig. 16) and the unknown (Fig. 17) and also the mass spectra (Figs. 18 and 19) were identical. It was concluded that the unknown compound collected from both the upper and lower end of the Arkansas arm of the reservoir was BHT. Confirmatory evidence was obtained by co-chromatography of the unknown and BHT on a Carbowax GLC column. The retention time of BHT (Fig. 20) was similar to peak # 3 of the unknown sample (Fig. 21), whereas the retention time of the mixture showed one peak which corresponded to peak # 3 (Fig. 22).

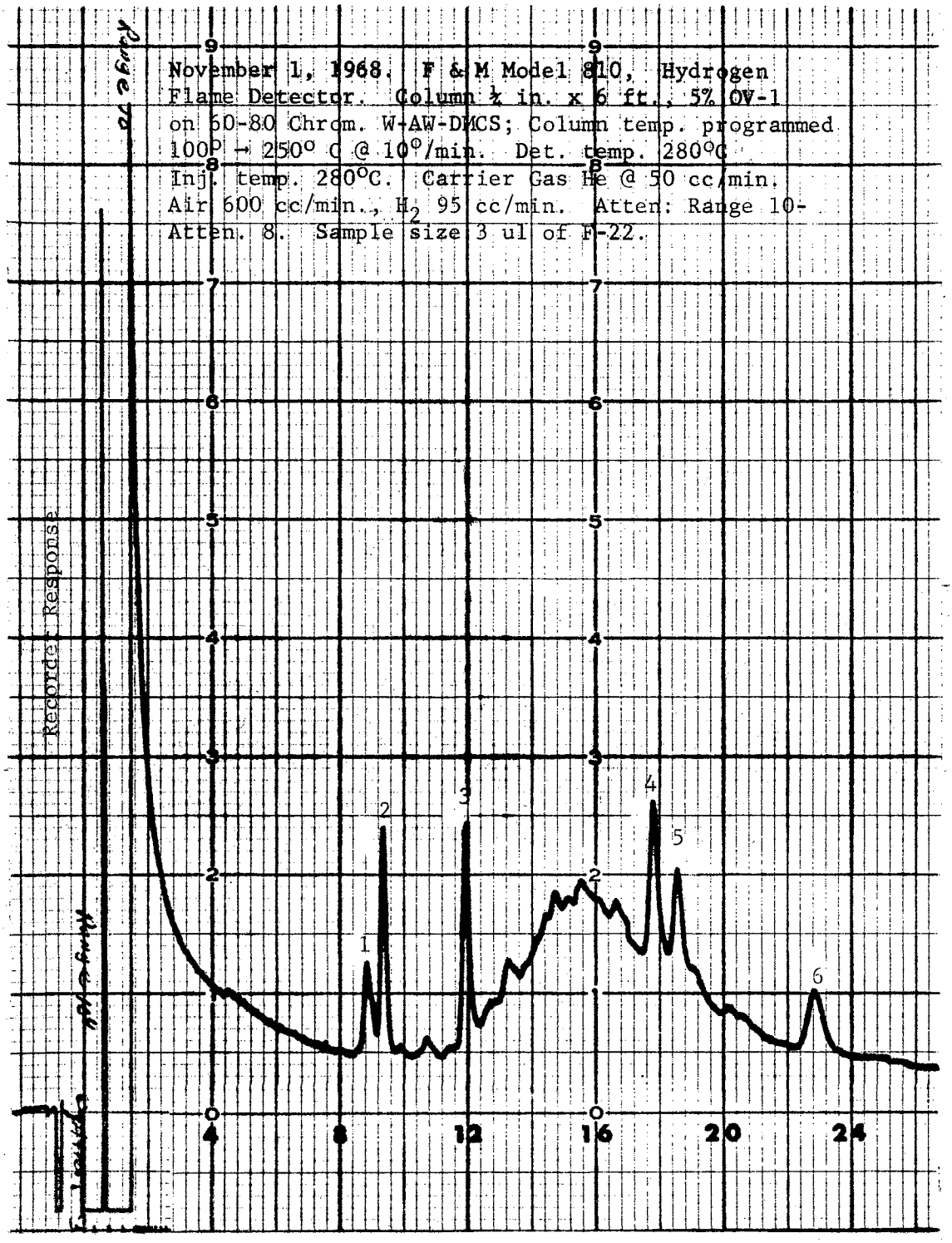



Figure 8. Chromatogram of Compounds Collected from Upper Arkansas River Arm of Keystone Reservoir.

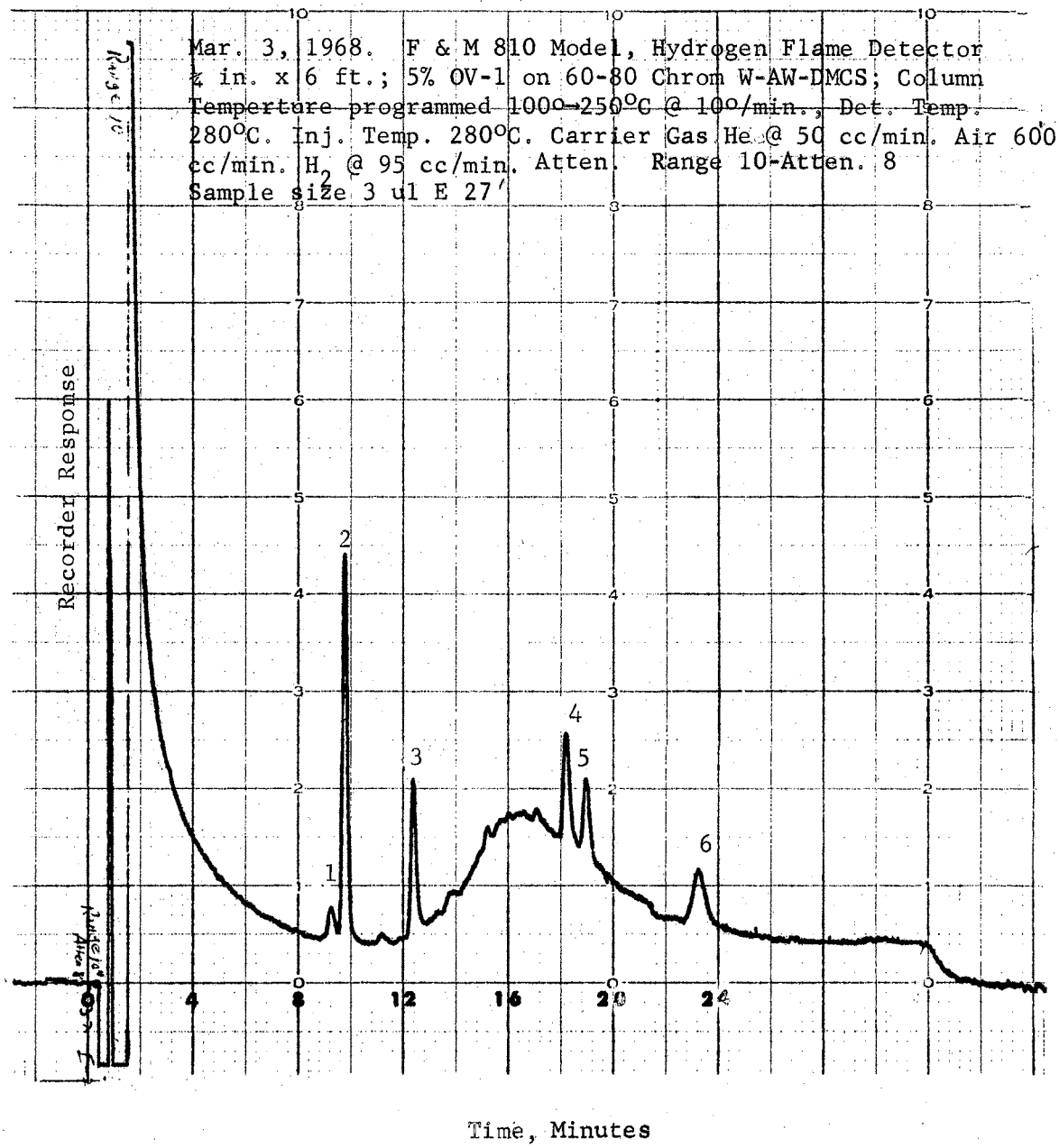



Figure 9. Chromatogram of Compounds Collected from Lower Arkansas River Arm of Keystone Reservoir.

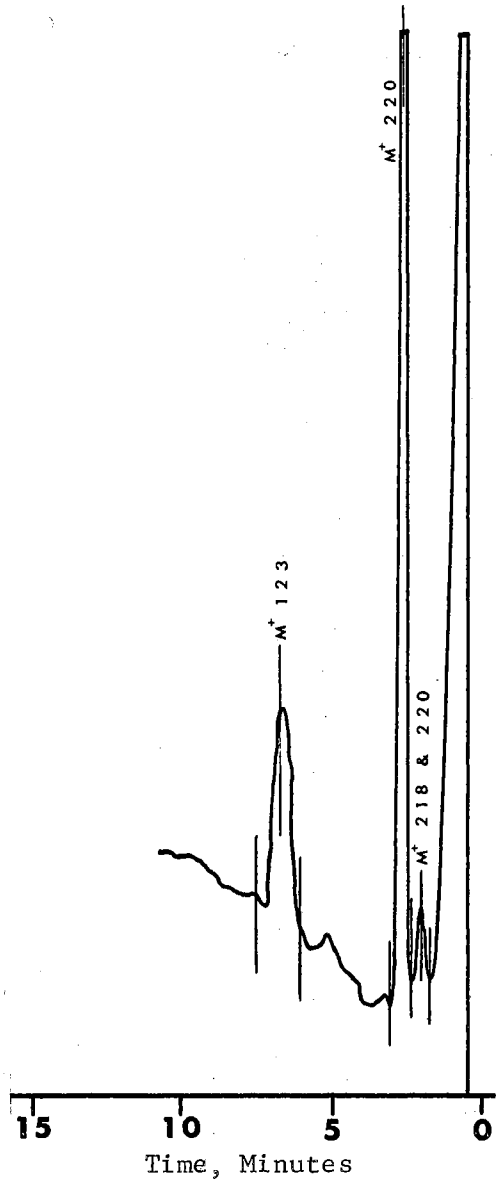



Figure 10. GC-MS Chromatogram of 1.0 µl of Sample E-27
Column temp. 150° C

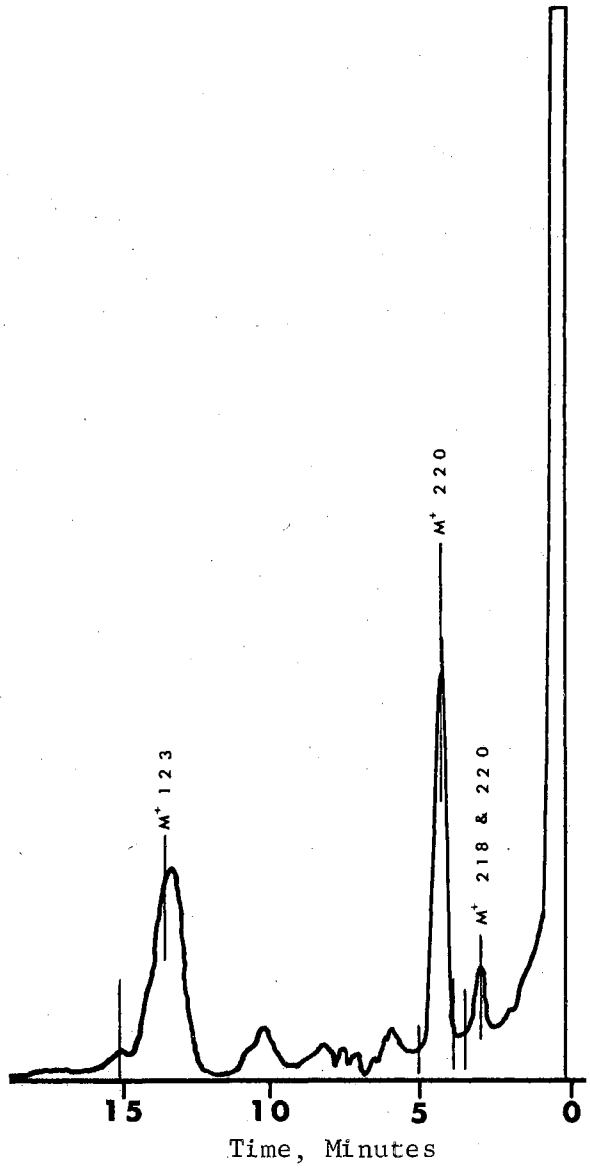



Figure 11. GC-MS Chromatogram of 4 µl of Sample F-22
Column temp. 130° C

GLC conditions for Figures 10 and 11: LKB 9000 ionization detector, 6 ft by 1/4 in glass, 5% Apiezon L on Chrom W-AW-DMCS, Mol. Sep. temp. 200° C; Inj. temp. 190° C; Car. Gas He @ 21 cc/min.

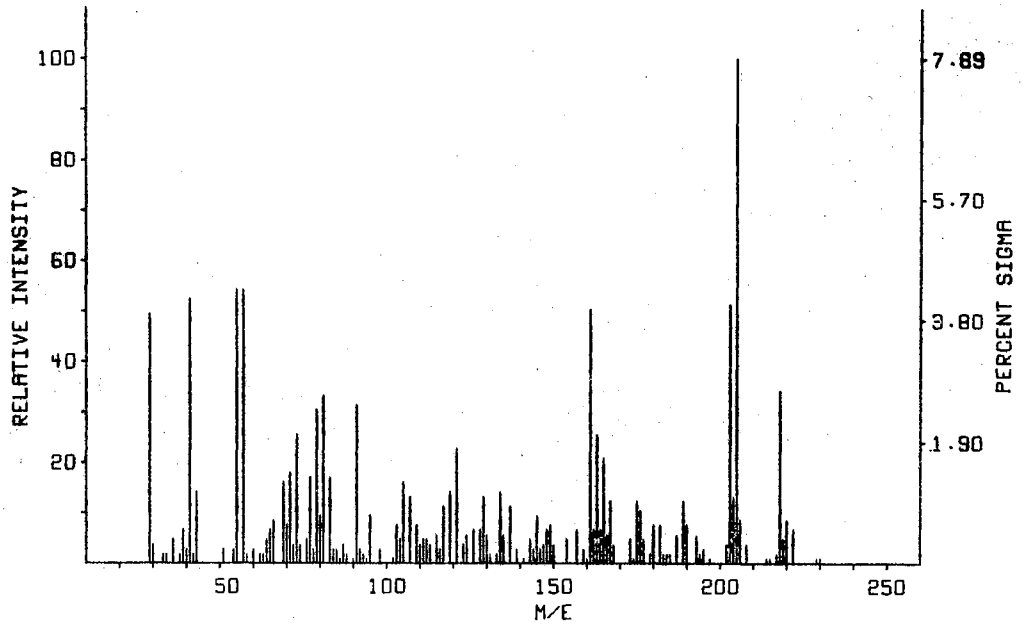



Figure 12. Mass Spectrum of GLC Peak #1 Collected from Lower Arkansas River Arm of Keystone Reservoir, Introduced via Gas Chromatograph.

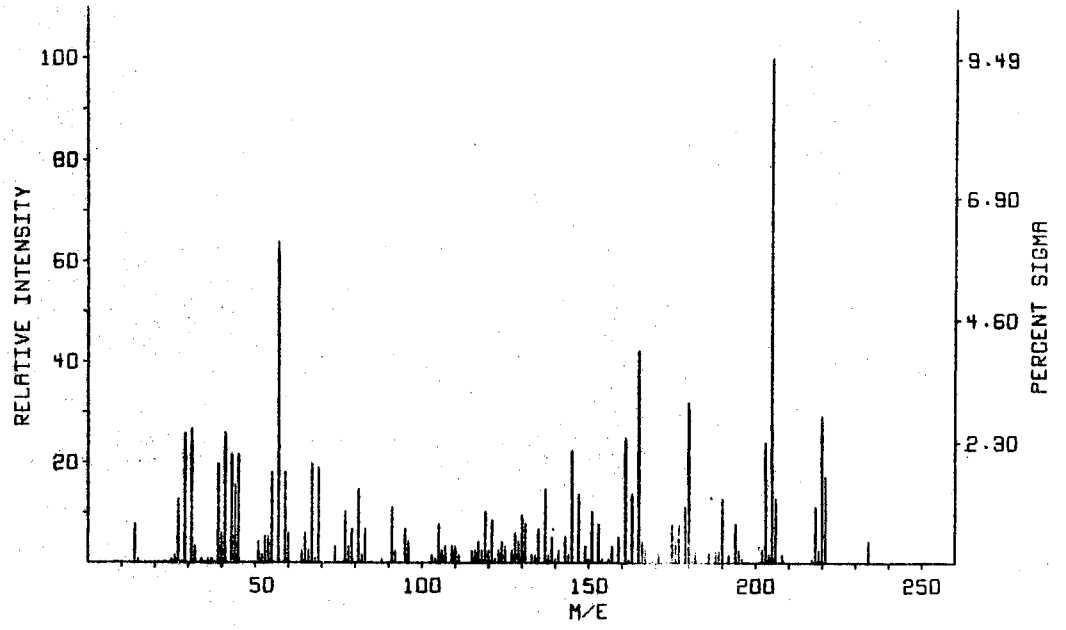



Figure 13. M.S. of GLC Peak #1 Collected from Upper Arkansas River Arm of Keystone Reservoir, Introduced via Gas Chromatograph.

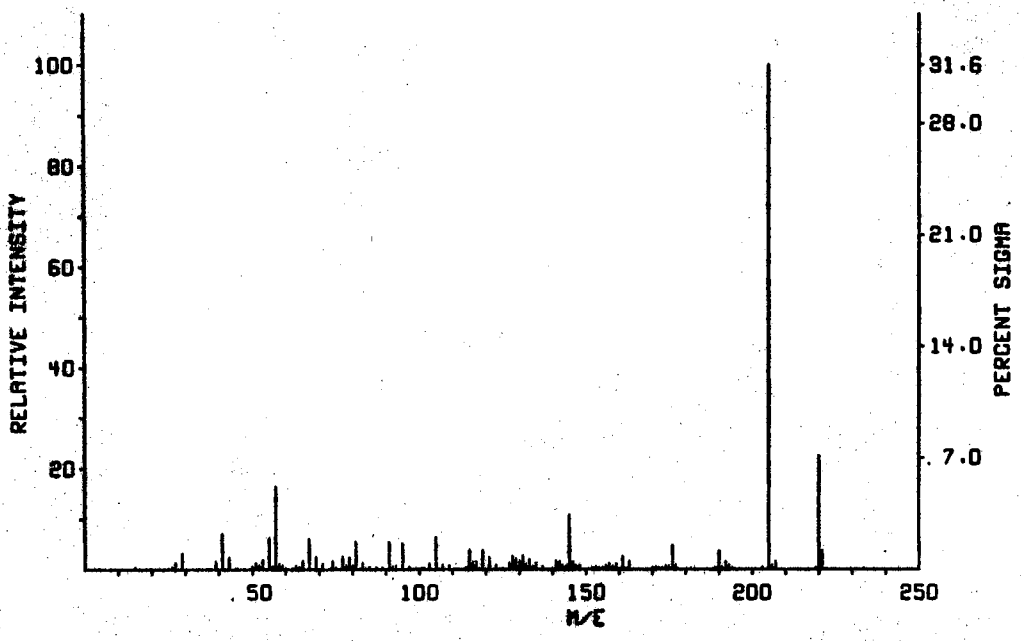



Figure 14. M.S. of Peak #2 Collected from Lower Arkansas River Arm of Keystone Reservoir, Introduced via Gas Chromatograph.

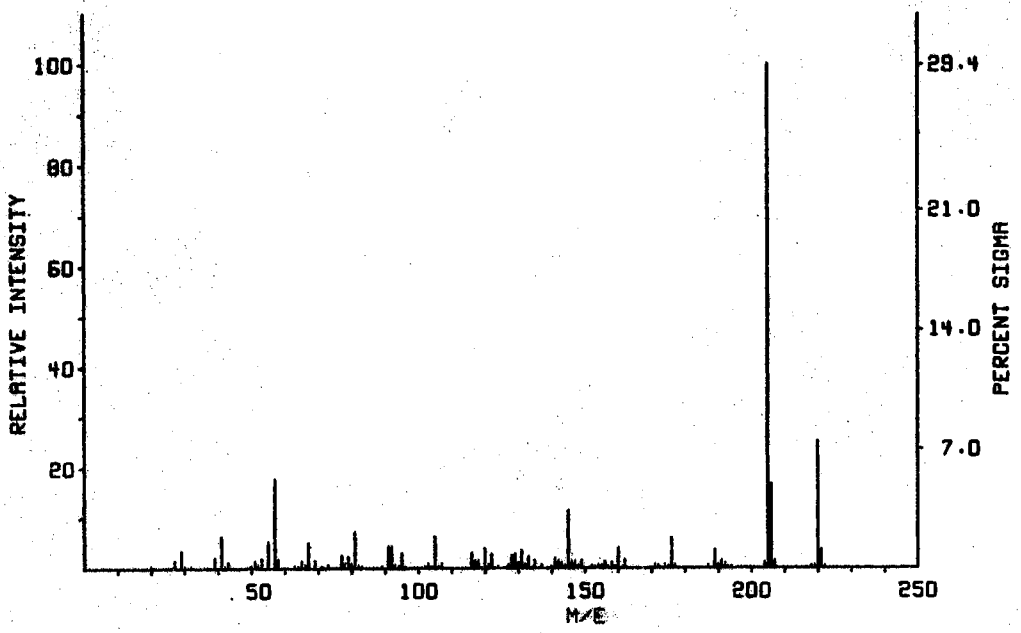



Figure 15. M.S. of Peak #2 Collected from Upper Arkansas River Arm of Keystone Reservoir, Introduced via Gas Chromatograph.

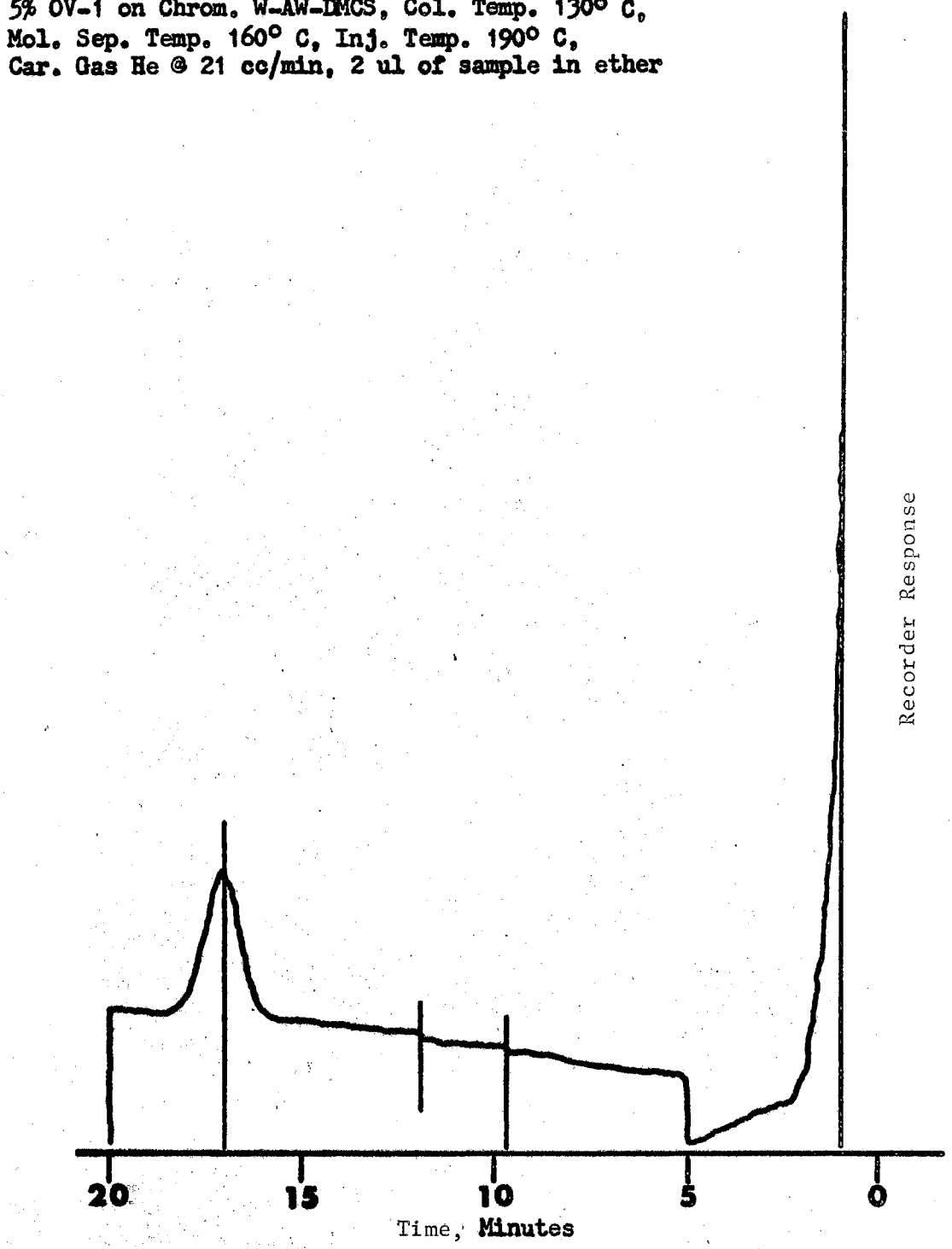



Figure 16. Gas Chromatogram of Reagent 2,6-di-tert-butyl-4-methylphenol. Vertical Lines Indicate Mass Spectral Scans.

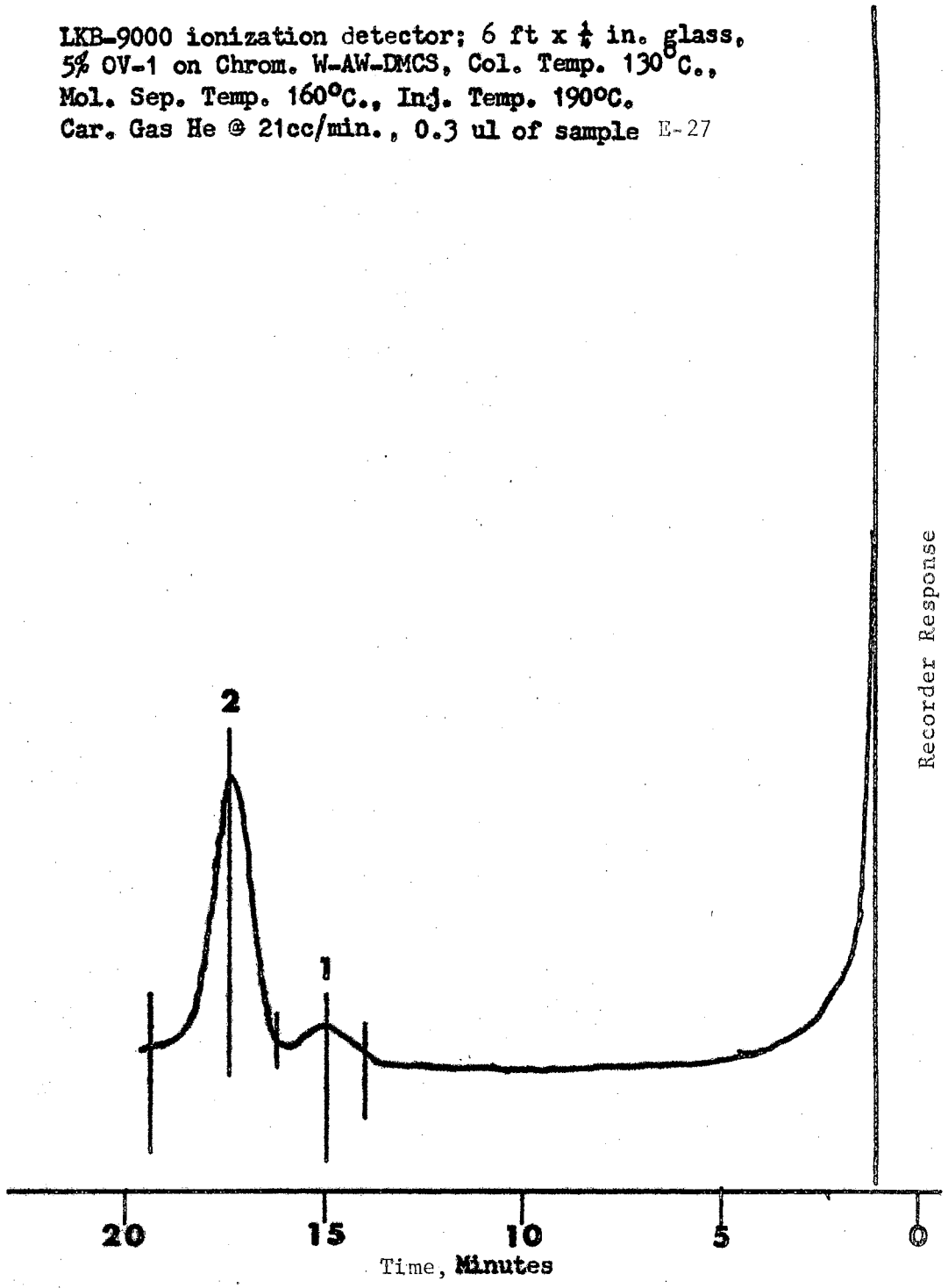



Figure 17. Partial Gas Chromatogram of Compounds Collected from the Lower End of the Arkansas River Arm of Keystone. Vertical Lines Indicate Mass Spectral Scans.

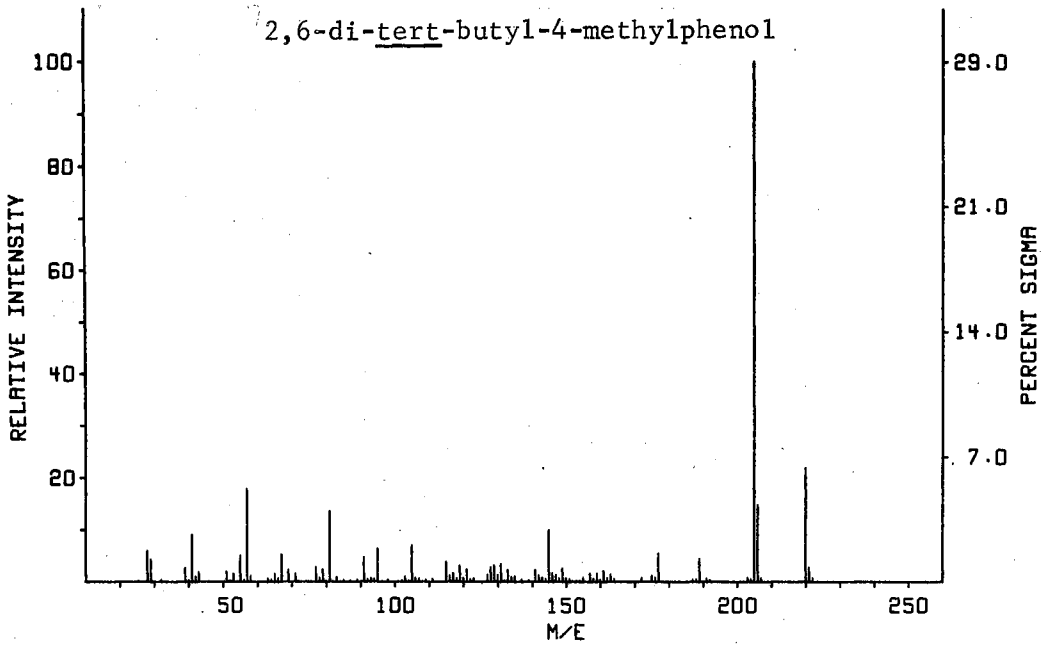



Figure 18. Mass Spectrum of Standard 2,6-di-tert-butyl-4-methyl-phenol, Introduced via Gas Chromatograph.

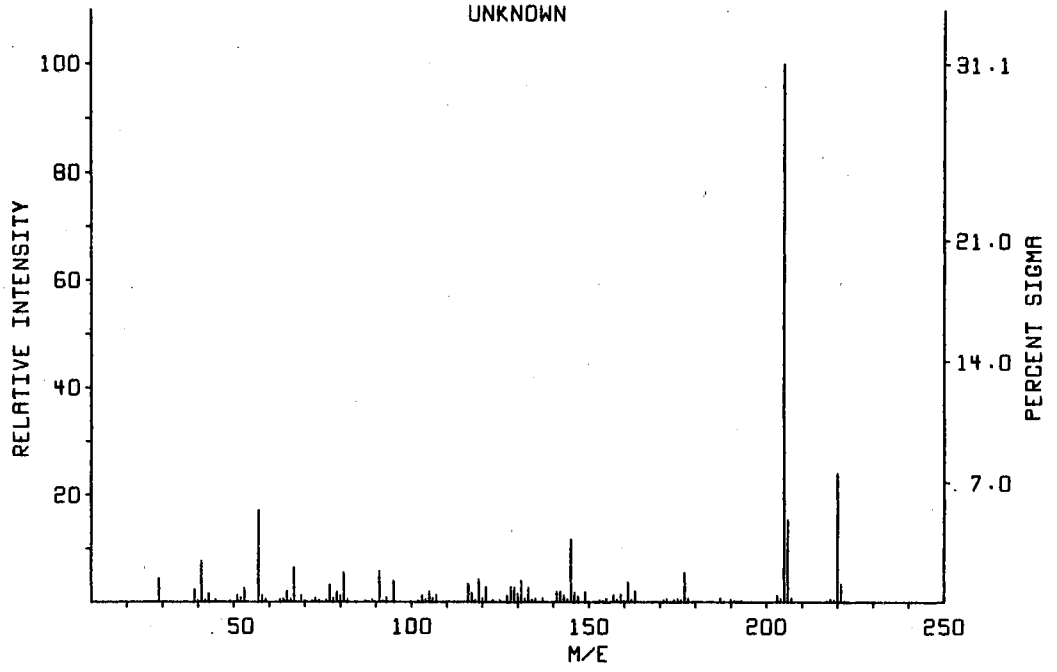



Figure 19. Mass Spectrum of Unknown Collected from Lower Arkansas River Arm of Keystone Reservoir, Introduced via Gas Chromatograph.

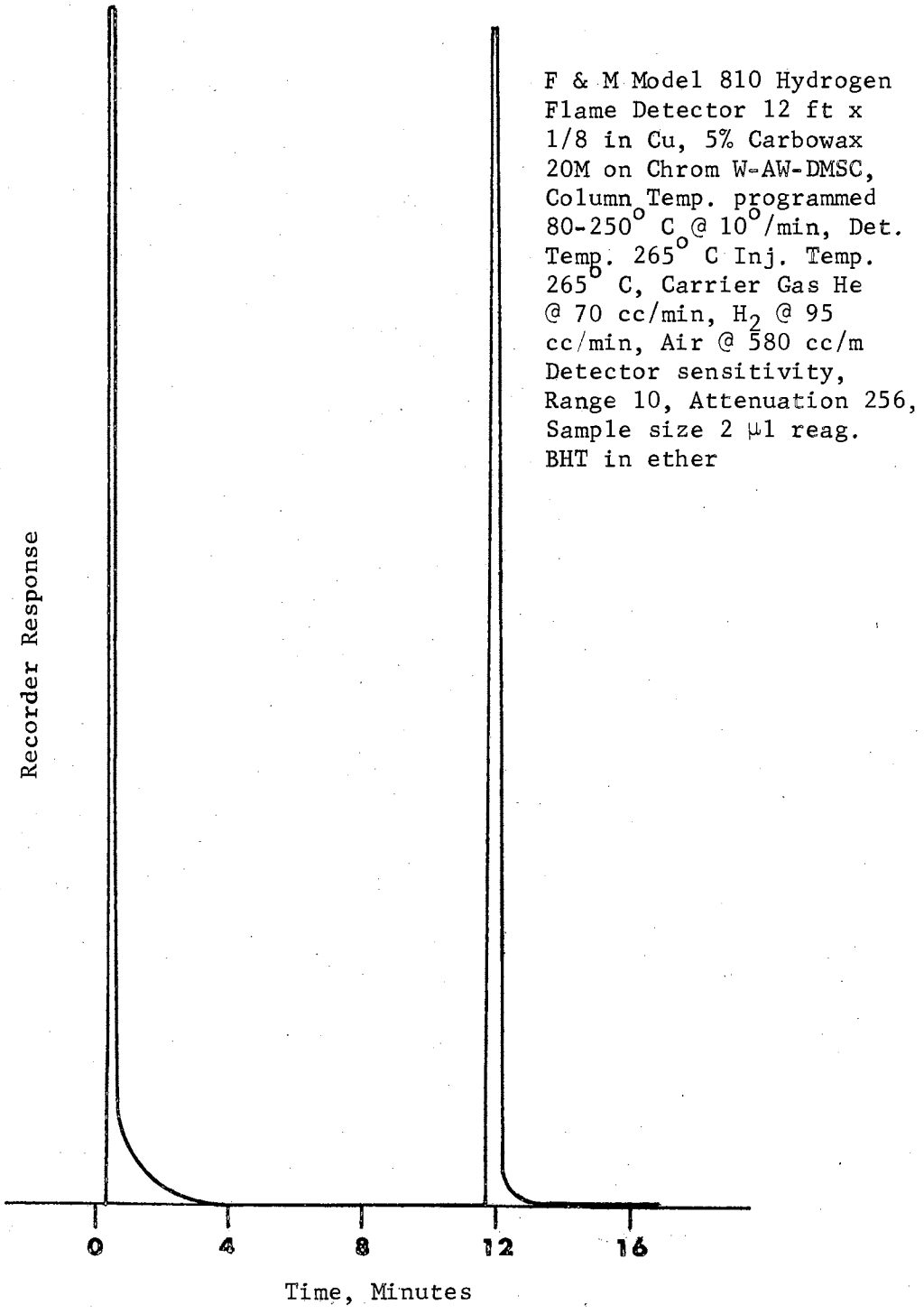



Figure 20. Gas Chromatogram of Standard 2,6-di-tert-butyl-4-methylphenol.

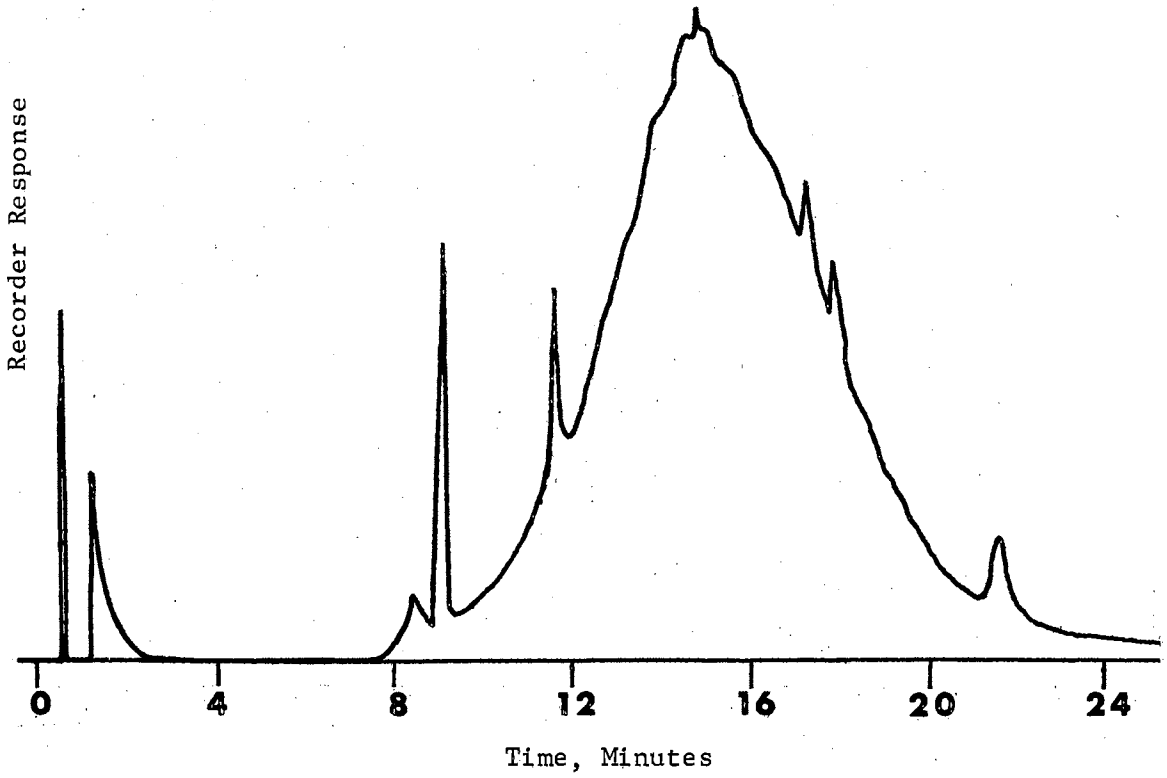



Figure 21. Gas Chromatogram of Sample E-27 Collected from Lower Arkansas River Arm of Keystone Reservoir.

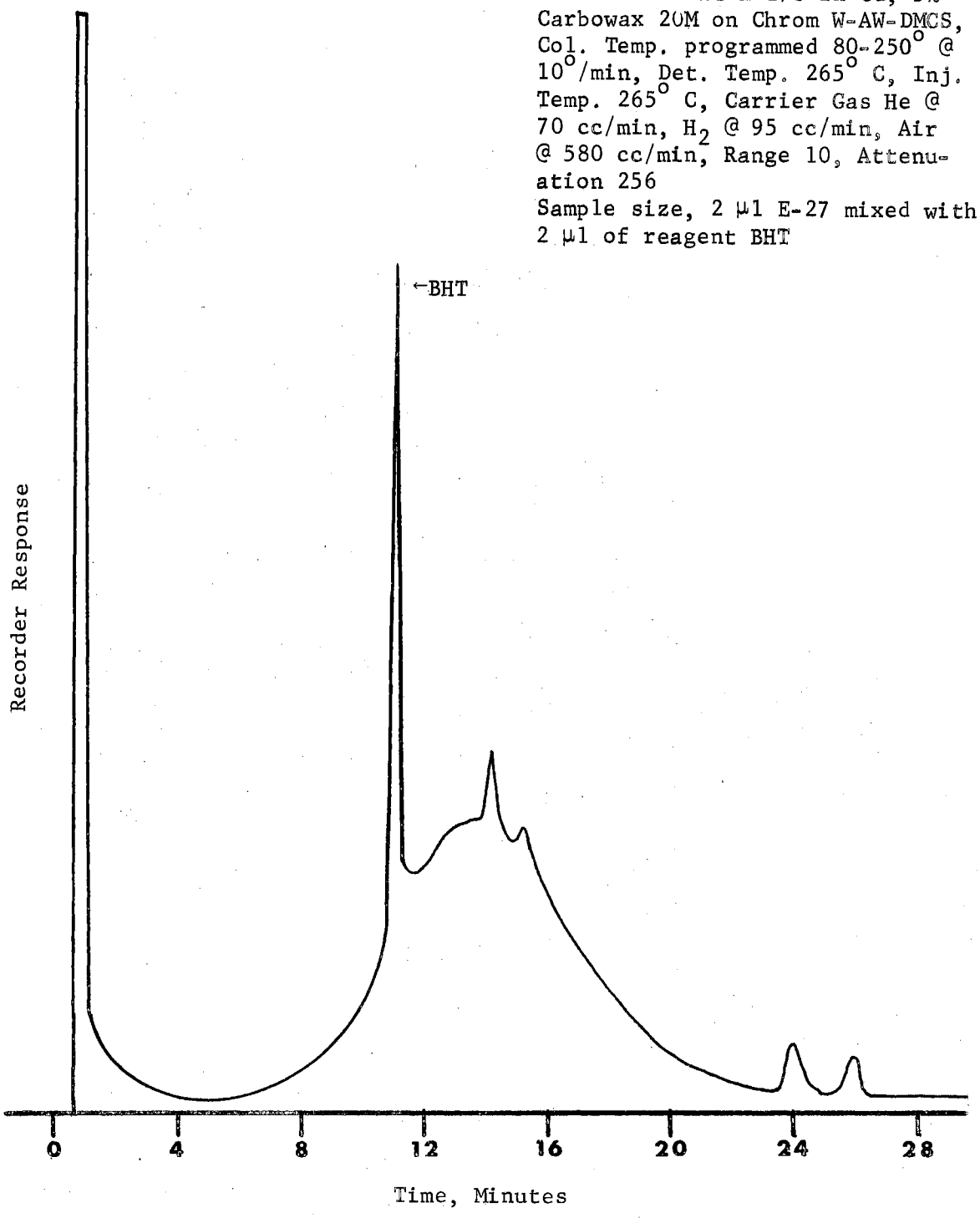



Figure 22. Chromatogram of Standard BHT and Steam Volatile Compounds Collected from E.

However, a shortening of the retention time by approximately one minute was observed in the mixture.

The third GLC peak in the steam volatile samples from the reservoir (Figs. 8 and 9) had a molecular weight of 123 (Figs. 23 and 24). The compound was not identified, however, the odd molecular weight indicates that the compound contained an odd number of nitrogen atoms. The fragmentation pattern indicates that it was probably aromatic.

BHT was not detected in samples from the Cimarron arm of the reservoir, which may indicate that the source of the compound was on the Arkansas River above Keystone Reservoir. BHT is used as an antioxidant in the manufacture of rubber and gasoline. It is also added to some foods, such as dry cereals, to retard spoilage (Merck Index 1960).

Pharmacological investigations indicate that BHT is not toxic at concentrations of 100 to 200 mg/liter in food consumed by rats (Gaunt, Gilbert, and Martin 1965) and by chickens (Frawley, Kay, and Calandra 1965). A concentration of 500 mg/liter of BHT in the diet of laying hens led to deposition of 20 mg/liter of BHT in the fat of the eggs (van Stratum and Vos 1965). At a dosage of 500 mg/Kg of rat body weight BHT reduced the level of glucose-6-phosphatase, increased the level of glucose-6-phosphodehydrogenase, and increased the size of the liver (Feuer, Gaunt, Goldberg, and Fairweather 1965). Recovery from the effects was rapid when it was removed from the diet.

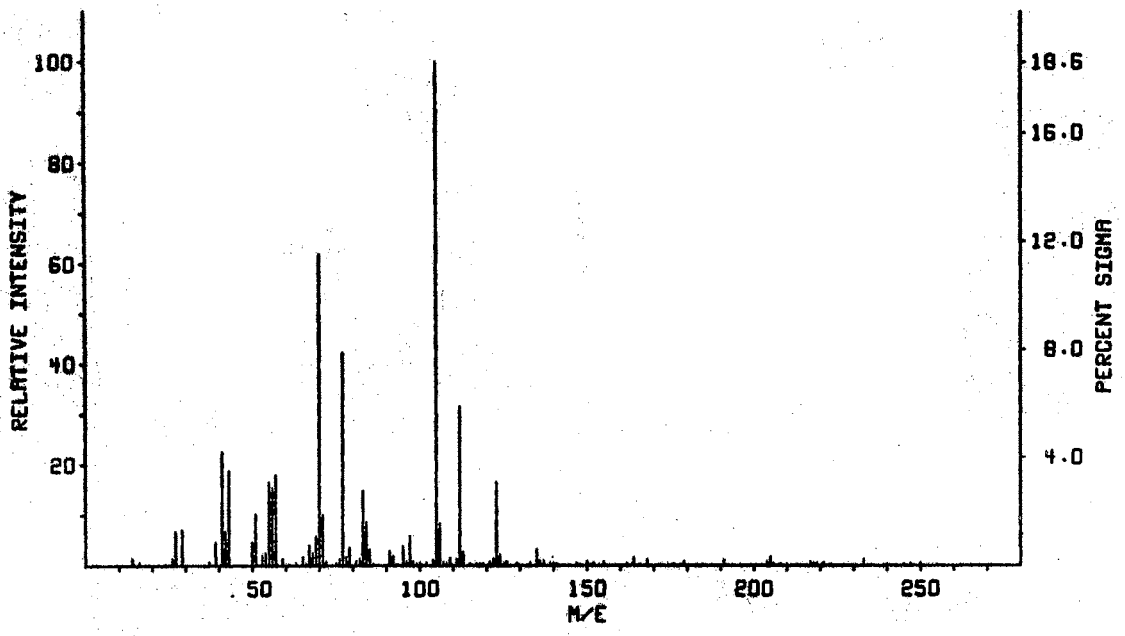



Figure 23. M.S. of Peak #3 Collected from Lower Arkansas River Arm of Keystone Reservoir, Introduced via Gas Chromatograph.

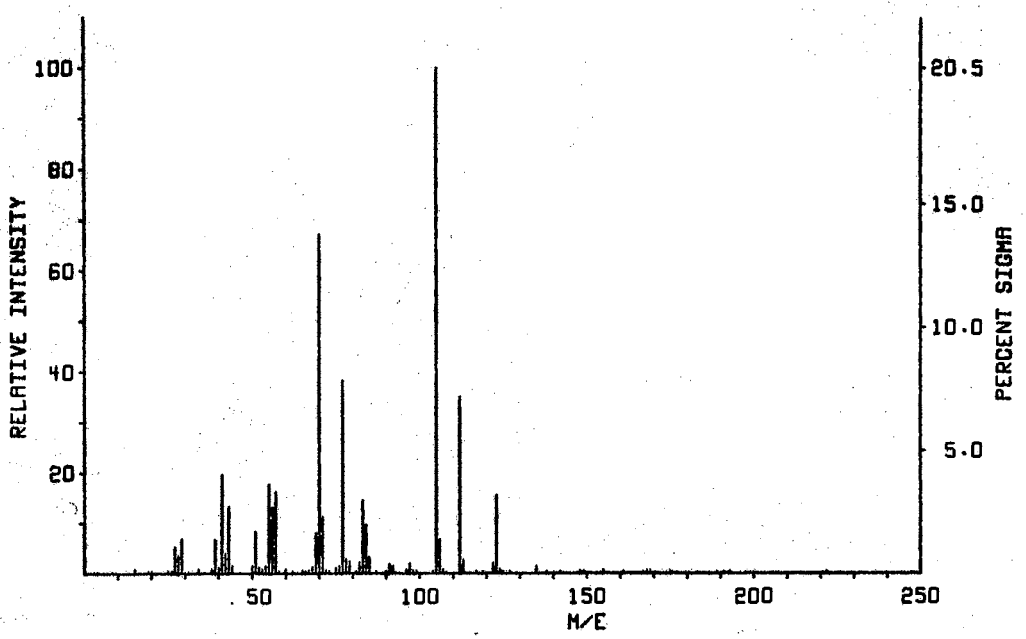



Figure 24. M.S. of Peak #3 Collected from Upper Arkansas River Arm of Keystone Reservoir, Introduced via Gas Chromatograph.

# CHAPTER V

## SUMMARY AND CONCLUSIONS

The carbon adsorption method was selected for continuous collection of semi-quantitative samples of trace aqueous organic compounds from Keystone Reservoir and the Arkansas River below Tulsa, Oklahoma. Qualitative analyses of the steam volatile compounds were performed on a combination gas chromatograph-mass spectrometer.

The concentration of organic compounds from the Arkansas River below Tulsa, Oklahoma exceeded that in Keystone Reservoir and also most published values from other locations. The Arkansas River arm contained somewhat higher concentrations than the Cimarron River arm of the reservoir. There was a decrease in concentration of CCE in both arms of the reservoir. CAE decreased from the upper to the lower end of the Cimarron River arm. The observed reductions in concentration were possibly due to dilution, sedimentation, or bio-oxidation. The concentration of CAE in the Arkansas River arm increased from the upper to the lower end of the reservoir. The increase may have been caused by sewage outfalls between the stations or by organic compounds from natural sources.

2,6-Ditertiary butyl-4-methylphenol (BHT) was identified in extracts from the upper and lower ends of the Arkansas River arm of Keystone Reservoir. This had not been detected as a persistent organic contaminant in a main stream reservoir. Sewage effluents may have

contained the compound, since it is a widely used anti-oxidant, and it probably was introduced into the Arkansas River upstream from the reservoir. Since BHT was detected at the lower end of the reservoir, it may be concluded that is was not amenable to metabolic oxidation. Identification of BHT in this study with the combination gas chromatograph-mass spectrometer is among the first successful applications of this instrument to analysis of an organic contaminant in surface receiving waters.

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# APPENDIX

TABLE I

CARBON ADSORPTION DATA FOR STATION A ON ARKANSAS RIVER NEAR BIXBY, OKLAHOMA FROM AUGUST, 1965 TO OCTOBER, 1966.

| Sampling Period | Liters Filtered | Net g CCE | µg/l CCE | Net g CAE | µg/l CAE | Flow Rate liters/min. |
|---|---|---|---|---|---|---|
| 8/24-9/22 | 888 | 0.4620 | 520 | 0.5203 | 586 | 0.60 |
| 10/12-11/10 | 4,923 | 1.3595 | 276 | 1.4711 | 299 | 0.50 |
| 11/17-12/1 | 4,400 | 4.3560 | 990 | 3.3692 | 766 | 0.60 |
| 12/1-12/23 | 8,005 | 63.1110 | 7,884 | 3.9599 | 495 | 0.61 |
| 12/23-1/5 | 3.361 | 66.0071 | 19,639 | 8.1199 | 2,416 | 0.63 |
| 1/5-1/12 | 2,982 | 1.1141 | 374 | 1.6950 | 568 | 0.67 |
| 1/12-1/18 | 1,558 | 0.3147 | 202 | 1.1524 | 740 | 0.62 |
| 1/18-2/5 | 825 | 0.2594 | 314 | 1.6255 | 1,970 | 0.57 |
| 2/5-2/25 | 264 | 0.1169 | 443 | 0.5160 | 1,954 | 0.92 |
| 2/25-3/11 | 4,523 | 2.3246 | 514 | 3.4986 | 773 | 0.70 |
| 3/11-3/22 | 2,258 | 2.5023 | 1,108 | 2.7914 | 1,236 | 0.53 |
| 3/22-3/30 | 2,452 | 0.7237 | 295 | 1,8660 | 761 | 0.60 |
| 3/30-4/13 | 3,314 | 1.6546 | 499 | 5.4816 | 1,654 | 0.56 |
| 5/25-6/2 | 3,391 | 1.9015 | 561 | 5.0330 | 1,484 | 0.86 |
| 6/2-6/8 | 2,892 | 6.3709 | 2,203 | 2.9535 | 1,021 | 0.72 |
| 6/8-6/15 | 3,032 | 0.9924 | 327 | 1.7796 | 587 | 0.75 |
| 6/15-6/22 | 3,473 | 1.3075 | 377 | 3.2567 | 938 | 0.80 |
| 6/22-7/5 | 4,629 | 1.5572 | 336 | 4,9122 | 1,061 | 0.83 |
| 7/5-7/15 | 2,277 | 1.6367 | 719 | 6.2084 | 2,727 | 0.75 |
| 7/15-7/29 | 1,640 | 0.5103 | 311 | 3.5873 | 2,187 | 0.63 |
| 7/29-8/11 | 1,788 | 0.6424 | 359 | 2.4395 | 1,420 | 0.71 |
| 8/11-8/26 | 2,519 | 1.5089 | 599 | 2.7176 | 1,089 | 0.26 |
| 8/26-8/31 | 1,046 | 0.4195 | 401 | 2.3837 | 2,279 | 0.31 |
| *8/26-8/31 | 1,046 | 0.2556 | 244 | 1.2841 | 1,228 | 0.31 |
| 8/31-9/6 | 2,151 | 1.2880 | 599 | 3.4436 | 1,601 | 0.67 |
| *8/31-9/6 | 2,151 | 0.1194 | 55 | 0.3829 | 178 | 0.67 |
| 9/6-9/13 | 1,433 | 0.7190 | 502 | 1.4062 | 981 | 0.63 |
| *9/6-9/13 | 1,433 | 0.0101 | 7 | 0.0541 | 38 | 0.63 |
| 9/13-9/29 | 2,745 | 0.9718 | 354 | 2.5445 | 927 | 0.80 |
| *9/13-9/29 | 2,745 | 0.0524 | 19 | 2.1197 | 772 | 0.80 |
| 9/29-10/10 | 3,776 | 2.1759 | 576 | 3.4104 | 903 | 0.74 |
| *9/29-10/10 | 3,776 | 0.0961 | 25 | 1.0203 | 270 | 0.74 |

*Carbon columns operated in series.

TABLE II

CARBON ADSORPTION DATA FOR STATION C ON LOWER END OF CIMARRON ARM OF KEYSTONE RESERVOIR FROM NOVEMBER, 1965 TO OCTOBER, 1966.

| Sampling Period | Liters Filtered | Net g CCE | µg/l CCE | Net g CAE | µg/l CAE | Flow Rate liters/min. |
|---|---|---|---|---|---|---|
| 11/11-11/18 | 3,454 | 0.3448 | 141 | 1.4949 | 433 | 0.54 |
| 11/29-12/9 | 4,689 | 0.3404 | 73 | 1.0456 | 223 | 0.54 |
| 12/11-12/16 | 3,035 | 0.5327 | 176 | 1.4304 | 472 | 0.54 |
| 12/20-12/27 | 6,700 | 0.5068 | 75 | 1.9064 | 285 | 0.57 |
| 12/27-1/4 | 4,629 | 0.8437 | 182 | 2.2175 | 479 | 0.55 |
| 1/4-1/11 | 5,615 | 0.5699 | 102 | 1.8104 | 322 | 0.52 |
| 1/11-1/21 | 4,097 | 0.7527 | 184 | 2.2035 | 538 | 0.50 |
| 1/21-2/2 | 11,396 | 1.8680 | 164 | 3.4348 | 301 | 0.50 |
| 2/2-2/11 | 4,011 | 0.7037 | 175 | 3.0802 | 768 | 0.40 |
| 2/11-2/18 | 7,254 | 0.9011 | 120 | 3.5376 | 488 | 0.62 |
| 2/18-2/25 | 6,324 | 0.6900 | 109 | 4.0727 | 644 | 0.62 |
| 2/25-3/6 | 2,988 | 0.9932 | 332 | 2.7991 | 937 | 0.86 |
| 3/6-3/11 | 4,827 | 0.5895 | 122 | 3.0299 | 628 | 0.80 |
| 3/11-3/23 | 2,963 | 1.1659 | 394 | 3.1411 | 1,060 | 0.75 |
| 3/23-3/30 | 1,519 | 0.1200 | 79 | 1.5518 | 1,021 | 0.62 |
| 3/30-4/13 | 1,948 | 1.3366 | 686 | 2.2918 | 1,176 | 0.74 |
| 4/13-4/20 | 5,912 | 1.2648 | 214 | 2.7607 | 467 | 0.62 |
| 4/20-4/27 | 6,951 | 0.7878 | 113 | 3.3029 | 475 | 0.60 |
| 4/27-5/4 | 9,459 | 0.3723 | 39 | 4.1239 | 435 | 0.60 |
| 5/4-5/13 | 10,216 | 0.7030 | 69 | 4.8611 | 476 | 0.75 |
| 5/13-5/20 | 8,803 | 1.3122 | 149 | 4.2372 | 481 | 0.69 |
| 5/20-5/25 | 6,867 | 0.8121 | 118 | 3.8134 | 555 | 0.90 |
| 5/25-6/1 | 9,119 | 1.3140 | 144 | 3.9264 | 432 | 0.78 |
| 6/1-6/8 | 6,638 | 0.5922 | 89 | 4.9781 | 750 | 0.45 |
| 6/8-6/15 | 9,633 | 1.2719 | 132 | 5.1541 | 535 | 1.00 |
| 6/15-6/22 | 8,539 | 1.0008 | 117 | 3.2377 | 279 | 0.71 |
| 6/22-7/5 | 12,727 | 0.9259 | 73 | 4.2802 | 336 | 0.80 |
| 7/5-7/15 | 12,971 | 1.8627 | 144 | 4.9470 | 381 | 0.88 |
| *7/15-8/3 | 18,437 | 3.6544 | 198 | 4.8849 | 265 | 0.87 |
| 8/3-8/11 | 7,739 | 1.4987 | 194 | 4.2347 | 547 | 0.78 |
| 8/11-8/26 | 12,651 | 2.4665 | 195 | 6.0742 | 480 | 0.61 |
| 8/26-9/6 | 8,894 | 1.7382 | 195 | 1.2349 | 139 | 0.57 |
| 9/6-9/23 | 18,019 | 2.5794 | 143 | 4.6435 | 258 | 0.62 |
| *9/28-10/12 | 884 | 0.6176 | 699 | 3.5402 | 4,005 | 0.46 |
| 10/12-10/31 | 3,569 | 0.5785 | 162 | 1.9343 | 542 | 0.55 |

* Volume measuring equipment not functioning properly, therefore these values will be discarded.

TABLE III

CARBON ADSORPTION DATA FOR STATION D ON UPPER END OF CIMARRON ARM OF KEYSTONE RESERVOIR FROM NOVEMBER, 1965 TO OCTOBER, 1966.

| Sampling Period | Liters Filtered | Net g CCE | µg/l CCE | Net g CAE | µg/l CAE | Flow Rate liters/min. |
|---|---|---|---|---|---|---|
| 11/4-11/8 | 2,808 | 0.1759 | 63 | 0.4308 | 153 | 0.60 |
| 11/16-11/18 | 2,317 | 0.0810 | 35 | 1.3770 | 594 | 0.75 |
| 11/29-12/6 | 4,532 | 0.6032 | 133 | 2.1550 | 476 | 0.54 |
| 12/6-12/11** | | | | | | |
| 12/14-12/20 | 3,956 | 0.4329 | 109 | 4.2722 | 1,079 | 0.67 |
| 12/20-12/27 | 6,224 | 1.1801 | 190 | 3.9313 | 632 | 0.62 |
| 12/27-1/4 | 6,317 | 2.3062 | 365 | 5.4367 | 861 | 0.58 |
| 1/4-1/11 | 8,807 | 1.7497 | 199 | 3.9443 | 448 | 0.86 |
| 1/11-1/21 | 10,944 | 1.4743 | 135 | 5.0172 | 458 | 0.67 |
| 1/21-2/2 | 9,370 | 5.8639 | 625 | 6.1278 | 654 | 0.46 |
| 2/11-2/18 | 8,080 | 2.3386 | 289 | 1.4959 | 185 | 0.83 |
| 2/18-2/25 | 7,557 | 1.0761 | 142 | 11.8213 | 1,564 | 0.80 |
| 2/25-3/6 | 7,948 | 1.3738 | 173 | 5.9628 | 750 | 0.72 |
| 3/6-3/11 | 4,505 | 0.5956 | 132 | 3.1686 | 703 | 0.67 |
| 3/11-3/18 | 2,695 | 0.4226 | 157 | 4.4640 | 1,656 | 0.70 |
| 3/23-3/30 | 6,653 | 0.7757 | 117 | 6.9525 | 1,045 | 0.75 |
| 3/30-4/13 | 5,841 | 4.3896 | 752 | 3.9138 | 670 | 0.80 |
| 4/13-4/20 | 4,979 | 1.0032 | 202 | 5.0011 | 1,004 | 0.67 |
| 4/20-4/27 | 4,395 | 0.9615 | 219 | 3.0742 | 700 | 0.80 |
| *4/20-4/27 | 3,676 | 0.7409 | 202 | 2.8508 | 776 | 0.46 |
| 4/27-5/4 | 2,776 | 0.6361 | 229 | 2.5847 | 931 | 0.51 |
| 5/4-5/13 | 5,362 | 1.3616 | 254 | 5.1573 | 962 | 0.20 |
| *4/27-5/13 | 7,866 | 1.9401 | 247 | 6.2008 | 788 | 1.05 |
| 5/13-5/20 | 1,264 | 0.5792 | 458 | 0.9405 | 744 | 0.99 |
| 5/20-5/25 | 6,975 | 1.9145 | 275 | 3.1445 | 451 | 0.95 |
| *5/13-5/25 | 6,859 | 2.2060 | 322 | 2.8672 | 418 | 0.98 |
| 5/25-6/1 | 5,610 | 2.7128 | 484 | 3.0485 | 543 | 1.07 |
| *5/25-6/1 | 138 | 0.0498 | 361 | 0.1113 | 806 | 0.41 |
| 6/1-6/8 | 5,463 | 1.7385 | 318 | 3.8545 | 706 | 1.01 |
| *6/1-6/8 | 4,153 | 1.1581 | 279 | 3.1308 | 754 | 0.68 |
| 6/8-6/15 | 3,789 | 1.1091 | 293 | 1.5190 | 400 | 1.07 |
| 6/15-6/22 | 3,909 | 1.7870 | 457 | 3.4803 | 890 | 0.82 |
| *6/8-6/22 | 3,334 | 1.0068 | 302 | 1.8811 | 564 | 0.63 |
| 6/22-7/5 | 5,837 | 1.6015 | 274 | 5.1320 | 879 | 0.94 |
| *6/22-7/5 | 4,492 | 1.2123 | 270 | Boiled Dry | | 0.50 |
| 7/5-7/15 | 1,615 | 0.7762 | 481 | 2.9684 | 1,838 | 0.97 |
| *7/5-7/15 | 501 | 0.1214 | 242 | 1.5470 | 3,087 | 0.50 |
| ***7/29-8/11 | 42 | 0.4744 | 11,295 | 2.0615 | 49,083 | 0.35 |
| *7/29-8/11 | 3,336 | 0.8001 | 239 | 2.4829 | 744 | 0.31 |

TABLE III (Continued)

| Sampling Period | Liters Filtered | Net g CCE | µg/l CCE | Net g CAE | µg/l CAE | Flow Rate liters/min. |
|---|---|---|---|---|---|---|
| ***8/23-8/31 | 752 | 0.8531 | 1,134 | 10.3665 | 13,758 | 0.62 |
| ***8/31-9/13 | 3,944 | 0.2947 | 74 | 4.8598 | 1,232 | 0.56 |
| 9/13-9/28 | 3,769 | 0.2588 | 68 | 2.8654 | 760 | 0.52 |
| *9/13-9/28 | 6,671 | 0.4446 | 66 | 3.9004 | 584 | 0.80 |
| 9/28-10/31 | 1,992 | 0.0132 | 6 | 1.3639 | 685 | 0.45 |

* Carbon columns operated in parallel.
** Did not extract, as the sample was molded.
*** Not accurate, volume measuring equipment not functioning properly, therefore these values will be discarded.

TABLE IV

CARBON ADSORPTION DATA FOR STATION E ON LOWER ARKANSAS ARM OF KEYSTONE RESERVOIR FROM DECEMBER, 1965 TO NOVEMBER, 1966.

| Sampling Period | Liters Filtered | Net g CCE | µg/l CCE | Net g CAE | µg/l CAE | Flow Rate liters/min. |
|---|---|---|---|---|---|---|
| 12/9-12/13 | 3,792 | 0.3798 | 100 | 0.7754 | 205 | 0.67 |
| 12/13-12/20 | 2,116 | 0.2055 | 97 | 1.2864 | 608 | 0.55 |
| 12/20-1/4 | 2,847 | 0.4909 | 172 | 1.4427 | 507 | 0.55 |
| 1/4-1/11 | 2,486 | 0.2825 | 114 | 1.6956 | 682 | 0.72 |
| 1/11-2/11 | 457 | Sample discarded, inaccurate liter measurement | | | | |
| 2/11-2/18 | 1,194 | 0.5643 | 473 | 3.8506 | 3,225 | 0.92 |
| 2/18-2/25 | 940 | 0.0532 | 57 | 1.4079 | 1,498 | 0.86 |
| 2/5-3/6 | 338 | 0.0043 | 13 | 1.2670 | 3,748 | 0.88 |
| 3/6-3/17 | 790 | 0.1055 | 133 | 1.3459 | 1,704 | 0.60 |
| 3/18-3/30 | 2,660 | 0.2709 | 102 | 4.3675 | 1,642 | 0.92 |
| 3/30-4/20 | 1,524 | 0.4143 | 272 | 1.7180 | 1,127 | 0.80 |
| 4/20-5/4 | 2,966 | 0.9260 | 312 | 2.4738 | 834 | 0.80 |
| 5/4-5/13 | 4,434 | 0.5151 | 116 | 3.1093 | 701 | 0.71 |
| 5/13-5/20 | 5,172 | 0.7066 | 137 | 4.2667 | 825 | 0.80 |
| 5/25-6/1 | 3,272 | 0.6402 | 196 | 2.9192 | 892 | 0.55 |
| 6/1-6/8 | 687 | 0.4544 | 661 | 3.7564 | 5,467 | 0.75 |
| 6/8-6/15 | 3,570 | 0.6627 | 186 | 2.4571 | 688 | 0.75 |
| 6/15-6/22 | 1,382 | 0.8513 | 616 | 3.8859 | 2,812 | 0.62 |
| 6/22-7/5 | 4,805 | 0.6263 | 130 | 1.5548 | 324 | 0.72 |
| 7/5-7/15 | 558 | 0.0404 | 72 | 0.1762 | 316 | 0.80 |
| 7/15-7/29 | 4,186 | 0.6559 | 157 | 3.6010 | 860 | 0.75 |
| 7/29-8/11 | 5,485 | 0.8955 | 163 | 4.2507 | 775 | 0.92 |
| 8/11-8/31 | 7,205 | 1.5000 | 208 | 3.8012 | 527 | 0.30 |
| 8/31-9/28 | 10,205 | 0.6712 | 66 | 3.5557 | 348 | 0.39 |
| 9/28-10/31 | 1,015 | 0.3653 | 360 | 2.4565 | 2,420 | 0.57 |
| 10/31-12/2 | 10 | Sample discarded, inaccurate liter measurement | | | | |
| 12/2-12/20 | 6,470 | 2.3810 | 368 | 3.0925 | 478 | 0.92 |

TABLE V

CARBON ADSORPTION DATA FOR STATION F ON UPPER ARKANSAS ARM OF KEYSTONE RESERVOIR FROM DECEMBER, 1965 TO JANUARY, 1967.

| Sampling Period | Liters Filtered | Net g CCE | µg/l CCE | Net g CAE | µg/l CAE | Flow Rate liters/min. |
|---|---|---|---|---|---|---|
| 12/7-12/14 | 5,700 | 0.5979 | 105 | 2.7474 | 482 | 0.67 |
| 12/16-12/27 | 9,565 | 1.0907 | 114 | 3.4195 | 358 | 0.67 |
| 12/27-1/4 | 800 | 0.2227 | 278 | 0.5932 | 742 | 0.57 |
| 1/11-2/25 | 500 | 0.2122 | 424 | 0.3602 | 720 | 0.92 |
| 2/25-3/30 | 5,444 | Sample discarded | | | | |
| 3/30-4/13 | 4,384 | 1.2749 | 291 | 3.7189 | 848 | 0.86 |
| 4/13-4/22 | 4,090 | 0.6698 | 163 | 3.0217 | 739 | 0.68 |
| 4/22-4/27 | 760 | 2.4183 | 3,181 | 0.5220 | 687 | 0.57 |
| 4/27-5/13 | 906 | 2.5691 | 2,835 | 0.5971 | 659 | 0.80 |
| 5/13-5/20 | 677 | 1.5534 | 2,295 | 1.1726 | 1,732 | 0.72 |
| 5/20-6/1 | 313 | 1.9536 | 6,241 | 0.3936 | 1,258 | 0.55 |
| 6/1-6/8 | 1,575 | 0.5152 | 327 | 0.9488 | 602 | 0.67 |
| 6/8-6/22 | 1,785 | 0,8347 | 468 | 1.9619 | 1,099 | 1.00 |
| 6/22-7/5 | 3,198 | 0.1426 | 44 | 0.7054 | 221 | 0.83 |
| 7/5-7/15 | 4,790 | 0.9685 | 202 | 1.9061 | 398 | 0.80 |
| 7/15-7/29 | 3,356 | 0.5146 | 153 | 1.9386 | 578 | 0.75 |
| 7/29-8/11 | 2,197 | 0.1892 | 86 | 0.7529 | 343 | 0.17 |
| 8/11-8/23 | 2,198 | 0.4336 | 197 | 0.8863 | 403 | 0.67 |
| 9/13-9/28 | 4,598+ | Sample discarded, inaccurate liter measurement | | | | |
| 9/28-10/12 | 2,656 | 0.2635 | 99 | 1.5986 | 602 | 0.47 |
| 10/12-10/31 | 4,680 | 0.3731 | 79 | 1.5249 | 326 | 0.48 |
| 10/31-1/3 | 3,025 | 0.4579 | 151 | 1.9709 | 651 | 0.34 |

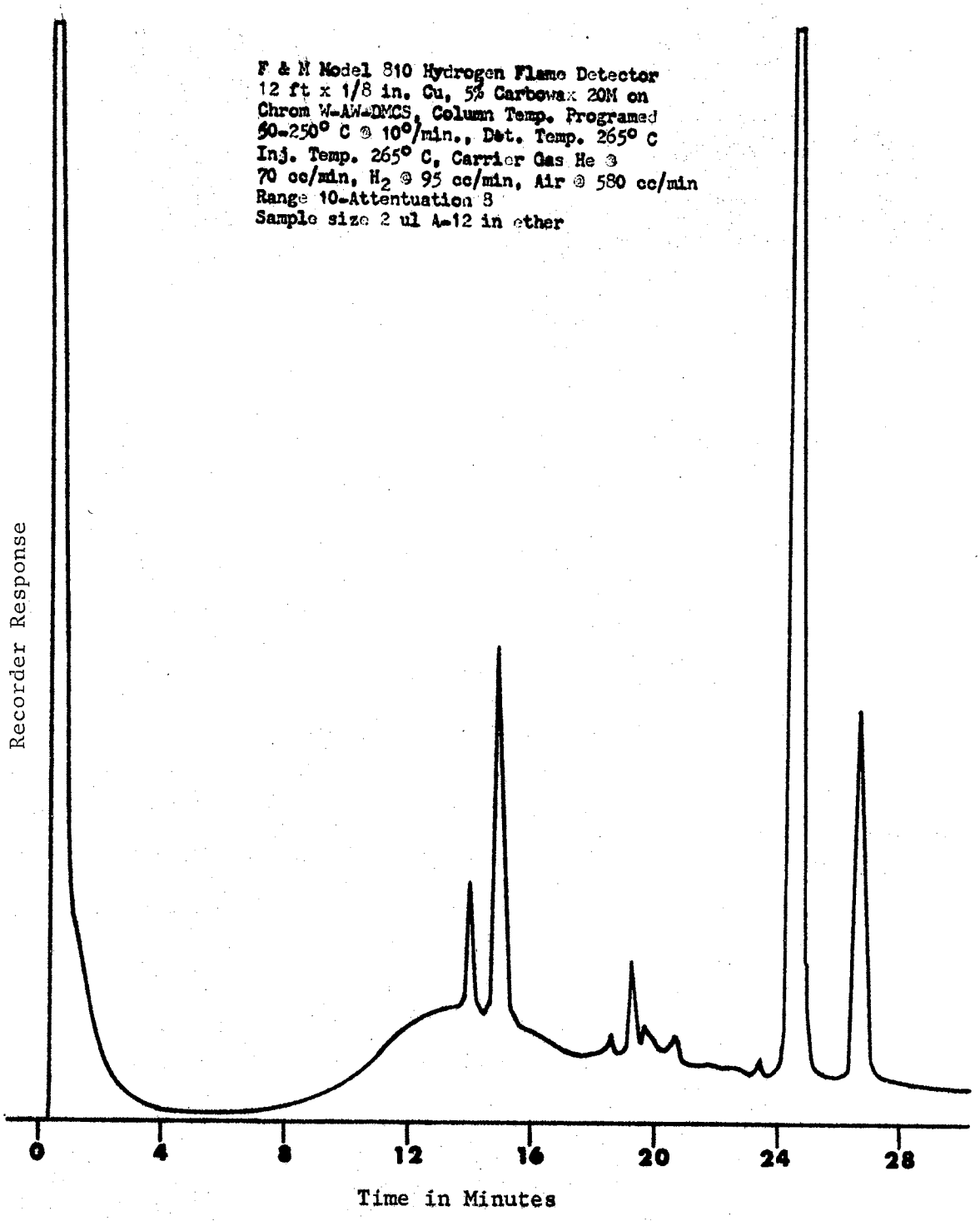


Figure 1. **Chromatogram of** Compounds Collected from Arkansas River below Tulsa.

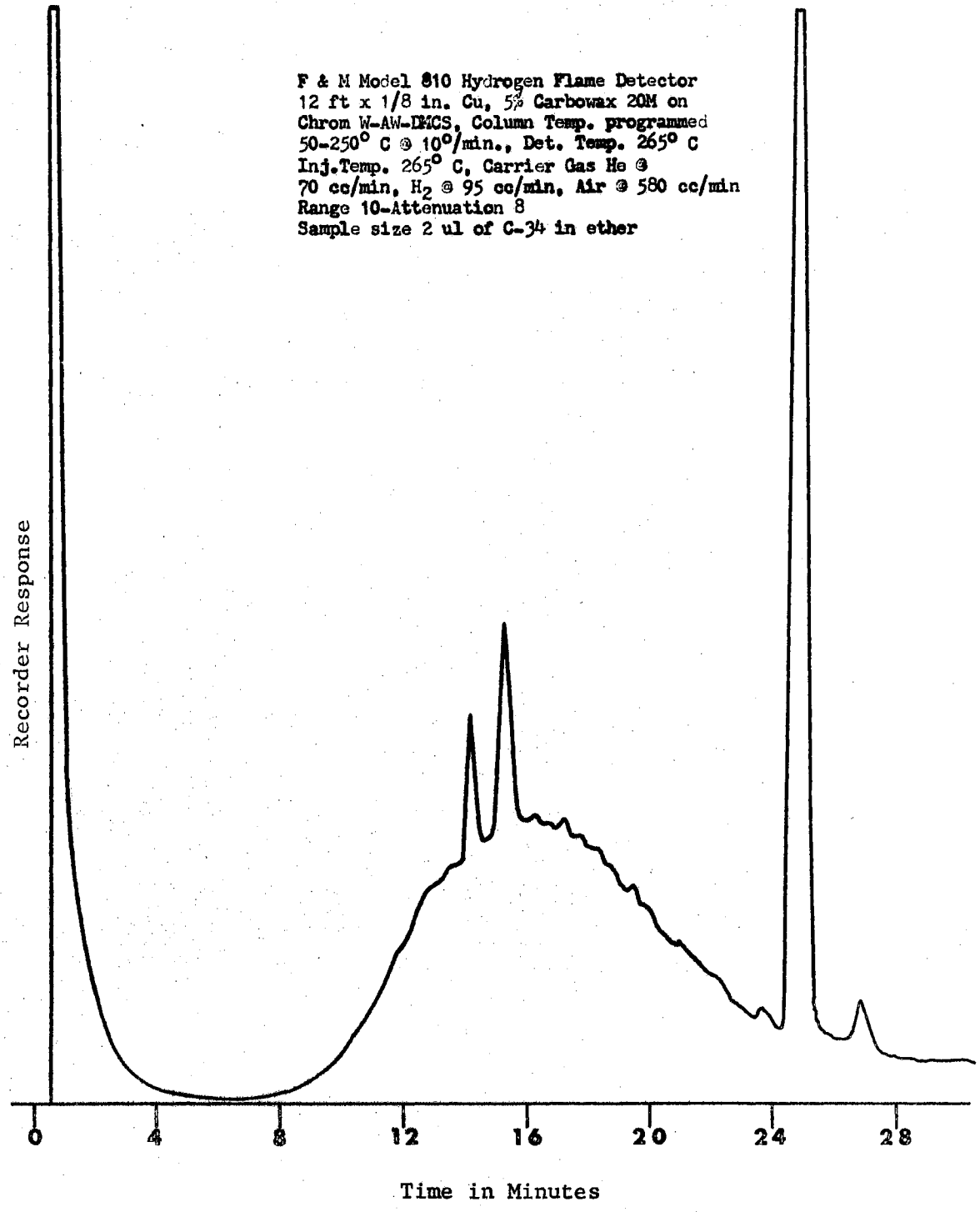


Figure 2. Chromatogram of Compounds Collected from Lower Cimarron River Arm of Keystone Reservoir.

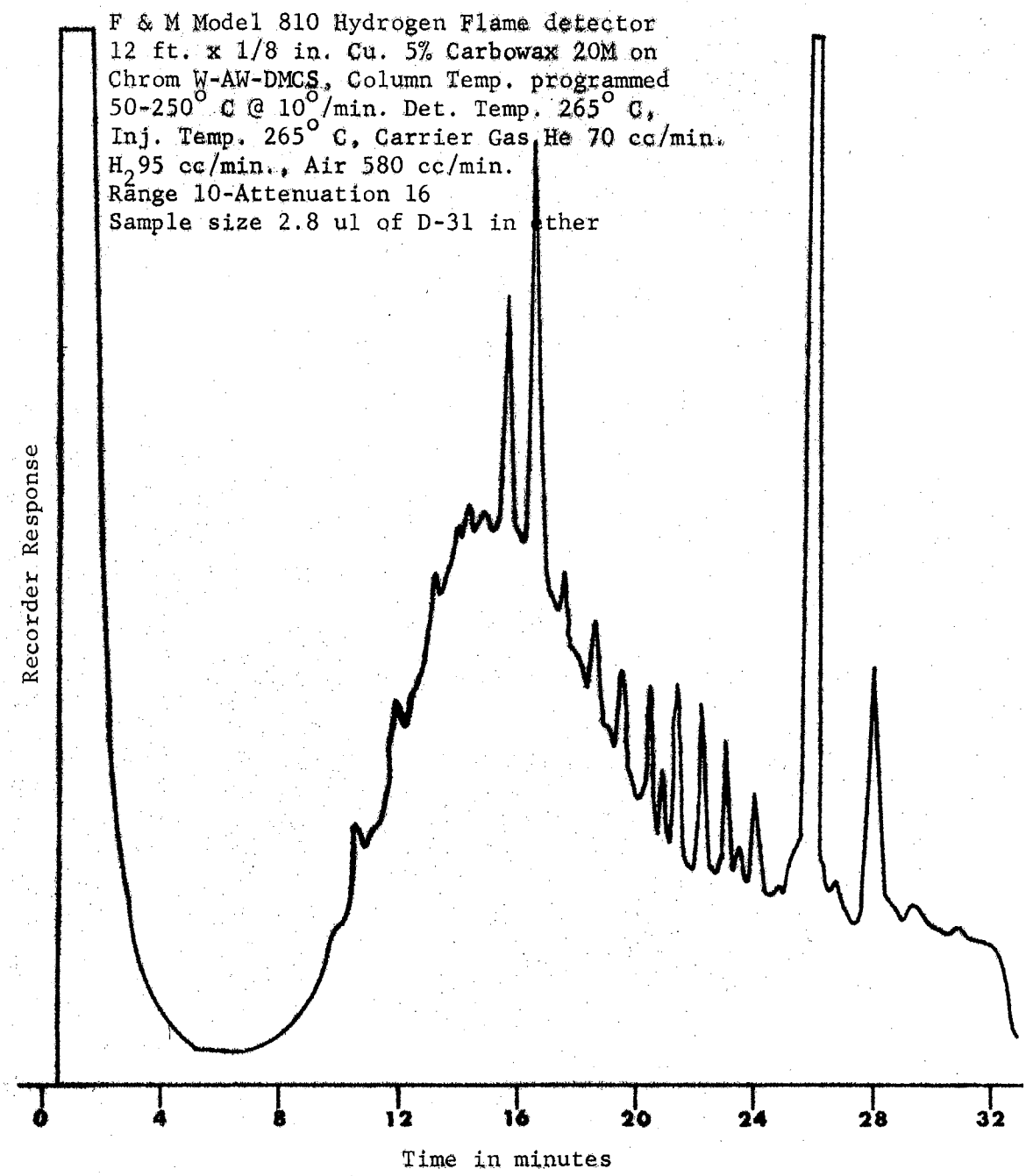


Figure 3. Chromatogram of Compounds Collected from Upper Cimarron River Arm of Keystone Reservoir.

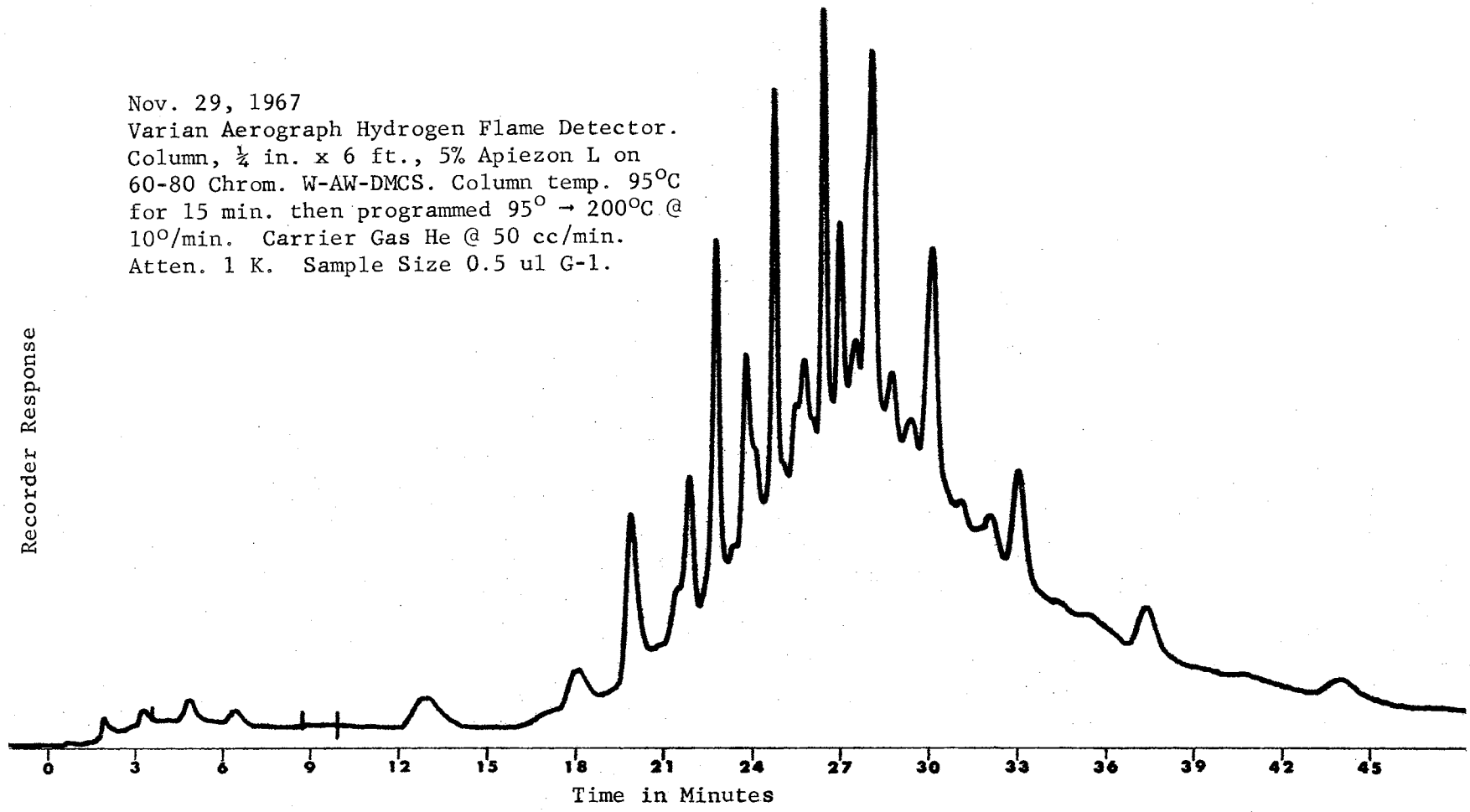


Figure 4. Gas Chromatogram of Compounds Collected from Oil Refinery on Arkansas River above Keystone Reservoir.

VITA

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Candidate for the Degree of

Doctor of Philosophy

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