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Determination of Acetone and Methyl Ethyl Ketone in Water

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The precision for two operators of the milligram-per-liter concentration procedure, expressed as the coefficient of variation, was generally less than 2 percent for concentrations ranging from 16 to 160 milligrams per liter. The precision from two operators of the microgram-per-liter concentration procedure was between 2 and 4 percent for concentrations of 20 and 60 micrograms per liter.

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UNITED STATES DEPARTMENT OF THE INTERIOR

CECIL D. ANDRUS, Secretary

GEOLOGICAL SURVEY

H. William Menard, Director

For additional information write to:

U.S. Geological Survey, WRD
Gulf Coast Hydroscience Center
Building 2101
NSTL Station, Mississippi 39529

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LIST OF SYMBOLS

C = Concentration of the components, in milligram per liter or microgram per liter;

C_i = A constant dependent on the sensitivity of the detector to the component of interest, in area units per milligram per liter atmosphere or area units per microgram per liter atmosphere;

C_A = Acetone concentration, in milligrams per liter or micrograms per liter;

C_{MEK} = Methyl ethyl ketone concentration, in milligrams per liter or micrograms per liter;

F = Daily correction factor for the standard solution;

PA = Area of gas chromatographic peak, in arbitrary area units;

P_{O_i} = Vapor pressure of pure component i, in atmosphere;

R_{HS} = Sensitivity of headspace analysis, in area units per milligram per liter or area units per microgram per liter;

γ_i = Activity coefficient of the component i; and

$\sum_{i=1}^{n}$ = Indicates the summation where n is the number of standard solutions and i is an integer.

CONVERSION TABLE: METRIC UNITS TO INCH-POUND UNITS

Multiply	By	To obtain
kilogram (kg)	2.205	pound (lb)
gram (g)	2.205×10^{-3}	pound (lb)
milligram (mg)	2.205×10^{-6}	pound (lb)
milliliter (mL)	3.38×10^{-2}	fluid ounce (fl oz)
microliter (µL)	3.38×10^{-5}	fluid ounce (fl oz)
meter (m)	3.281	foot (ft)
millimeter (mm)	0.03937	inch (in.)
milligram per liter (mg/L)	62.44×10^{-6}	pound per cubic foot (lb/ft^3)
microgram per liter (µg/L)	62.44×10^{-9}	pound per cubic foot (lb/ft^3)
milliliter per minute (mL/min)	35.31×10^{-6}	cubic foot per minute (ft^3/min)
millimeter per minute (mm/min)	25.4	inch per minute (in./min)
degree Celsius (°C) + 17.78	1.8	degree Fahrenheit (°F)

DETERMINATION OF ACETONE AND METHYL ETHYL KETONE IN WATER

By Doreen Y. Tai

ABSTRACT

Analytical procedures for the determination of acetone and methyl ethyl ketone in water samples were developed. Concentrations in the milligram-per-liter range were determined by injecting an aqueous sample into the analysis system through an injection port, trapping the organics on Tenax-GC at room temperature, and thermally desorbing the organics into a gas chromatograph with a flame ionization detector for analysis. Concentrations in the microgram-per-liter range were determined by sweeping the headspace vapors over a water sample at 50°C, trapping on Tenax-GC, and thermally desorbing the organics into the gas chromatograph.

The precision for two operators of the milligram-per-liter concentration procedure, expressed as the coefficient of variation, was generally less than 2 percent for concentrations ranging from 16 to 160 milligrams per liter. The precision from two operators of the microgram-per-liter concentration procedure was between 2 and 4 percent for concentrations of 20 and 60 micrograms per liter.

INTRODUCTION

The concern over the presence of trace quantities of organic compounds in water has increased significantly in recent years. A survey by Shackelford and Keith (1976) showed that acetone was one of the most prevalent compounds found in waters. In the National Organics Reconnaissance Survey (Environmental Protection Agency, 1975), the finished waters of 10 cities at various locations in the United States were analyzed for trace organics, and the only two compounds in all 10 finished waters were acetone and chloroform. Acetone has also been identified in landfill leachates (Khare and Dondero, 1977) and may be present in the wastewater discharges from sewage treatment plants operated at above optimum capacity (Abrams and others, 1975). Acetone may, under some conditions, be a precursor to the formation of chlorinated hydrocarbons during the chlorination of drinking water supplies (Stevens and others, 1976).

Acetone is a common, widely used chemical solvent. In terms of annual production, it ranked number 40 in the United States in 1977 when 0.971 billion kg were produced (Chem. and Eng. News, 1978). Thus, it is important from an industrial and an environmental point of view. Improved procedures for its measurement in water are needed.

GENERAL ANALYTICAL CONSIDERATIONS

Most of the procedures for the measurement of volatile organic compounds in water samples at the microgram-per-liter concentration level are based on a stripping and trapping procedure. For example, the Bellar and Lichtenberg (1974) procedure consists of stripping the volatile organics from the water with helium gas, trapping them at room temperature on a high-molecular-weight polymeric material, usually Tenax-GC[1/], thermally desorbing the organics, and flushing them into a gas chromatograph for analysis. This procedure works well for slightly soluble compounds.

Acetone, however, is a polar organic compound that is infinitely soluble in water. Thus, complete stripping of acetone from a water sample is very difficult, even with lengthy stripping times. Kuo, Chian, DeWalle, and Kim (1977) reported that 93.8 percent of the acetone was stripped from water at 95°C after a 60-minute stripping period. This temperature, however, results in considerable water vapor carryover through the Tenax-GC trap, and subsequently into the chromatograph. It induces significant baseline shifts with concomitant inaccurate measurements. Also, the higher temperatures may increase the rate of the reaction between acetone and any residual chlorine present in natural water to form halomethanes (Kuo, Chian, DeWalle, and Kim, 1977).

Kuo, Chian, DeWalle, and Kim (1977) discussed a few possibilities for reducing the water problem. The first is to strip the sample at a lower temperature. This requires considerable stripping time for quantitative recovery. The second is to install a fractionation column between the stripper and the trap. The third possibility is to continue passage of helium through the trap after the completion of the stripping process and before the initiation of thermal desorption. This must be done with care to insure that breakthrough of the adsorbed organics does not occur. The problem of breakthrough can be minimized somewhat by using a longer Tenax-GC trap.

Other approaches have been used for the analysis of acetone in water samples at the microgram-per-liter concentration level. Cowen, Cooper, and Highfill (1975) described an evacuated gas sampling valve for quantitative headspace sampling; Chian and others (1977) described a distillation-headspace procedure; and Kuo, Chian, and DeWalle (1977) described a distillation method. Concentrations at the milligram-per-liter range have been determined by a direct aqueous injection gas chromatography-mass spectrometry procedure (Harris, Budde, and Eichelberger, 1974).

[1/] The use of the brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

All the procedures applicable to microgram-per-liter concentrations require a time-consuming concentrating step and therefore pose an analytical problem for routine analysis of a large number of samples. A significant problem is the decontamination of the stripping chamber between samples, since complete stripping of acetone from a water sample is almost impossible to achieve.

This report describes two procedures for the measurement of acetone in water samples. These procedures were developed on the basis of methods described in the literature and have the advantages that they are relatively rapid and easy to use, have good precision, and are suitable for routine analytical work. The first procedure is applicable to milligram-per-liter concentration levels; the second procedure is applicable to microgram-per-liter concentration levels. These procedures may also be used for the measurement of methyl ethyl ketone in water samples, either as a single component or in mixtures with acetone.

ANALYTICAL PROCEDURES

General Description of the Procedure

The basic procedure consists of three steps. These are:

(1) preconcentration of the acetone on a Tenax-GC trap at room temperature;

(2) thermal desorption of the acetone from the trap; and

(3) flushing of the acetone into a gas chromatograph for analysis.

The preconcentration step in the procedure for the milligram-per-liter concentrations consists of direct aqueous injection of a 5- to 10-µL aliquot of the sample through a port and septum just prior to the Tenax-GC trap. The preconcentration step in the procedure for the microgram-per-liter concentrations consists of sweeping the headspace vapors over a 20-mL sample in a standard 125-mL Erlenmeyer flask with helium, and trapping on Tenax-GC. Descriptions of the instrumentation and accessory equipment and detailed procedures are presented in the following paragraphs.

Instrumentation and Accessory Equipment

A Varian 2700 gas chromatograph with a flame ionization detector was used. The column was a 1.83-m length of 6.35-mm OD stainless steel tubing packed with Chromosorb 103 and conditioned at 250°C for 2 hours with carrier gas flow. The helium carrier gas flow rate was 60 mL/min and the air and hydrogen flow rates to the detector were 300 mL/min and 30 mL/min, respectively. The helium flow rate used in the stripping or sweeping preconcentration step was 20 mL/min. The helium was filtered through activated carbon and molecular sieve 5A, and the air and hydrogen

were filtered through Drierite and molecular sieve 5A. Two-stage regulating valves were used on all cylinders, and the flows were further controlled with metering valves on each line. The oven temperature was maintained at 150°C, the injection port temperature at 200°C, and the detector temperature at 200°C. Most of the samples were analyzed at an attenuation of 16 and an electrometer range of 10^{-12} amps/mV, although attenuations of 32 and 8 were used for some concentrations. The signal from the electrometer was recorded on a 1 mV full scale strip chart recorder with a chart speed of 5 mm/min. Peak areas were used in the analysis of the results, and a digital electronic integrator was used for determining the areas. Both an Auto Lab Model 6300 and a Columbia Scientific Industries Supergrator I have been used for this purpose.

The main component of the accessory equipment was an eight-port valve with two Tenax-GC traps. In the milligram-per-liter concentration procedure, this arrangement permitted the trapping of one sample while a second sample was being desorbed and flushed into the gas chromatograph. This system resulted in almost no dead time and greatly increased the number of samples that could be analyzed in a specific time period as compared to a single trap system. In the microgram-per-liter concentration procedure, the second trap was used simply for flushing all traces of the previous sample from the system while the sample was being analyzed in the chromatograph.

The Tenax-GC traps were constructed from 3.18-mm OD stainless steel tubing. The traps were U-shaped with arms about 160 mm long and a distance of about 30 mm between the arms. About 70 mg of Tenax-GC was used in each trap, and the traps were conditioned at about 300°C for 1 hour prior to use.

Two heating cups for desorbing the acetone from the Tenax-GC traps were constructed from 200-mm lengths of 30-mm diameter steel pipe and heating tapes. The pieces of pipe were flattened so as to just fit around the U-tube Tenax-GC traps; the heating tapes were wrapped around the flattened pieces of pipe; and these arrangements were sealed in a metal can with refractory cement. A wooden handle was attached to the can for ease in handling. Figure 1 is a photograph of the heating cups. The temperature of the cups was controlled at about 170 to 180°C with line voltage and a variable transformer.

Figure 2 is a photograph showing one of the heating cups in place around the Tenax-GC trap, and the second Tenax-GC trap is visible directly to the right of the heating cup. The eight-port valve, and all tubing from the injection port to the gas chromatograph, were wrapped with heating tape, as shown in figure 2, to prevent condensation of acetone. The temperature was maintained at about 100°C.

The injection port for direct aqueous injection of sample aliquots was constructed from a standard 6.35-mm stainless steel Swagelok tubing

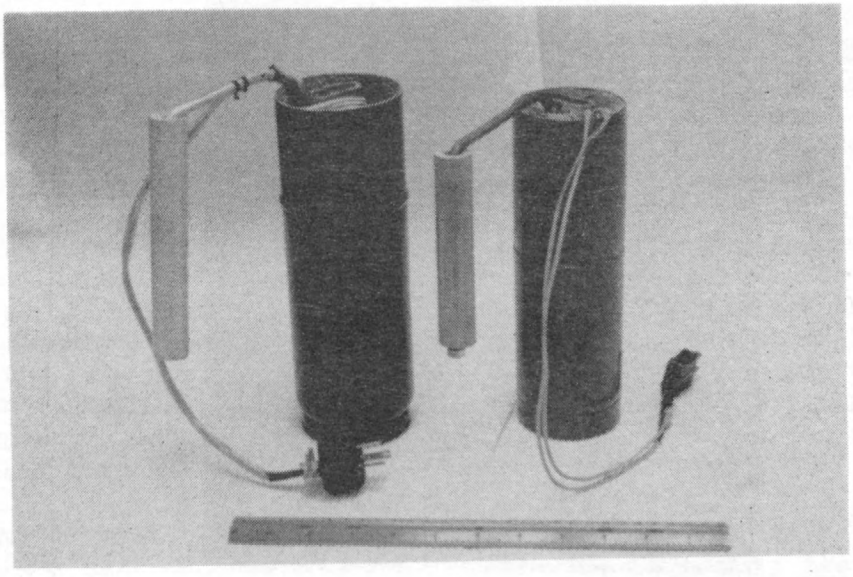

Figure 1.--View of the heating cups used in desorbing the organic compounds from the Tenax-GC traps; the scale is 305 mm long.

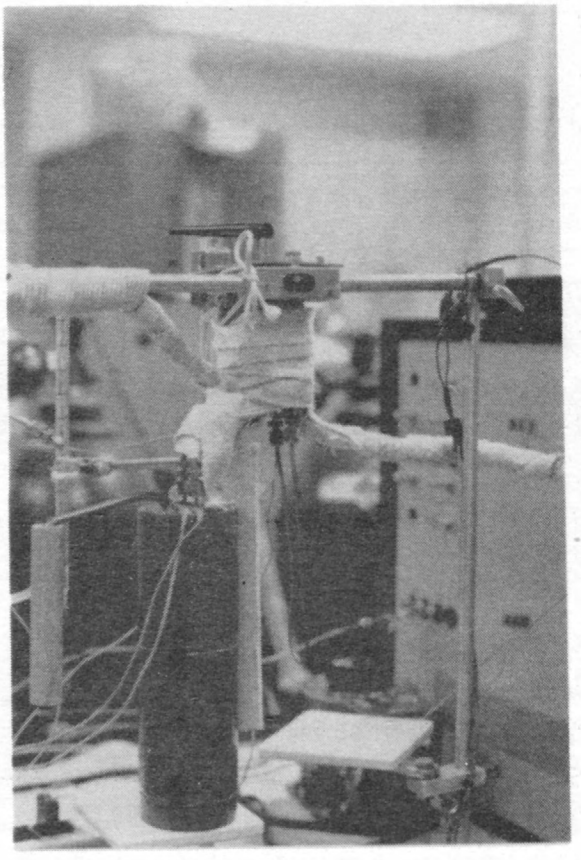

Figure 2.--View of the eight-port valve with one of the heating cups in place around the Tenax-GC trap; the second trap is visible at the right.

tee, a teflon-coated septum, and a needle guide as used for gas chromatograph injection ports. The guide permitted introduction of the sample at the same point in the port for each injection, and also prevented the syringe needle from being bent as a result of contact with the sides of the tee. Figure 3 is a schematic drawing of the injection port. The injection port was wrapped with heating tape and maintained at about 150°C.

The flasks used for the preconcentration step in the procedure for microgram-per-liter concentrations were standard 125-mL Erlenmeyer flasks with a 24/40 standard taper fitting. Use of a standard flask permits the use of a clean flask for each sample, and thus eliminates the problem of decontamination of the stripping and sweeping chamber between samples. A condenser bulb was placed on the outlet of the sweeping flask. The outlet of the condenser bulb was specially constructed so as to restrict the flow and to condense some of the water vapor carried over by the stripping gas. Figure 4 is a photograph of the sweeping flask and condenser bulb.

The water bath used for heating the sweeping flasks and the samples was constructed of stainless steel, and it was 250 mm by 200 mm and 100 mm deep. It was heated by an immersion heater and a thermoregulator was used to control the temperature at 50°C. A magnetic stirrer was placed under the bath for stirring the sample in the sweeping flask. Figure 5 is a photograph showing the water bath with a sweeping flask in place. The condenser bulb and the flexible teflon tubing used for connecting the flask into the system are also shown.

Tubing used throughout the system was 3.18-mm OD stainless steel, except for that used to connect the sweeping flask into the system. This was 3.18-mm OD teflon tubing which was sufficiently flexible to permit changing of the flasks between samples. The line to the chromatograph is connected directly to the internal plumbing of the instrument so as to bypass the flow-measuring device and to have the shortest route possible to the column.

Reagent grades of acetone and methyl ethyl ketone were used without further purification. Water from a Millipore Corporation Milli-Q system, further purified by boiling for 1 hour and cooling, was used in the preparation of samples and standard solutions. Boiling the water substantially reduced the concentration of some unknown organic that was not removed by the Milli-Q system. This organic had a retention time approximately the same as that of acetone, thus necessitating a blank correction at small concentrations.

Schematic diagrams of the complete systems are presented in figures 6 and 7. Figure 6 shows trap A being used for trapping a sample and trap B desorbing a sample into the chromatograph, and figure 7 shows trap A desorbing a sample into the chromatograph and trap B trapping a sample.

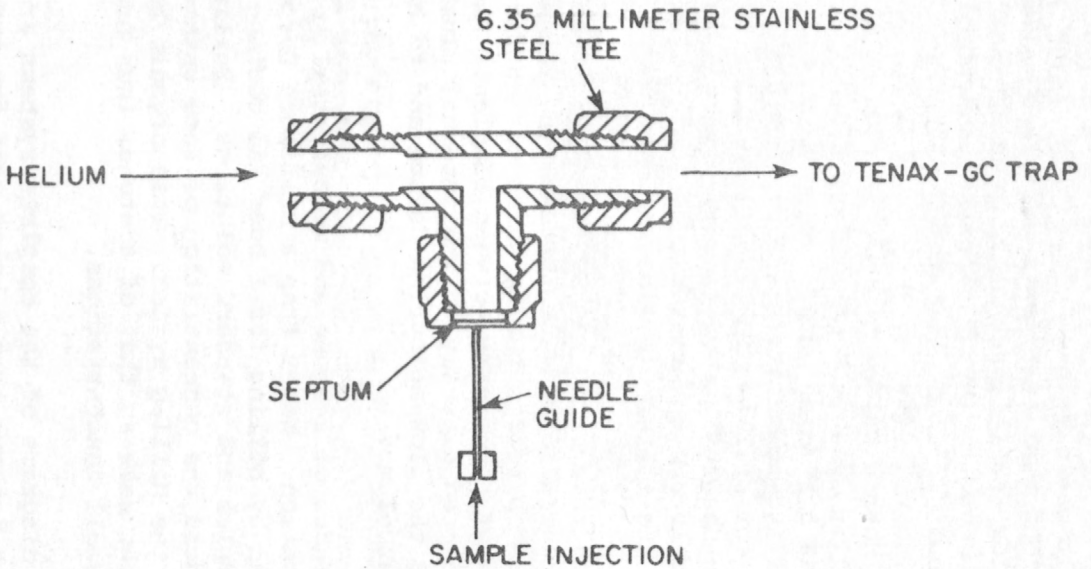

Figure 3.--Schematic diagram of the injection port for direct aqueous injection of sample aliquots in the milligram-per-liter concentration procedure.

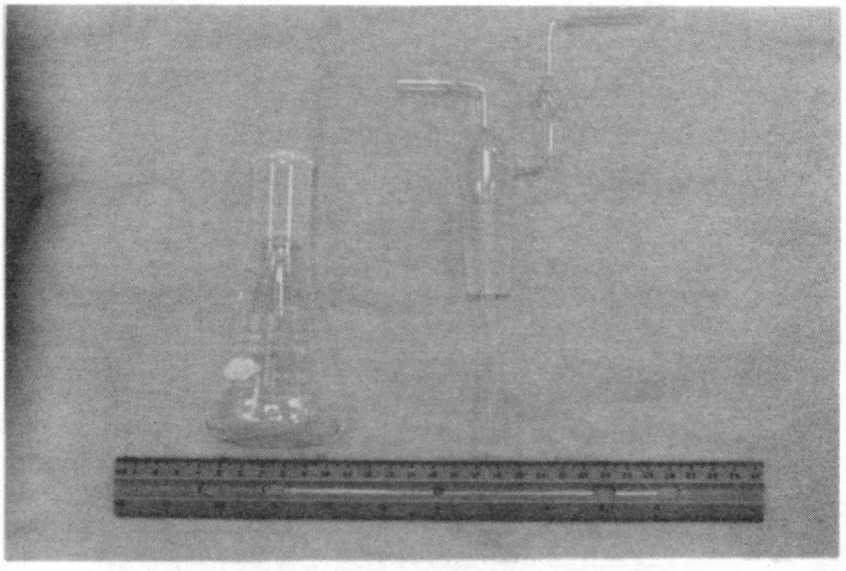

Figure 4.--View of the sweeping flask and condenser bulb; the scale is 305 mm long.

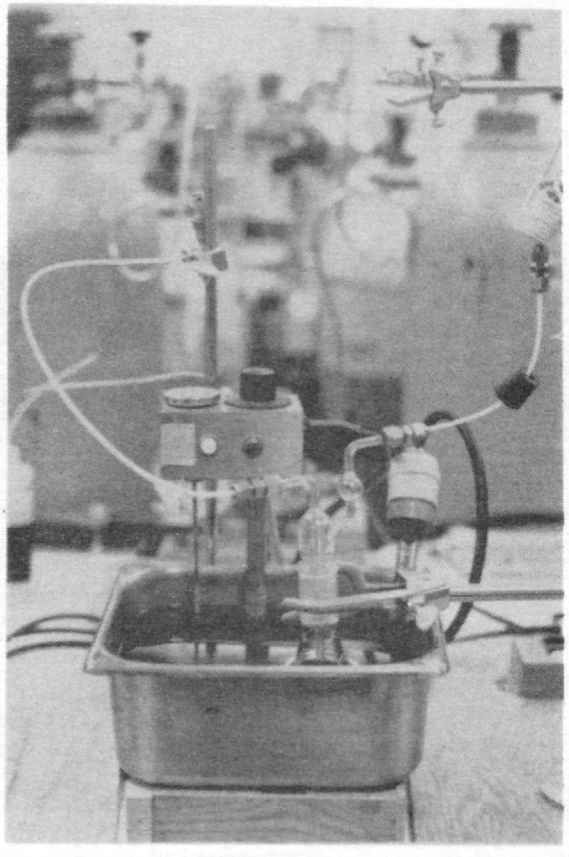

Figure 5.--View of the constant temperature bath and thermoregulator.

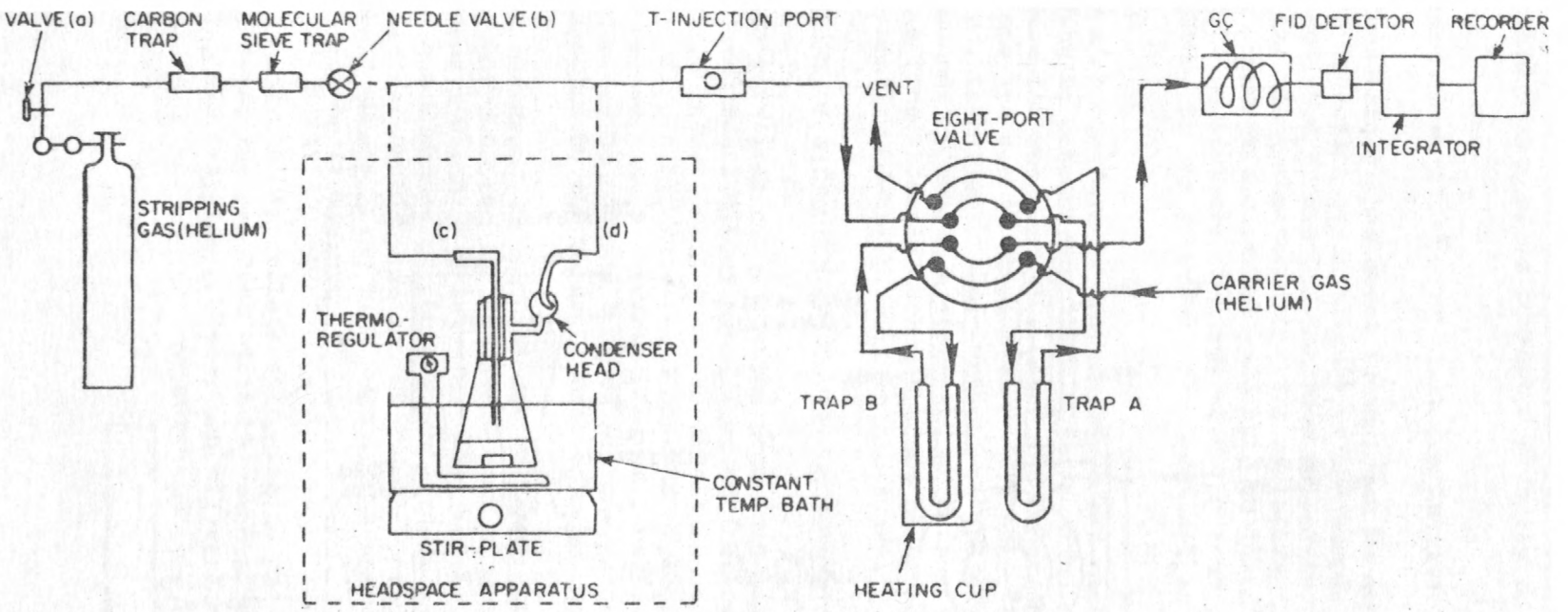

Figure 6.--Schematic diagram of the stripping, trapping, and gas chromatographic system; Trap A trapping, Trap B desorbing.

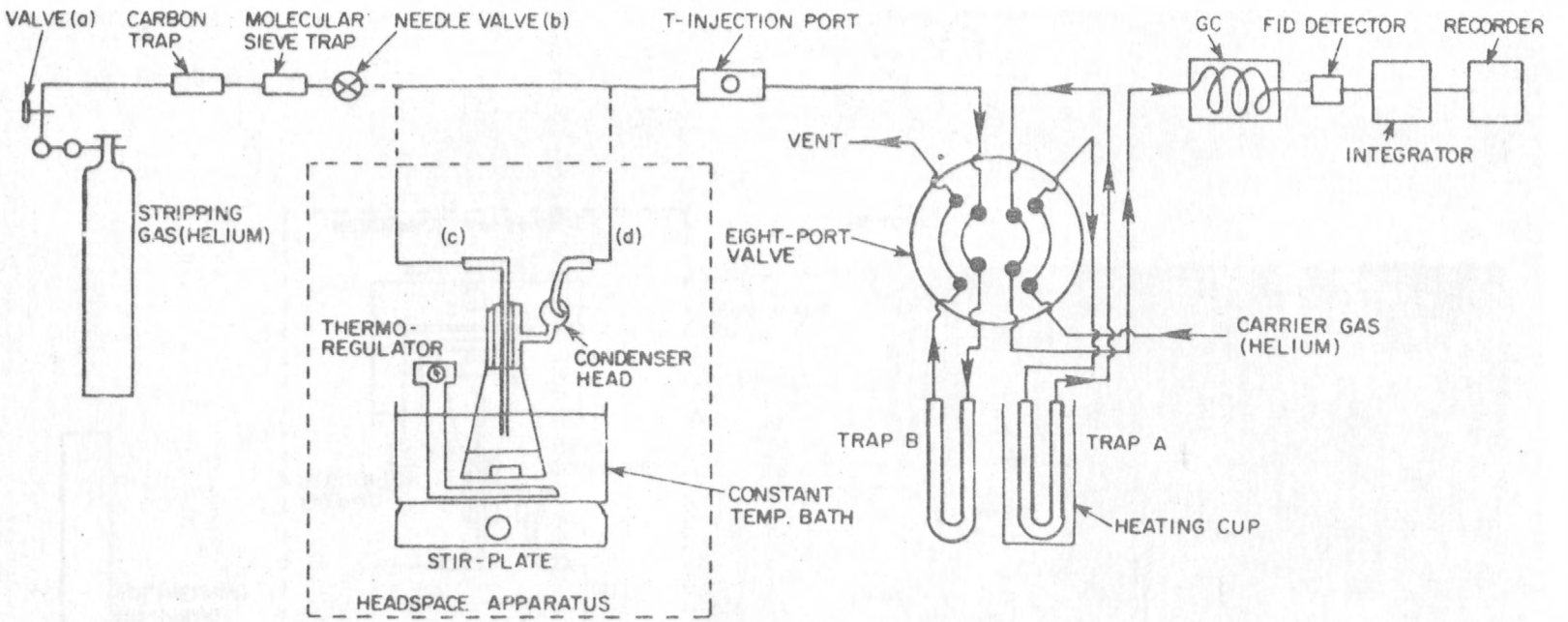

Figure 7.--Schematic diagram of the stripping, trapping, and gas chromatographic system; Trap B trapping, Trap A desorbing.

For measurement of microgram-per-liter concentrations, the line from needle valve (b) is connected to (c), the inlet of the sweeping flask, and the outlet of the condenser bulb (d) is connected to the injection port. For measurement of milligram-per-liter concentrations, the line from needle valve (b) is connected directly to the injection port.

MEASUREMENT OF MILLIGRAM-PER-LITER CONCENTRATIONS

Concentrations larger than about 10 mg/L can be accurately measured by direct aqueous injection of an aliquot of the sample through the injection port, followed by trapping at room temperature, thermal desorption, and analysis in the gas chromatograph. The procedure is routine and readily learned. Student assistants were able to learn the procedure in a short time and to perform the analyses with the same precision as professionals. Steps in the procedure are described in Supplementary Procedure I.

Figure 8 is a chromatogram showing acetone and methyl ethyl ketone peaks corresponding to concentrations of 60 mg/L. The analyses described in this report were for water samples where the major constituents were known to be acetone and methyl ethyl ketone. If natural water samples are being analyzed, then blank samples should be analyzed to determine if there are compounds appearing at the same retention times as acetone and methyl ethyl ketone. Should such compounds be present, use of a second column to confirm identity would be necessary.

MEASUREMENT OF MICROGRAM-PER-LITER CONCENTRATIONS

The milligram-per-liter concentration procedure described previously has an absolute detection limit of about 5 ng of acetone which is equivalent to a 5-µL injection of a sample with a concentration of 1 mg/L. To obtain reproducible results, a minimum of about 50 ng of acetone would be needed. At a concentration of 1 µg/L, a sample size of 5 mL would be necessary to provide 5 ng of acetone, and this volume of water cannot be handled by the Tenax-GC trap and the gas chromatograph.

An extensive review of the literature and experimental evaluation of several techniques resulted in the development of a headspace sweeping procedure which uses a standard Erlenmeyer flask as the sweeping chamber, thus permitting a quick change of the chamber between samples. This eliminates the need for decontamination of the stripping or sweeping chamber, which would be a problem with some of the more sophisticated designs presented in the literature.

On the other hand, the incomplete stripping of the sample requires some way of quantifying the results. This has been done in two ways. First, the sweeping and trapping process, and all variables involved in

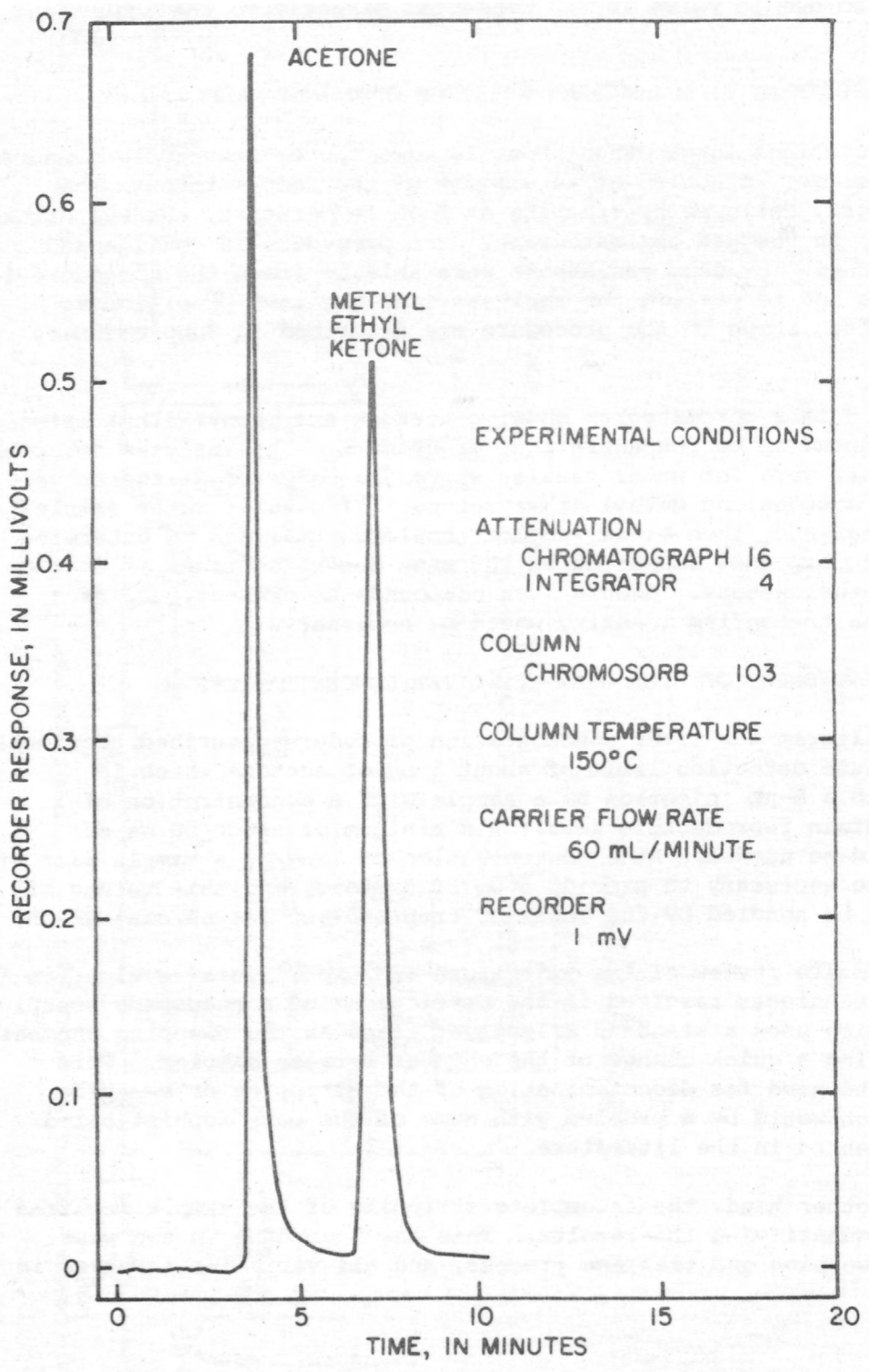

Figure 8.--Chromatogram from the milligram-per-liter concentration procedure; acetone and methyl ethyl ketone concentrations of 60 mg/L.

the process, were carefully controlled so that exactly the same procedures were used for the samples as were used for the standard solutions. Second, methyl ethyl ketone was used as an internal standard.

The basic procedure consists of removing the acetone vapor by sweeping the headspace with helium, trapping the acetone on the Tenax-GC trap, followed by thermal desorption and flushing into the gas chromatograph for analysis. The proportion of acetone in the vapor phase was increased, and thus, the efficiency of the sweeping process was improved by heating to 50°C and by adding sodium sulfate to the sample. The headspace sweeping flask and the condenser bulb are shown in figure 4, and a schematic of the complete system is shown in figures 6 and 7. The apparatus within the dotted area is added to the system for the measurement of the microgram-per-liter concentrations. Steps in the procedure are described in Supplementary Procedure II.

Figure 9 is a chromatogram showing the water peak and acetone and methyl ethyl ketone peaks corresponding to a concentration of 20 µg/L.

RESULTS

Numerous samples of various concentrations were analyzed by the milligram-per-liter and microgram-per-liter concentration procedures to permit determination of their precisions and also for the purpose of the determination of calibration curves. Results are presented in terms of the coefficient of variation, C_V, which is the standard deviation divided by the mean, expressed as a percentage. The percentage difference was used when only two replicates were completed. These results are presented and discussed in the following sections.

Milligram-Per-Liter Concentration Procedure

Results of the determination of the precision of the milligram-per-liter concentration procedure for acetone and methyl ethyl ketone are presented in table 1. Concentrations of acetone and methyl ethyl ketone ranged from 160 mg/L to zero, and chromatograph attenuations of 8, 16, and 32 were used. Blank corrections generally were applied for concentrations of 60 mg/L and smaller, but were neglected for the larger concentrations because of their insignificant effect on the peak areas.

Consideration of table 1 shows that the coefficients of variation are generally less than 2 percent for the concentrations between 16 and 160 mg/L, are from 3 to 5 percent for the concentrations of 8 and 13 mg/L, and 8 percent for a concentration of 0.8 mg/L. A significant problem in the analysis of samples with concentrations near the lower limit of applicability of the milligram-per-liter concentration procedure is the baseline shift caused by the water peak. This shift results in an incorrect reference point, and as a result, the electronic integrator incorrectly adjusts the baseline. This problem has been avoided somewhat by turning on the integrator only after the chart recorder indicates that the baseline has returned nearly to zero after the water peak.

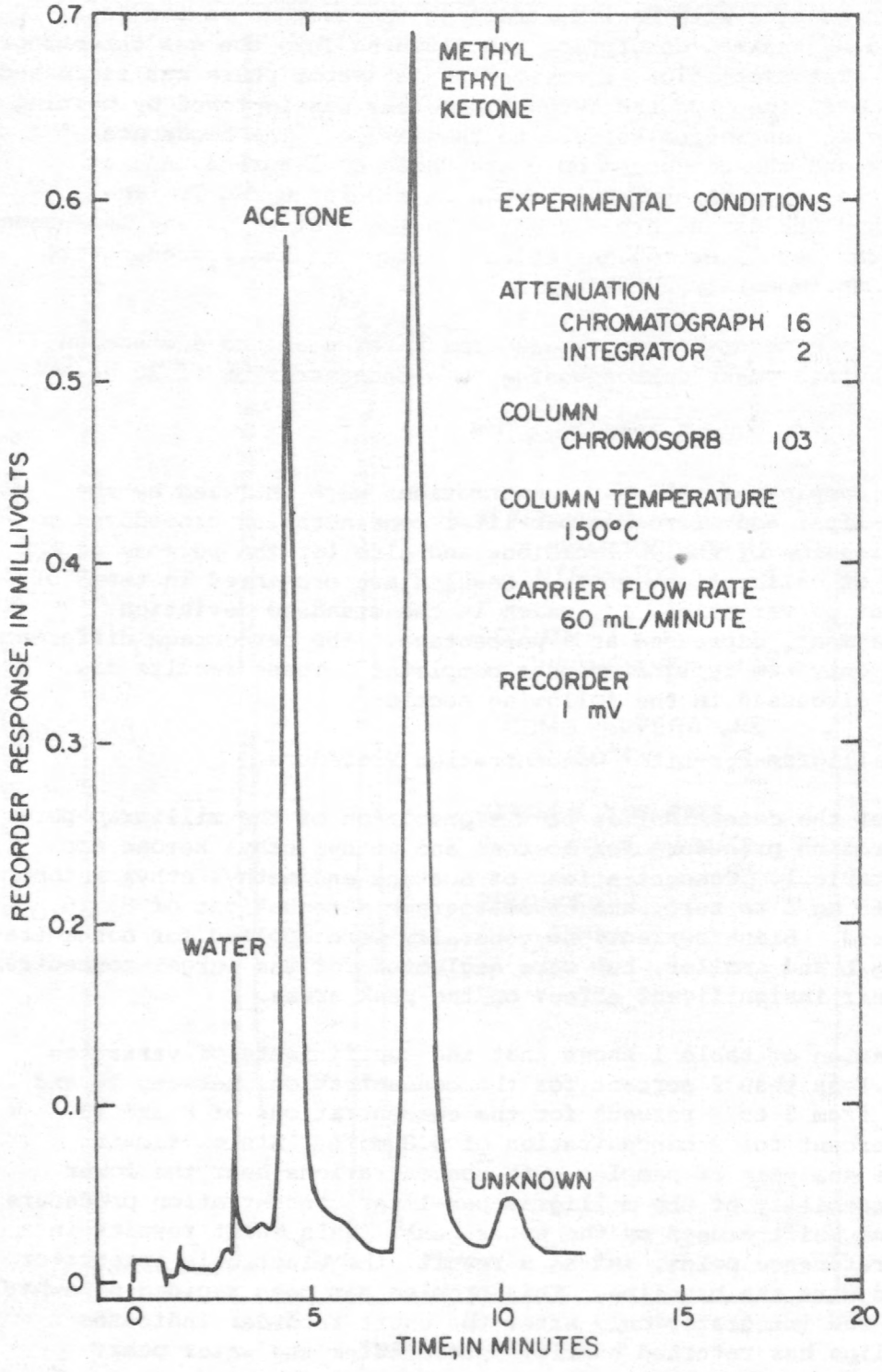

Figure 9.--Chromatogram from the microgram-per-liter concentration procedure; acetone and methyl ethyl ketone concentrations of 20 µg/L.

Table 1.--Determination of the precision of the milligram-per-liter concentration procedure

Date of analysis	Number of analyses	Acetone		Methyl ethyl ketone		Acetone/methyl ethyl ketone C_V (percent)
		Concentration (mg/L)	C_V (percent)	Concentration (mg/L)	C_V (percent)	
04/12/77	3	12.66	2.78	12.88	3.85	2.85
04/14/77	3	12.66	4.99	12.88	3.84	1.23
04/14/77	3	31.64	1.06	32.20	0.83	1.56
04/14/77	3	63.28	2.08	64.40	2.93	1.15
04/14/77	3	79.10	1.92	80.50	1.92	1.07
04/14/77	3	126.6	0.72	128.8	.48	.82
04/14/77	3	158.2	0.93	161.0	1.05	.75
07/19/77	10	79.10	1.82	80.50	1.41	2.15
11/15/77	6	79.10	1.00	80.50	.76	1.14
11/21/77	14	79.10	1.23	80.50	1.48	1.31
02/10/78	6	79.10	1.54	80.50	.63	1.72
03/03/78	6	59.32[1]	1.43	60.38	.40	1.08[1]
03/02/78	6	31.64[1]	2.03	32.20	1.07	1.44[1]
03/02/78	6	15.82[1]	1.75	16.10	.83	1.15[1]
03/03/78	5	7.91[1]	2.47	8.05	2.18	3.63[1]
02/22/78	10	0.79[1]	7.54	0.80	6.60	12.42[1]
02/22/78	3	0	7.20	0	----	----
03/02/78	2	0	1.38	0	----	----
03/03/78	2	0	4.04	0	----	----

[1]Corrected for blank

This, however, is tedious and probably introduces some error into the measurement of these small concentrations. Use of an integrator that can be programmed to automatically eliminate the effect of the water peak would be advantageous.

Also shown in table 1 are the coefficients of variation of the acetone/methyl ethyl ketone peak area ratios. Several compounds including isopropanol and methyl ethyl ketone were evaluated as internal standards for use with acetone. Because methyl ethyl ketone showed a better separation from acetone than did isopropanol and also because it was more similar in its chemical and physical properties to acetone, methyl ethyl ketone was selected for use as an internal standard. Consideration of the results in table 1 shows that the ratios can be determined with good precision, suggesting that methyl ethyl ketone is a good internal standard. Thus, field samples can be spiked with a known amount of methyl ethyl ketone to detect possible changes in the acetone concentration during storage, transportation, or any other operation that might occur before analysis. It will be necessary, however, to analyze blank samples of the natural water to insure that there are no compounds eluting at the same times as acetone and methyl ethyl ketone.

The results of the analysis of standard samples for the determination of calibration factors are presented in tables 2 and 3 for chromatograph attenuations of 32 and 16, respectively. Results are presented for each of the two Tenax-GC traps because usually it is difficult to pack the traps so that the flow resistances are the same. Because the carrier gas for the chromatograph flows through one or the other of the traps during analysis (figs. 6 and 7), the carrier flow rate, and thus, the sensitivity could change slightly if the resistances are different. Consideration of the results in tables 2 and 3 show, however, that the percentage differences are very small.

Assuming a linear relation between peak area and concentration, calibration factors in the form of least-squares slopes of lines forced through the origin, and 95-percent confidence limits for the slopes, were computed from the data presented in tables 2 and 3. The results are presented in table 4.

Microgram-Per-Liter Concentration Procedure

Results of the determination of the precision of the microgram-per-liter concentration procedure for acetone and methyl ethyl ketone are presented in table 5. Acetone concentrations of 20 and 60 µg/L and a methyl ethyl ketone concentration of 20 µg/L were used. The chromatograph attenuation was set at 16. Blank corrections were applied to all the acetone peak areas, however, blank corrections for methyl ethyl ketone were usually negligible.

Table 2.--Determination of calibration factors for the milligram-per-liter concentration procedure, attenuation of 32

Trap	Acetone				Methyl ethyl ketone			
	Concentration (mg/L)	Peak area (area units)	Mean (area units)	Percent difference (percent)	Concentration (mg/L)	Peak area (area units)	Mean (area units)	Percent difference (percent)
A------19.78		9,432	------	----	-----	------	------	----
A------39.55		18,496	18,638	1.52	40.25	22,782	23,167	3.32
B------39.55		18,780			40.25	23,551		
A------59.33		29,309	29,622	2.11	60.38	36,365	36,621	1.40
B------59.33		29,935			60.38	36,877		
A------79.10		39,157	39,582	2.14	80.50	48,964	49,134	0.69
B------79.10		40,006			80.50	49,305		
A------98.88		48,565	48,914	1.43	100.6	59,750	59,983	0.78
B------98.88		49,263			100.6	60,217		
A-----118.6		57,970	57,894	0.26	120.8	73,056	73,016	0.11
B-----118.6		57,817			120.8	72,976		
A-----158.2		76,630	77,203	1.48	161.0	97,040	97,165	0.26
B-----158.2		77,776			161.0	97,290		

Table 3.--Determination of calibration factors for the milligram-per-liter concentration procedure, attenuation of 16

Trap	Acetone				Methyl ethyl ketone			
	Concentration (mg/L)	Peak area (area units)	Mean (area units)	Percent difference (percent)	Concentration (mg/L)	Peak area (area units)	Mean (area units)	Percent difference (percent)
A------39.55		38,689			40.25	48,626		
			38,689	0.00			48,119	2.11
B------39.55		38,690			40.25	47,613		
A------59.33		58,259			60.38	72,552		
			59,099	2.84			73,169	1.69
B------59.33		59,939			60.38	73,786		
A------79.10		79,910			80.50	99,248		
			79,515	0.99			98,610	1.29
B------79.10		79,120			80.50	97,972		
A------98.88		98,504			100.6	121,206		
			99,635	2.27			122,116	1.49
B------98.88		100,766			100.6	123,026		
A-----118.6		117,542			120.8	149,436		
			117,520	0.037			148,386	1.42
B-----118.6		117,498			120.8	147,336		

Table 4.--Least-squares slopes and 95-percent confidence limits, milligram-per-liter concentration procedure

Attenuation	Acetone			Methyl ethyl ketone		
	Number of samples	Slope (area units/ mg/L)	95-percent confidence limits	Number of samples	Slope (area units/ mg/L)	95-percent confidence limits
32	13	490.5	4.18	12	602.7	4.17
16	10	997.9	8.80	10	1221	9.60

Table 5.--Determination of the precision of the microgram-per-liter concentration procedure

Compound	Concentration (µg/L)	Number of analysis	C_V (percent)
Acetone----------	20	5	3.85
Methyl ethyl ketone--	20	5	1.74
Ratio (acetone/MEK)--	--	5	3.06
Acetone----------	60	5	3.04
Methyl ethyl ketone--	20	5	3.03
Ratio (acetone/MEK)--	--	5	1.80

Consideration of table 5 shows that the coefficients of variation ranged from 2 to 4 percent.

The results of the analysis of standard samples for the determination of calibration factors are presented in table 6. The concentration of methyl ethyl ketone used as the internal standard was 20 µg/L. The percentage differences for replicate samples were less than 5 percent for all concentrations considered. Also, the percentage differences for replicate determinations of the acetone/methyl ethyl ketone ratio were less than 4 percent for all ratios considered. This suggests that the procedures of carefully controlling the variables and the use of methyl ethyl ketone as an internal standard are comparable.

Calibration factors in the form of least-squares slopes of lines forced through the origin and 95-percent confidence limits for the slopes were computed for the data presented in table 6. For acetone, the slope is 1,433 area units/µg/L with 95 percent confidence limits of 27.81. For the procedure using methyl ethyl ketone as an internal standard, the slope is 0.4962 with 95 percent confidence limits of 0.00832.

DISCUSSION

The most significant problem in the analysis of organic compounds with a very high solubility in water, such as acetone, is the separation of the compounds from the water. A stripping and trapping procedure can be used for separation; however, complete stripping of a very soluble compound from water at room temperature is a difficult and time-consuming procedure. Stripping at a higher temperature results in a larger quantity of the acetone being transferred to the trap but with a large carryover of water as well. Tenax-GC does not absorb water, but the passage of great quantities of water through the trap and out of the vent reduces the retention volume resulting in acetone breakthrough. Also, large quantities of water disturb the chromatographic baseline, inducing errors in the integration of the peaks. Drying agents such as anhydrous calcium sulfate and silica gel were evaluated for water removal, but it was found that acetone was also removed. These agents should not be used. To prevent water condensation in the plumbing and to minimize acetone dissolution in this water, the system was wrapped with heating tape and maintained at a temperature of about 100°C.

The sensitivity of the milligram-per-liter concentration procedure is controlled by the volume of the sample aliquot that can be injected for analysis and the flow rate of the stripping gas. The size of the sample aliquot can be increased by using a higher flow rate of stripping gas. This results in a greater amount of water being transported through

Table 6.--Determination of the calibration factors for the microgram-per-liter concentration procedure

Acetone concentration (µg/L)	Ratio concentration acetone / concentration MEK	Acetone			Methyl ethyl ketone			Ratio acetone/MEK		
		Peak area (area units)	Mean (area units)	Percent difference (percent)	Peak area (area units)	Mean (area units)	Percent difference (percent)	Peak area ratio	Mean	Percent difference (percent)
0	0	5,015 5,225	5,120	4.10	1,406 1,314	1,360	6.76	-----	-----	----
20	1.0	27,348 27,892	27,620	1.97	57,395 56,896	57,145	0.87	0.477 0.490	0.484	2.69
40	2.0	58,773 57,541	58,157	2.12	59,156 58,608	58,882	0.93	1.003 0.967	0.985	3.65
60	3.0	83,504 80,400	81,952	3.79	57,487 54,911	56,199	4.58	1.453 1.464	1.456	0.76
83.2	4.2	118,126 120,726	119,443	2.18	58,381 58,263	58,322	0.20	2.023 2.073	2.048	2.44
104.3	5.2	153,750 149,218	151,484	2.99	57,712 57,398	57,555	0.55	2.664 2.600	2.632	2.43

the trap, but there is also the danger of breakthrough and the resultant loss of the acetone. A 5-μL sample aliquot with 15 minutes stripping at a flow rate of 20 mL/min has proved to be satisfactory for sample concentrations ranging from about 10 mg/L to about 160 mg/L.

To increase the sensitivity to permit the determination of microgram-per-liter concentrations requires the analysis of a proportionately larger aliquot of the sample. The sensitivity of the microgram-per-liter concentration procedure depends on the volume of the headspace vapor transferred to the trap and the concentration of acetone in the vapor. The volume of the headspace vapor transferred to the trap depends on the flow rate of the sweeping gas and the duration of the sweeping period. As in the aforementioned procedure, water transferred into and through the system and acetone breakthrough are the primary limitations.

The concentration of the acetone in the vapor phase is dependent on the temperature and the activity coefficient of acetone in the liquid phase. The sensitivity of the headspace analysis can be expressed on the basis of Raoult's Law in the form (Hachenberg and Schmidt, 1977)

$$R_{HS} = \frac{PA}{C} = C_i P_{o_i} \gamma_i \qquad (1)$$

where R_{HS} is the sensitivity of the headspace analysis; PA is the peak area for a sample with a concentration of C; C_i is a constant dependent on the sensitivity of the detector to the component of interest; P_{o_i} is the vapor pressure of the pure component; and γ_i is the activity coefficient of the component. Thus, the headspace sensitivity can be increased by increasing the pure component vapor pressure, increasing the activity coefficient, or increasing both of these factors.

The vapor pressure can be increased by raising the temperature at which the headspace sweeping is accomplished. There are, however, several disadvantages in doing this. First, the increased temperature also increases the vapor pressure of the water, resulting in transfer of increased amounts of water to the trap, as discussed previously. Second, leaks are more of a problem at the higher temperatures and vapor pressures. For these reasons, an intermediate temperature of 50°C was used in the present study.

The activity coefficient can be increased by the addition of an electrolyte to the sample according to the traditional "salting out" procedure. Sodium chloride, sodium sulfate, ammonium sulfate, and sodium citrate were evaluated for this purpose, and it was concluded that sodium sulfate was the most efficient for increasing the activity coefficient of acetone in water. It was found, however, that reagent grade sodium sulfate contained small amounts of organic impurities, some of which had about the same retention time as acetone. Most of these impurities could be removed by baking for 2 hours at 600°C, however, a small residual necessitated the determination of a blank correction.

It was found that sweeping the headspace vapors over a 20-mL water sample at 50°C with 10 g of sodium sulfate added produced peak areas sufficiently large to give good precision for sample concentrations ranging from about 20 to 100 µg/L. A sweeping gas flow rate of 20 mL/min and a sweeping period of 15 min were used for the apparatus described in this report.

The milligram-per-liter and microgram-per-liter concentration procedures permit the measurement of a very wide range of concentrations of acetone and methyl ethyl ketone in water samples. Concentrations in the interval between the maximum microgram-per-liter concentration and the minimum milligram-per-liter concentration considered in this report can be determined using the microgram-per-liter concentration procedure. In the milligram-per-liter concentration procedure, use of the eight-port valve permits stripping and trapping of one sample while another sample is being flushed through the gas chromatograph for analysis, thus giving a very efficient operation. In the microgram-per-liter concentration procedure, use of the eight-port valve permits flushing of the system with stripping gas to remove all traces of the previous sample while the sample is being flushed through the chromatograph. Transfer from one procedure to the other is easily accomplished (figs. 6 and 7); the only change necessary being the connection of the sweeping flask into the system. Approximately 15 to 20 samples can be analyzed per day using the milligram-per-liter concentration procedure, and the precision of this procedure is of the order of about 2 percent. Approximately 10 to 12 samples can be analyzed per day using the microgram-per-liter concentration procedure, and the precision of this procedure is generally less than 4 percent.

Because of the level of concentrations measured by the microgram-per-liter concentration procedure, experimental conditions must be closely controlled. Glassware must be thoroughly cleaned and baked to insure the absence of organics. The flasks must be flushed with organic-free nitrogen or helium before the addition of a sample. The temperature, stripping gas flow rate, stripping time, and heating cup temperature used for desorption must be carefully controlled. With these precautions and rigid experimental control, it is possible to obtain reproducible results for microgram-per-liter concentrations.

SUMMARY AND CONCLUSIONS

Gas chromatographic procedures were developed for the determination of acetone and methyl ethyl ketone in water samples. The basic procedure consisted of trapping the organics at room temperature on Tenax-GC followed by thermal desorption and flushing into a gas chromatograph with a flame ionization detector for analysis. Two procedures were developed for the introduction of the samples into the system. For milligram-per-liter concentrations, a direct aqueous injection of an

aliquot of the sample through an injection port just upstream of the Tenax-GC trap was used. For microgram-per-liter concentrations, headspace sweeping of the vapors over the water sample was used. The proportion of the organics in the vapor phase was increased by heating the sample to 50°C and by using sodium sulfate as a salting out agent. The microgram-per-liter concentration procedure was quantified by either carefully controlling the experimental conditions or by using methyl ethyl ketone as an internal standard.

An eight-port valve with two Tenax-GC traps was used. In the milligram-per-liter concentration procedure, this arrangement permitted stripping and trapping of one sample while another sample was being flushed through the chromotograph for analysis. This system permitted approximately 15 to 20 samples to be analyzed per day. In the microgram-per-liter concentration procedure, the two-trap arrangement facilitated flushing the system with stripping gas to remove completely all traces of the previous sample while the sample was being flushed through the chromatograph. About 10 to 12 samples per day can be analyzed with the microgram-per-liter concentration procedure.

The most difficult problem in measuring very soluble organic compounds in aqueous solution is separating the compounds from the water. The procedures described in this report can be used to accomplish such a separation and thereby permit the precise determination of acetone and methyl ethyl ketone in water samples.

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SUPPLEMENTARY PROCEDURES

SUPPLEMENTARY PROCEDURE I

The steps necessary for measuring acetone and methyl ethyl ketone by the milligram-per-liter concentration procedure are described in the following paragraphs. Refer to figures 6 and 7 for the location of the various valves and other components of the system.

A. Condition the Tenax-GC traps: (only at the beginning of each day)

(1) Turn on the helium stripping gas at valve (a) and adjust needle valve (b) to give a flow rate of 20 mL/min. Measure the flow rate with a soap-film meter connected to the vent of the eight-port valve (figs. 6 and 7).

(2) Turn on the variable transformer controlling the voltage (about 45 volts) to the heating tape on the tubing, the eight-port valve, and the injection port. This will maintain the injection port at about 150°C and the eight-port valve and the tubing at about 100°C.

(3) Turn on the integrator and recorder.

(4) Apply about 75 volts with a variable transformer to one of the heating cups. Allow about 15 minutes for the temperature to reach 160-180°C.

(5) Turn the eight-port valve to trap A stripping position (fig. 6). Place the hot heating cup on trap A for 15 minutes.

(6) Repeat the procedure for trap B.

B. Sample analysis:

(1) Turn the eight-port valve to the trap A stripping position (fig. 6).

(2) Remove the heating cup from trap A and plug into the variable transformer for reheating. Allow trap A to cool for 5 minutes.

(3) Using a 10-µL syringe, inject a 5-µL aliquot of the sample through the septum of the injection port.

(4) Set the timer for 15 minutes and allow the sample to strip.

(5) At the end of 15 minutes, turn the eight-port valve to the trap A desorb position (fig. 7) and place the heating cup on trap A.

(6) Start the integrator and strip chart recorder. Set the instrument parameters according to the expected peak areas.

(7) Remove the heating cup from trap B and plug into the variable transformer for reheating. Allow trap B to cool for 5 minutes, then repeat steps (3) to (6).

(8) Simultaneously with step (7), check the recorder to see if the chromatogram for the sample from trap A is completed. When complete, turn off the chart recorder and stop the integrator. Record the peak areas of the sample components.

For continuous operation, when trap A is at steps (5) and (6), trap B is at steps (3) and (4), and conversely.

C. Calibration factors:

(1) Prepare standard solutions with concentrations ranging from zero to 160 mg/L at 20-mg/L intervals.

(2) Analyze the standard solutions according to the procedure discussed previously.

(3) Determine a blank for the water used in the preparation of the standards and correct the standard sample peak areas for the blank peak area. Experience has shown that small amounts of organics remain in the water, even after boiling the high purity Milli-Q system water for 1 hour.

(4) Plot the corrected peak areas as a function of the concentration and determine the slope of a least-squares line forced through the origin from the equation

$$\text{Slope} = \frac{\sum_{i=1}^{n} (\text{Peak Area})_i \, (\text{Conc})_i}{\sum_{i=1}^{n} (\text{Conc})_i^2} \qquad (2)$$

where n is the number of standard solutions.

D. Calculation of sample concentrations:

The calibration factor determined in C is valid as long as the instrument operating conditions and sample analysis procedures are not changed. Experience has shown that small variations of about 2 to 3 percent may occur in the calibration from day-to-day because conditions cannot be easily controlled to any greater degree of precision. Analysis each day of the complete range of samples used in the determination of the calibration factor is impractical because of the time required. Therefore, it is suggested that a daily correction factor be determined by analyzing

only one standard solution and assuming the same relative proportion for all concentrations. Define the daily correction factor, F, as

$$F = \frac{\text{Peak Area from standard curve analysis of Sample C}}{\text{Peak Area from daily analysis of Sample C}} \qquad (3)$$

where the standard sample with concentration C chosen for this purpose has a concentration in about the middle of the range of the sample concentrations analyzed that day. The acetone concentration, C_A, in milligrams per liter, is calculated from

$$C_A = \left(\frac{\text{Peak Area of Sample}}{\text{Slope}}\right) (F) \qquad (4)$$

Experience has shown that the daily correction factor varies randomly rather than systematically. This suggests that the variation is a result of small random fluctuations in operating conditions, rather than a permanent change in the system such as deterioration of the column. Therefore, the assumption that the daily calibration factor applies to all concentrations should be reasonable.

SUPPLEMENTARY PROCEDURE II

The steps necessary for measuring acetone by the microgram-per-liter concentration procedure are described in the following paragraphs. Refer to figures 6 and 7 for the location of the various valves and other components of the system.

A. Preliminary preparations:

(1) Bake the sodium sulfate at 600°C for at least 2 hours to remove any organics, then cool in a dessicator.

(2) Wash the flasks and stoppers (125 mL, $\overline{\$}$ 24/40) and bake in an oven for at least 2 hours at 200 to 250°C.

(3) After the flasks have cooled in a dessicator flushed with pure nitrogen, add 10 g of sodium sulfate to each flask and cap. Keep all the flasks in the dessicator and flush with pure nitrogen.

(4) Place a clean empty flask tightly in place on the condenser head (figs. 6 and 7).

(5) Condition both of the Tenax-GC traps following the procedures described previously. This should be done at the beginning of each day.

B. Sample analysis:

(1) Turn the eight-port valve to the trap A stripping position (fig. 6).

(2) Remove the heating cup from trap A and plug into the variable transformer for reheating in preparation for step 10. Allow trap A to cool for 5 minutes.

(3) Place a magnetic stirrer bar (25 mm long, ceramic or teflon coated) in the flask with the 10 g of sodium sulfate.

(4) Measure 20.0 mL of the water sample with a graduated cylinder and pour with as little mixing as possible into the flask and cap the flask. If methyl ethyl ketone is to be used as an internal standard, a known amount should have been added to the sample at the time the sample was collected. Steps (3) and (4) should be completed as quickly as possible. A pipet could be used to transfer the sample aliquot to the sweeping flask. However, it is expected that errors resulting from volatilization losses during the filling and draining of the pipet would exceed the error involved in measuring the aliquot with a graduated cylinder.

(5) Stop the helium sweeping gas flow temporarily by shutting valve (a) (fig. 6). Check to see that the magnetic stirrer is in the off position.

(6) Replace the empty flask with the sample flask, insuring that the condenser head is tightly attached to the flask.

(7) Place the flask in the water bath at 50°C and clamp it in position to the stand (fig. 5). Allow 5 minutes for equilibrium to be established.

(8) Start the helium sweeping gas flow [fig. 6, valve (a)] and set the flow at 20 mL/min. Start the magnetic stirrer.

(9) Set the timer for 15 minutes and sweep and trap the headspace vapors for this time period.

(10) Turn the eight-port valve to the trap A desorb position (fig. 7), place the heating cup on trap A, and desorb the organics into the chromatograph.

(11) Start the chart recorder and the integrator. Set the instrument parameters according to the expected peak areas.

(12) Remove the flask containing the stripped sample and replace with a dry, empty flask, and connect the condenser head. During the next 10 minutes, continue the sweeping and stripping process through trap B to remove any residual organics that might still be in the system. Trap B is continuously heated.

(13) Return to step (1) and begin the analysis of the next sample.

(14) Simultaneously with step (13), check the recorder to see if the chromatogram for the last sample is completed. When complete, turn off the chart recorder and stop the integrator. Record the peak areas of the sample components.

C. Calibration factors:

Calibration factors were determined for both procedures used in the measurement of microgram-per-liter concentrations. The first procedure consisted of carefully controlling experimental conditions so that the samples and standards were analyzed in precisely the same way, and the second procedure consisted of the use of methyl ethyl ketone as an internal standard. Steps are as follows:

(1) Prepare standard solutions with concentrations ranging from zero to 100 µg/L at 20-µg/L intervals. If methyl ethyl ketone is to be used as an internal standard, it should be added to the standards.

(2) Analyze the standard solutions according to the procedure discussed previously.

(3) Determine a blank for the water used in the preparation of standards and correct the standard sample peak areas for the blank peak area.

(4) For the first procedure, plot the corrected peak areas as a function of the concentration. For the second procedure, plot the peak area ratio of the acetone and the internal standard as a function of the concentration ratio of the acetone and the internal standard. Determine the slopes of the least-squares lines using equation 2 presented previously.

D. Calculation of sample concentrations:

The calculation of the sample concentrations for the first procedure is as described previously. It is suggested that a daily correction factor as defined by equation 3 be determined and the sample concentrations be calculated from equation 4. For the second procedure, the acetone concentration, C_A, in micrograms per liter, is calculated from

$$C_A = \frac{\left(\frac{\text{Peak Area: Acetone}}{\text{Peak Area: MEK}}\right)_{\text{Sample}}}{\text{Slope}} (F) (C_{MEK}) \qquad (5)$$

where $(\text{Peak Area: Acetone/Peak Area: MEK})_{\text{Sample}}$ is the ratio of the peak areas for acetone and methyl ethyl ketone in the sample, slope is the least-squares slope of the peak area ratio versus concentration ratio data for the standard sample, and C_{MEK} is the concentration of methyl ethyl ketone, in micrograms per liter, added to the sample as an internal standard.