DEVELOPMENT OF METHODS FOR TRACE ANALYSIS OF DRINKING WATER

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ABSTRACT

This paper describes a study designed to develop an analytical protocal for the analysis of contaminants in drinking water believed to have originated in substandard galvanized pipe. These contaminants were both organic and inorganic in nature. The low levels of organic contamination necessitated the evaluation of four methods of preconcentration:

1) inert gas phase stripping onto a precolumn for subsequent direct heat desorption (Purge and Trap);
2) closed loop inert gas phase stripping ("Grob Stripping");
3) concentration on XAD resins; and
4) liquid-liquid extraction with hexane.

Each of these preconcentration techniques was used in conjunction with glass capillary gas chromatography except the Purge and Trap, which utilized packed column chromatography.

The "Grob Stripping" method was found most suitable and was used in the analysis of samples from five locations plumbed with suspected galvanized pipe. Two samples were obtained at each site, one at the water meter (i.e., before the galvanized piping) and the other inside the structure.

The organic contamination in samples originating after the galvanized pipe consisted of a wide variety of compounds at levels ranging from 20 to 800 parts per trillion.

Heavy metal content was examined using X-ray fluorescence and Inductively Coupled Argon Plasma spectroscopies. Elevated levels of zinc and lead were found in samples obtained within the structure.

I. INTRODUCTION

The use of imported galvanized pipe began about seven years ago when domestically produced galvanized pipe became rather scarse and imported pipe became less expensive to use. With this came an increase in the number and severity of complaints about taste, odor, and the overall quality of the water being distributed by these pipes. A number of minor illnesses, such as nausea, diarrhea, and gastrointestinal problems, were believed linked to the water, but this could not be substantiated.

Work done by the EPA (Region X), the Oregon Department of Environmental Quality, and various independent laboratories indicated that both organic and inorganic contaminants were possibly contributing to poor drinking water quality in sites where these pipes were being used. Inorganic analyses revealed relatively high levels of zinc in water samples from such locations. These levels were sometimes in excess of the water quality criteria standards for drinking water of 5 ppm.[1] When some sections of pipe were removed from these sites and physically inspected, it was found that the galvanization was uneven and tended to chip off easily. This poor coating probably contributed to the elevated zinc levels.

Organic contamination in the water delivered by these pipes appeared to exhibit an "oily" character and existed at levels reportedly as high as several parts per million (ppm) in some sites. This led to the hypothesis that residual cutting oil, used during the pipe's installation, was responsible for the contamination. However, unlike most residual cutting oil, this contamination persisted over long periods of time. Although

no tie could be established, this led to speculation that some organic coating associated with the manufacture or shipping of the pipe might be responsible. A preliminary gas chromatographic-mass spectroscopic analysis of a water sample containing these organic contaminants was done by the EPA Health Effects Research Laboratory (HERL) in Cincinnati. The presence of a large number of organic compounds, some of which are known to be toxic and/or carcinogenic, was shown to exist in this sample (e.g., 3-methyl-2-butanone, 2,4-hexadienal, dimethylfuran).[2]

This study was intended to develop and apply an analytical protocol useful in routine analysis of water samples and applicable pipe sections to further establish the nature of the link between the poor water quality and the use of imported galvanized pipe. Due to the subclinical nature of the problem, this protocol was also intended to serve as an inexpensive method for screening the more severely effected sites. For the organic contaminants, this necessitated a method sensitive for a broad range of possible compounds and compound classes at varying concentration levels. Through a literature search it became apparent that a clearly superior preconcentration method, useful for the broad range of compounds of interest, was not available. For example, the Purge and Trap (PT) method was useful only for highly volatile, relatively low molecular weight compounds.[3-5] The Grob Stripping (GS) method provided analysis capabilities up to the medium molecular weight range, but had little sensitivity toward polar compounds.[6-9] Resin methods, on the other hand, were more sensitive to polar compounds and higher molecular weight compounds than either of the other methods.[10-13]

Since the organic contamination was said to impart a strong odor

to the water, it was thought that volatile low molecular weight compounds might be responsible for a major portion of the contamination. However, the "oily" character described by some suggested higher molecular weight compounds. This made it unclear which preconcentration method was best suited for this project. It was decided that the merits and faults of each method would have to be directly determined. One additional method was also tested for its applicability to this project, the Micro Pentane Extraction method.[7]

It was felt that glass capillary gas chromatography $(GC)^2$ would be best suited to this project because of its greater sensitivity and the ability to produce a high resolution gas chromatogram. This chromatogram might then provide a pattern or "fingerprint" of the organic contamination found in the water. Such a fingerprint could then be used for a direct comparison between water entering a galvanized pipe distribution system (sample taken at the meter) and the water distributed by that system (sample from a tap in the building).

For the analysis of inorganic components in the sample, X-ray fluorescence (XRF) analysis coupled with ion exchange resin preconcentration was considered. This technique was attractive since it was an inexpensive method for the simultaneous determination of a large number of potentially toxic elements. Inductively Coupled Argon Plasma (ICAP) analysis was also considered as an alternative method of analysis.

II. EXPERIMENTAL APPARATUS

A. Chemicals and Reagents

All organic solvents used were distilled in glass and obtained

from Burdick & Jackson (Muskegon, Michigan). Chemical standards were purchased through Chem Services (West Chester, Pennsylvania). The silver nitrate standard used in the XRF analysis was purchased from Alfa Division of Ventron Corp. (Danvers, Massachusetts). Unless otherwise stated, all inorganic reagents used were reagent grade.

An internal standard of 75 ng/μL of chlorohexane, chlorooctane and chlorodecane in acetone was used for organic analyses. The column evaluation standard consisted of the following compounds at the 2 ng/μL level in hexane: decane, n-octanol, undecane, 2,6-xylenol, 2,6-dimethylaniline, methyl decanoate, dicyclohexylamine, methyl hendecanoate and methyl dodecanoate. For PT analysis an appropriate dilution of chlorohexane to 10 ng/μL in methanol was used as the internal standard.

The column packing materials used for PT analysis were Tenax GC (60/80 mesh), Chromasorb 102 (60/80 mesh) and 0.2% Carbowax 1500 on Carbopac C (80/100 mesh).

The macrorenticular resin used in the resin elution method was Rohn & Hass XAD-2. The resin fines were removed by wet sieving to the 20-60 mesh size and then sequentially washed with methanol, acetonitrile, diethyl ether, and methylene chloride in a Soxhlet extractor. It was then stored under methanol until used.

B. Glassware

The glassware used in the PT and GS methods will be shown and described with the discussion of each apparatus. The Micro Extraction procedure required only a standard 1 liter volumetric flask, a separation tube (to enhance the phase difference for separation after extraction), and a small container in which to place the extract.[7] The separation

device was merely a tube sealed at one end approximately 15 cm long by 3 mm I.D.

A 10 cm x 0.5 cm resin bed was used in the Resin Elution Method (RE) of preconcentration. With a ground glass joint at the top of this column, a 2-liter sample container was attached. The column also had a standard Teflon stopcock to control the flow rate.

The eluant from the column was collected in a concentrating flask designed to minimize losses of solutes (see Figure 1). The Snyder distillation column used for the concentration step is also designed to minimize solute losses. A sample container calibrated to 0.5 ml was used to collect the final concentrate and assure equivalent sample size.

The grab samples for organic analyses were collected in amber 4-liter glass bottles. These bottles were first washed with laboratory detergent followed by warm sodium dichromate/H_2SO_4 cleaning solution. After thorough rinsing with tap water and then organic free water (zero water), the bottles were baked at 500°C and fitted with Teflon-lined screw caps. For PT analysis, 125 mL septum vials with Teflon-lined septa were used to collect samples. This enabled samples to be taken which had no head-space. These vials were also baked out at 500°C to ensure cleanliness.

Inorganic samples were taken in 1-liter Teflon bottles. These containers were cleaned by soaking for 4 hours first in 8 N nitric acid, then for 4 hours in 6 N hydrochloric acid. This was followed by extensive rinsing with deionized water.

C. Purge and Trap Apparatus[3-5]

The apparatus used is pictured in Figure 2. It consisted of an

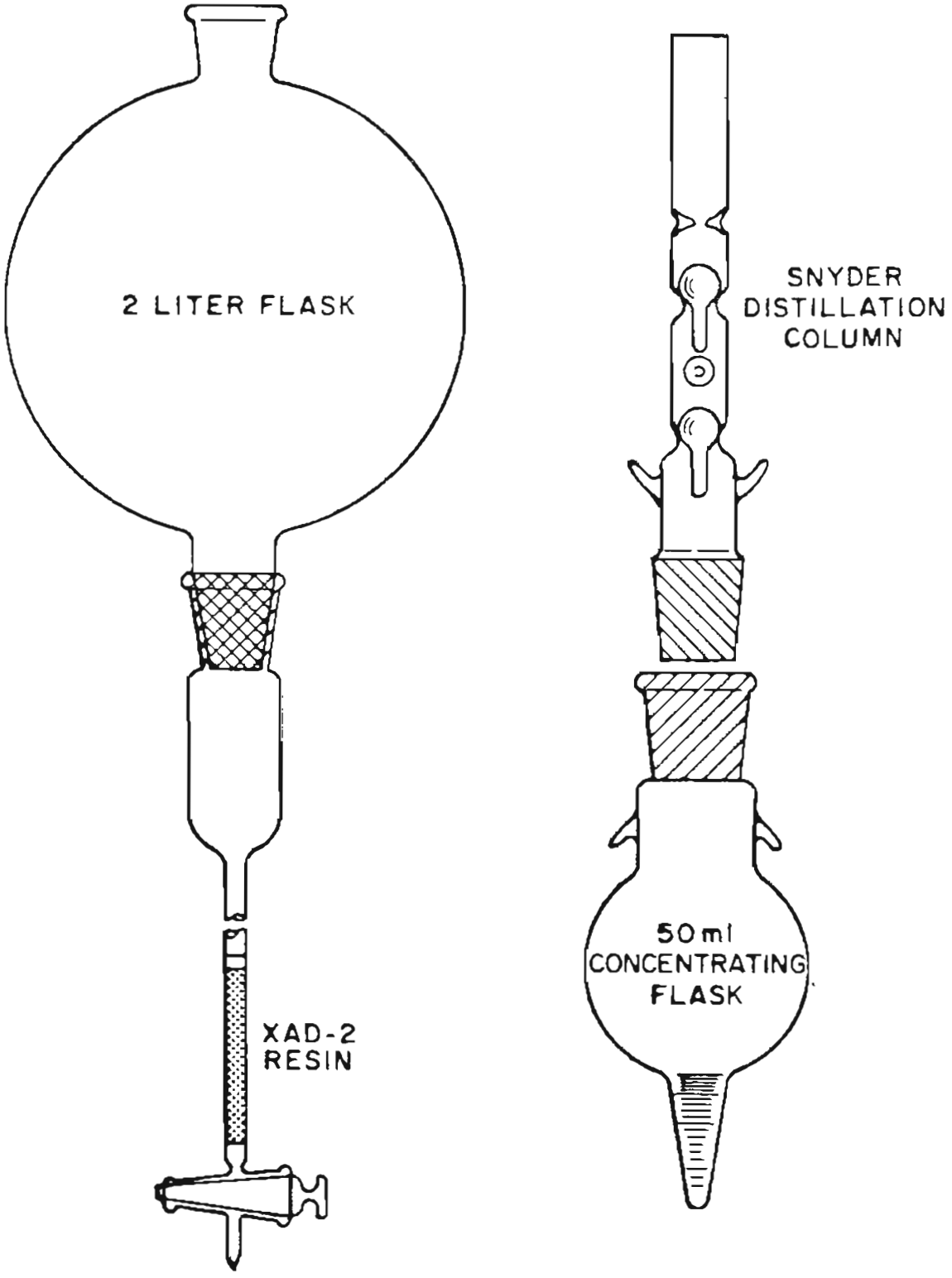
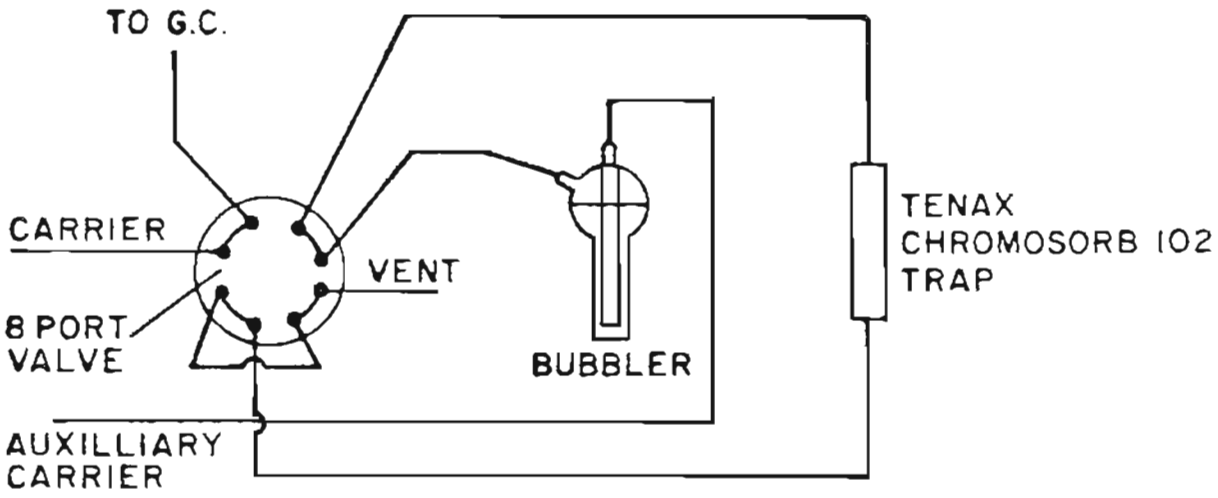
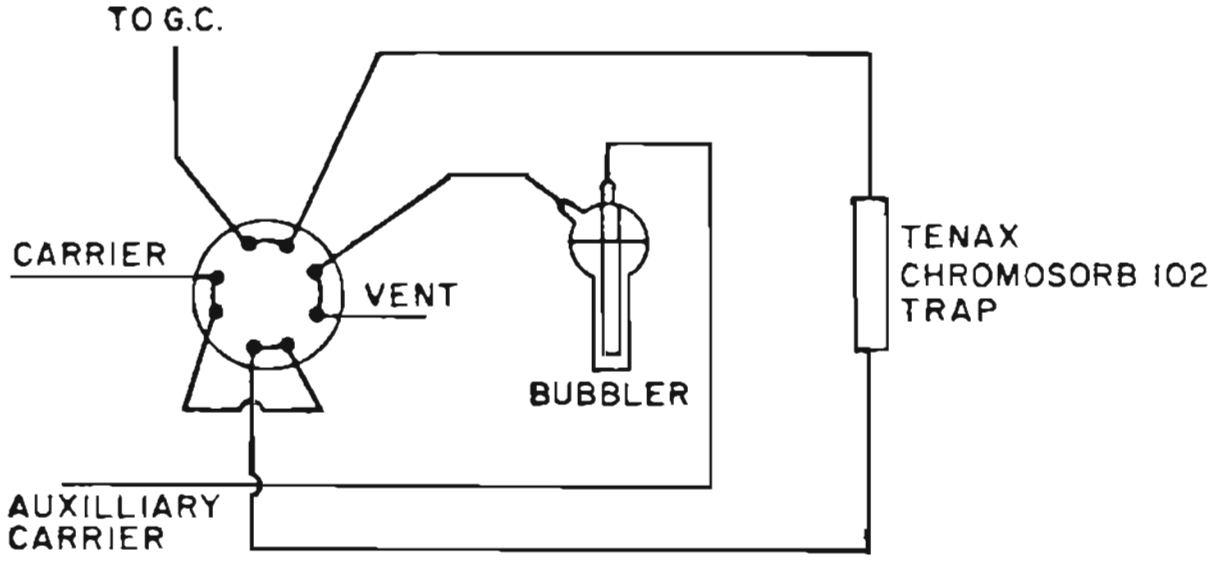


Figure 1. Resin Elution apparatus.



PURGE MODE



DESORPTION MODE

Figure 2. Purge and Trap apparatus.

8-port valve used to direct gas flows through the bubbler, Tenax/Chromasorb 102 trap, and onto the column. The bubbler was constructed of a glass sample container in which the auxiliary carrier gas was bubbled through a coarse glass frit near the bottom of the container to facilitate good mixing. The container was sealed by a size 2-026 rubber "O"-ring between the upper and lower portions. A 10-mL Luer-Lok glass syringe with a 10 cm needle was used to transfer samples from the septum vials to the bubbler.

The trap consisted of a 15 cm, 1/8", stainless steel tube filled with about 5 cm Chromosorb 102 and 10 cm of Tenax GC. These packings were arranged such that compounds emerging during the purge cycle were first adsorbed on the Tenax GC and then the Chromosorb 102 (see Figure 3). This tube was then wound with nichrome wire as a heating coil. Power was supplied to the heating coil by a variac which raised the temperature (determined by a thermocouple) to 180°C in 30 seconds. A control circuit was included to cut the power to the coil so that the additional heat conducted by the trap would not exceed 180°C.

The carrier gas lines were 1/16" stainless steel. All the lines from the Tenax/Chromosorb 102 trap through to the GC, including the 8-port valve, were maintained at a nominal 80°C to reduce condensation in them.

A Perkin-Elmer 900 gas chromatograph was dedicated to the PT apparatus for this work. An 8-foot, 2 mm I.D. glass column packed with 0.2% Carbowax 1500 on Carbopac C was used with Flame ionization detection at a carrier gas flow rate of 35 mL/min. The flow rate of the hydrogen and air to the detector were 35 mL/min and 300 mL/min respectively. The chromatograph was programmed for an initial temperature of 60°C to remain for 3 minutes, then to increase to 160°C @ 10°/min.

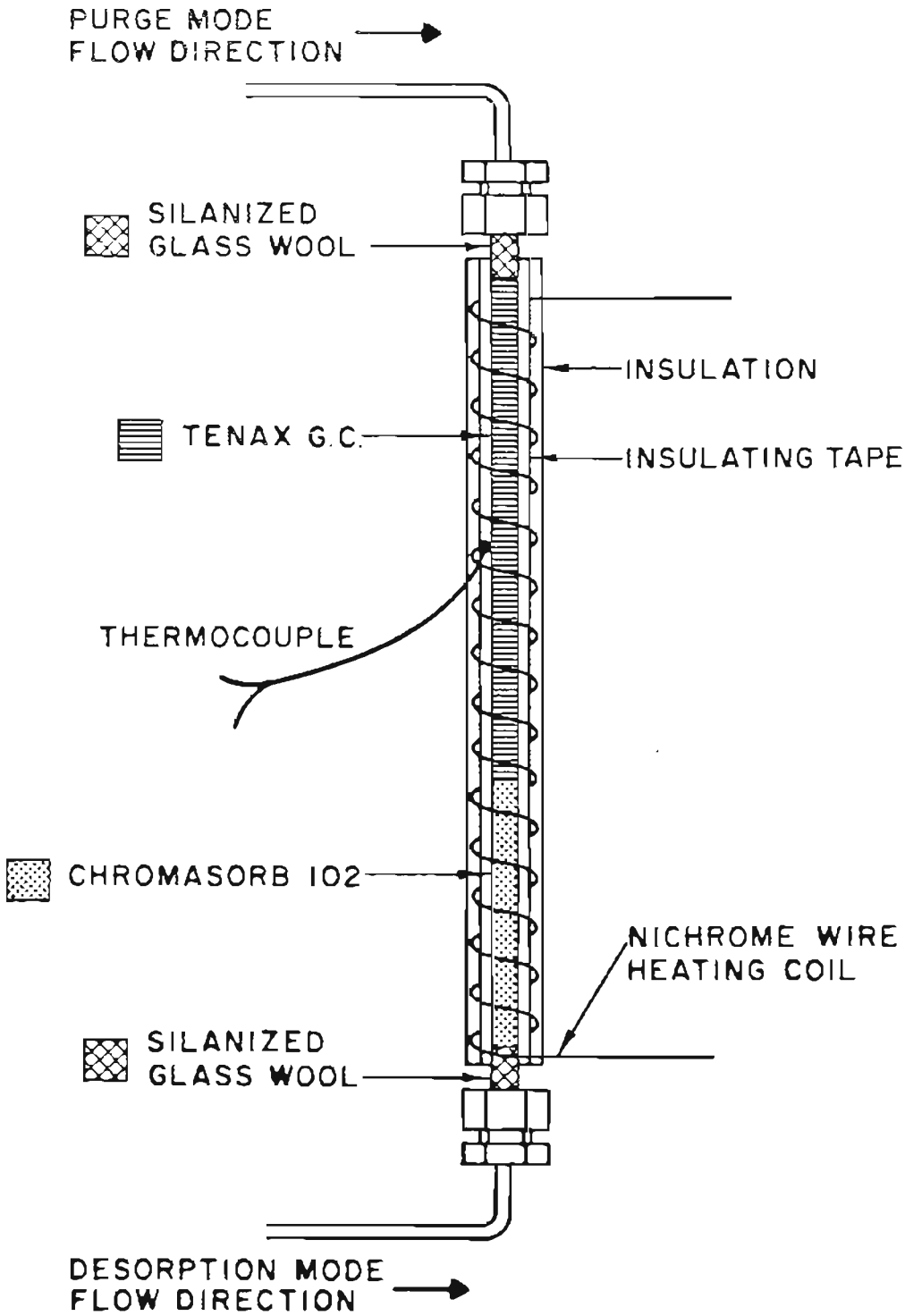


Figure 3. Tenax/Chromosorb 102 Trap

D. Grob Stripper[6-9]

The closed loop of the GS system was constructed with 1/8" stainless steel tubing and is shown in Figure 4. In this system a Metal Bellows pump (Metal Bellows Corp, Sharon, Massachusetts, Model MB-21) circulated precleaned nitrogen through a 1-liter Pyrex sample flask using a coarse frit as the bubbler. A heating block designed to prevent condensation in the Grob filter was constructed of aluminum and wound by the stainless steel tubing. A variac-controlled soldering iron fitted to the center was used to control the temperature. Clamped ground glass ball joints served to connect the sample flask to the remainder of the system.

The Grob filter holder was precision-ground so that almost all of the circulating gas passed through the filter rather than around it. The filter itself contained 1.5 mg of activated charcoal sealed between 2 disks in a 5 mm precision glass tube purchased from Bender & Hobein AG (Zurich, Switzerland). The filter extraction device pictured in Figure 5 was constructed and the collection tube was calibrated to contain 20 µL.

E. Gas Chromatograph

The solvent used in each preconcentration method was chromatographed on a Varian 1400 GC equipped with a flame ionization detector and a splitless "Grob-type"[14] injector, coupled to a Spectra-Physics 4100 chromatography data system. All analyses were carried out using a 20-meter SP2100 (Grade A) capillary column. The chromatograph was programmed for an initial temperature of 40°C, to increase at 4°/min., 1.00 min after initiation of injection, until the final temperature of 260°C was achieved. These standard operating conditions are outlined in Table 1.

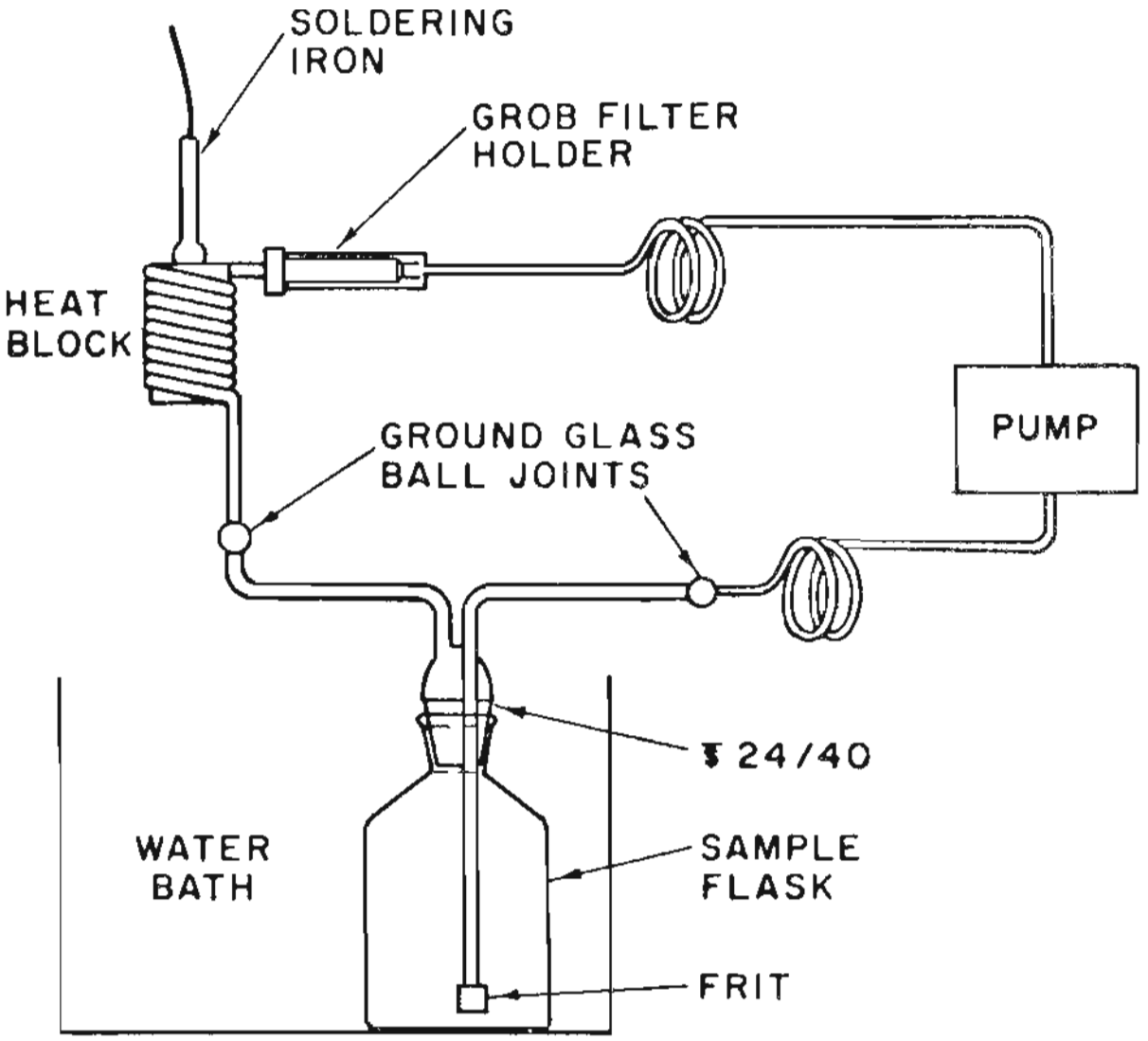


Figure 4. Grob Stripping apparatus.

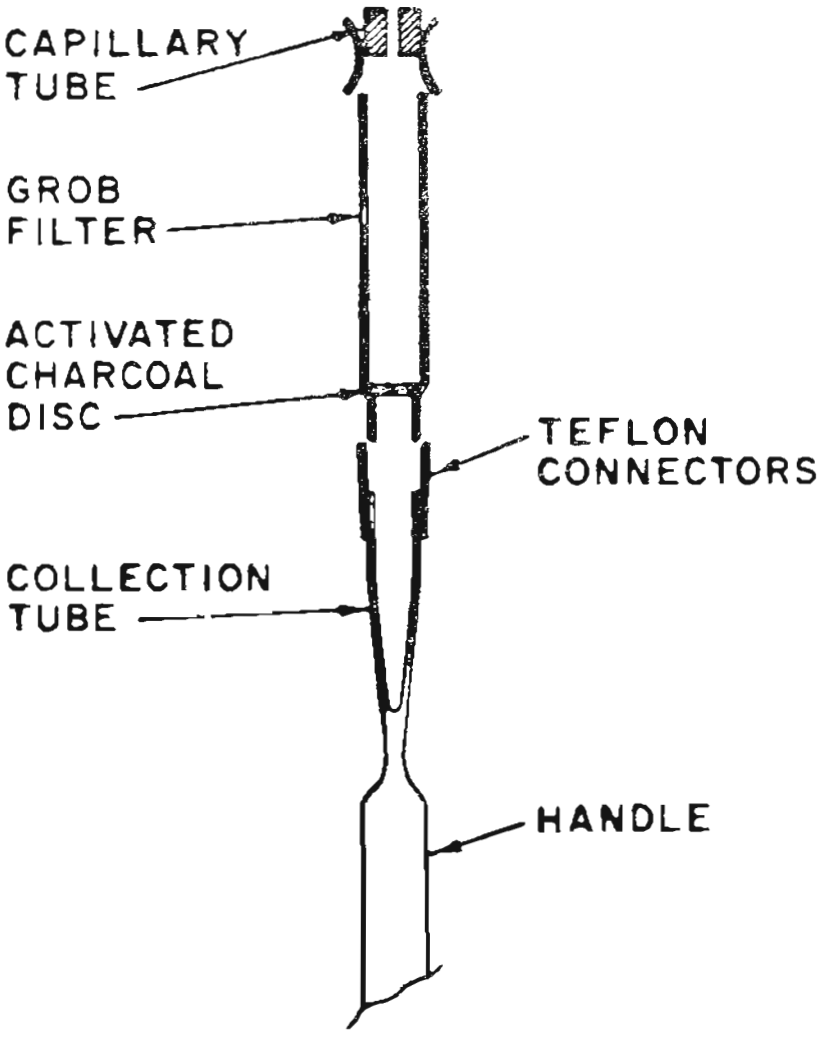


Figure 5. Grob filter extraction apparatus.

TABLE 1.

OPERATING CONDITIONS FOR GAS CHROMATOGRAPH

Carrier gas	He
Carrier gas linear flow rate	25 cm/sec
Septum purge rate	5 ml/min
Split flow rate	50 ml/min
Initial oven temperature	40°C
Final oven temperature	260°C
Injector temperature	250°C
Detection temperature	270°C
Oven program rate	4°C/min
Sample volume	2 µl
Column	Glass WCOT (methyl silicone)

F. Inorganic Analyses

Inductively Coupled Argon Plasma (ICAP) analysis of the samples was performed by the EPA Research Laboratory, Corvallis, Oregon, on an Instrumentation Laboratories (ICAP) instrument.[15] Samples were run directly or as 1:10 dilutions for elements which were too concentrated.

X-Ray Fluorescence (XRF) analysis was performed on an ORTEC TEFA Model 6110 X-ray fluorescence analyzer. A molybdenum anode with molybdenum filter was used under conditions of 50 kV excitation energy, 100 μ Amp excitation current, and a 1000 sec counting interval. 150 mL of the acidified water sample was evaporated to about 2 mL with a silver internal standard previously added to each. The remaining 2 mL were carefully transferred and evaporated on a 4 cm^2 sheet of Whatman 41 filter paper for analysis. Pipe scrapings were analyzed in a spectral cup.

III. EXPERIMENTAL TECHNIQUE

A. Sample Collection

1. Organic samples

At each site samples were taken before the water reached the suspect plumbing (at the meter) and after it had emerged from this plumbing (from an inside tap). In addition, a sample container filled with zero water was transported to and from each sample site as a method blank. Since there appeared to be a correlation between the length of time the water stood in the pipe and the degree of contamination, arrangements were made so that a standing time of at least 24 hours was achieved. The meter sampling apparatus was extensively flushed before sampling of the meter commenced.

Septum vials for PT samples were filled to the rim with sample. The Teflon-lined septum cap was slid onto the vial (Teflon facing sample) so that no head space was left in the vial. This cap was then sealed with a krimp cap.

All samples taken for organic analysis were analyzed within 48 hours of collection.

2. Inorganic samples

Samples were taken both at the meter and after the suspect plumbing for comparison. 1 mL of concentrated nitric acid (reagent grade) was added to each sample immediately after collection. The samples for inorganics were taken immediately following the samples for organics.

B. Purge and Trap Procedure

The septum of the sample vial was punctured with a clean needle to relieve the vacuum created as samples were withdrawn via a 10 mL syringe. This syringe was rinsed twice with about 3 mL of sample before the 10 mL needed for analysis was removed through the vial's septum. With the sample in the container of the bubbler, 30 mg of internal standard (chlorohexane) was added before the purging device was sealed into the system.

In the purge mode, precleaned helium carrier gas was bubbled through the sample, thereby sparging volatile organic compounds from the sample which were in turn caught on the Tenax/Chromosorb 102 trap (see Figure 2). This purging would continue for 15 minutes at a flow rate of 40 mL min.

The carrier gas flow was then reversed by rotation of the 8-port valve, and the trap was placed on line with the gas chromatograph. The

compounds collected were immediately heat desorbed from the trap into the GC by resistive heating of the nichrome wire coil surrounding the trap (Figure 3). Heat desorption took place at 180°C and the carrier gas (He) flow rate in the GC was optimized at 35 mL/min for these analyses.

C. Grob Stripping Procedure

1. Preparation of Grob apparatus

Two consecutive zero water samples were run on the Grob apparatus. The first cycle served to clean out any compounds remaining from the previous sample, and the second cycle served as a blank. The methylene chloride extract from the second cycle was chromatographed before the analysis of a field sample was initiated.

2. Extraction of water sample

A 1 liter volume of the sample was spiked with 5 µL of the internal standard and placed in the GS flask (see Figure 4). The Grob filter was cleaned with 3 mL of methylene chloride and the residual solvent evaporated in a clean nitrogen stream. After installation of the filter in the filter holder, the holder and connecting tubing were flushed with clean nitrogen. The sample flask was then attached to the outlet side of the pump and clean nitrogen was purged through the sample for 10 seconds to flush the air from the headspace of the sample flask. (This short purge no doubt caused a small loss of some of the more volatile compounds, but overall detrimental effects were probably minimal.) The other side of the flask was then connected to complete the circuit. With the nitrogen line still connected to the system, 5 psi pressure was applied. Zero water was applied to each joint to test for leakage. When the system was leak-tight,

the nitrogen line was removed and that port sealed. The GS was then run for two hours. The temperature of the water bath was maintained at 30°±2°C. The temperature of the heating block was maintain at 45°±2°C.

3. Extraction of the Grob Filter

When the stripping was complete, the filter was removed and attached to the collection tube via a Teflon connection (see Figure 5). A capillary cap was attached to the top of the filter. Using a 10 µL syringe inserted through the capillary cap, 5 µL of methylene chloride was applied to the filter. This first 5 µL portion was allowed to equilibrate with the filter for five minutes. The filter was then extracted with 3 additional 5 µL portions of methylene chloride. Each portion was passed back and forth through the charcoal three to five times by repeated heating and cooling of the volume enclosed under the charcoal filter. The extract portions were in turn brought down into the collection tube by first cooling with ice, then lightly shaking the liquid down, as is done with a fever thermometer. When 20 µL was reached, the filter was removed for immediate regeneration, and the collection tube was capped with a glass stopper. The extract was then analyzed by GC.

4. Cleaning of the GS between runs

The regeneration of the filter was accomplished by flushing it with 5 mL of methylene chloride. The residual solvent was removed under a nitrogen flow. The collection tube was cleaned by rinsing with methylene chloride several times, then heating with a heat gun. The sample bottle was prepared for another analysis by rinsing it with 50 mL of zero water five times. Any iron or other inorganic material which may have deposited in the frit was removed by soaking the frit in 1 N nitric acid

before rinsing with zero water.

D. Micro Extraction Procedure

The Micro Hexane Extraction (MHE) procedure used was a modification of Grob's micropentane extraction.[7] The samples were chilled to about 4°C before extraction to enhance the recovery of hexane. Vigorous shaking of about 0.9 L of sample with 400 µL of hexane in a 1 L volumetric flask for 2 minutes was used to remove organics from the water. The water level was raised into the neck of the volumetric flask by adding zero water. The application of a moderate vacuum resulted in the froth flotation of the hexane to the surface where it was then removed to a separation tube using a Pasteur pipet. Two more 50 µL extractions were made and added to the separation tube to increase recovery efficiencies (the separation tube facilitates the separation of the hexane and any residual water.) The extract was then chromatographed.

E. Resin Elution Procedure

1. Column preparation and sample adsorption

A resin bed 0.5 x 10 cm was made from the methanol slurry of XAD-2 resin prepared as described earlier. Before the first run, the resin bed was cleaned with 3-5 cycles of sequential elution with 30-40 mL of acetone, diethyl ether, methylene chloride and methanol. An additional 30 mL of methanol was used in the last cycle. Two 10 mL portions of zero water were then run through the bed to prepare it for the subsequent sample. A clean 2-L sample reservoir was attached to the top of the column and it was rinsed with two 20 mL portions of zero water. It should be noted that every effort was made to prevent the resin bed from standing "dry" during any portion of the resin elution procedure to prevent "cracking" of the

resin beds with accompanying release of contaminants.

Two liters of sample were then spiked with 25 µL of internal standard, this was poured into the sample reservoir, and the flow rate was set to 30-50 mL/min. As the sample moved through the resin bed, the organic compounds present in the water were removed by the resin. When the water level had dropped to just above the bed, the reservoir was rinsed with three 20 mL portions of zero water allowing each rinse to drain to the top of the bed. The final rinse was allowed to drain completely through the bed.

2. Solvent elution

In order to remove the organics from the resin bed, elution with acetone and methylene chloride was used. The acetone served to remove the residual water left in the column as well as to make the resin "wetable" for the methylene chloride, which was the primary solvent responsible for the elution of compounds from the column. The reservoir walls were first washed down with two 5 mL portions of acetone and collected in the resin bed. These portions were allowed to equilibrate for 5 minutes with the column capped off before they were eluted into the concentrating flask. Thereupon, three 10 mL portions of methylene chloride were eluted through the column and into the concentrating flask. The concentrating flask was then capped off and saved for concentration while the resin bed was immediately regenerated.

3. Regeneration of resin bed

The column was filled with about 15 mL of methanol, the upper layer of silanized glass wool removed and the column capped off. It was then repeatedly inverted to remove any air bubbles left in the bed volume.

With this accomplished, five more 10 mL portions of methanol were eluted through the column, saving the last portion in the bed. A new plug of glass wool was added to the top of the bed, and it was ready for another sample or storage.

In some cases the resin bed exhibited a yellow or brown color even after regeneration. In these cases the resin bed was cleaned by soaking in 1 N hydrochloric acid overnight to dissolve any inorganic solids present. If the discoloration persisted the resin bed was flushed and soaked with 1 N sodium hydroxide to remove the humic substituants. Following the acid/base treatment the resin bed was rinsed with zero water and then regenerated as usual.

4. Solvent concentration

After the excess water was removed with a Pasteur pipet, the eluant was concentrated to 0.5 mL using a Snyder distillation column (Figure 1). Acetone (2-3 mL) was added to the eluant before concentration to ensure that the remaining water was removed by azeotropic distillation with the acetone and methylene chloride. Gas chromatographic analysis of the concentrate followed immediately.

F. Inorganic Analysis

Analysis of inorganics present at the ppb-ppm level by X-ray fluorescence spectroscopy (XRF) requires preconcentration techniques which are cumbersome for routine work. Therefore, XRF analysis was not chosen for the routine analysis of water samples. Inductively Coupled Argon Plasma spectroscopy (ICAP) is better suited for simultaneous determination of many trace metals in water. Arrangements were made to have these analyses carried out by Mr. Jerry Wagner of the EPA research center in Corvallis, Oregon.[15]

A semi-quantitative XRF analysis, however, was used to supply a crosscheck of the ICAP results, as well as provide additional data regarding the levels of lead, an element for which ICAP is inadequately sensitive. Samples for XRF were prepared by evaporating 150 mL of acidified water samples to about 2 mL. The remaining 2 mL was carefully transferred and evaporated to dryness on a 4 cm^2 piece of Whatman 41 filter paper. Prior to evaporation silver nitrate was added as an internal standard. An additional check on the validity of the XRF data was provided by a comparison of the elements common to both XRF and ICAP techniques.

G. Pipe Analyses

The interior walls of suspect pipe samples obtained from a condominium where taste and odor problems had been experienced were also analyzed. Separate sections of pipe were extracted with both an organic solvent and zero water. The solvent extraction was accomplished by flushing a one-foot section of pipe with 25 mL of methylene chloride. This volume was then reduced to 5 mL under a nitrogen stream. Gas chromatography of this concentrate followed immediately.

In order to simulate the conditions present in a distribution system, a 30-inch section of pipe was filled two-thirds full with 100 mL of zero water and shaken overnight. A 25 mL aliquot of this water was then diluted to 1 L and run on the GS for comparison with water samples from the field sites.

IV. COMPARISON OF ORGANIC ANALYSIS METHODS

A. Synthetic Samples

To test the applicability of each of the preconcentration schemes

for trace organic analysis, synthetic samples were made and used in recovery studies. Minimum detectable concentration levels (MDL) were also determined. These synthetic samples were made by spiking a mixture of standard compounds, dissolved in acetone or methanol (methanol only used for PT samples), into a prescribed volume of zero water. Recoveries were determined by comparison of a direct GC analysis of the standard mixture to what was retrieved by each analysis method from the synthetic water samples.

PT analysis did not lend itself to standard recovery studies. It was found that even for the smallest direct injection, the solvent peak was so large and generated such a large tail that all compounds of interest were swamped out by this peak. In an effort to obtain an idea of how much of each compound was coming through to the detector, a simple test of the purging efficiency was undertaken. To determine this efficiency, a synthetic water sample was purged and analyzed twice without opening the purging device between analyses. The compounds emerging in the second analysis were incompletely purged in the first cycle. An upper limit of the purgeability of these compounds could be determined by assuming that 100% of the compound was sparged from the water in 2 purge cycles. Then the purging efficiency for each compound would be the amount removed by the first cycle divided by the total removed in both cycles. This admittedly gives a very rough estimate of the purging efficiencies, but showed the applicability of this procedure.

Table 2 shows these upper limit purging efficiencies. The important point illustrated here is that highly volatile non-polar compounds are purged well from water samples. The more polar compounds are not

TABLE 2

PURGING EFFICIENCIES FOR PURGE & TRAP ANALYSIS*

	% Removed by One Purge Cycle
Chloroform	100
1,1,1 Trichloroethane	100
1,2 Dichloropropane	100
Benzene	100
Tetrachloroethylene	100
Toluene	100
Carbon tetrachloride	98
1,1,2 Trichloroethane	84
1,2 Dichloroethane	81
Bromoform	75
1,1,2,2 Tetrachloroethane	68
Methanol impurity #1	62
Methanol impurity #3	59
Methanol impurity #2	54

*Based on the assumption that two purge cycles removed 100% of each compound (i.e., upper limit estimate).

purged very well from the water. It should be noted here that the compounds labeled methanol impurities were indeed traced back to originating in the methanol solvent. It was felt that these compounds, being impurities of the polar methanol, were also polar compounds, and therefore help demonstrate the applicability of the PT analysis to non-polar compounds as opposed to polar compounds.

The MDL of the PT method was found to be comparable to other methods for trace organic analysis (Table 4). These values are, however, limited to the compounds for which the analysis is applicable (i.e., non-polar, volatile compounds). The primary advantages of the PT methodology for this study were its small sample size requirement and the ease and speed with which it could be used. The technique's specificity toward very volatile compounds was both an advantage and a disadvantage. It enabled analysis of very low molecular weight compounds which could not be determined by the other methods investigated, however, it also limited the technique's useful range.

Table 3 shows the recoveries obtained on some selected polar and non-polar compounds for the RE, MHE and GS methods of analysis. The RE method appears to work fairly well for a broad range of compounds, expecially the more polar compounds. It did suffer, however, from relatively high blank levels. This contamination obscures much of the first quarter of the gas chromatogram. Such blank problems could possibly be alleviated by connecting the resin bed directly to a faucet and allowing a large volume of water to flow through the resin. Presumably this method of <u>in situ</u> collection would raise the level of the absorbed contaminants well above the blank level. A second problem experienced with the RE method was that it

proved to be very difficult to clean the columns of materials which discolored the resin bed when field samples were studied.

The MHE method works relatively well for non-polar compounds, but is very poor for polar compounds. Its major advantages are that it is inexpensive and resuires a minimum of analysis time (∿15 min).

The main advantage of the GS method is that it is one to two orders of magnitude more sensitive for compounds of low to medium molecular weight than the other two methods (see Table 4). This sensitivity made the GS method very attractive as the primary procedure to be employed during this study. A disadvantage of the method is its limited applicability to higher molecular weight compounds (i.e., > C_{22}) and polar compounds.

The Grob Stripper, however, does suffer from several problems which tend to make the routine use of this procedure quite tedious. The primary difficulty is that the system is very sensitive to air leakage. Such leakage might occur at either: a) the ground glass ball connectors; or b) the pump itself (due to vibration). Secondly, the GS apparatus displayed serious memory effects. (This has not been noted by previous investigators.) This necessitated that two extra cycles be run between samples, one to clean the system and a second to ensure that the system was, in fact, clean. The advantages and disadvantages of these preconcentration methods are summarized in Table 5.

B. Field Samples

Each of these methods was used to preconcentrate the organics in some preliminary field samples to determine which methods were most applicable to this project. The $(GC)^2$ analysis of these preconcentrates indicated that the level of organic contamination was generally in the low ppt

TABLE 3

RECOVERY EFFICIENCIES FOR ORGANIC EXTRACTION METHODS (%)

	XAD-2 Resin (5 ppb level*)	Hexane Micro Extraction (5 ppb level*)	Grob Stripper (0.5 ppb level*) 2-hr run	16-hr run
1-Chlorohexane	**	40-60	60-90	84.6
Ethylbenzene	**	20-50	80-100	98.4
Cumene	**	20-50	90-100	105.1
Decane	50-80	40-60	65-75	81.3
1-Chlorooctane	30-50	45-60	50-70	87.1
Undecane	30-50	40-60	65-75	--
1-Chlorodecane	40-60	40-55	50-80	79.8
Hexadecane	10-30	20-50	35-55	86.3
Anthracene	60-85	20-50	0	0
Docosane	10-30	5-20	0	0
Chrysene	40-70	3-15	0	0
			3-hr run	
1-Octanol	50-80	0	0-5	--
o-Cresol	50-80	0	0-5	--
2,6 Dimethylphenol	60-80	0	0-10	--
Methyl decanoate	60-90	25-40	50-70	--
Dibutyl phthalate	60-90	15-20	0-5	--
Docosanol	65-100	0	--	--

* 1 liter sample volume
** Obscured by resin blank

TABLE 4

COMPARISON OF MINIMUM DETECTABLE CONCENTRATIONS
FOR SELECTED METHODS

Purge & Trap: (C_1-C_7)(10 ml sample)	0.1-2.0 ppb
Grob Stripper: (C_7-C_{18}, 2-hr run)(1-liter sample)	1-5 ppt
Micro Hexane Extraction: (C_7-C_{30})(1-liter sample)	0.1-1.0 ppb
Resin Elution (XAD-2): (2-liter sample)	0.1-1.0 ppb
(10-liter sample)	20-300 ppt

TABLE 5

METHODS USED FOR TRACE ORGANIC ANALYSIS

	ADVANTAGES	DISADVANTAGES
1. Purge & Trap	A - quick and easy B - small sample size C - best for low molecular weight compounds	A - discriminates against polar compounds B - limited to low molecular weight compounds
2. Resin Elution	A - low cost B - well suited to in situ sample collection C - better for collection of polar compounds	A - high blank levels B - tedious procedure C - difficult to clean between samples
3. Micro Hexane Extraction	A - quick and easy B - inexpensive	A - discriminates against polar compounds
4. Grob Stripper	A - very low detection limits B - low cost	A - tedious procedure B - sensitive to leakage C - discriminates against heavier compounds D - memory effects

(parts per trillion) range. This automatically excluded the use of all but the GS method for analysis of most samples because only the GS method had the sensitivity required to detect compounds at that level. It was therefore used exclusively for field samples throughout the remainder of the study.

V. RESULTS AND CONCLUSIONS

A total of 15 samples were collected, both before and after the galvanized plumbing lines suspected of contaminating the drinking water at six different sites (see Table 6). The organic and selected inorganic constituents in these samples were analyzed according to the procedures outlined in the experimental section.

A. Organic Analyses

Of the four methods used (PT, RE, MHE, and GS), only the GS procedure was capable of detecting any organic contamination in these samples. Several major and many minor peaks were visible in the $(GC)^2$ chromatograms of the samples collected from the galvanized piping. If it is assumed that the compounds responsible for these major peaks have the same recovery efficiency and relative response as the internal standard (chlorodecane), then the major contaminants are present at the low ppt level (see Table 6).

Figures 6-10 are $(GC)^2$ chromatograms obtained using the GS method to analyze water samples collected at sites where taste and odor problems are currently being reported. Samples taken at sites where such problems existed at one time but are no longer being experienced indicated only minor contamination in excess of that present in the meter water sample.

TABLE 6. SAMPLING LOCATIONS

Site	Type of Water Sample	Number of Samples Taken	Detection of Odor*	Approximate Level of Most Concentrated Component (ppt)
#1 House in Scholls, Oregon	Meter	1	-	---
	Inside Faucet	1	+	---
	Outside Faucet	2	+	150
#2 First Apartment from Complex in Portland, Oregon	Meter	1	-	---
	Cold Tap	1	-	---
	Hot Tap	2	+	200
#3 Second Apartment from Complex in Portland, Oregon	Meter	1	-	---
	Hot Tap	1	++	750
#4 House in Gresham, Oregon	Meter	1	-	---
	Bathtub Tap	1	++	350
#5 House in Scappoose, Oregon	Well Head	1	-	---
	Hot Tap	1	-	---
#6 School in Gladstone, Oregon	Meter	1	-	---
	Shower-room Tap	1	+	20

* ++ Strong Odor. + Slight Odor. - No Odor.

The comparison of Figures 6 and 7 as well as Figures 8 and 9 indicates that the galvanized plumbing is contaminating the drinking water delivered at sites 2 and 6 with compounds which elute relatively early as well as with a more diffuse contamination characterized by the large number of unresolved peaks which elute as a large hump during the later stages of the chromatogram. The sample taken from inside the structure at site 2 had a greater odor than did the inside sample obtained at site 6. It should be noted that the greater contamination evidenced at site 2 by GS seems to be correlated with its stronger odor. This tendency was noticed in most of the samples and is illustrated in Table 6.

When the methylene chloride extract of the one-foot section of contaminated pipe was analyzed, it yielded an extremely complex chromatogram with a broad "hydrocarbon envelope" which seemed to range from about C_{11} ($\sim$MW = 140) to about C_{22}(MW = 310). A field desorption mass spectrum of the extract indicated, however, that many compounds of molecular weight up to $\sim$550 were present. An "envelope" of compounds was also found in the GS analysis of the aliquot of water extract from the 30-inch pipe section, but this envelope was not quite as broad as that found in the methylene chloride extract. This was probably due to the tendency of the GS method to discriminate against heavier compounds.

A comparison of the $(GC)^2$ from the GS analysis of field samples and that obtained from the water extract of the pipe section revealed an important similarity. The width as well as the location of the apex were the same for the "envelope" of compounds in each chromatogram. This lends additional weight to the argument that the plumbing is the source of organic contamination contributed to the drinking water delivered in structures where it

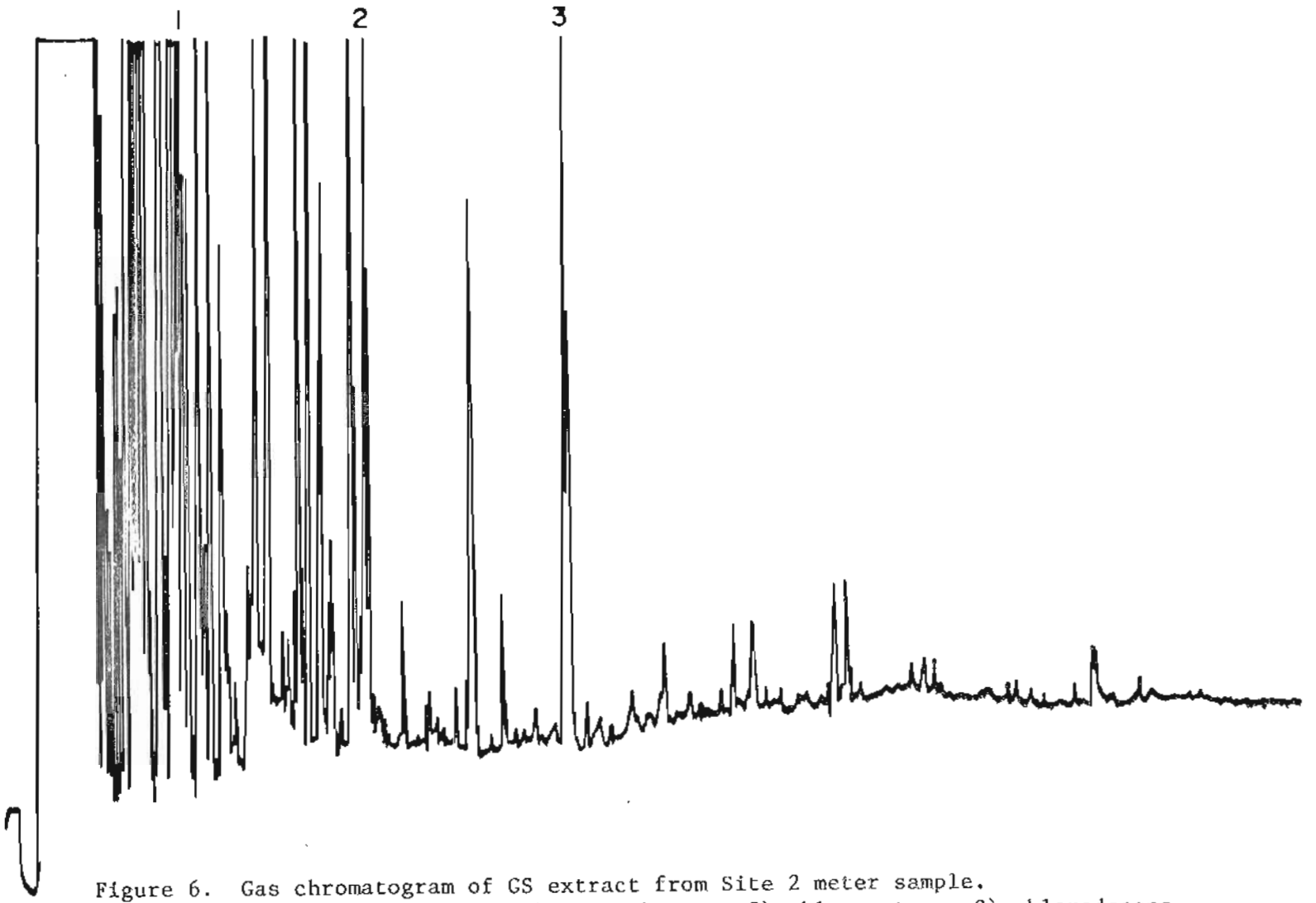


Figure 6. Gas chromatogram of GS extract from Site 2 meter sample.
Internal standards: 1) chlorohexane; 2) chlorooctane; 3) chlorodecane.
See Table 1 for gas chromatographic conditions.

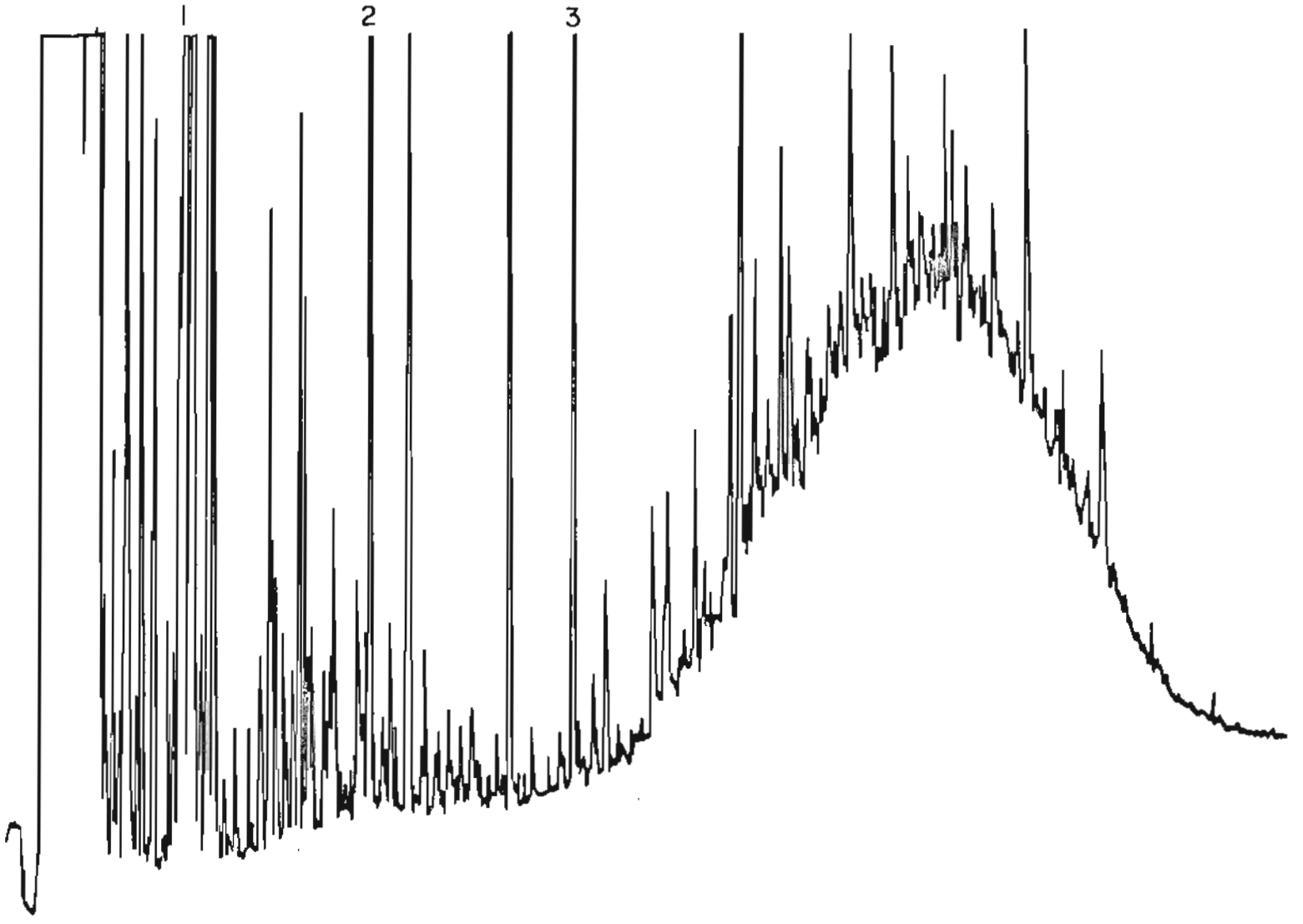


Figure 7. Gas chromatogram of GS extract from Site 2 house sample.
Internal standards: 1) chlorohexane; 2) chlorooctane; 3) chlorodecane.
See Table 1 for gas chromatographic conditions.

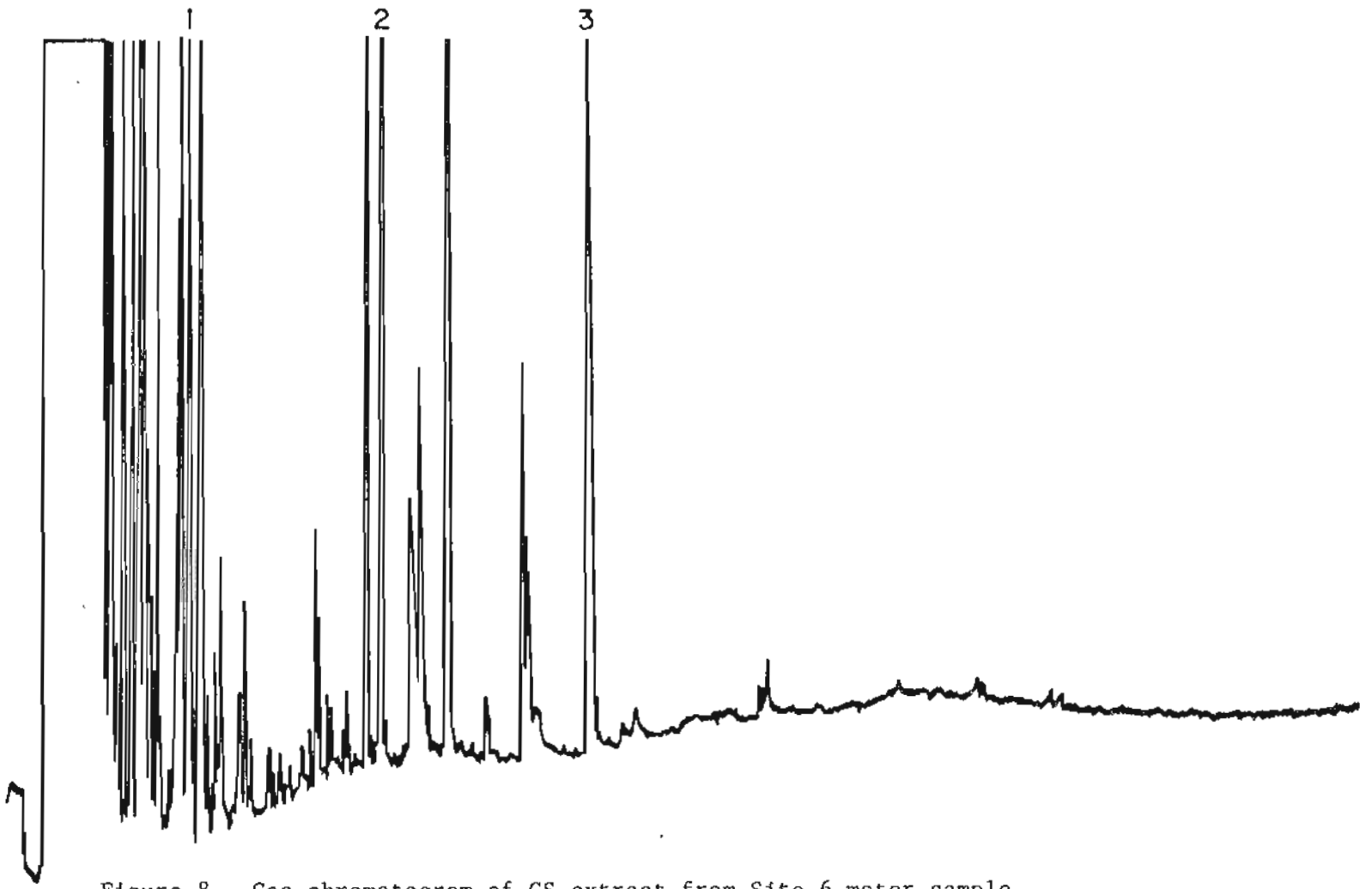


Figure 8. Gas chromatogram of GS extract from Site 6 meter sample.
Internal standards: 1) chlorohexane; 2) chlorooctane; 3) chlorodecane.
See Table 1 for gas chromatographic conditions.

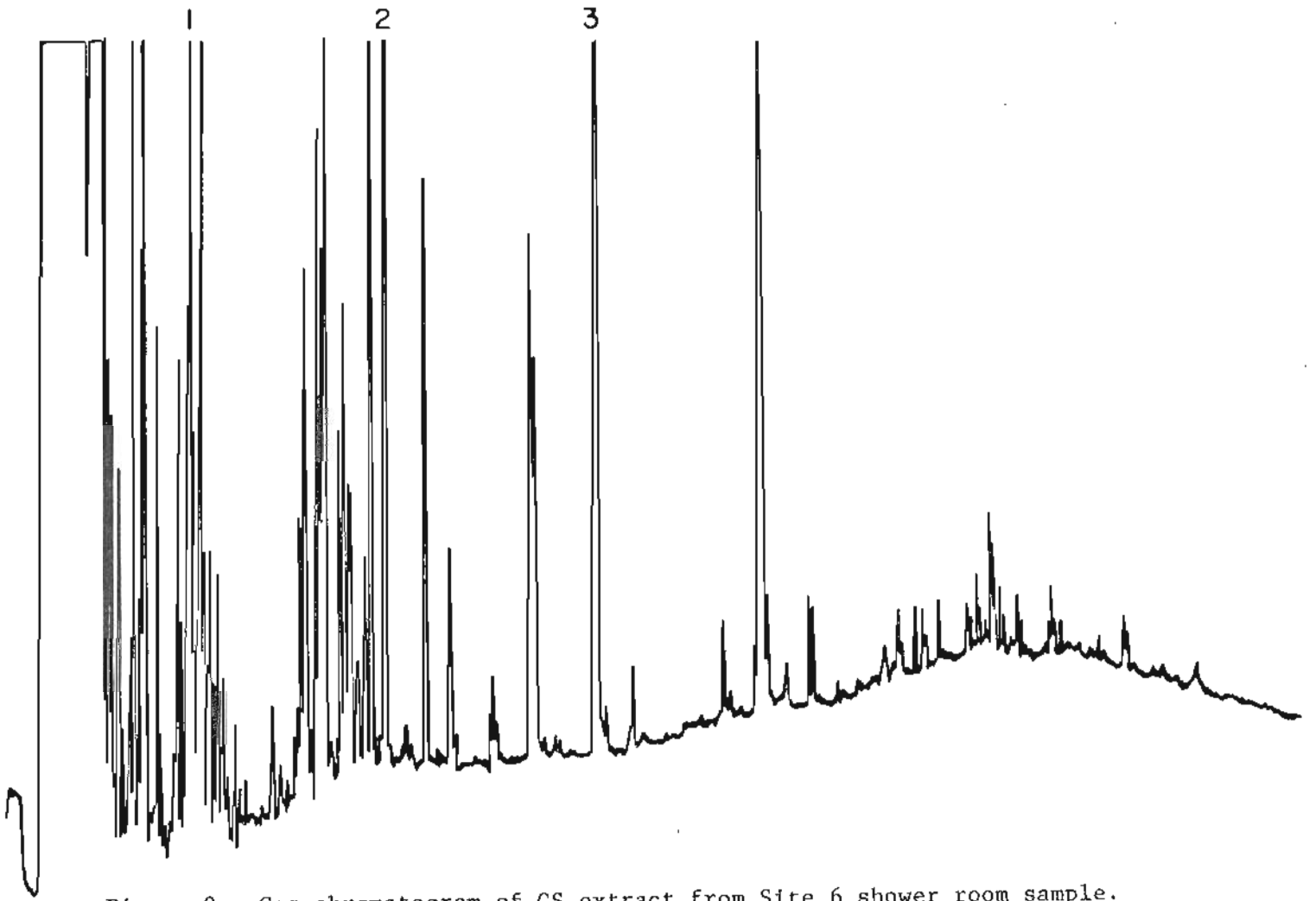


Figure 9. Gas chromatogram of GS extract from Site 6 shower room sample. Internal standards: 1) chlorohexane; 2) chlorooctane; 3) chlorodecane. See Table 1 for gas chromatographic conditions.

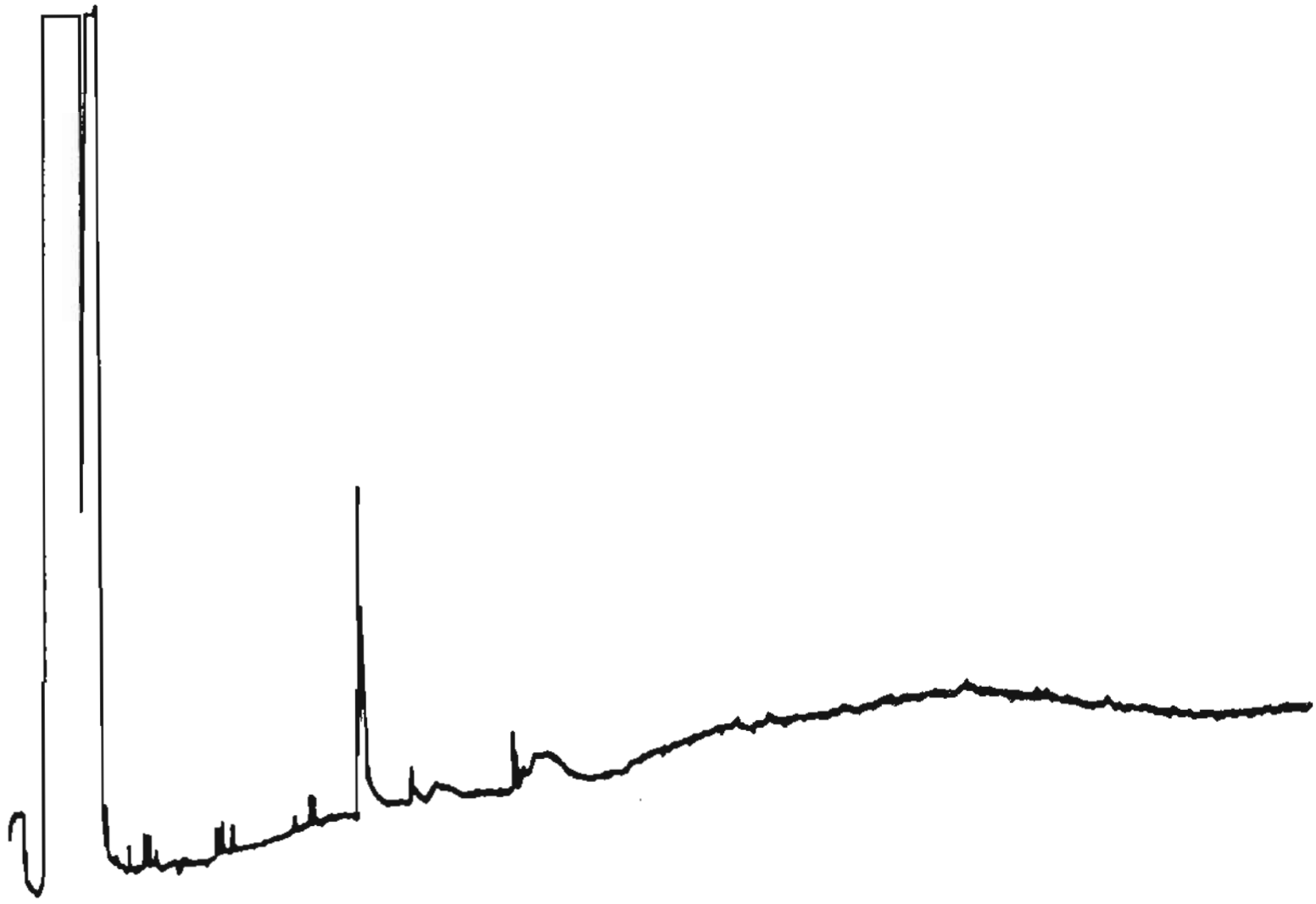


Figure 10. Gas chromatogram of system blank (GS extract).

is used.

With regard to the aliquot of water analyzed from the section of contaminated pipe, it should be noted that the level of contamination (even in its diluted form) was far in excess of anything seen from any field samples. This resulted in gross contamination of the Grob Stripper. The procedure required to clean the GS apparatus included: a) solvent washing of all tubing; b) removal, disassembly, and acid cleaning of the pump valve body; c) solvent cleaning of the pump and especially the metal bellows; and d) solvent cleaning of all glassware. To prevent such severe contamination of the Grob Stripper, it is suggested that a preliminary MHE be performed on any sample which is believed to contain high levels of organic contaminants.

B. Inorganic Analyses

The results of the ICAP and XRF analyses of the water samples are shown in Table 7.[15] The XRF results agree reasonably well with the ICAP data. The important feature indicated by these data is that water samples coming from the galvanized plumbing contain elevated zinc and lead levels. In general, the zinc values are below the minimum detectable limit for water samples taken at the meter, but after passing through the galvanized pipe, the zinc concentrations have risen to the low parts per million level, approaching the maximum drinking water standard of 5 ppm.[1] The lead levels behave similarly. In this case the highest concentration encountered was 30 ppb, which approaches the USEPA drinking water standard for lead of 50 ppb.[16] (XRF analyses of the galvanized coating scraped from the interior walls of two pipe samples revealed that this coating was approximately 1% lead.) Since these water samples were allowed to stagnate

TABLE 7. RESULTS OF INORGANIC ANALYSIS

	ICAP Results ±10% (in ppm)							XRF Results ± Factor of 2 (in ppm)					
	Zn	Cd	Pb	Mn	Fe	Cu	Sr	Zn	Pb	Mn	Fe	Cu	Sr
Site 2													
Meter	<	<	<	0.39	1.1	<	0.042	0.007	0.011	0.27	(1.10)	0.005	0.027
House	3.9	<	<	0.01	0.81	0.006	0.036	(3.90)	0.009	0.013	0.76	0.012	0.016
Site 4													
Meter	<	<	<	0.17	0.74	<	0.030	0.007	<	0.11	(0.74)	0.003	0.017
House	2.9	<	<	0.04	0.73	0.058	0.029	(2.90)	0.019	0.021	0.65	0.050	0.016
Site 5													
Well Head	0.04	<	<	0.01	0.26	0.113	0.047	(0.040)	0.009	0.009	0.24	0.083	0.028
House	3.6	<	<	0.02	0.14	0.149	0.055	(3.60)	0.031	0.010	0.22	0.107	0.028
Site 6													
Meter	0.06	<	<	0.08	0.11	0.012	0.222	(0.060)	0.005	0.057	0.15	0.015	0.105
Shower	6.7	0.01	<	0.13	0.56	0.020	0.224	(6.70)	0.016	0.071	0.49	0.035	0.088
Blank	<	<	<	<	<	<	<	0.017	<	<	0.019	<	<
QA Standard*	1.00	0.015 ±.005	<	<	<	<	<	(1.00)	0.065	<	0.006	<	<
Minimum Detectable Levels	0.005	0.005	0.04	0.005	0.005	0.005	0.005	0.003	0.005	0.005	0.005	0.003	0.005

*QA Standard consists of zero water spiked with 1.0 ppm Zn, 0.01 ppm Cd, 0.05 ppm Pb.
( ) indicates value of element which each set of data has been normalized to.

TABLE 7. (Cont.): RESULTS OF INORGANIC ANALYSIS

	ICAP Results ±10% (in ppm)												
	Mg	Ca	Co	Ni	As	Cr	Mo	Se	Zr	Sb	Al	B	V
Site 2													
Meter	1.1	6.9	<	<	0.12	<	<	<	<	<	0.38	<	<
House	2.0	5.6	<	<	0.16	<	<	<	<	<	<	0.012	<
Site 4													
Meter	1.1	4.1	<	<	<	<	<	<	<	<	0.19	<	<
House	1.2	3.6	<	<	<	<	<	<	<	<	<	0.007	<
Site 5													
Well Head	2.3	7.0	<	<	0.04	<	<	<	<	<	<	<	<
House	3.6	7.8	<	<	0.10	<	<	<	<	<	<	<	<
Site 6													
Meter	8.1	22.0	<	<	0.14	<	<	<	<	<	0.30	0.012	<
Shower	8.7	22.0	<	<	0.16	<	<	<	<	<	<	0.014	<
Blank	<	<	<	<	0.12	<	<	<	<	<	<	0.007	<
QA Standard*	<	<	<	<	0.12	<	<	<	<	<	<	0.010	<
Minimum Detectable Level	0.1	0.1	0.04	0.04	0.04	0.005	0.1	0.04	0.005	0.04	0.01	0.005	0.005

*QA Standard consists of zero water spiked with 1.0 ppm Zn, 0.01 ppm Cd, 0.05 ppm Pb.

in the galvanized pipes for several days before they were sampled, these heavy metal levels are probably upper limits of the exposure levels expected for occupants consuming such waters. During higher flow situations, the levels are likely to be lower.

VI. SUMMARY

An analytical protocol for the analysis of both water and pipe samples associated with poor water quality and the use of substandard galvanized pipe has been developed. The applicability of the protocol was evaluated by analyzing water samples from six different sites for both organic and inorganic contamination. For analysis of the organic contaminants, a Grob Stripper coupled with glass capillary column gas chromatography provides a fingerprint or profile useful for source comparison purposes. Detection limits for the system are at the low ppt level. Inorganic contaminants are best analyzed by ICAP with preconcentration to extend the detection limits for lead to the 10 ppb level.

Although application of the Grob Stripper reveals an adequate fingerprint, several modifications in the system are recommended to facilitate routine sample analysis. These changes are aimed at lowering the possibility of contamination and the elimination of memory effects, and include the following: use of improved connectors to insure against leaks, minimizing the amount of stainless steel tubing in the system, and the minimization of any dead volumes. The above modifications would help greatly in reducing the amount of time and thus the cost of analysis.

The application of the protocol to actual field samples confirms that the suspect galvanized piping is in fact contributing both inorganic

and organic contamination to drinking water. Inorganic contamination is associated with the breakdown of the galvanized coating. The nature of the organic contamination, while apparently pipe-related, is yet to be determined.

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VITA

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