DEPARTMENT OF THE ARMY
U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND
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REPLY TO
ATTENTION OF

August 25, 1998

Freedom of Information and Privacy Act Office

Mr. John Greenewald, Jr.

Dear Mr. Greenewald:

I am writing in response to your June 4, 1998, Freedom of Information Act (FOIA) request.

Enclosed you will find a copy of "The Determination of Trace Quantities of BZ (3-Quinuclidinyl Benzilate) In Air and Water".

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Attention: AMSCB-CIH, Building E5232
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Cheryl S. Fields
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Methods were developed for the analysis of BZ (3-quinuclidinyl benzilate) in the emissions and waste materials from demilitarization processes using gas chromatography.

BZ was quantitatively removed from aerosol filters using acidic aqueous solvents. Extraction of BZ from water samples and from the aerosol filter extracts involved the use of chlorinated solvents. Recoveries of BZ at different concentrations and in the presence of possible interferents are given.

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PREFACE

The work described in this report was authorized under project C23, Disposal of Incapacitating BZ/Agent Munitions and funded by US Army Toxic and Hazardous Materials Agency. The work was started in April 1978 and was completed in February 1980. The experimental data are recorded in Chemical Systems Laboratory notebooks 9787, 9811, and 9926.

The use of trade names in this report does not constitute an official indorsement or approval of the use of such commercial hardware or software. This report may not be cited for purposes of advertisement.

Acknowledgement

The authors acknowledge the assistance of Mr. Raymond E. Herd, Research Division, Chemical Systems Laboratory, for the preparation of BZ standard solutions.

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CONTENTS

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THE DETERMINATION OF TRACE QUANTITIES OF BZ (3-QUINUCLIDINYL BENZILATE) IN AIR AND WATER

1. INTRODUCTION

BZ (3-quinuclidinyl benzilate) was introduced into the United States chemical agent munitions inventory in the early 1960's. In late 1976, a program was initiated by the US Army Toxic and Hazardous Materials Agency for the demilitarization of the remaining stores of bulk agent, the M43 and M44 munitions, contaminated residues, and scrap.

The most promising disposal methods outlined in the Concept Plan[1], prepared for the demilitarization action, were incineration and chemical neutralization (hydrolysis or transesterification). Since the ultimate disposal method was not specified, a sensitive and specific analytical method was needed that could analyze for BZ in the emissions and waste materials produced by either disposal method.

Based on earlier work on the analysis of BZ, the most promising methods appeared to be gas chromatography (GC) or spectroscopy. GC had been investigated by both Sass[2] and Ellin[3]. Sass demonstrated that GC could be used to separate and quantitate BZ in the presence of known process intermediates. Ellin was able to detect BZ in such complex media as blood and urine by a simple extraction and concentration technique. However, the levels analyzed in both studies were at least 1000 times greater than the levels required by current emission standards. Spectroscopic methods such as Tropaeolin 00[4] and iodine complexation[5] were shown to have sufficient sensitivity, but suffered from interference from the products of hydrolysis (e.g., 3-quinuclidinol).

To determine which of the available methods should be developed further, an evaluation was performed by Battelle Columbus Laboratories (BCL) under contract number DAAK40-73-C-0142[6]. This evaluation concluded that the best choices would be GC or gas chromatography/mass spectrometry (GC/MS). It was found that GC, equipped with a flame ionization, nitrogen/phosphorus, or electron capture detector had sufficient sensitivity for the analysis of BZ at the emission levels. At the time, it was anticipated that GC could be used for stack, waste stream, and wash-down samples after a simple extraction. It was also felt that a simple cleanup procedure would be required for more complex samples such as hydrolysis brines. It was postulated that GC/MS, being more specific, could be used to detect BZ even in complex brine samples after a simple extraction into an organic solvent.

From the BCL study, GC was chosen over the spectroscopic techniques as the method to be developed for most of the routine analyses needed in the BZ demilitarization program. The nitrogen-phosphorus detector (NPD) offered the most selectivity of the detectors evaluated by BCL for routine analyses. Detector selectivity was desirable in that it might eliminate the need for any complex cleanup methods. The GC/MS was to be used only for very complex samples that could not be analyzed by simpler GC detectors and as a referee method for more specific analysis of BZ in any questionable samples.

As part of the BCL evaluation, the question arose as to whether BZ would be lost from aerosol filters during sampling. In one test, less than 10 percent of 1 µg of a BZ spike applied to a filter was recovered after aerating with 500 liters of air. Losses of this magnitude would have seriously hampered the development of analytical methods for BZ particulates.

Initiated shortly after contract DAAK40-73-C-0142 was completed, a study at Chemical Systems Laboratory (CSL) first looked at aeration losses from filters. Based on the BCL methods evaluated, GC with an NPD was chosen as the analytical method for this work. The BZ levels and aeration times used in the CSL work[7] were based on the then existing chronic exposure monitoring requirements, 4 mg-min/m^3. Assuming an 8-hour workday, the permissible chronic exposure concentration would be 8.3×10^{-3} mg/m^3. If a real-time monitor (RTM) were assumed to operate at 10 l/min for 10 minutes, the amount of BZ on the filter at the maximum permissible concentration would be 0.8 µg.

No firm requirements were available at the time for a personnel monitor. It was assumed that a level of one-tenth the requirement for a RTM would approximate the level for this purpose. The levels used in the filter study were set at the maximum levels for the RTM and the personnel monitor. The aeration volumes were set at the assumed total volumes for the RTM and the personnel monitor.

In 1978, BCL was awarded a second contract (DAAK11-78-C-0096) for conducting the laboratory phase studies required for the design of the BZ munitions demilitarization facility. Part of this work involved the development and verification of analytical methods to support BZ agent incineration and neutralization tests. BCL was also tasked to prepare analytical methods manuals for eventual plant operation. Early in this work, incineration became the preferred agent destruction process. Analytical tasks were quickly shifted to support an operating plant utilizing incineration equipment. Key analytical methods involved determinations of BZ in furnace effluent gases, as an aerosol particulate in the workplace and in plant washdown/scrubber liquids.

Work was performed at CSL to supplement BCL's analytical methods development. CSL's efforts were directed toward developing an analysis for BZ in water.

Problems with the NPD during the filter study at CSL and later work at BCL during a detector evaluation[8] led to the determination that the NPD was too unstable and fragile for routine use. As a result, GC with a flame ionization detector (FID) was chosen for subsequent methods development. The FID was chosen because of its ruggedness, reliability, ease of operation, and wide linear dynamic range.

The BZ levels used in this part of the study were set at one-quarter the maximum permissible BZ concentration (1 ppb), the maximum concentration (4 ppb), and 10 times the maximum concentration (40 ppb)[7]

in water. At the time, it was believed that the aqueous analysis would be a minor part of the analytical program. As the BCL study progressed, however, it became apparent that the methods for air and water would merge into a singularity, namely, extraction from an aqueous matrix into an organic solvent with final quantification of the BZ by GC or by GC/MS.

The final results of the methods development for air samples using the NPD and for water samples using the FID are documented herein.

2. MATERIALS AND METHODS

2.1 Aerosol Studies.

2.1.1 Equipment:

- Gas chromatograph - Hewlett-Packard Model 5840A with a Hewlett-Packard Model 18847A/8A nitrogen-phosphorus thermionic flame ionization and a 4 ft x 1/8-inch ID glass column packed with 2 percent OV101 on 100/120 Chromsorb WHP®. (The 2 percent OV101 column was used because the NPD needed a low bleed column.)

- Reflux timer - Maximum setting 120 seconds (Eagle Signal Company, Davenport, Iowa).

- Solenoid - Valve number V52DB2052, 10 watts, 50 psi, 3/16-inch orifice (Skinner Electric Valves Division, New Britain, Connecticut).

- Filters - Gelman Type A/E glass fiber.

- Filter holders - Gelman product no. 1220 or the equivalent.

- Syringes - (10 µl, 25 µl, 50 µl, 100 µl) Hamilton Models 701N, 702LT, 705LT, and 710LT.

- Volumetric glassware to conform to NBS Class A specifications.

2.1.2 Gas Chromatographic Conditions:

- Temperatures - Oven - 230°C

  Detector and injection port - 260°C

- Helium - 30 ± 1 ml/min

- Air - 50 ml/min

- Hydrogen - 3 ml/min

2.1.3 Reagents:

- BZ - Obtained from Analytical Branch, Research Division. Analysis by a standard titrimetric method gave a purity of 99+ percent.

- 1,4-dioxane - Distilled-in-glass (Burdick and Jackson Laboratories, Muskegon, Michigan) or freshly purified and distilled ACS reagent grade.

- Methanol - ACS reagent grade.

- Isopropanol - ACS reagent grade.

- Sodium hydroxide - ACS reagent grade.

- Toluene - ACS reagent grade.

All other reagents were ACS or CP in quality.

2.1.4 Purification Procedures.

If distilled-in-glass, 1,4-dioxane is not available, ACS reagent grade 1,4-dioxane may be purified and distilled by the following procedures developed during the course of this study; this procedure will produce dioxane that is suitable as a chromatographic solvent.

Three liters of 1,4-dioxane were gently refluxed for 6 to 8 hours with 50g of sodium hydroxide pellets, stoppered, and allowed to cool overnight.

The next morning, the material was placed into a distillation apparatus having an 18-inch insulated Vigreaux column. The material was brought to boiling and allowed to reflux for 1 hour. Distillation was then started.

All material boiling below 100°C was discarded (approximately 400 ml). The fraction boiling between 100°C and 102°C was collected (approximately 2 liters). The remaining material in the still was discarded.

The collected fraction was placed into pint size, narrow neck, brown glass bottles which were tightly sealed, and frozen in a refrigerator until use.

2.2 Water Studies.

2.2.1 Equipment:

- Gas chromatograph - Hewlett-Packard Model 5840A with a Hewlett-Packard Model 18812B FID and a 4 ft x 1/8-inch ID glass column packed with 3 percent OV17 on 80/100 Chromsorb WHP®. (The 3 percent OV17 column gave better chromatographic separation than the 2 percent OV101 column. The higher bleed column was not a problem with the FID).

- Reflux timer - Maximum setting 120 seconds (Eagle Signal Company, Davenport, Iowa).

- Solenoid - Valve number V52DB2052, 10 watts, 50 psi, 3/16-inch orifice (Skinner Electric Valves Division, New Britain, Connecticut).

- pH Meter - Beckman Model 4500.

- Chlorine Test Kit - LaMotte Chemical Products Company, Model P-30 (Code 44370).

- Balance - Mettler Instrument Corp., Model B5.

- Volumetric glassware to conform to NBS Class A specifications.

- Eppendorf Microliter Pipette - Brinkman Instruments, Model 2235 080-3.

- Adjustable Pipette - Oxford Model 8900.

- Syringe - (10 µl) Hamilton Model 701N.

2.2.2 Gas Chromatographic Conditions:

- Temperatures - Oven - 260°C

  Detector and injection port - 300°C

- Helium - 40 ml/min.

- Air - 240 ml/min.

- Hydrogen - 30 ml/min.

2.2.3 Reagents:

- BZ - Obtained from Analytical Branch, Research Division. Analysis by a standard titrimetric method gave 99+ percent purity.

- Chloroform - ACS reagent grade, washed to remove ethanol and acids as described in section 2.2.4

- Sodium carbonate - ACS reagent grade.

- Sodium hydroxide - ACS reagent grade.

- Sulfuric acid - ACS reagent grade.

- 2-Butanone (methyl ethyl ketone) - ACS reagent grade.

- Toluene - ACS reagent grade.
- Cyclohexane - ACS reagent grade.
- Sodium sulfate - ACS reagent grade.
- Sodium metabisulfite ($Na_2S_2O_5$) - ACS reagent grade.
- Water (double distilled) - distilled H_2O was redistilled from a well-leached, all-glass distillation apparatus.
- 4,4-bis (dimethylamino) benzophenone [Michler's Ketone] - purified and recrystallized as described in 2.2.4.

All other reagents were ACS or CP in quality.

2.2.4 Purification Procedures.

Chloroform - The ethanol which is used as a preservative in chloroform could destroy the BZ by causing it to transesterify. Acids which form as chloroform ages can also react with the BZ. To remove the ethanol and acids, the chloroform was washed with a sodium carbonate solution, then with double-distilled water as follows:

> Approximately 1500 ml of chloroform was washed by vigorously stirring for at least 1 hour with 200 ml of 0.5 M aqueous sodium carbonate. The chloroform was then separated and vigorously stirred three times for 10 minutes each with double-distilled water. The fourth and final double-distilled water wash was performed by shaking for 5 minutes in a 2-liter separatory funnel. After the aqueous and chloroform layers separated, the chloroform was drawn off into a brown-glass bottle.

The Michler's Ketone was dissolved in acetone, treated with decolorizing charcoal, and gently boiled for 5 minutes. The solution was filtered while hot to remove the charcoal. The filtrate was heated to boiling and distilled water was added dropwise to the point just before crystallization occurred. The filtrate was then allowed to cool undisturbed. The resulting crystals were vacuum filtered. The recrystallization from acetone and water was repeated once again. The product was vacuum filtered and dried in a vacuum dessicator set at 40°C for 48 hours. The resulting product was pure white leaflets with a melting point of 172°C. Merck Index cites 172°C.[9]

3. INVESTIGATIONAL PROCEDURES

3.1 Aerosol Studies.

3.1.1 Preparation of BZ Standards.

BZ stock solution was prepared by dissolving BZ in toluene. The solution was sealed in serum vials with Teflon® lined septa and stored under refrigeration.

The BZ standards used for the analysis by GC were prepared by dilution of the stock solution with dioxane. Dioxane was chosen because BZ was soluble in it, and the dioxane gave a low background on the NPD. The standards were sealed in serum vials with Teflon® lined septa. The standards were prepared fresh daily for the low concentration, and every other day for the high concentration.

3.1.2 Internal Standard Interferences.

A problem was encountered with the internal standard chosen (1-(N-piperidyl) isopropyl benzilate). An impurity in the concentrated extracts had the same retention time as the internal standard on the column used. This made quantification of the BZ using the internal standard impossible. Time limitations precluded a search for another standard, so efforts were made at eliminating the interference.

The Gelman glass fiber type A/E filters were extracted with dioxane for 8 hours in a Soxhlet extractor. The dioxane was discarded and the filters were extracted for 8 hours with isopropanol. The filters were then dried for 16 hours in a heated vacuum desiccator. This extraction eliminated some of the contamination observed in the chromatogram and greatly improved the baseline stability but did not completely remove the impurity interferring with the internal standard.

Both the distilled-in-glass and freshly-purified and distilled dioxane were concentrated in the same manner as the filter extracts to determine if the impurity was in the dioxane. The results did not conclusively point to the dioxane as the source of contamination.

An effort was made to identify the interferring gas chromatographic peak. A concentrated filter extract sample containing this interference was submitted to BCL for gas chromatographic and mass spectrophotometric analysis under contract DAAK11-78-C-0096[10]. Computer identification of the separated interference pointed to a structure similar to trioctylphosphate. Compounds of this type are widely used as plasticizers in spinning fibers and are common pollutants.

The source of contamination was not determined.

3.1.3 Extraction of BZ from Filters.

The first part of the study determined the efficiency of the procedure used for extracting BZ from glass-fiber filters.

For this study, the filters were impregnated with BZ by administering BZ solutions dropwise with a syringe and air drying for 15 minutes. The filters were transferred to a centrifuge tube and then macerated with about 5 ml of dioxane. The suspension was centrifuged for 3 minutes. The supernatent liquid was decanted into a concentration tube. This extraction, maceration, and centrifugation procedure was repeated twice more. The dioxane extracts were combined and concentrated to about 0.5 ml by heating in a constant-temperature water bath set at 80°C while purging with nitrogen. The nitrogen flow was controlled by a reflux timer connected to a solenoid. This alternately started and stopped the nitrogen at 30-second intervals. The purpose of the interrupted flow was to set up a reflux to help wash down the walls of the concentration tube. When the concentrates reached a level between 0.2 ml and 0.5 ml, they were removed from the bath and diluted to a total volume of exactly 0.5 ml with dioxane. The concentrates were stirred on a Vortex mixer before analyzing by GC.

It was found that the syringe used for injecting samples into the GC had to be thoroughly rinsed with methanol between injections to remove the BZ. It was found that injections had to be made immediately after taking a sample to prevent adsorption of the BZ onto the walls of the syringe barrel. It was also found that BZ could be chromatographed without apparent breakdown at temperatures above its decomposition point if the BZ was injected directly onto the column packing and not onto the glass wool or the dead space above the glass wool.

The interference problem precluded quantification of BZ using an internal standard, so the amount of BZ in the concentrates was determined by direct comparison of concentrate peak heights and areas to standard peak heights and areas.

The extraction efficiency was calculated by dividing the amount of BZ recovered by the amount deposited on the filter.

3.1.4 Aeration Study.

The second part of the study compared the recovery of BZ from aerated filters to the recovery from unaerated filters. Two aeration volumes were studied. The low volume (100 liters) represented sampling at a low rate for a long period such as in the case of a personnel monitor. The high volume (1000 liters) represented sampling at a very high rate such as would be done in stack sampling or area monitoring. The low volume filters were aerated at 4.4 l/min for 25 minutes. The high volume filters were aerated at 13.5 l/min for 75 minutes.

For the aeration study, the filters were spiked with BZ and air dried for 15 minutes. The filters were then aerated by pulling room air through them with a vacuum pump. After aeration, the filters were extracted, and the extracts were concentrated and analyzed in the same manner as in the extraction study.

The recovery from the aerated filters was compared to the recovery for the unaerated filters to determine if any loss of BZ occurred during aeration.

3.1.5 Concentration Study.

BZ solutions were concentrated in the same manner as the filter extracts to determine if any BZ was lost during the concentration step. The two levels of BZ studied (0.1 µg and 1.4 µg) were the same as in the extraction and aeration studies.

The BZ solutions were prepared by adding 5 ml of dioxane and a known amount of BZ stock solution to a concentration tube. Additional dioxane was then added to bring the final volume to 12 ml. This was done to approximate the final volume of the filter extracts. The solutions were stirred on a Vortex mixer before they were concentrated. The recoveries were calculated by direct comparison of the concentrate peak heights.

3.2 Water Studies.

3.2.1 Preparation of BZ Standards.

- BZ (base) - BZ stock solutions were prepared by dissolving BZ in toluene. The solutions were sealed in serum vials using Teflon® lined septa and stored under refrigeration. The BZ standards used for the analysis by GC were prepared by dilution of the stock solution with methyl ethyl ketone. The standards were dissolved in methyl ethyl ketone because it was a readily available solvent in which both the BZ and the Michler's ketone were soluble and stable. The standards were sealed in serum vials using Teflon® lined septa.

- BZ·HCl - A stoichiometric amount of 0.1N HCl was added dropwise with swirling and gentle heating to dissolve the BZ (base). The solution was diluted to volume with double-distilled water, sealed in a serum vial, and stored under refrigeration. The BZ·HCl standards used for spiking the tap water were prepared by diluting the stock solution with double-distilled water.

3.2.2 Preparation of Michler's Ketone Standards.

The stock solutions were prepared by dissolving Michler's Ketone in methyl ethyl ketone and sealing in serum vials using Teflon® lined septa. The vials were made opaque by wrapping in aluminum foil. The stock solutions were stored under refrigeration.

The Michler's Ketone standards that were used for the analysis by GC were prepared by dilution of the stock solution with methyl ethyl ketone. The standards were sealed in serum vials using Teflon® lined septa.

3.2.3 Extraction of BZ from Tap Water.

The first extraction study for tap water determined the efficiency of the procedure for extracting BZ. One hundred grams of sodium sulfate were added to 1 liter of tap water in a 2-liter separatory funnel and dissolved by shaking for approximately 15 seconds. The sodium sulfate was used to increase the ionic strength of the water solution in an effort to "salt out" the BZ.

It was found that the amount of active chlorine (1.0 - 1.5 ppm) in the tap water, when made alkaline to pH 10-11, was sufficient to destroy BZ at the concentrations under study.

The active chlorine was removed by adjusting the pH of the sample to 3.0 using 10 ml of 1N H_2SO_4 and followed by the addition of 1 ml of 0.2 percent sodium metabisulfite. The removal required less than 30 seconds for complete reaction.

After the chlorine level was checked using the test kit, BZ was added to the tap water in concentrations ranging from 1 ppb to 40 ppb.

To extract the BZ, the tap water was made basic (pH 10.5) by adding 100 ml of a 0.5 M sodium carbonate/0.1 M sodium hydroxide solution. Fifty milliliters of chloroform were added, and the mixture was shaken for 3 minutes. The layers were allowed to separate for 5 minutes before the chloroform layer was drawn off into a 250-ml separatory funnel. Another 50 ml of chloroform was added to the water in the 2-liter separatory funnel, and the mixture was again shaken for 3 minutes. The layers were allowed to separate for 10 minutes before the chloroform layer was drawn off and combined with the first chloroform extract.

Twenty-five milliliters of 0.001N H_2SO_4 were added to the $CHCl_3$ solution in the 250-ml separatory funnel, and the mixture was shaken for 3 minutes. The layers were allowed to separate for 5 minutes. The aqueous layer was transferred with a disposable Pasteur pipette to a 125-ml separatory funnel. Another 25 ml of 0.001N H_2SO_4 were added to the $CHCl_3$, and the mixture was shaken for 3 minutes. The layers were allowed to separate for 5 minutes before the $CHCl_3$ layer was drawn off and discarded. The aqueous layer was combined with the first aqueous extract.

The pH of the aqueous extract was adjusted to 11.0 using 1 ml of 0.5 M sodium carbonate. Five milliliters of $CHCl_3$ were added, and the mixture was shaken for 3 minutes. The layers were allowed to separate for 5 minutes. The $CHCl_3$ layer was drawn off into a conical centrifuge tube. Another 5 ml of $CHCl_3$ layers were allowed to separate for 5 minutes before the $CHCl_3$ layer was combined with the first extract.

The combined $CHCl_3$ extracts were concentrated to approximately 0.1 ml in a constant-temperature water bath set at 80°C while purging with nitrogen. The nitrogen flow was controlled by a reflux timer connected to a solenoid. This alternatively started and stopped the nitrogen flow at 30-second intervals. The purpose of the interrupted flow was to set up a reflux to help wash down the walls of the centrifuge tube. When the concentrates reached a level of approximately 0.1 ml, they were removed from the bath, the internal standard (Michler's Ketone) was added, and the solutions were diluted to 0.2 ml with $CHCl_3$. The concentrates were stirred on a Vortex mixer before analyzing by GC.

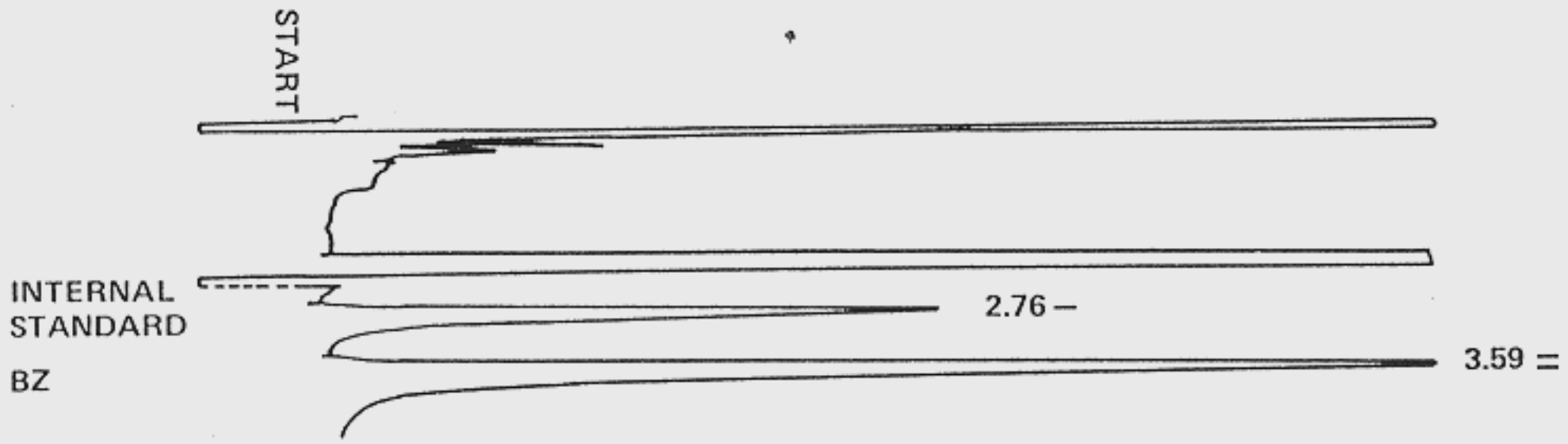

Figure 1. Chromatogram of BZ Standard With Internal Standard

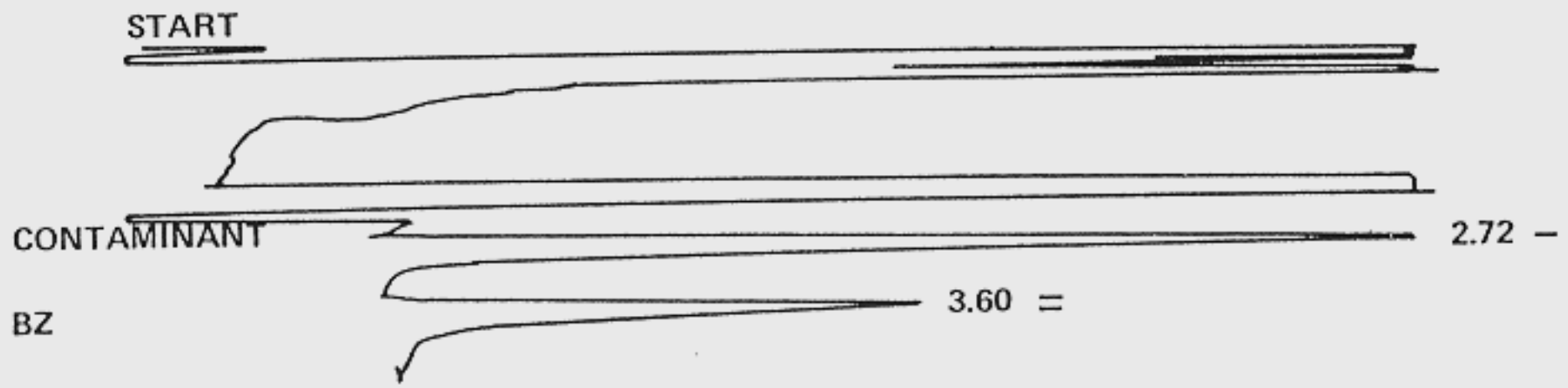

Figure 2. Chromatogram of Sample Extract Containing Contaminant Peak

Tables 1 and 2 present the BZ recovery from unaerated and aerated filters at the two BZ levels. The recovery shows the amount of BZ extracted from the filter as a percentage of the amount deposited on the filter. Both the peak height measurement and the area measurement recoveries are shown for the unaerated and aerated filters. The average recovery ($\bar{X}$) and the standard deviation (S) are given for each measurement method. All recoveries were calculated by comparison to the peak height and areas of the external standard run before the sample.

Tables 3 and 4 present the recovery of the two levels of BZ from solution after concentration. This was done to check for loss of BZ during the concentration step. Recoveries were calculated as for tables 1 and 2.

4.2 Water Studies.

Table 5 is a step-by-step outline of the method for water developed by CSL. An outline of the BCL method for air is also given for comparison. As can be seen, both methods are very similar and are complex, time consuming, and labor intensive. The prolonged procedure and long turnaround time makes the method not entirely suitable for most of the routine analyses in the BZ demilitarization plant.

Figures 3 and 4 illustrate the effect of chlorine on the recovery of BZ from tap water. Figure 3 is a chromatogram of an extraction of BZ from tap water without chlorine. Figure 4 shows the extraction of BZ from tap water containing chlorine. The BZ concentration in figure 4 is the same as in figure 3. In figure 3, BZ has a retention time of 3.10 minutes and Michler's Ketone has a retention time of 7.26 minutes. In figure 4, no peak appears at the retention time of BZ, but two extraneous peaks are evident at the retention times of 4.96 and 5.74 minutes. The peak of 7.30 minutes is Michler's Ketone. It was not determined whether the extraneous peaks were BZ degradation products.

Table 6 presents the recovery of BZ from tap water using the procedure described in 3.2.3. The recovery was calculated by comparison of the amount of BZ in the extract to a prepared GC standard. The GC standard had a BZ concentration that would approximate that in the extract if 100 percent of the BZ were recovered.

Depicted in table 7 is the recovery of BZ from tap water in the presence of contaminants, using the procedure described in 3.2.4. The effect on the recovery with and without the cyclohexane is shown. The recovery was calculated in the same manner as for table 6.

Table 8 shows the effect of salting on the recovery of BZ at the drinking water level (4 ppb). The recovery was calculated in the same manner as for table 6.

Tables 9 and 10 show the detection limit as calculated by the method of Hubaux and Vos.[11]

Figures 5 and 6 show the 90 percent confidence limits as calculated by the method of Hubaux and Vos.

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Table 1. BZ Recovery at the 0.1 µg Level

Unaerated (N=25)					Aerated: 100 Liters (N=25)					Aerated: 1000 Liters (N=25)				
			Recovery (%)				Recovery (%)					Recovery (%)		
Sample	Peak Height (mm)	Area (counts)	Peak Height	Area	Sample	Peak Height (mm)	Area (counts)	Peak Height	Area	Sample	Peak Height (mm)	Area (counts)	Peak Height	Area
External Standard	92.5	1034	-	-	External Standard	82.0	1135	-	-	External Standard	78.0	1375	-	-
1	80.0	1032	86.5	99.8	1	49.0	566	59.8	49.9	1	38.5	1410	49.3	29.4
2	80.0	919	86.5	88.9	2	62.5	730	76.2	64.3	2	34.5	1004	44.2	56.7
External Standard	92.0	1003	-	-	External Standard	74.0	848	-	-	External Standard	75.5	1751	-	-
3	53.5	645	58.2	64.3	3	43.5	609	58.8	71.8	3	30.0	1065	39.7	60.8
4	66.0	778	71.7	77.6	4	49.0	652	66.2	76.9	4	31.0	1005	41.1	57.4
External Standard	96.0	816	-	-	External Standard	75.5	869	-	-	External Standard	71.5	1685	-	-
5	43.0	435	44.8	53.0	5	41.0	525	54.3	60.4	5	39.5	1412	55.2	83.8
6	28.0	297	29.2	33.2	6	32.0	306	42.4	35.2	6	46.0	1299	64.3	77.1
External Standard	106.0	905	-	-	External Standard	67.0	743	-	-	External Standard	114.5	2717	-	-
7	39.5	385	37.3	43.0	7	42.5	427	63.4	57.5	7	44.5	1041	38.9	38.3
8	58.0	595	54.7	66.4	8	44.5	454	66.4	61.1	8	49.0	1218	42.8	44.8
External Standard	98.0	915	-	-	9	45.0	433	67.2	58.3	External Standard	119.0	2783	-	-
9	41.5	368	42.4	40.2	External Standard	73.5	810	-	-	9	63.5	1797	53.4	64.4
10	49.0	452	50.0	49.4	10	43.0	440	58.5	54.3	10	64.0	1627	53.8	58.5
External Standard	97.0	1006	-	-	11	56.0	565	76.2	69.8	External Standard	104.0	2822	-	-
11	63.0	693	65.0	68.9	12	51.5	517	70.1	63.8	11	56.5	1626	54.3	57.4
12	54.0	505	55.7	50.2	External Standard	69.0	740	-	-	12	57.0	1497	54.8	53.0
External Standard	90.0	975	-	-	13	42.0	482	60.9	65.1	13	66.5	1939	63.9	68.7
13	55.0	640	61.1	65.6	14	56.0	561	81.2	75.8	14	77.0	2021	74.0	71.6
14	61.5	690	68.3	70.8	15	43.0	410	62.3	55.4	External Standard	93.5	2595	-	-
15	56.5	596	62.8	61.1	External Standard	96.5	1124	-	-	15	72.5	1966	77.5	75.8
16	79.0	894	87.8	91.7	16	32.0	529	33.2	47.1	16	71.5	1868	76.5	71.2
External Standard	98.0	1106	-	-	17	37.0	333	38.3	29.6	External Standard	98.0	2606	-	-
17	52.0	652	53.1	59.0	External Standard	100.0	1095	-	-	17	74.5	1995	75.2	76.6
18	66.5	779	67.9	70.4	18	42.5	308	42.5	28.1	18	73.0	1896	73.7	72.8
External Standard	83.0	877	-	-	External Standard	121.5	1342	-	-	External Standard	93.0	2522	-	-
19	30.5	396	36.8	45.2	19	39.0	568	32.1	42.3	19	57.0	1434	55.9	56.9
20	35.0	363	42.2	41.1	20	49.5	445	40.7	33.2	20	57.0	1618	61.3	64.2
21	36.0	348	41.0	39.7	21	52.5	473			External Standard	106.0	2885	-	-
External Standard	86.5	821	-	-	External Standard	101.5	1189	-	-	21	65.0	1625	61.3	56.3
22	36.5	358	42.2	43.6	22	68.0	744	43.2	35.2	22	71.0	1785	67.0	61.9
23	51.0	541	59.0	65.9	23	38.0	426	67.0	61.6	External Standard	93.0	2681	-	-
External Standard	102.0	1058	-	-	24	52.0	448	37.4	36.4	23	55.0	1372	59.1	51.2
24	69.0	987	67.7	93.3	External Standard	95.5	1037	-	-	24	58.0	1451	62.4	54.2
25	62.0	733	60.8	69.3	25	57.5	542	51.2	40.0	External Standard	91.5	2772	-	-
										25	50.0	1749	52.9	46.1
	$\bar{x}$ (mean)		57.3	62.1				56.4	53.2				56.4	53.2
	s (standard deviation)		15.9	18.4				14.2	14.7				14.2	14.7

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Table 2. 8Z Recovery at the 1.4 µg Level

Unaerated (N-2S)					Aerated: 600 Liters (N-2S)					Aerated: 1000 Liters (N-2S)				
			Recovery (%)					Recovery (%)					Recovery (%)	
Sample	Peak Height (mm)	Area (counts)	Peak Height	Area	Sample	Peak Height (mm)	Area (counts)	Peak Height	Area	Sample	Peak Height (mm)	Area (counts)	Peak Height
External Standard	124.0	19540	-	-	External Standard	141.0	22490	-	-	External Standard	141.0	23280	-
1	78.5	12390	63.3	65.5	1	75.0	12170	53.2	54.1	1	73.5	12180	51.4
2	83.0	14320	66.1	73.3	2	79.5	13980	56.4	62.2	External Standard	140.5	22880	-
External Standard	106.0	16410	-	-	External Standard	134.5	21670	-	-	2	70.5	11660	50.2
3	87.0	13940	82.1	84.9	3	82.0	13510	61.0	62.3	External Standard	133.0	21810	-
4	74.0	12220	69.8	74.5	4	72.5	16140	53.9	74.5	3	75.5	12920	56.8
External Standard	131.0	20860	-	-	5	91.5	14980	58.0	69.1	4	49.0	8652	34.8
5	75.0	12560	57.2	60.2	6	84.0	13610	62.4	62.8	External Standard	145.5	23730	-
6	76.0	11920	58.0	57.1	External Standard	130.0	21340	-	-	5	84.5	14350	58.1
7	82.5	16730	63.0	80.2	7	83.0	13700	63.9	64.2	6	78.5	13350	54.0
External Standard	128.0	20270	-	-	8	90.5	15000	69.6	70.3	External Standard	145.0	23220	-
8	91.5	18600	71.5	91.8	9	99.0	16420	76.2	76.9	7	80.0	13690	55.2
9	106.5	23310	83.2	115	10	97.5	16660	75.0	78.1	8	79.0	13380	54.5
External Standard	143.5	22860	-	-	External Standard	130.5	6208	-	-	External Standard	106.5	36840	-
10	81.0	13100	56.5	57.3	11	104.0	6916	79.7	79.2	9	73.5	25230	69.0
External Standard	99.5	9028	-	-	12	102.5	6821	78.5	77.7	10	71.5	23190	67.1
11	56.0	5402	56.3	59.9	13	93.0	6366	71.3	70.3	External Standard	125.5	6092	-
12	77.0	7246	77.4	80.3	External Standard	129.0	6140	-	-	11	85.5	6300	68.1
13	62.5	5922	62.8	65.6	14	120.0	5807	93.0	94.6	12	84.0	6081	66.9
External Standard	97.0	9084	-	-	15	97.0	6666	75.2	76.0	External Standard	130.0	6162	-
14	57.0	4910	58.8	54.0	16	78.0	3412	60.5	55.6	13	90.5	4634	69.6
15	61.0	5599	62.9	61.6	17	88.0	4180	68.2	68.1	14	80.0	4172	61.5
16	65.5	6163	67.5	67.8	External Standard	129.5	6178	-	-	External Standard	101.5	4909	-
17	51.0	4536	52.6	49.9	18	102.0	4846	78.8	78.4	15	78.5	3804	77.3
External Standard	106.5	9680	-	-	19	108.5	5114	83.8	82.8	External Standard	102.0	4914	-
18	48.5	4161	45.3	43.0	20	91.0	4305	70.3	69.7	16	80.0	3815	74.8
19	53.5	4742	50.2	49.0	External Standard	132.0	6363	-	-	External Standard	94.5	4547	-
20	62.0	5874	58.2	60.7	21	104.5	5145	79.2	80.9	17	54.0	2438	57.1
21	58.5	5352	54.3	55.3	22	104.5	5049	79.2	79.4	18	48.5	2342	51.3
External Standard	78.0	7166	-	-	External Standard	123.5	6051	-	-	19	58.0	2908	61.4
22	64.0	6008	82.1	83.8	23	91.5	4445	74.1	73.5	20	71.0	3275	75.1
23	54.0	5006	69.2	69.9	24	113.0	5489	91.5	90.7	External Standard	97.0	4651	-
External Standard	130.5	6208	-	-	25	101.0	4289	81.8	79.8	21	69.0	3432	71.1
24	97.0	4510	74.3	72.7						22	70.5	3281	72.7
25	92.0	4434	70.5	71.4						External Standard	101.0	5046	-
										23	71.0	3606	70.3
										24	70.5	3564	69.8
										External Standard	82.5	4356	-
										25	69.5	3390	84.2
	X (mean)		64.5	68.2				71.8	73.2					83.4
	σ (standard deviation)		10.2	15.6				11.0	9.80					10.7

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Table 3. BZ Recovery After Concentration - 0.1 µg Level

Sample	Peak Height (mm)	Area (counts)	Recovery (%) Peak Height	Recovery (%) Area
External Standard	98.0	5538	-	-
1	102.5	5379	105.0	97.1
2	89.5	4752	91.3	85.8
3	88.0	4592	89.8	82.9
4	79.5	4200	81.1	75.8
External Standard	94.5	5148	-	-
5	91.0	4837	96.3	94.0
6	101.0	5319	107.0	103.0
7	99.5	5205	105.0	101.0
8	83.0	4370	107.0	103.0
External Standard	105.5	5731	-	-
9	104.0	5459	98.6	95.3
10	97.0	5120	91.9	89.9
	$\bar{x}$		95.3	91.0
	s		8.57	8.63

Table 4. BZ Recovery After Concentration 1.4 µg Level

Sample	Peak Height (mm)	Area (counts)	Recovery (%) Peak Height	Recovery (%) Area
External Standard	111.5	93500	-	-
	89.5	72160	80.3	77.2
	93.0	74460	83.4	79.6
	95.0	76180	85.2	81.5
	118.5	95160	106.0	102.0
External Standard	104.5	86740	-	-
	90.0	72560	86.1	83.6
	109.0	87520	104.0	101.0
External Standard	89.5	74180	-	-
	97.0	79080	108.0	107.0
	92.0	74640	103.0	101.0
	111.0	90780	124.0	122.0
	106.0	86380	118.0	116.0
	$\bar{x}$		99.8	97.1
	s		15.3	15.8

Table 5. Comparison of Methods

Step #	Method Developed by CSL Operation	Estimated Time (min)	Step #	Method Developed by BCL Operation	Estimated Time (min)
1	Add H_2SO_4 and dissolve	1	1	Spike filter with BZ-d_{10}	1
2	Adjust pH to 3.0	0.25	2	Add 0.1N HCl or acetic acid	0.5
3	Add 0.2% $Na_2S_2O_5$	0.25	3	Shake	2
4	Let solution stand	0.5	4	Add cyclohexane	0.5
5	Check chlorine level	1	5	Shake	2
6	Add cyclohexane	0.5	6	Let settle	2
7	Shake	1	7	Remove cyclohexane	0.5
8	Allow layers to separate	5	8	Add cyclohexane	0.5
9	Draw off water layer into 2-liter separatory funnel	0.5	9	Shake	2
10	Adjust pH to 10.5	0.25	10	Let settle	2
11	Add $CHCl_3$	0.5	11	Remove cyclohexane	0.5
12	Shake	3	12	Add $CHCl_3$	0.5
13	Allow layers to separate	5	13	Add Na_2CO_3 to pH 11 (check pH)	2
14	Draw off $CHCl_3$ layer into 250ml separatory funnel	0.5	14	Shake	2
15	Add fresh $CHCl_3$	0.5	15	Filter into separatory funnel	2
16	Shake	3	16	Let settle	2
17	Allow layers to separate	10	17	Remove $CHCl_3$ into 250ml Erlenmeyer	0.5
18	Draw off $CHCl_3$ into 250ml separatory funnel	0.5	18	Add fresh $CHCl_3$	0.5
19	Add 0.001% H_2SO_4	0.5	19	Shake	2
20	Shake	3	20	Let settle	2
21	Allow layers to separate	5	21	Remove $CHCl_3$ into same Erlenmeyer	0.5
22	Transfer H_2SO_4 to 250ml separatory funnel	2	22	Add fresh $CHCl_3$	0.5
23	Add fresh 0.001N H_2SO_4	0.5	23	Shake	2
24	Shake	3	24	Let settle	2
25	Allow layers to separate	5	25	Remove $CHCl_3$ into same Erlenmeyer	0.5
26	Draw off & discard $CHCl_3$ layer	0.5	26	Add K_2CO_3 (to dry)	0.5
27	Draw off H_2SO_4 into 125ml separatory funnel	0.5	27	Filter into 250ml rb flask	2
28	Adjust pH to 11.0	0.25	28	Rinse (2x)	1
29	Add $CHCl_3$	0.25	29	Attach to rotovaporator	1
30	Shake	3	30	Evaporate	15
31	Allow layers to separate	5	31	Remove from rotovaporator	1
32	Draw off $CHCl_3$ into centrifuge tube	0.5	32	Pour into KD concentrator	1
33	Add fresh $CHCl_3$	0.25	33	Rinse (2x)	1
34	Shake	3	34	Concentrate	15
35	Allow layers to separate	5	35	Transfer to vial	0.5
36	Draw off $CHCl_3$ into centrifuge tube	0.5	36	Seal vial	0.5
37	Evaporate $CHCl_3$ to 0.1ml	15	37	Place in autosampler rack	0.5
38	Add internal standard	0.25			
39	Dilute to 0.2ml	0.25			
	TOTAL	86.5		TOTAL	71.5

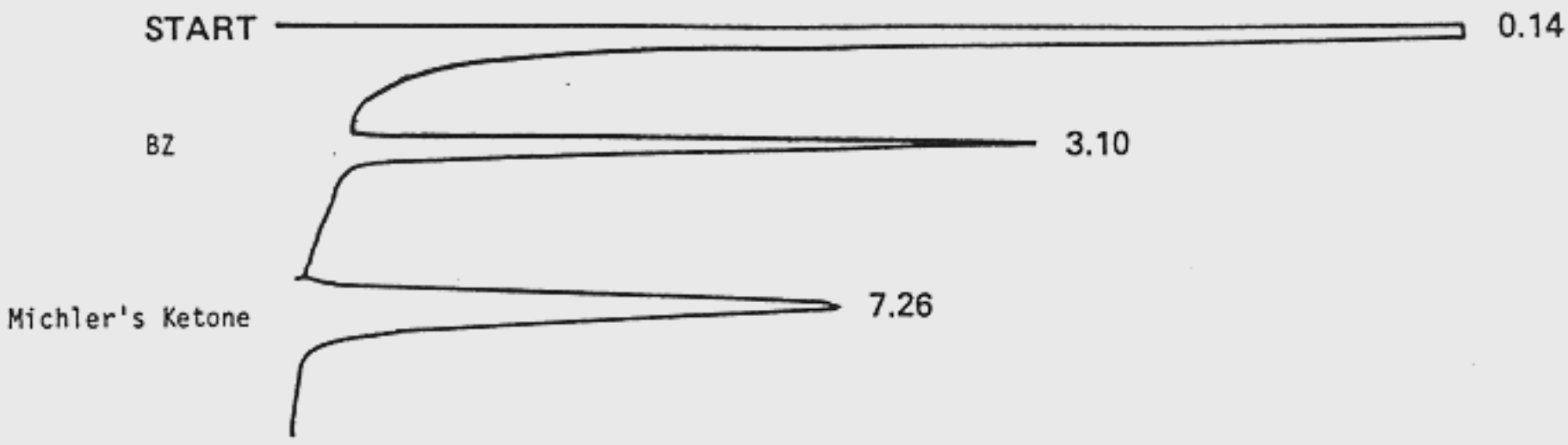

Figure 3. Chromatogram of Extraction of BZ from Tap Water

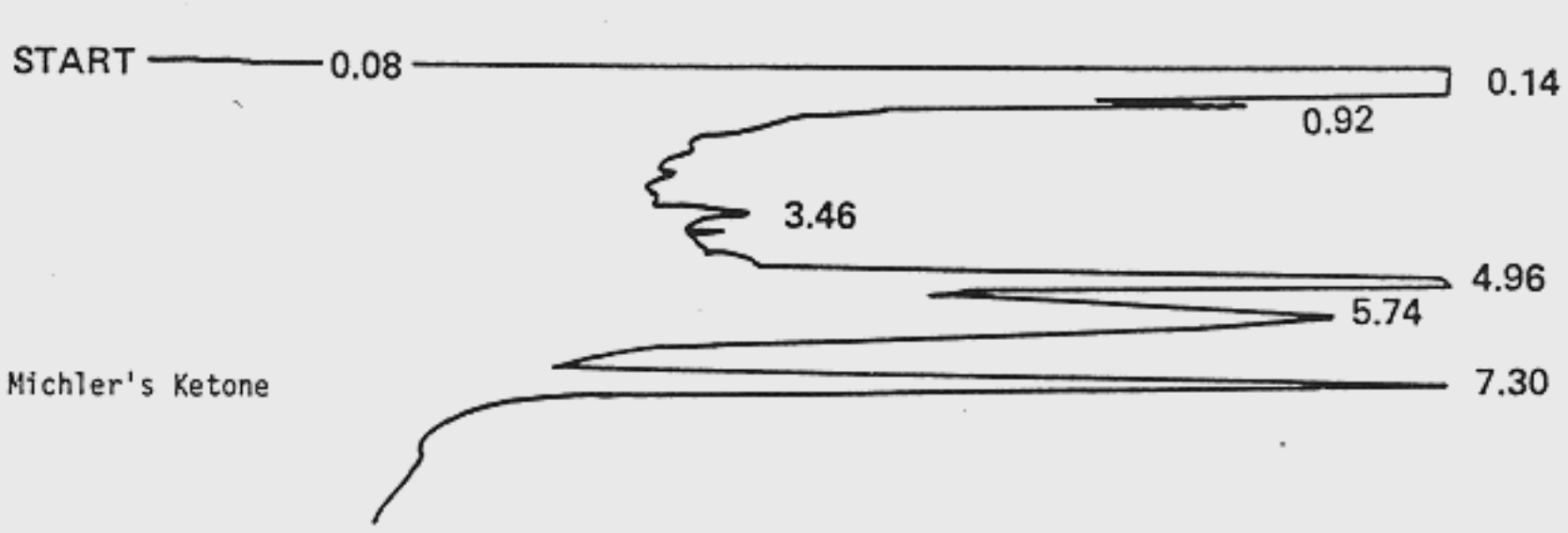

Figure 4. Chromatogram Showing Effect of Chlorine on Extraction of BZ from Tap Water

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Table 6. Recovery of BZ From Tap Water

BZ Concentration (ppb)	Nichler's Reagent Peak Height (mm)	BZ Peak Height (mm)	Recovery (%)	BZ Concentration (ppb)	Nichler's Reagent Peak Height (mm)	BZ Peak Height (mm)	Recovery (%)	BZ Concentration (ppb)	Nichler's Reagent Peak Height (mm)	BZ Peak Height (mm)	Recovery (%)	BZ Concentration (ppb)	Nichler's Reagent Peak Height (mm)	BZ Peak Height (mm)	Recovery (%)
Standard	54.0	312.0	-	Standard	84.5	77.0	-	Standard	15.0	98.0	-	Standard	68.5	68.0	-
50	58.5	184.25	84.4	4	68.0	42.75	53.0	2	84.5	62.0	30.3	1	76.25	35.5	47.0
Standard	71.5	268.25	-	4	80.5	46.25	55.0	2	78.0	38.5	30.9	1	65.25	23.25	37.1
50	71.25	215.0	61.2	Standard	82.5	76.75	-	Standard	75.25	91.0	-	Standard	67.0	65.25	-
Standard	69.5	327.0	-	4	58.5	39.0	68.4	2	61.5	27.5	35.8	1	69.5	21.0	32.0
50	62.0	95.0	80.8	Standard	64.0	72.5	-	Standard	74.0	100.5	-	Standard	68.25	68.0	-
Standard	61.0	331.5	-	4	68.0	30.5	38.5	2	85.75	39.5	36.3	1	71.5	33.5	51.7
50	61.5	149.25	81.0	Standard	73.0	82.75	-	Standard	73.0	91.75	-	1	71.0	32.75	48.5
Standard	53.25	137.5	-	4	83.0	34.75	52.6	2	82.25	37.0	35.4	Standard	69.0	69.5	-
50	61.0	103.3	80.4	4	86.25	43.25	68.1					1	61.25	24.25	33.3
Standard	63.0	337.3	-	Standard	73.0	78.25	-					Blank	36.5	5	Blanks were
50	57.0	91.75	78.9	4	77.5	43.75	53.1					Blank	80.0	0	compared to standards shown.
Standard	67.5	179.0	-									Blank	51.5	0	
50	64.0	100.0	77.6									Blank	72.0	0	
Standard	66.0	174.75	-												
50	61.5	101.25	84.0												
Standard	61.25	150.3	-												
50	67.5	81.5	84.3												
Standard	66.25	133.25	-												
50	65.0	111.0	83.9												
		$\bar{x}$	83.1				51.0				30.8				-1.9
		s	3.93				2.69				1.88				7.46

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Table 7. Recovery of BZ From Tap Water in the Presence of Contaminants

Without Cyclohexane Wash

BZ Concentration (ppb)	Contaminant	Contaminant Concentration (ppm)	Recovery (%)	$\bar{X}$	S	%S
1.24	Sodium Benzilate	11.2	0 0	----	----	----
1.24	Benzophenone	10.0	0 0	----	----	----
1.24	3-Quinuclidinol	7.75	45.4 40.0 41.7	42.4	2.76	6.51

With Cyclohexane Wash

BZ Concentration (ppb)	Contaminant	Contaminant Concentration (ppm)	Recovery (%)	$\bar{X}$	S	%S
1.24	----	----	44.7 37.3 29.3	37.1	7.70	20.8
1.24	Sodium Benzilate	11.2	16.6 29.2 21.1	22.3	6.39	28.7
1.24	Sodium Benzilate	1.12	33.6 21.4 19.1	24.7	7.79	31.5
1.24	Benzophenone	10.0	13.8 34.6 16.3	21.6	11.4	52.8
1.24	Benzophenone	1.00	17.5 24.8 25.4	23.8	4.39	18.4

Table 8. Effect of Salting on Recovery of BZ

Without Salting

BZ Concentration (ppb)	Michler's Ketone Peak Height (mm)	BZ Peak Height (mm)	Recovery (%)
Standard (3.98)	67.5	71.0	-
4.0	63.5	22.5	33.7
4.0	79.5	24.0	28.5
Standard (3.98)	66.0	72.5	-
4.0	81.0	33.0	37.0
		$\bar{x}$	33.1
		s	4.29

With Salting

BZ Concentration (ppb)	Michler's Ketone Peak Height (mm)	BZ Peak Height (mm)	Recovery (%)
Standard (4.02	69.5	72.0	-
4.0	60.0	32.75	53.0
4.0	80.5	46.25	55.8
Standard (4.02)	67.5	74.75	-
4.0	54.5	29.0	48.4
Standard (3.98)	66.0	72.5	-
4.0	68.0	38.5	51.5
		$\bar{x}$	52.2
		s	3.08

Table 9. Hubaux - Vos Detection Limit

Target Value (ppb)	Found Value (ppb)
40	34.6
40	32.5
40	32.3
40	32.7
40	32.2
40	31.8
40	31.0
40	33.6
40	33.7
40	34.4
4	2.12
4	2.23
4	1.94
4	2.06
4	2.10
4	1.96
4	2.08
2	0.77
2	0.78
2	0.70
2	0.73
2	0.71
1	0.48
1	0.37
1	0.36
1	0.52
1	0.46
1	0.34
0	0
0	0
0	0
0	0

Detection Limit x(d) = 3.2 ppb

Table 10. Hubaux-Vos Detection Limit

Target Value (ppb)	Found Value (ppb)
4	2.12
4	2.23
4	1.94
4	2.06
4	2.10
4	1.96
4	2.08
2	0.77
2	0.78
2	0.70
2	0.73
2	0.71
1	0.48
1	0.37
1	0.36
1.	0.52
1	0.46
1	0.34
0	0
0	0
0	0
0	0

Detection Limit x(d) = 0.95

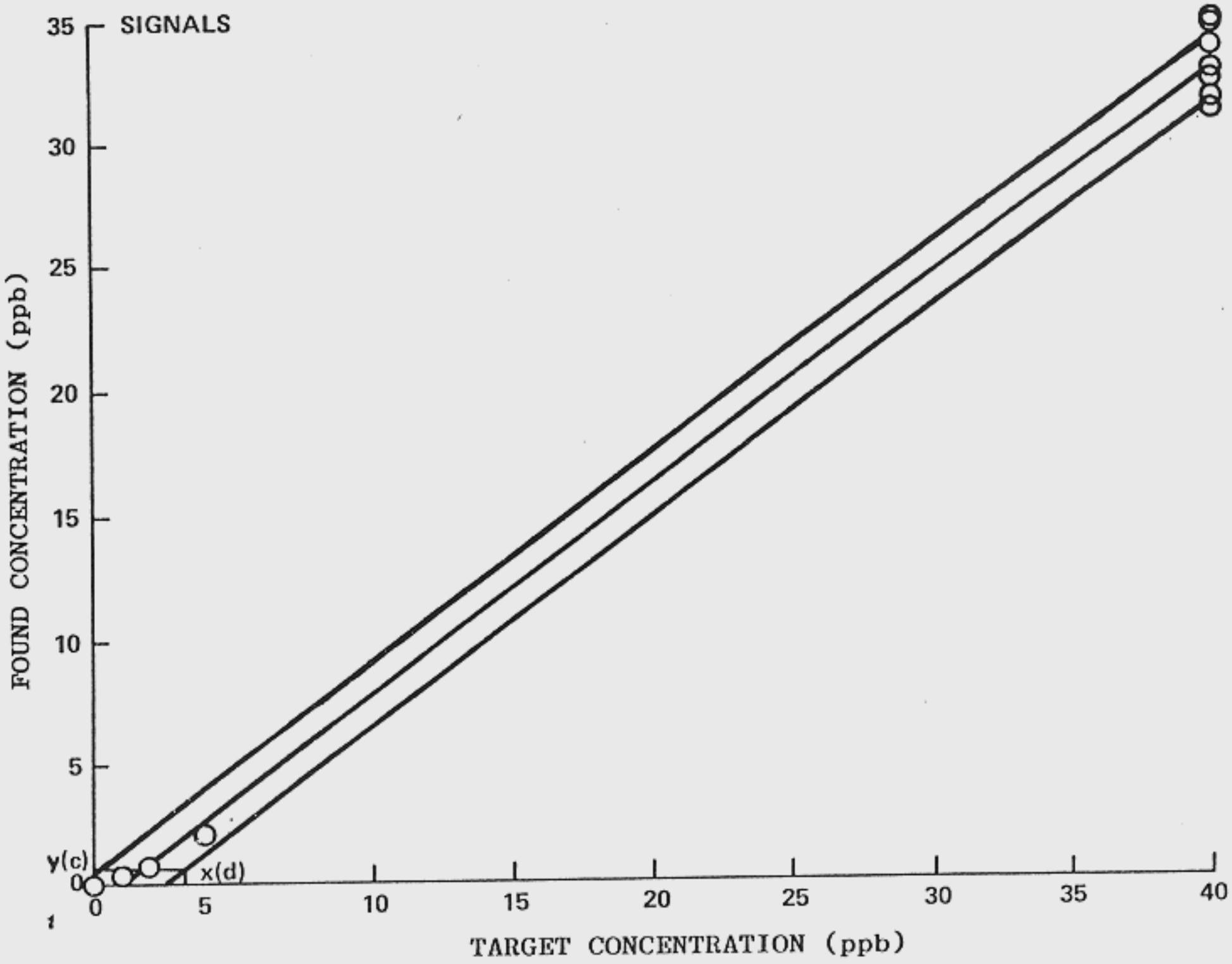

Figure 5. 90 Percent Confidence Limit

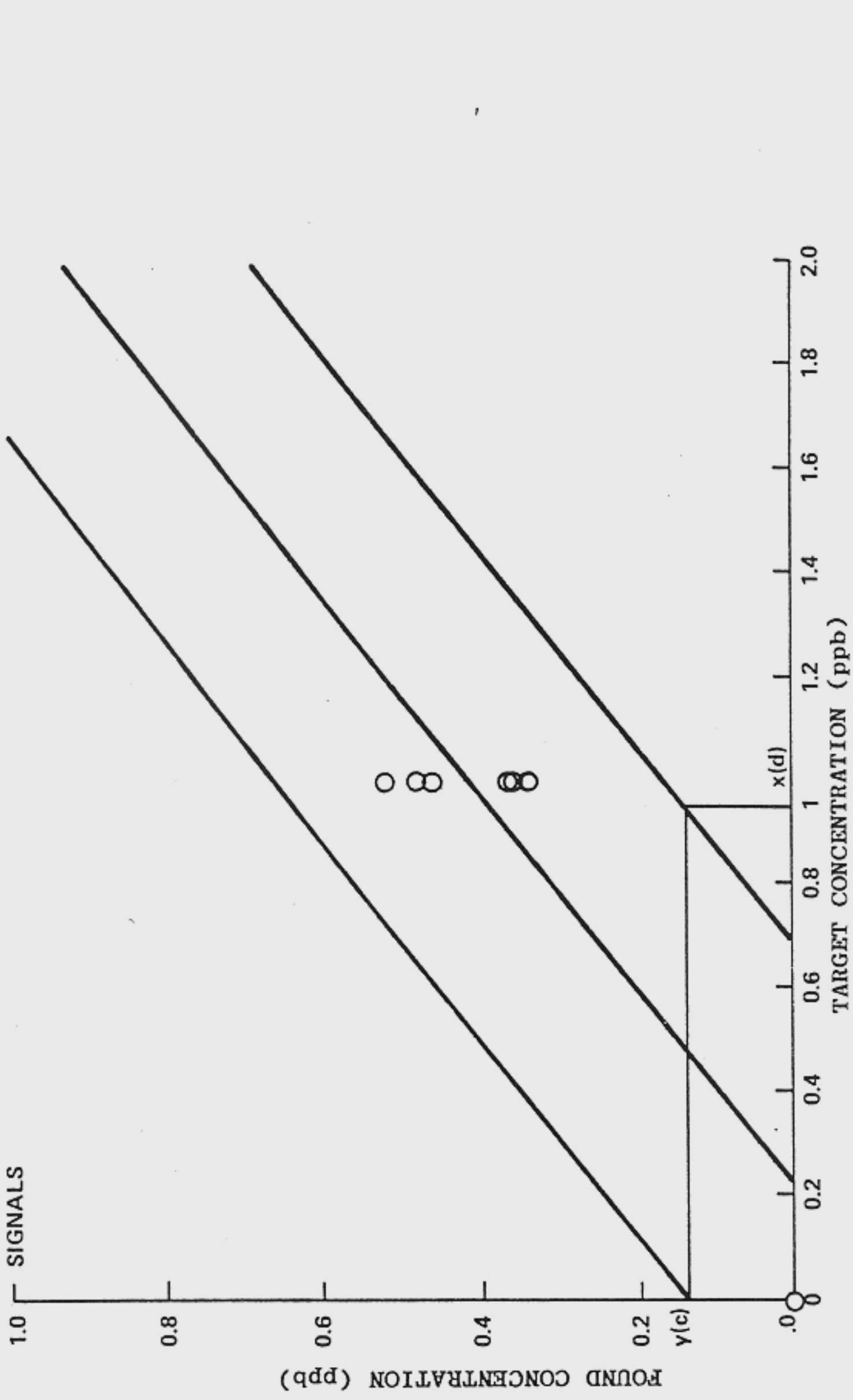

Figure 6. 90 Percent Confidence Limit

5. DISCUSSION OF RESULTS

5.1 Aerosol Studies.

The BZ recoveries were lower and more variable than would be desired for routine laboratory analysis. The low and variable recovery from the filters could be due to the polarity of the glass fiber filters which bound the BZ to the filters and the inability of dioxane to remove it. Deiner, Herd, and Vigus, Munitions Division, CSL,* showed that 100 percent recoveries from glass-fiber aerosol filters were attainable using an aqueous acidic medium. It is concluded that dioxane employed as a solvent is not sufficiently polar to afford complete removal of BZ from the filter.

In addition, much of the variability could be due to the NPD. The detector is very sensitive and selective for nitrogen and phosphorus compounds, but it can also be nonreproducible in its response to a sample. The NPD does not show long-term response stability. Attempts to quantitate BZ in a sample by comparing it to a previously injected standard may produce variable results. It is now thought that the lack of a suitable internal standard to help overcome the effects of the detector instability may be the cause for much of the variation in the results of the tests conducted. As a result of BCL's efforts, it was shown that Michler's Ketone could be successfully employed as an internal standard[12] with the NPD.

The results of the concentration tests did not show any appreciable loss of BZ at either dosage level.

5.1.1 Statistical Analysis of the Data.

A statistical analysis of the data was done to determine if there was any significant difference at the two BZ levels between the amount of BZ recovered from the aerated filters and the amount of BZ recovered from the unaerated filters.

The data obtained from peak height measurements and from area measurements were analyzed separately.

5.1.1.1 Peak Height Measurements.

The frequency distribution of the peak height measurement data from tables 1 and 2 are shown in figure 7.

Analysis of Variance.

Based upon Bartlett's test shown below, there would be a 17.2 percent risk of error if it were concluded that a significant difference did exist in the variability of the different samples. It was concluded that the variances of the samples were equivalent regardless of the aeration or BZ level used.

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*Deiner, A., Herd, R. E., and Vigus, E. S. The Utilization of an Ion-Pairing Reaction to Trace Concentrations of 3-Quinuclidinyl Benzilate (BZ) and Application to Demilitarization Operations. (unpublished data, June 1983).

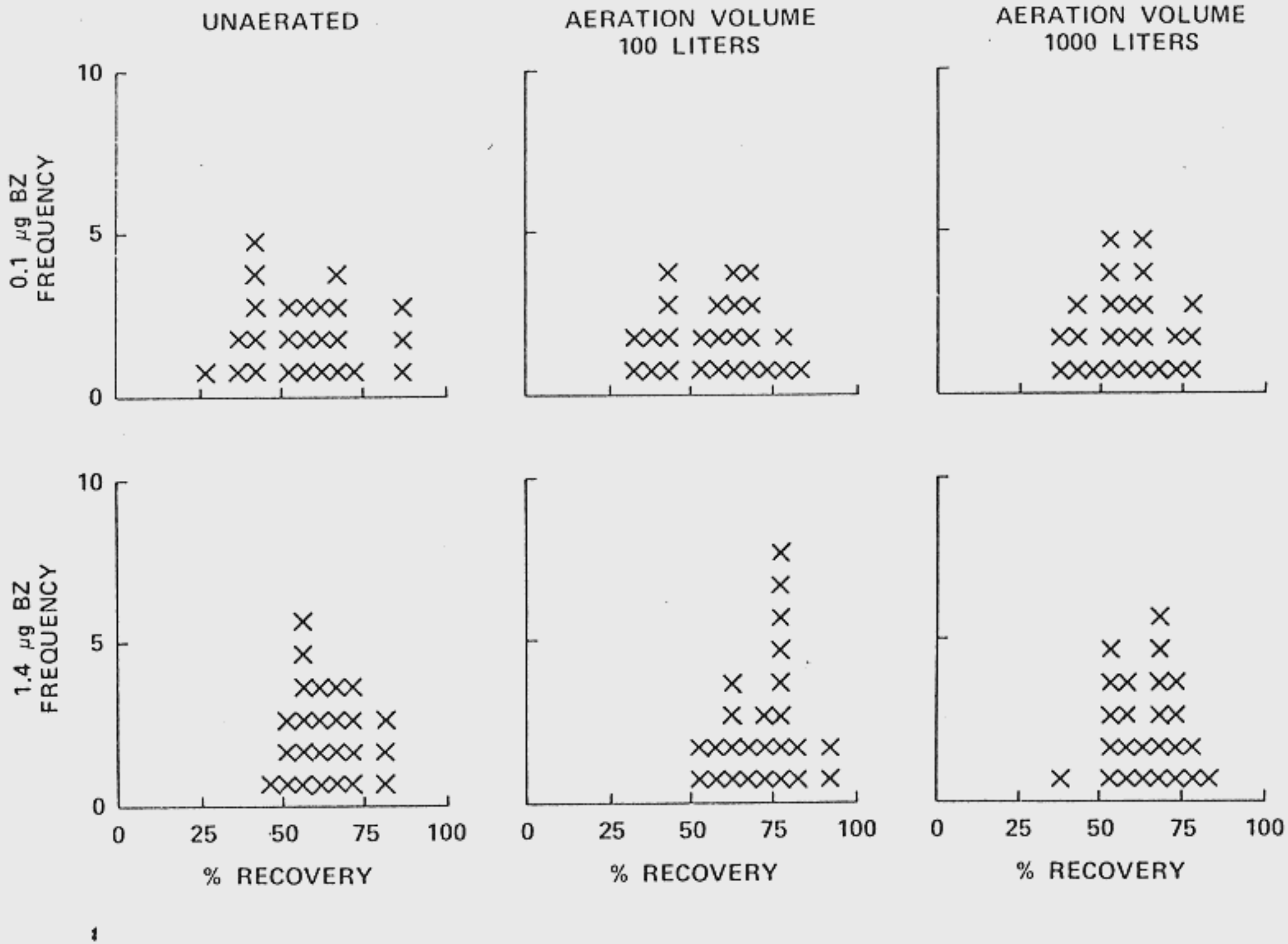


Figure 7. FREQUENCY DIAGRAM FOR PEAK HEIGHT DATA OF TABLES 1 & 2

BARTLETT'S TEST

$M = 2.3025 (\nu \log (\Sigma_i S_i^2/\nu - \Sigma \nu_i \log S_i^2)$

$= 7.853$

$C = 1 + \frac{1}{3(g-1)} \left(\frac{1}{\nu_i} - \frac{1}{\nu}\right)$

$= 1.016$

$M/C = 7.728 = \chi^2_{0.172,5}$

$\nu = \Sigma \nu_i$

ν_i = degrees of freedom of the i_{th} sample.

S_i^2 = independent estimate of the i_{th} variance.

g = number of variances compared.

$\chi_{\alpha, g-1}$ = percentage point of the Chi-Square distribution at the α point and g-1 degrees of freedom.

Assuming a completely cross-classified, random effects model, the analysis of the variance presented in table 11 shows that:

(1) There would be a 31.5 percent risk of error if it were that aeration had an effect on the process.

(2) There would be less than 0.05 percent risk of error if it were concluded that the BZ level had an effect on the process.

(3) There would be a 9.5 percent risk of error if it were concluded that there was an effect on the process due to the interaction of the BZ level and the aeration volume.

From (1) above, it was concluded that aeration may have an effect on the amount of BZ recovered.

From (2) above, it was concluded that the level of BZ had no effect on the percent of recovery.

From (3) above, it was decided that more testing would be necessary before any firm conclusions could be drawn concerning the effect of the BZ level or the effect of the interaction of the BZ level and the aeration volume on the amount of BZ recovered.

Table 11. Analysis of Variance of Peak Height Measurement Data

Source	Degree of freedom	Sum of squares	Mean square	Mean square ratio	Level for H_0 rejection
BZ Level	1	3247.096	3247.096	20.922	<0.0005
Aeration	2	358.0769	179.038	1.154	0.315
Interaction	2	768.9266	364.463	2.348	0.095
Residual	144	22347.8088	155.193		
Total	149	26681.9083			

5.1.1.2 Sample Size.

The residual mean square shown in table 11 is an estimate of the experimental error of the peak height measurement method. Assuming that the residual mean square is the population variance (S^2), the number of GC injections (n) needed to reliably estimate the population can be calculated using the following equation:

$$n = \left(t^2_{1-\alpha/2,\ \phi}\ \hat{S}^2\right)/d^2$$

$t_{1-\alpha/2,\ \phi}$ - $(1-\alpha/2)$ percentile of the t distribution at ϕ degrees of freedom (ϕ = 144)

$\hat{S}^2$ - estimate of the population variance ($\hat{S}^2$ = 155.193)

d - error in the estimate of the population mean

Table 12 shows the calculated number of GC injections needed depending upon the 100 (1-α) percent confidence level and the interval $\bar{X} \pm d$ percent one is willing to accept. It can be seen from the table that if the average value for a sample is to be within ± 10 percent of the true average value ($\bar{X}$) 95 percent of the time, then at least six injections would be necessary.

Table 12. Sample Size

100 (1-α)% Confidence	n		
	d = 5	d = 10	d = 15
99	43	11	5
98	35	9	4
95	25	6	3
90	17	5	2
80	11	3	2

5.1.1.3 Area Measurement.

The frequency distributions of the area measurement data from tables 1 and 2 are shown in figure 8.

An analysis of variance was not done on the area measurement data because the assumption of homogeneity of variance between samples was proven not valid by a Bartlett's Test for the homogeneity of variances (shown below). The results of this test showed that there would be a 1.1 percent risk of error if it were concluded that a significant difference exists in the variability of the different samples. It was, therefore, concluded that the variability between samples was not constant.

BARTLETT'S TEST

$$M = 2.3026\ (\nu \log\ (\Sigma \nu_i S_i^2\ \nu) - \Sigma \nu_i \log\ s_i^2)$$

$$= 15.142$$

$$C = 1 + \frac{1}{3(g-1)} \left(\frac{1}{\nu i} - \frac{1}{\nu} \right)$$

$$= 1.016$$

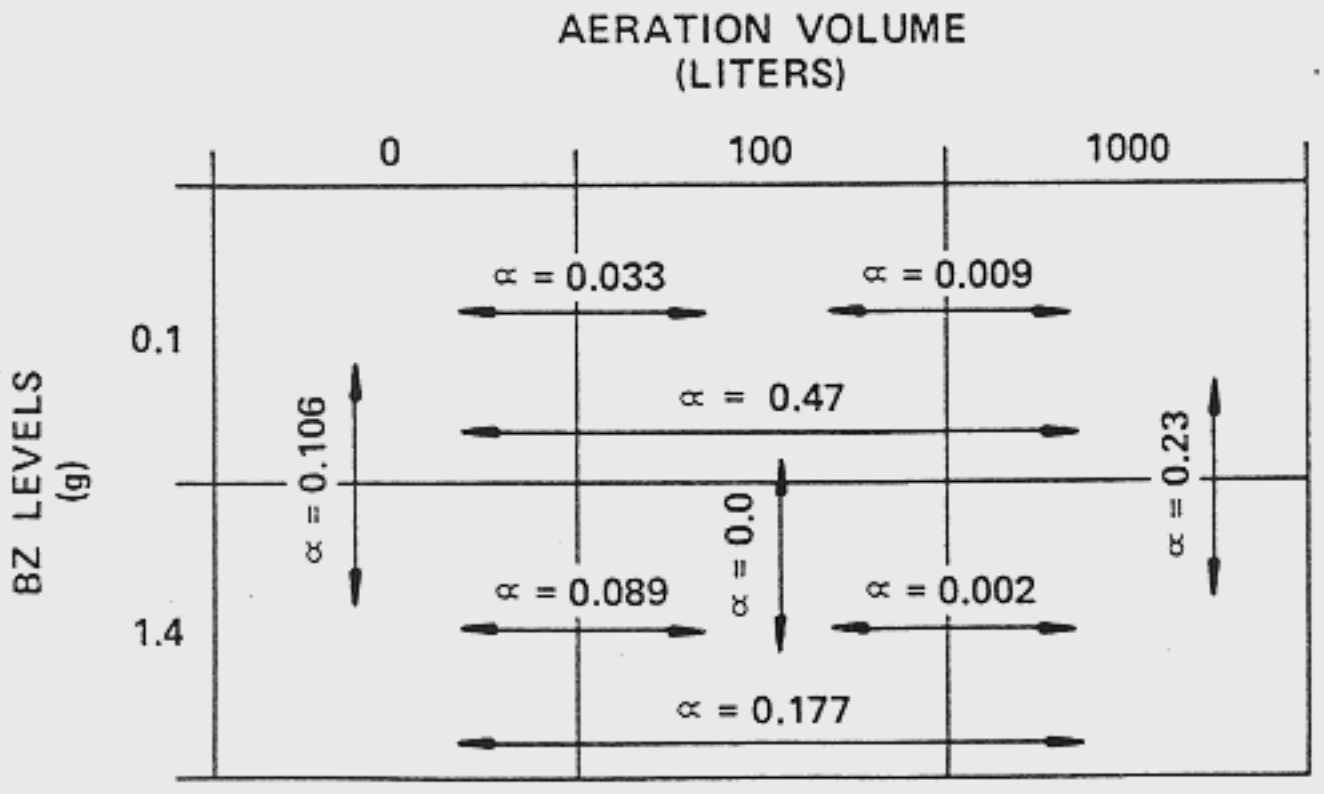
$$M/C = 14.901 = \chi^2_{0.11,5}$$

5.1.1.4 t-Test and F-Test.

Differences in the mean and variance between individual samples were checked by t-tests and F-tests (see tables 13 and 14). While differences were found to exist between the mean and variances of individual samples, no pattern was found which would indicate an effect on the amount of BZ recovered by either the aeration volume or the BZ level used.

Table 13. t-Test of Area Measurement Data

Levels at which H_0 would be rejected



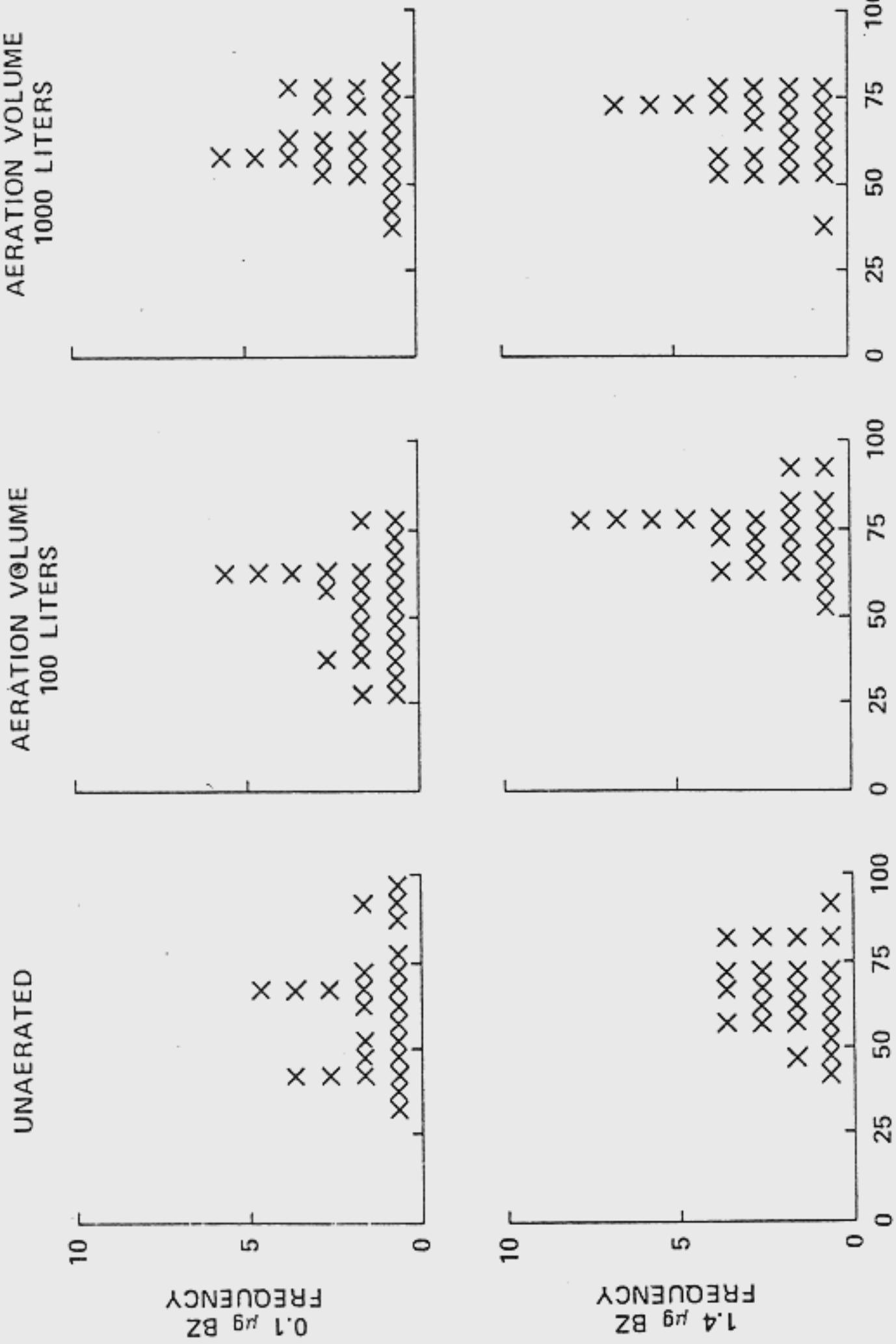
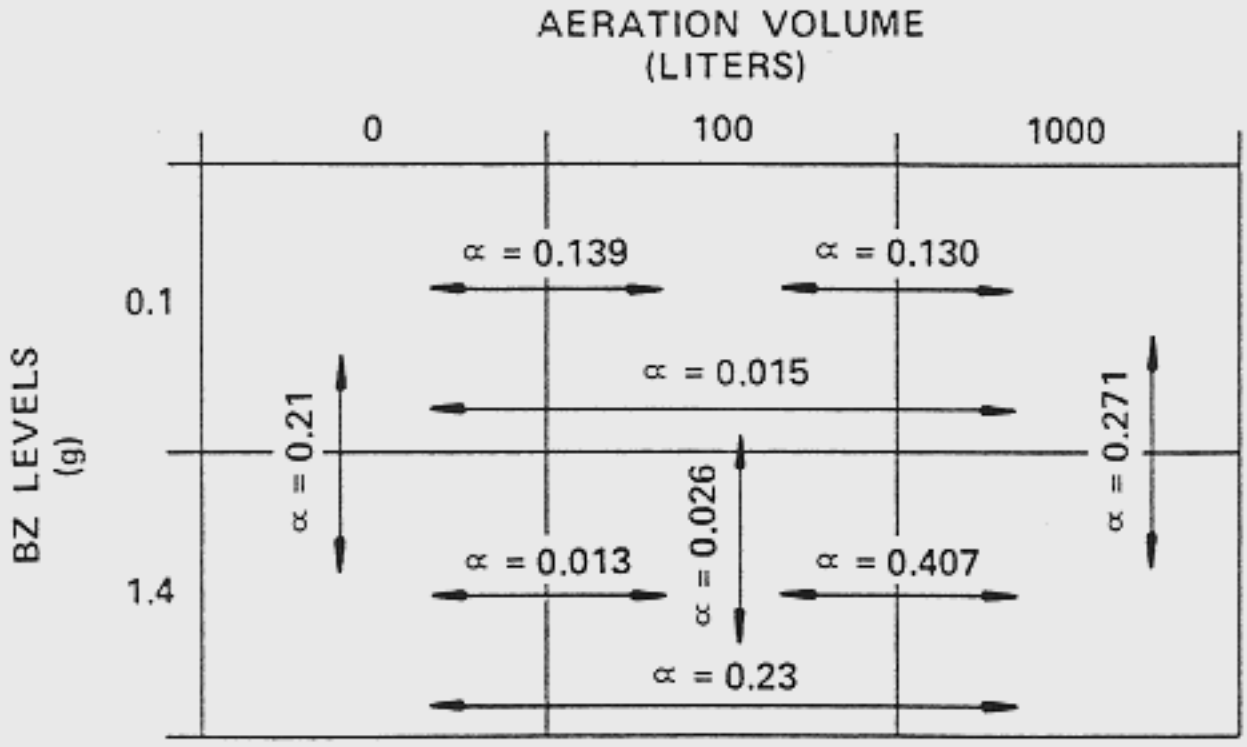


Figure 8. FREQUENCY DIAGRAM FOR AREA DATA OF TABLES 1 & 2

Table 14. F-Test of Area Measurement Data

Levels at which H_0 would be rejected



Area Measurement Method Versus Peak Height Measurement Method. Statistical analysis of the data showed that the peak height measurement method was more reliable than the area measurement method. The authors believe that this is true because it was possible to visually determine where the BZ peak began, but the change in slope frequently was not sufficient to trigger the electronic integrator at the true beginning and end of the BZ peak. This caused erroneous area count readings.

5.2 Water Studies.

The presence of active chlorine in water presents a potential problem for accurate analysis. Though BZ is stable to oxidants at pH 3-4[13] used in this assay, at a pH greater than 7, BZ at the 10-fold drinking water level is rapidly degraded. This is aptly illustrated in figures 3 and 4. The procedure developed to measure and destroy active chlorine is rapid and sufficiently accurate to preclude degradation of BZ samples prior to analysis.

Shown in figure 9 is the average recovery of BZ from tap water at various spike levels. The low recoveries at the low spike levels are due to intrinsic solubility of BZ in water.

From the data base,[7] the solubility of BZ base in water ranges from 11.8 ppm to 540 ppm. The data base also cites the solubility of BZ in CCl_4 as 4.5 gm/liter while the solubility in $CHCl_3$ is cited as 130 gm/liter. The distribution coefficient listed for CCl_4 is approximately 3.3×10^2. One may expect a far more favorable distribution coefficient with $CHCl_3$ due to the greater solubility of BZ in this solvent. From the data at the lowest level, the total loss of BZ is approximately 0.58 ppb. This reflects the ultimate efficiency one may expect using the procedure.

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The losses observed at the low levels of spiking were minimized by "salting" the BZ out of aqueous solution using 10 percent Na_2SO_4. Shown in table 8 are the results of using Na_2SO_4 to "salt out" BZ. This effect at the low level is appreciable and results in being able to quantitate BZ at one-quarter of the drinking water level (1ppb).

It was anticipated that under field conditions, large levels of contaminants would be present in process water. As part of this work, the effects of high levels of contaminants present along with the BZ were determined using the cleanup method in section 3.2.4.

The three contaminants studied were 3-quinuclidinol, sodium benzilate, and benzophenone. Sodium benzilate is highly soluble in water. Under acidic conditions such as in scrubbing for SO_2 and in venturi washing, it is converted to benzilic acid. Benzilic acid has a solubility of 168.2 mg/100 ml (1682 ppm).* This high solubility could result in benzilic acid being present in the final extract.

The anticipated degradation product of BZ due to incineration is benzophenone. This material has a solubility of 6.9 mg/100 ml (690 ppm).* Though benzophenone is a neutral, nonionic species, its inherent high solubility in water could result in some benzophenone not being completely removed by the initial cyclohexane wash.

Early in our study we found that benzophenone and benzilic acid, injected on-column with BZ, results in almost complete degradation of the BZ. Monsanto, under contract DA18-035-AMC-136(A)[14] and Sass[15] showed that the rate of degradation of BZ was increased when benzophenone or benzilate was present. BCL has shown that benzilate degrades to benzophenone when injected on-column.[14]

A study was performed to measure the adequacy of the cleanup technique to remove this interference. Table 7 shows that removal of these interferences by the extraction technique is reasonably adequate. Some losses of BZ were observed, but total destruction was prevented.

The detection limit for tap water, as determined by the method of Hubaux and Vos,[15] was found to be 3.2 ppb when all data are included (table 9). When the values at 40 ppb are excluded, a detection limit of 0.95 ppb is obtained (table 10). Detection limits were calculated at the 90 percent confidence level.

6. CONCLUSIONS

6.1 Employment of NPD for BZ Analysis.

The manufacturer of the NPD recommends that chlorinated solvents not be used. BZ can be quantitatively removed from aerosol filters with acidic aqueous solvents. Extraction of the BZ from the aqueous phase must be performed with neutral, low-boiling, halogen-free, water-immiscible, organic solvents if the NPD is employed. The use of alcohols, aldehydes, ketones, and esters is precluded due to their water solubility; leaving neutral hydrocarbons as the only viable extraction

solvents. Unfortunately, BZ has a low solubility in neutral hydrocarbons. Due to the intrinsic solubility of BZ in water, it is believed that even with multiple extractions of the aqueous phase with hydrocarbon, extraction efficiencies approaching those obtained with a chlorinated hydrocarbon would be hard to achieve. In addition, the inherent instability of the NPD precludes its use on a routine basis.

It is recommended that the NPD not be employed for routine analysis of BZ.

6.2 Employment of FID for BZ Analysis.

Our studies show that sodium metabisulfite is an effective reducing agent to remove active chlorine from process water. In order to preserve water samples, it is recommended that the samples be acidified to a pH of 4, and that the active chlorine be removed by the process described. At this pH, adsorption of BZ on the glass walls of containers is negligible. As a further precaution, the samples should be stored at 10°C or lower if there are long delays in analysis.

It has been the experience of these laboratory personnel that the routine use of an internal standard to quantitate trace levels of BZ by GC with any detector is a fundamental requirement. Day-to-day variations in the GC detector sensitivity require the employment of a standard directly in the solution being analyzed. We find that Michler's Ketone is a suitable material as a reference standard. It is easy to purify, highly stable in solution, and does not react with BZ. The only drawback is that the retention time of Michler's Ketone is longer than desired. However, this drawback does not appreciably add to the length of the analysis.

The effect of interferences on the analysis was investigated. The cleanup technique effectively removes these materials and allows the quantification of BZ to one-quarter the drinking water level (1 ppb).

The procedures developed at CSL and at BCL are virtually identical. The method must be performed by highly-trained personnel who understand the necessity of carrying out the complex steps in the analytical scheme correctly and diligently. The procedure is long and labor-intensive. It appears that there are no means of shortening the analysis. Carried out correctly, the method is capable of quantitating BZ in water with good precision. It is recommended that the procedures developed at CSL and BCL (using GC-MS with BZd_{10} as the internal standard) be employed to analyze process water, brines, and scrubber effluents. Presently, we do not feel that GC analysis is the best analytical tool to analyze a large number of filter samples. It is recommended that another analytical method be sought to analyze the large number of filter samples that will be generated every day at the actual demilitarization site.

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