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ABSTRACT

Title of Thesis : Quantitative Determination of Formaldehyde in Ambient Air

Name of Candidate : Wen-Shao (Cheryl) Chou
Master of Science
in Environmental Science - Toxics Option
1989

Thesis Directed by :

Dr. B. Kebbekus Date
Associate Chairman
Department of Chemical Engineering,
Chemistry & Environmental science

Formaldehyde has been shown in the laboratory to play a critical role in the chemistry of polluted air. The method which we discuss in this paper was evaluated under practical field conditions in the Northern New Jersey Staten Island Urban Air Toxics Project. Formaldehyde in ambient air is concentrated and derived by passing a known quantity of air through a silica column impregnated with 2,4-dinitrophenylhydrazine (DNPH). The silica is eluted with acetonitrile and the concentration of formaldehyde is determined by High Performance Liquid Chromatograph (HPLC) with UV detection. A description of procedural details for coating silica cartridges with 2,4-DNPH acidified with hydrochloric acid, the preparation of calibration standards, analytical testing, a series experiments of quality control and assurance and the results of atmospheric sampling in Carteret and Elizabeth are included.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made to my advisor, Dr. Barbara Kebbekus, for giving me the opportunity to join this interesting and challenging research topic. All through the year, under her careful guidance, I learned not only advanced analytical methods but techniques; moreover I learned practical experimental skills which will be very helpful in my future work. A special thanks goes to Dr. Dai for his valuable suggestions which helped me a lot during the year.

I should like to extend my appreciation to my husband and families for their love and support, and lastly I would also like to dedicate this thesis to my parents for their encouragement in pursuing higher education.

Quantitative Determination of Formaldehyde in Ambient Air

by

Wen-Shao (Cheryl) Chou

Thesis submitted to the faculty of the Graduate School of

the New Jersey Institute of Technology

in Partial fulfillment of the requirements for the degree of

Master of Science in Environmental Science - Toxics Option

1989

90

APPROVAL OF THESIS

Title of Thesis : Quantitative Determination of Formaldehyde in Ambient Air

Name of Candidate : Wen-Shao (Cheryl) Chou
Master of Science
in Environmental Science - Toxics Option 1989

Thesis and Abstract Approved by :

Dr. Barbara Kebbekus — Date
Professor of Chemistry & Environmental Science
Department of Chemical Engineering, Chemistry
& Environmental Science
Associate Chairman of the Division of Chemistry
Co-Director of the Air Pollution Research Laboratory

Dr. C. R. Huang — Date
Professor of Chemical Engineering
Department of Chemical Engineering, Chemistry
& Environmental Science

Dr. R. Trattner — Date
Professor of Chemistry & Environmental Science
Department of Chemical Engineering, Chemistry
& Environmental Science
Associate Chairman of the Division of Environmental Science

VITA

Name : Wen-Shao (Cheryl) Chou

Permanent Address :

Degree and Date To Be Conferred : Master of Science in Environmental Science - Toxics Option 1989

Date of Birth :

Place of Birth :

Collegiate Institutions	Date	Degree	Date of Degree
Taipei Medical College in Taiwan	1979 - 1984	B.S.	1987
New Jersey Institute of Technology	1987 - 1989	M.S.	1989

Major : Environmental Science - Toxics Option

Minor : Instrumental Analysis

Position Held : Research Assistant
Department of Chemical Engineering, Chemistry & Environmental Science
Air Pollution Research Laboratory
New Jersey Institute of Technology
Newark, New Jersey 07102

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FIGURES (continued)

FIGURES (continued)

FIGURES (continued)

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SECTION I

INTRODUCTION

(A): BACKGROUND

Carbonyl compounds, especially aldehydes and ketones, have been shown in the laboratory to play critical roles in the chemistry of polluted air and also play a key role in the photochemical smog-forming process [1]. They are emitted from the tailpipes of automobiles, are produced during the photooxidation of hydrocarbons, and are active participants in free radical chain reactions, such as those induced by hydroxyl and hydroperoxyl radicals [1,2].

Because of the key role of aldehydes and ketones in atmospheric chemistry, their analysis has received considerable attention [1]. Only very limited speciated aldehyde (formaldehyde, acetaldehyde, acrolein, crotoanaldehyde) data in source emissions and in ambient air are available in the literature despite the great need for these data in air quality assessment and health-related studies. Most of the published data is limited to formaldehyde which is not only an extremely important industrial chemical but also a toxic air contaminant on the EPA list of priority pollutants [3].

For the quantitative and qualitative determination of ambient pollutants such as formaldehyde in a particular

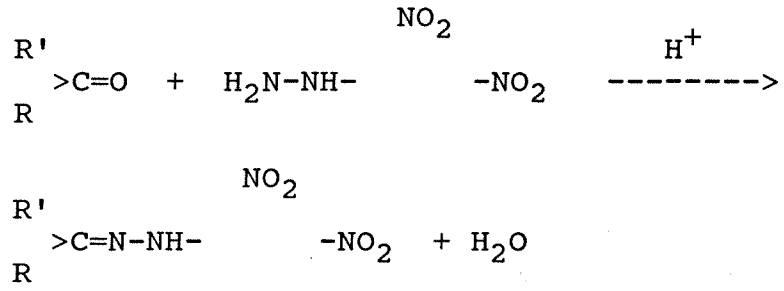
area, the United States Environmental Protection Agency (US EPA) and the New Jersey Department of Environmental Protection (NJDEP) are conducting a Project called the Staten Island / New Jersey Urban Air Toxics Project (SI/NJUATP) which is a three year project encompassing indoor as well as outdoor air sampling and analysis to determine levels of selected ambient organic compounds (VOCs) in air samples at four sites (two sites in Union County and two in Middlesex County) for formaldehyde, along with the improvement of the analytical method (Figure 1).

Several sensitive, specific, and convenient analytical methods for measuring and determining the very low concentrations (ppb) of formaldehyde gas in ambient air have been described in publications [4]. Selecting the appropriate sampling and analytical technique is of critical importance and must be consistent with the type of environment to be sampled and the anticipated concentration levels [5].

The method which we used in this project was developed by Silvestre B. Tejada and John E. Sigsby, Jr. for the US EPA's Mobile Source Emissions Research Branch (MSERB), Atmospheric Sciences Research and Exposure Assessment Laboratory, Research Triangle Park, NC.

The following Experimental Section is done according to a procedure developed by Tejada [3,6].

The method widely used to date is based on the reaction of organic carbonyls (aldehydes and ketones) with 2,4-dinitrophenylhydrazine (DNPH) in the presence of an acid to form stable derivatives (dinitrophenylhydrazones, here often termed "hydrazones") according to the following equations:



R and R' can be any organic group or hydrogen [6].

Section II describes experimental details for collecting formaldehyde in ambient air by passing the air sample through a silica gel Sep-PAK cartridge coated with acidified 2,4-dinitrophenylhydrazine (DNPH). The resulting hydrazone derivatives are extracted with acetonitrile and quantified by high performance liquid chromatography separation, with UV detection at 354 nm. Formaldehyde was measurable for concentrations greater than 0.1 ppbv [2]. The analytical data were reported to both the US EPA and the NJDEP every quarter. At the same time, duplicates were sent to EPA, and ongoing analysis of data were being carried out. EPA's data should be the only one used for comparison with the results of our laboratory.

The coated cartridge method described earlier is

simpler than most procedures in the literature, is applicable to a variety of sampling situations and can be applied to the determination of carbonyl compounds in automotive emissions as well as in residential indoor and ambient outdoor atmospheres [6].

(B): **PHYSICAL PROPERTIES OF FORMALDEHYDE**

Formaldehyde (HCHO, MW 30.03) is a flammable colorless gas at ordinary temperature. On chilling, it condenses to form a liquid that boils at - 19^{o} C and freezes at - 118^{o} C. The gas has a pungent suffocating odor. It is intensely irritating to the mucous membranes of the eyes, nose, and upper respiratory tract, and high concentrations are intolerable. Formaldehyde is very reactive, combines readily with many substances, and polymerizes easily. The most commonly encountered aqueous solution, often referred to as formalin, contains about 37% by weight of formaldehyde gas, usually with 10 - 15% methanol added to prevent polymerization [5 & 7-10].

(C): **CHEMICAL PROPERTIES OF FORMALDEHYDE**

Formaldehyde is a highly reactive and unstable molecule possessing a single carbonyl group flanked by two hydrogen atoms, $H_2C=O$. Formaldehyde, when irradiated in a dilute mixture of NO_2 in air, promotes the formation of

photochemical ozone. Even in the absence of NO_x, formaldehyde has been observed to induce photochemical oxidation of higher hydrocarbons when exposed to ultraviolet light. Most reactions are of three types, as illustrated by the following reaction sequences [5 & 7-10].

Oxidation-Reduction

$$2\ HCHO \rightarrow HCOOH + CH_3OH$$

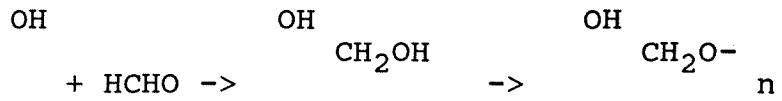
Addition

$$HCHO + NaHSO_3 \rightarrow HOCH_2SO_3Na$$

Condensation

$$HCHO + R'(R'')CHCOR \rightarrow HOCHCR'(R'')COR$$

Polymerization (Methylol Formation)



(D): **OCCUPATIONAL AND ENVIRONMENTAL EXPOSURE**

The current federal standard for formaldehyde exposure in the workplace calls for an 8-hr time-weighted-average exposure limit (TWA = 8 hrs./day of Threshold Limit Value) of 3 ppm, a 10 ppm short-term exposure limit (STEL = 15 minutes TWA) and a 5 ppm ceiling which is the upper concentration limit and should never be exceed at any time and any place [11]. In 1976, the National Institute for Occupational Safety and Health (NIOSH) recommended that the limit for an 8-hr time-weighted-average

exposure to formaldehyde be reduced to 1 ppm [12].

Substantial exposure of more than 1.5 million full- or part-time workers to formaldehyde has been noted in several industries, with sample means of 1 ppm or more in the following industries and occupations: formaldehyde production including the manufacture of rubber, photographic film, leather, explosives, dyes, cosmetics, corrosion inhibitors, and embalming fluids; resin and plastic materials production; apparel manufacture; plywood, particleboard, and wood furniture manufacture; paper and paperboard manufacture; urea-formaldehyde foam insulation dealers and installers; mushroom farms; funeral homes; and pathology and biology laboratories. High concentrations of formaldehyde have also been reported in individual air samples from iron foundries and plastic molding facilities [13-17].

Numerous sources of environmental exposure have been reported. These include motor vehicle exhaust, especially in large cities; the burning of gas, oil, coal, wood, and rubbish as well as photochemical smog [18 - 20].

The most important source of indoor formaldehyde exposure is formaldehyde resins in wood products such as plywood panelling, particle board underlays, and fiberboard furniture [5].

Formaldehyde is formed in the atmosphere by chemical breakdown of higher hydrocarbons, and emitted into the atmosphere as a by-product of incomplete combustion of many organic substances, and from certain chemical industrics and operations. Several methods are available for determining the level of formaldehyde in air. Most of the available methods have been developed for use in occupational settings [5], where concentrations can be relatively high and detection limits are in the ppm range.

(E): **RISKS ASSOCIATED WITH FORMALDEHYDE**

Risk is the potential realization of unwanted consequences of an action. The available data collected during the project will be used to develop the risk of formaldehyde exposure in humans.

The data on the carcinogenicity of formaldehyde from experimental and epidemiologic studies have demonstrated that formaldehyde produces nasal cancer in rats and mice at 14 ppm and in rats at 6 ppm [5], which is within the domain of present permissible human exposure (8-hr time-weighted average of 3 ppm, a 5 ppm ceiling, and a 10 ppm short-term exposure limit) [11]. Formaldehyde is carcinogenic and mutagenic in the laboratory, but the extent of the carcinogenic risk of formaldehyde exposure in humans has not yet been defined.

SECTION II

EXPERIMENTAL

(A): APPARATUS AND EQUIPMENT

1. All-glass tube container with polypropylene screw cap
2. Melting point apparatus
3. Timers
4. Cartridge drying manifold with multiple standard male Luer connectors (at least 5). The manifold is connected to a cylinder of nitrogen (Figure 2).
5. 10-mL and 2-mL syringe with Luer end fitting
6. Syringe rack
7. Polyethylene gloves
8. Pasteur pipet equipped with a medicine dropper rubber bulb.
9. Desiccator
10. Soap bubble flow meter
11. 0.45 um disposable disk filters

(B): REAGENTS

1. 2,4-Dinitrophenylhydrazine - Fluka, reagent grade
2. Acetonitrile - Fluka, Puriss grade
3. Water - resin filtered deionized water by Millipore Water System apparatus.
4. Concentrated hydrochloric acid - analytical grade

5. Concentrated sulfuric acid - analytical grade
6. Formaldehyde solution - Fluka guarantee grade
7. 95% Ethanol or methanol
8. Nitrogen gas - zero grade, Liquid Carbonic
9. Sep-PAK silica gel cartridge, purchased from Waters Associates (Milford, MA) contain about 0.7 g. of silica gel (approximately 100 mesh) compactly sealed in a plastic tube (1 cm 0.d. * 2 cm long) by inert plastic filter frits. The cartridge body terminates at both ends as small tubes that can be conveniently connected to a standard male Luer syringe port.

(C): **PURIFICATION OF 2,4-DINITROPHENYLHYDRAZINE (DNPH) REAGENT**

DNPH is purified by multiple recrystallization in HPLC grade ACN. Prepare a supersaturated solution of DNPH by boiling excess DNPH in 200 mL of ACN. Transfer the supernatant to a beaker through fluted filter paper and allow the clear filtrate to cool gradually to 40-60^{o} C by putting the beaker on a low heat plate. Allow about 95% of the solvent to evaporate slowly at this temperature range. This maximizes crystal size and purity. Decant the last remaining saturated solution to waste and rinse the crystals twice with about three times their apparent volume of ACN.

Transfer the crystals to another clean beaker, add 200

mL of ACN, heat to boiling, and again allow the crystals to grow slowly at 40-60^{o} C until 95% of the solvent has evaporated. Nitrogen gas may be used to enhance the evaporation of the solvent. Repeat the rinsing process. The large crystals obtained in the purification process not only enhance the removal of surface impurities but also minimize the loss of the purified material during rinsing (due to decreased solubility rate of the crystals) as a direct consequence of significant decrease in specific surface area of the crystals.

Take an aliquot of the second rinse, dilute 10 fold with ACN, acidify with hydrochloric acid, and analyze by HPLC. The impurity level should be comparable to that shown in Figure 3. Repeat the crystallization process with ACN if the impurity level is unsatisfactory. Store the purified crystals in a 25 mL all- glass reagent bottle, capped and sealed with parafilm. The bottle is repeatedly filled with ACN above the purified crystals at all times as the source of saturated DNPH stock solution for various analytical applications. The purified crystals should be stored in a refrigerator and should not be allowed to contact the carbonyl-contaminated laboratory air except for a brief moment when additional solvent is being added to the crystal reservoir [3,6].

(D): **PREPARATION OF STOCK DNPH REAGENT**

Before using the saturated DNPH solution, pour off the original solution (which might become contaminated during the storage) and rinse the crystals again to get a fresh purified DNPH solution. Shake the mixture gently and allow it to stand overnight. The saturated solution above the large excess of purified crystals is used as stock reagent in the preparation of the absorbing solution. Use a clean pipet and a rubber bulb when taking aliquots of the saturated solution. Do not pour from the reagent bottle [3,6]. Impurity level of the stock solution is checked by HPLC analysis. The impurity level should be similar to that shown in Figure 3.

(E): **PREPARATION OF DNPH-COATED SEP-PAK SILICA CARTRIDGE**

This procedure must be performed in a very low aldehyde background atmosphere. All glassware and plastic ware must be scrupulously cleaned and rinsed with deionized water and aldehyde-free ACN. Contact of reagents with laboratory air must be minimized. Polyethylene gloves are worn when handling the cartridges [3,6].

(1) **DNPH COATING SOLUTION**

Dilute 12.5 mL of the saturated DNPH stock solution to 500 mL with ACN in a volumetric flask. Acidify with 0.5 mL of concentrated HCl. Dispense an aliquot to a sample vial

and check the impurity level of the acidified solution by HPLC analysis using a gradient program similar to those given in the Instrumentation and Optimization of Chromatographic Conditions section I and II. [3,6]. The impurity level may be larger than that shown in Figure 1, but should be still acceptable (Figure 4).

(2) **COATING PROCEDURE**

Open the Sep-PAK packet and connect the long end of the cartridge to a 10-mL syringe and place in the syringe rack. Prepare as many cartridges and syringes as the syringe rack can hold. For lot consistency, it is important that a large batch is coated in assembly line fashion. In our experiment, 5 cartridges constitutes one batch (Figure 5). Each cartridge is washed by gravity feed elution of 10 mL of ACN from a syringe to a waste reservoir. Remove any air bubbles which may be trapped between the syringe and the silica cartridge by displacing it with ACN in the syringe. A long tipped disposable Pasteur pipet equipped with medicine dropper rubber bulb is convenient for this purpose.

Once the ACN rinse solution is completely drained into the cartridge and the effluent flow at the outlet of the cartridge has stopped, dispense 7 mL of acidified DNPH-coating solution into each of the syringes. Air is usually trapped between the cartridge and syringe and should be displaced with the coating reagent in the same manner

mentioned above. Allow the coating reagent to drain by gravity until flow at the other end of the cartridge stops. Wick the excess liquid from the outlet of each of the cartridges with clean tissue paper.

Remove the batch of cartridges from the syringes and connect the long ends of the cartridges to the Luer ports of the drying manifold (see Figure 2). The cartridges are dried in batches of five at a time using nitrogen at a controlled flow rate for 15 minutes. The flow rate should be monitored by a rotameter. After 15 minutes drying, stop the nitrogen flow. Each coated cartridge is capped at both ends with plastic male Luer plugs and then placed in individual glass tube container with polypropylene screw cap. Pre-printed labels containing the sampling date and site are then placed on the side of every glass tube container. Store the DNPH-coated cartridges in the refrigerator as soon as possible [3,6].

The cartridges are usually mass produced in lots. Randomly select a cartridge from the lot and determine background impurity levels according to procedures detailed in the HPLC Analysis section. The range of typical concentrations of impurities as hydrazones when a cartridge is eluted with 5 mL ACN should be acceptable for aldehydes and ketones respectively, especially formaldehyde (see Figure 4).

(F): **PREPARATION OF CARBONYL-DNPH DERIVATIVE**

A solution of the formaldehyde carbonyl compound in ethanol is prepared by dissolving 0.5 g. of the compound in 20 mL of 95% ethanol. To 0.4 g. of 2,4-dinitrophenylhydrazine in a 25-mL Erlenmeyer flask is added 2 mL of concentrated sulfuric acid. Water (3 mL) is added dropwise, with swirling or stirring until solution is complete. To this warm solution is added 10 mL of 95% ethanol. The freshly prepared 2,4-dinitrophenylhydrazine solution is added, and the resulting mixture is allowed to stand at room temperature. Crystallization of the 2,4-dinitrophenylhydrazone usually occurs within 5 to 10 minutes. If no precipitate is formed, the mixture is allowed to stand overnight.

Recrystallization can usually be effected in the following way. The 2,4-dinitrophenylhydrazone is heated on a hot plate with 30 mL of ethanol (95%). If solution occurs immediately, water is added slowly until the cloud point is reached or until a maximum of 5 mL of water has been added. If the dinitrophenylhydrazone does not dissolve, ethyl acetate is added slowly to the hot mixture until solution is attained. The hot solution is filtered through a fluted filter and stands at room temperature until crystallization is complete (about 12 hours).

Filter the colored precipitate and rinse with ACN twice through a flute paper. Then, place the free DNPH

formaldehyde hydrazone crystals in a desiccator until the weight is stable [3,6].

(G): **PREPARATION OF STANDARDS**

Prepare standard stock solutions containing free DNPH formaldehyde hydrazone derivative by dissolving accurately weighed amounts in a 100 mL volumetric flask with acetonitrile (ACN). Prepare a working calibration standard from the standard stock solutions. Nominal concentrations of the derivative ranged from 0.5 mg/L to 20.7 mg/L. Store all standard solutions in the refrigerator. They should be stable for several months. Use standard samples to make calibration table. A typical calibration run is illustrated in Figures 6 - 11.

(H): **SAMPLING**

Sampling has been carried out at the Mattano Park in Elizabeth, and the Carteret sites since July 27th, 1987 (Figure 1). RENU and KUSU samplers were installed on the roof of the Police Station Building in Carteret. HEMA sampler was installed at Mattano Park in Elizabeth. Seven DNPH-coated Sep-PAK cartridges (two for each sampler and one for the blank) are used on each sampling trip, samples were taken for twenty-four hours, once per six days with few interruptions.

Formaldehyde sampling procedure is as follows [3,6]:

1. Record the date, site, and operator on the sampling sheet, in the formaldehyde record area.

2. The coated cartridges should be allowed to warm to room temperature in a capped vial prior to connection to the sampling train. Remove one cartridge from vial, remove plastic plugs from both ends and press into the tubing on the pump. The cartridge should be connected to the sampling train so that its long end becomes the sample inlet. Store the empty vial inside the pump box.

3. Turn on the pump and adjust required flow setting point.

4. Record the start time and flow setting on the sample sheet.

5. Return the unused cartridge to laboratory as the blank sample.

6. The next day, after the sampling is completed, read and record the final flow. Record the end time of the sample. Turn off the pump. Remove the trap and plug both ends of the cartridge before replacing it in the vial.

7. On return to the laboratory, place the traps in the appropriate box in the refrigerator as soon as possible.

Typical flow rate through 2 cartridges in series is about 0.8 L/min. In practical field sampling, the maximum flow rate obtained with two cartridges in series is about 300-500 mL/min for 24 hours at different sampling

sites. The sampling train using the cartridges is shown schematically in Figure 12.

An individual pumping system for each cartridge sampler in conjunction with a calibrated flow meter is recommended, especially at low sample flow rates and short sampling times. The flow meter and pumping system should be periodically checked against a soap bubble flow meter. Then, the flow rate calibration curve is plotted using the Engineering Graphic software package. For example, the calibration curve for the KUSU pump is shown in Figure 13.

(I): HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) ANALYSIS

(1) INSTRUMENTATION AND OPTIMIZATION OF CHROMATOGRAPHIC CONDITIONS

HPLC chromatographic conditions are optimized for the separation of DNPH derivatives of formaldehyde, acetaldehyde, acrolein, propionaldehyde, benzaldehyde and ketones. The gradient HPLC LDC/Milton Roy system conditions at ambient temperature were as follows [3,6] (Figure 14):

A Dupont Zorbax ODS analytical column (4.6 mm I.D. * 250 mm)

A Dupont Zorbax ODS guard column (4.6 mm I.D. * 50 mm)

A 20 uL injection loop

A variable wavelength UV-VIS (354 nm) detector

Absorbance range 0.05 - 0.1

An electronic integrator

Pressure: 1000 psi - 6000 psi

Flow: 1 mL per minute

Solvent of metering pump A : Deionized water

Solvent of metering pump B : Acetonitrile

Linear gradient program :	Mobile phase	Time(min)
	60% B to 100% B	10
	100% B	2
	100% B to 60% B	1
	60% B	5

(2) **ELUTION PROCEDURE**

Allow the cartridge to reach ambient temperature in its glass container prior to elution.

Elution Procedure [3,6] (Figure 15) :

1. Remove the cartridge from its glass bottle.
2. Remove the plastic plugs.
3. Connect the short end (outlet end during sampling) of the cartridge to a clean 10-mL syringe (without the plunger).
4. Place the syringe on a syringe holder or rack.
5. Place a 5-mL volumetric flask underneath the cartridge. Make sure that the cartridge extends into the collecting flask.
6. Dispense about 6 mL of acetonitrile (ACN) into the

syringe and let the ACN flow through the cartridge by gravity. To assure continuous flow, remove any air that is trapped between the cartridge filter and the syringe Luer tip by displacing it with ACN. A long tipped Pasteur pipet is convenient for this purpose.

7. Bring the eluate to the 5-mL mark with ACN and shake/stir to make sure that the resulting solution is homogeneous.
8. Use 2-mL syringe to draw the sample from the sample flask. Inject it through a 0.45 um disc filter into the 20 ul sampling loop, then begin analysis.
9. Clean the 2-mL syringe with methanol a couple of times before the next use.

Cartridge samples should not be eluted if they cannot be analyzed within 24 hours. They should be stored, preferably plugged at both ends, in capped all glass reagent bottles in the refrigerator.

(J): **COMPOUND IDENTIFICATION**

The retention times of formaldehyde hydrazone standards are very important because formaldehyde in the samples is identified by comparison of its retention times. In order to get a reasonable estimate of the formaldehyde hydrazone, retention times of synthetic standards and analytical

samples have been reproduced by multiple injections to get each control chart. For example, we compared the retention times of standards with samples from January to April 1989 (Table 1, Figures 16 and 17). We found that the retention time of formaldehyde hydrazone is around 6.88 - 8.15 minutes in our final analysis. After analysis, we can add a little high concentration standard solution to the sample and reanalyze. The formaldehyde hydrazone peak increases, so it easy to be sure which is the formaldehyde peak. This is especially helpful for distinguishing very small peaks from the other peaks. Therefore, formaldehyde is identified with high degree of confidence.

(K): **CALCULATIONS**

The concentration C in parts per billion (ppb, v/v) of the formaldehyde is calculated according to the following equations [3,6]:

$C' = a * As + b$

$C = C' * Vs * Vstd * 10^9 / (t * f * M)$

where C' = concentration in g/L of the DNPH derivative of the formaldehyde in the sample solution

As = area of sample

a = slope of standard solution calibration curve

b = intercept of standard solution calibration curve

C = concentration in parts per billion (ppb, v/v) of the formaldehyde

Vs = volume of diluted sample solution, 0.005 liter

Vstd = mole volume under standard situation, 24.5 liter

t = sampling time in minutes

f = flow rate in liters per minute

M = molecular weight of the DNPH derivative of the Formaldehyde ($C_7H_6N_4O_4$), 210.17 g/mole

These calculations are conveniently done using linear regression with the Lotus 1-2-3 software package. We selected analytical chromatograms of KUSU sampler in Carteret in January 22nd 1989 (Figures 18 and 19) for an example, showing a completed data and report form (Table 2).

SECTION III

QUALITY CONTROL AND ASSURANCE

(A): REPRODUCIBILITY OF FORMALDEHYDE HYDRAZONE HPLC

Past experiences with formaldehyde hydrazone standards had shown that reproducibility at about 0.0093 g/L level at about 0.97 % relative standard deviation (RSD) (10 runs over 8 months) had been achieved in peak area measurements under favorable conditions.

Under similar analytical conditions, the results of replicates (8 runs over 9 months) of our standards, which cover the usual range of concentrations in ambient air are shown in Table 3 and Figures 20-24. As shown in Table 3, the RSD% of the different concentrations of standards are within 9%.

The formaldehyde hydrazone standard solutions have been sealed and stored at room temperature for more than nine months without significant change in concentration.

(B): INDOOR AND OUTDOOR COMPARISON STUDY FOR AIR SAMPLING

As more of these comparisons are made, the confidence in the technique will grow. In order to assess the utility and quality of the DNPH-silica gel cartridge technique for sampling formaldehyde in ambient air, both indoor and outdoor parallel air sampling were compared.

(1) **DUPLICATE SAMPLING**

The study was done for four continuous weeks. Two ambient air samplers, HEMA and KUSU, were installed at Mattano Park in Elizabeth. HEMA was our regular detecting sampler. Compared with HEMA, KUSU would be the replicate sampler. Ambient atmospheres were sampled at about 500 mL/min with two cartridges in series for 24 hours. The final analytical results are shown in Table 4. The deviation between the sample averages 7.20% +/- 5.74%. There was little difference between the two detected values. The reproducibility is good.

(2) **INTERLABORATORY COMPARISON STUDY**

As part of the SI/NJUAT project, a parallel sampling called a "Shootout" was held by EPA at Susan Wagner High School in Staten Island , New York. The objective of this project was to assure the quality of the project data. For four days, samples were collected simultaneously and analyzed by the individual laboratories involved in this project.

"Shootout #2" was held during the week of July 25, 1988. Each organization performed sampling during four dry days. An ambient air formaldehyde sampler was installed on the roof of Susan Wagner High School. Ambient atmospheres were sampled at about 500 mL/min with two cartridges in series. All samples were processed according to procedural

details for formaldehyde in the Experimental Section. The final analytical results were reported to EPA and should be used for comparison with the results of other laboratories. The data can be used for qualitative comparisons of the different sampling and analytical methods being used in the study. Comparing our results for formaldehyde with the values from EPA, the % difference is within 17.6% (Table 5).

(3) AGREEMENT BETWEEN NJIT AND EPA STANDARDS

In order to evaluate the quality of preparation of carbonyl-DNPH derivatives and standard solutions, we had an opportunity to compare with primary standards since EPA supplied us with a set of "pure" derivative crystals (formaldehyde, acetaldehyde, etc.) to use as analytical standards for the "Round Robin" project, which is explained in Section IV.

Under favorable analytical conditions, the reproducibility of formaldehyde from a five carbonyl calibration mix was within 12% RSD (5 runs over 6 months) (Table 6). Here, we only show the comparison of the average concentration of NJIT's and EPA's formaldehyde hydrazone standard solution in Table 7. The % difference is within 11.4%, except for concentration 0.005g/L ACN (16.7%).

SECTION IV

ROUND ROBIN ANALYSIS OF ALDEHYDES ON DNPH-COATED SILICA GEL CARTRIDGES

(A): INTRODUCTION

The "Round Robin" was initiated by Mobile Source Emissions Research Branch (MSERB) of USEPA to assess the utility of the cartridge technique for sampling aldehydes in mobile sources.

While formaldehyde is the only aldehyde presently recognized by those concerned with regulation, several others are showing promise of coming to the fore. These include acetaldehyde, acrolein, propionaldehyde and benzaldehyde. The concern is primarily from those in the "toxics" field and is currently focused on alternative - fueled vehicles. The twenty participating laboratories were solicited through official correspondence and/or through the Coordinating Research Council (CRC) of the Air Pollution Research Advisory Committee (APRAC).

(B): EXPERIMENTAL

(1) SAMPLES AND BLANKS

A set of pure derivative crystals to use as analytical standards and a set of samples were sent to participating laboratories as follows :

5 vials containing "pure derivative crystals

1 vial Formaldehyde hydrazone standard

1 vial Acetaldehyde hydrazone standard

1 vial Acrolein hydrazone standard

1 vial Propionaldehyde hydrazone standard

1 vial Benzaldehyde hydrazone standard

3 DNPH-coated blank cartridges

3 DNPH-coated cartridges spiked with standard hydrazones at different concentration levels.

1 DNPH-coated cartridge exposed to a known volume of diluted automotive exhaust.

A few sample sets (designated as control samples) were retained and analyzed by MSERB.

(2) **HPLC ANALYSIS**

We used HPLC chromatographic conditions that were described in detail in Section II(J) as currently practiced in our laboratories except that the flow was increased to flow 1.5 mL/min and the following gradient program was used : linear gradient from 60% to 75% ACN in 20 minutes, linear gradient from 75% to 100% ACN in 5 minutes, 5 minutes hold at 100% ACN, then reversed gradient from 100% to 60% ACN. At least 9 minutes equilibration at 60% ACN was allowed before the next sample injection.

(3) **PREPARATION OF STANDARDS**

Following the procedure of Section II(H), we prepared formaldehyde, acetaldehyde , acrolein, propionaldehyde and benzaldehyde hydrazone standards. The retention times of aldehyde hydrazone standards were used for compound identifications. At the same time, a standard solution containing 5 standard DNPH derivatives was prepared as a mixture of individual volume aliquots in a 100 mL volumetric flask with ACN (Figures 25-29). Finally, five different aldehyde hydrazone standard calibrations were done, as shown in Figures 30-34. The correlation coefficients for each calibration were very high for each standard hydrazone. Then, the five hydrazone standards were used to quantitate our results and all results were reported as DNPH derivatives in ug/cartridge.

(C): **RESULTS AND DISCUSSION**

The results from individual laboratories were logged into a Lotus spreadsheet as they were received. The average value is calculated and is used in the statistical data reduction.

All laboratories are coded. EPA's code is "A" which is obvious from the number of replicates and should be the one used for comparison to the results of other laboratories. The code for our laboratory is "O".

(1) **BLANK CARTRIDGE DATA SET**

The analytical data for the cartridges blanks are summarized in Table 8. Figure 35 shows bar graphs for formaldehyde and acetaldehyde in the blank cartridges as analyzed by the individual laboratories.

(2) **THE SPIKED CARTRIDGE DATA SET**

These data set contains three subsets, Level 1, Level 2 and Level 3 (Table 9 and Figure 36).

(3) **THE EXHAUST DATA SET**

The exhaust samples consisted of 13 sets of 4 cartridges which were used to collect diluted exhaust samples from a gasoline-powered vehicle. Four parallel samples were collected during the hot test phase for each of the thirteen repetitive operations of the vehicle using the Federal Test Procedure (FTP). Table 10 shows the exhaust sample data. The formaldehyde results are graphically summarized in Figures 37 and 38.

(D): **CONCLUSIONS**

A round robin study has been completed for the group at EPA who are involved with formaldehyde sampling. A series of loaded traps and several phenylhydrazone standard materials were supplied to us. Our results for formaldehyde are summarized:

Formaldehyde Round Robin Data

Cartridge	Formaldehyde EPA	Formaldehyde NJIT	% Difference
Blank	0.74	0.86	----
Spike 1	5.78	5.44	5.9%
Spike 2	45.67	45.92	0.55%
Spike 3	113.53	112.07	1.3%
Exhaust Sample	6.327	6.98	10.3%

The results for propionaldehyde and benzaldehyde agreed within about 15% for the standards and were within the range of the EPA's results for the exhaust sample . However, our results for acetaldehyde and acrolein were not good. We have not explored the reasons for this non-agreement, but high blanks were found for these compounds. We could consider adding propionaldehyde and benzaldehyde to our analyses, however, we would have to prepare the standard compounds for these, since EPA supplied us with the standards for the Round Robin.

SECTION V

RESULTS AND DISCUSSION

(A) STATISTICAL ANALYSIS OF FORMALDEHYDE DATA

Table 11 presents the data for formaldehyde on a weekly time series in Carteret and Elizabeth from June 1988 to 1989. The whole year's data distribution was plotted in Figures 39-40. Comparing the average between two sites, the formaldehyde concentration in Elizabeth was a little higher than in Carteret. The average of two sites was about 3.99 ppb. Both maximums occurred in summer (June - August) and minimums occurred in winter (December - March). The winter and summer show a large difference in formaldehyde levels because they are affected by different meteorological conditions and because the influence of space heating be easily identified.

In order to trace the formaldehyde concentration with the change of seasonal weather condition, Table 12 listed statistical average concentrations. The average values were calculated as the following steps: The first average value contained the first four weekly data. Then, the second through fifth weekly data was averaged. The computation proceeded this way until the last data was calculated, containing the last four weekly data of the original series. The trend of statistic average concentration for

formaldehyde in Carteret and Elizabeth can be roughly described as follows (Figures 41-42):

(1) The higher concentrations mostly occurred in two sites between June and August (summer time).

(2) For Elizabeth site described from late August 1988 to May 1989, the trend was moving up and down around 3 - 5 ppb which was lower than in summer and there was no significant change during the time.

(3) For Carteret site described during the same time period, the trend was more unstable and the maximum happened in October. Because three months data (November - January) were not included for seasonal comparison, it was hard to describe the seasonal changes. But, we still see the same trends as in Elizabeth, that is, the average concentrations were much lower in winter than in summer.

(B) **THE IMPURITIES OF THE BLANKS**

From a series of analytical results, the impurity level in the blank cartridges was mostly acceptable, as shown in Figure 43, but some appeared high, like Figure 44.

Figure 44 shows carbonyl profiles of background impurities observed from three randomly selected DNPH-coated silica unexposed blank cartridges which were prepared at different times in the analytical chemistry laboratory. The profiles show that these unexposed cartridges interfered

with the quantitation of the carbonyl compounds, especially formaldehyde. The problem may be caused by any of the procedures from purification of DNPH reagent to preparation of DNPH-coated silica cartridge which is detailed in Section II (C) - (E). We attempted to decrease the background impurities by keeping the fume hood open all day and night before and during experimental work and by doing no other experiments at the same time, to keep a low aldehyde background in the atmosphere. Then, the DNPH-coated cartridges were stored in the refrigerator properly to eliminate moisture contamination. The results indicated that the concentrations of formaldehyde in blank cartridges were decreased and more acceptable after these precautions were taken.

(C) OZONE INTERFERENCE WITH FORMALDEHYDE MEASUREMENTS

For short-term respiratory effects of formaldehyde, peak concentrations and episodes are important for pollutants such as ozone [21]. A preliminary investigation of ozone interference with formaldehyde measurements was made, using samples taken at Tiernan Hall, Newark. A copper tubing inlet coated with potassium iodide, as recommended by Tejada of EPA, was used as a pretreatment to remove the ozone. Similar inlet coated with sodium thiosulfate was also tried.

The formaldehyde appears to be reduced by 10-30% when

ozone is not removed. The amount of formaldehyde loss does not seem to be related to the ozone concentration at the time of sampling. The iodide denuder increased the formaldehyde detected in all cases, while the thiosulfate appeared to give erratic results, sometime increasing the formaldehyde detected, and sometimes showing no positive effect. The results are listed in Table 13. Further study will be done to determine the best way of removing the ozone or reducing its effect.

SECTION VI.

CONCLUSION

The New Jersey Institute of Technology has had a long history of maintaining an analytical air pollution program and thus is able to draw upon its past experience in examining problems and correcting them. This has been especially evident in the analysis of formaldehyde where problems in the earlier part of 1988 has resulted in the invalidation of some data. The quality assurance for the DNPH method with respect to formaldehyde samples has been in place. However, according to the results of presented here, we conclude the following and make recommendations for further research :

(1) The cartridge is very convenient for field applications. The advantages we see in the cartridges are, handling ease - no glassware or liquids during the sampling phase, portability and ease of shipping.

(2) We can make up the cartridges ahead when the workload is appropriate and store them for use later in a refrigerator for over a month without significant deterioration. Even EPA's sampled traps, when properly packed, can be sent back to EPA's laboratory for analysis within about few days without compromise of sample integrity.

(3) Significantly higher analytical sensitivity is attainable with the cartridge method due to high degree of preconcentration of the analytes in the HPLC analytical samples. There is also the potential benefit in a lower limit of detection since the sample is eluted into a smaller total volume.

(4) The reproducibilities of formaldehyde hydrazone standards are within 9%. Simultaneously, we get very high agreement between NJIT and EPA's standards. The error of a duplicate sampling is 7.2% +/- 5.74% ; the % difference of an interlaboratory comparison (spiked test) is within 17.6%. From a series of quality control and assurance experiments, qualitative and quantitative data show that the DNPH-coated silica cartridge method is practical and efficient for trapping formaldehyde in ambient air.

(5) The DNPH reagent (if no acid is added) and the standard solutions are very stable when kept in glass-capped containers for up to a half year. The preparation method detailed above is recommended.

(6) The sampled cartridges appear to be stable for at least few weeks after sampling if they are refrigerated. But, we still recommend that analyses be performed within two weeks after sampling.

(7) The statistical average concentrations of formaldehyde data, in both Carteret and Elizabeth, show that higher concentrations mostly occurred in summer time and the average was lower in winter than in summer.

(8) Formaldehyde was the only aldehyde analyzed regularly in our laboratory. Since EPA supplied us with five different aldehyde hydrazone standards for the Round Robin, and we got very high correlation coefficients for each calibration for each standard hydrazone, if we are asked to provide data on the other aldehydes while formaldehyde is analyzed, the analysis should be relatively easy to implement.

(9) The accuracy of most of the NJIT data is currently difficult to deterimine due to the fact that no results from the traps sent by NJIT to EPA have been reported.

(10) Method accuracy is difficult to assess because of the difficulty in generating an accurate formaldehyde gas standard.

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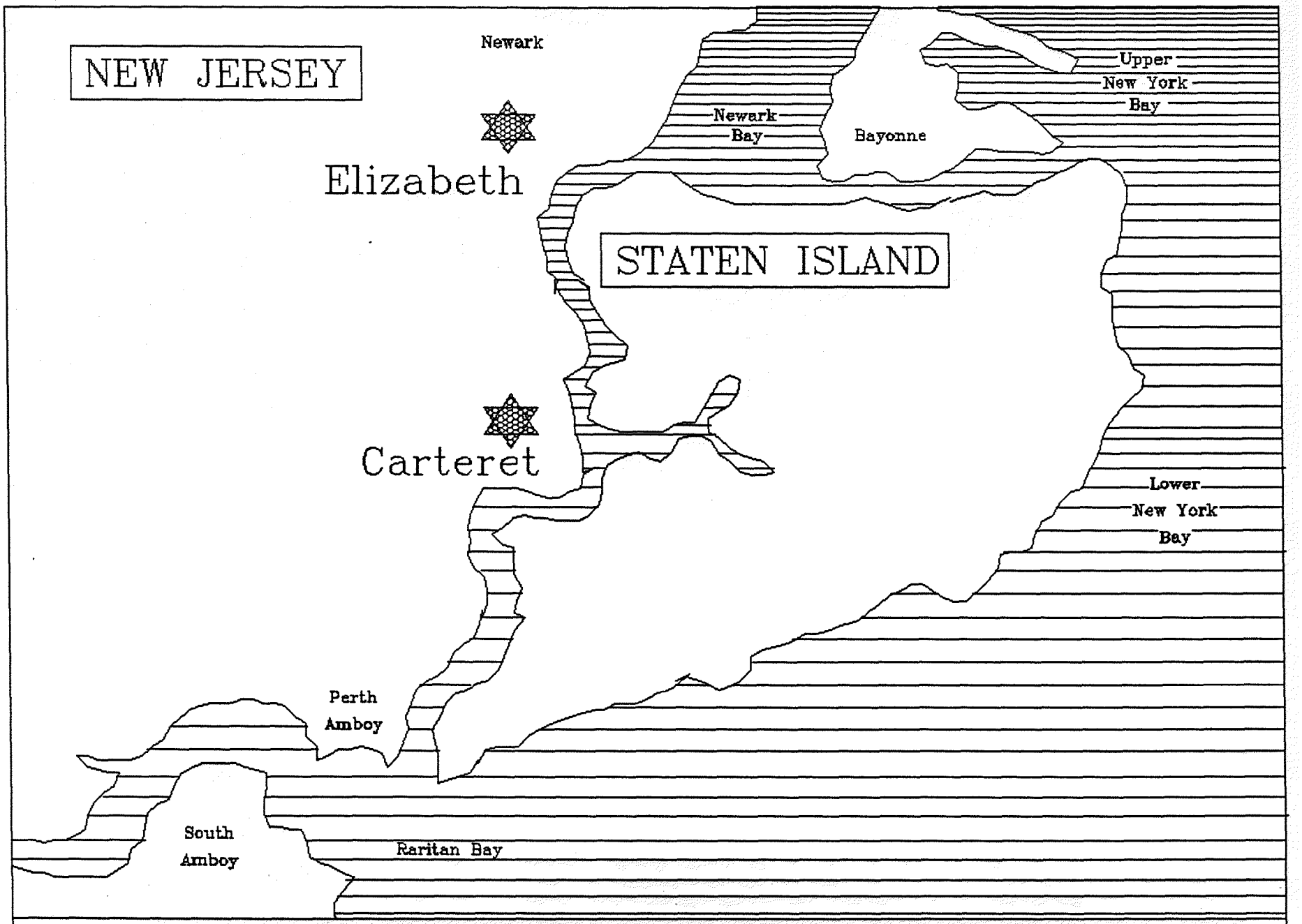
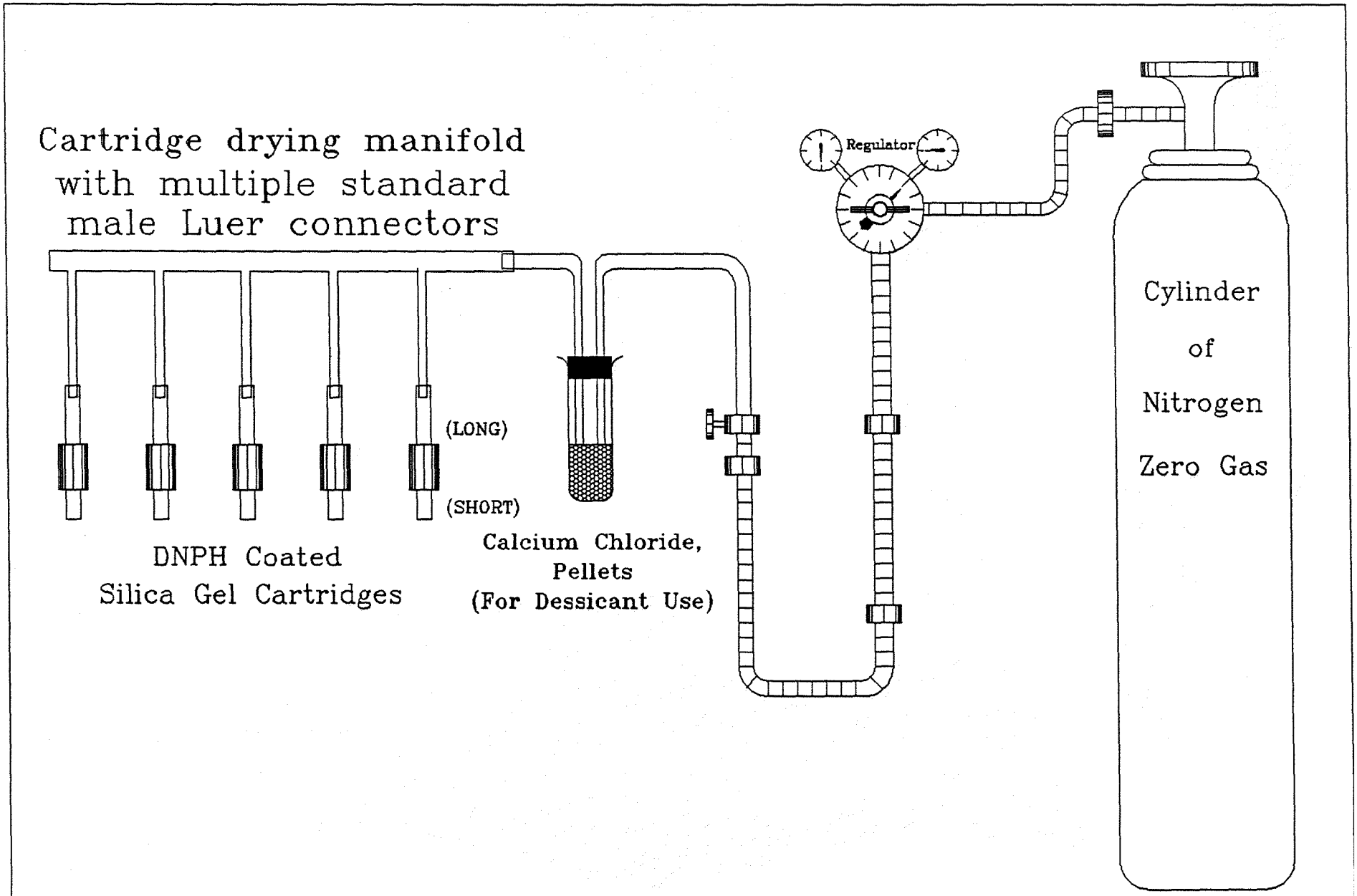
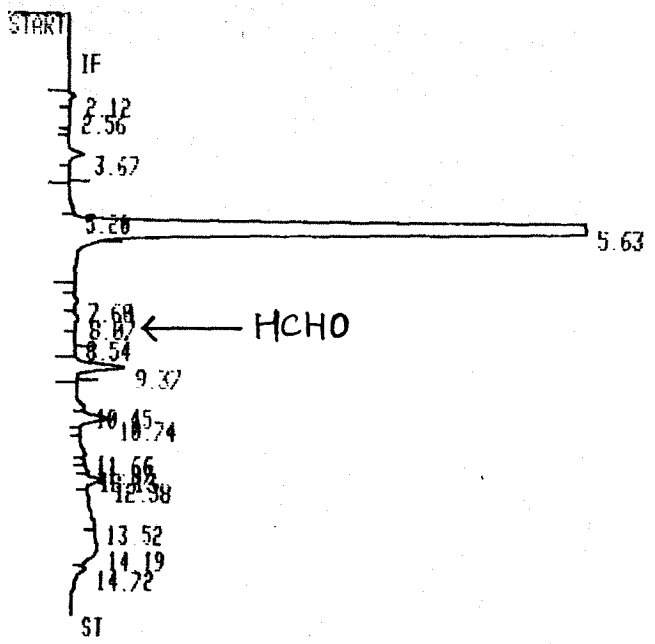


Figure 1 : Sampling Site

Figure 2:Configuration for Drying DNPH Coated Silica Gel Cartridges





RUN # 10 FEB/02/89 14:48:12

AREA%

	RT	AREA	TYPE	AR/HT	AREA%
	2.12	11253	PB	0.151	0.116
	2.56	3531	BB	0.230	0.036
	3.67	31451	PB	0.161	0.324
	5.20	0	PB	0.000	0.000
	5.63	9342900	BB	0.187	96.347
	7.60	7005	PB	0.186	0.072
→	8.07	8772	BB	0.170	0.091
	8.54	528	BB	0.122	0.006
	9.37	122400	PB	0.182	1.262
	10.45	0	PB	0.000	0.000
	10.74	63880	BB	0.173	0.659
	11.66	0	PB	0.000	0.000
	11.87	617	BB	0.107	0.006
	12.13	1980	BB	0.103	0.020
	12.38	32640	BB	0.150	0.337
	13.52	3322	BB	0.097	0.034
	14.19	66826	BB	0.529	0.689
	14.72	0	I BP	0.000	0.000

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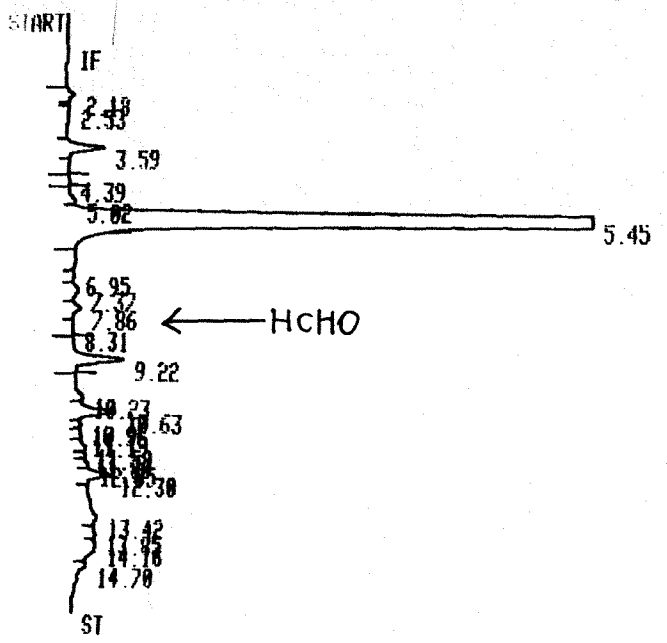
MUL FACTOR= 1.0000E+00

Figure 3. An Acceptable Chromatographic Impurity Level of the Purifed 2.4-Dinitrophenylhydrazine Reagent



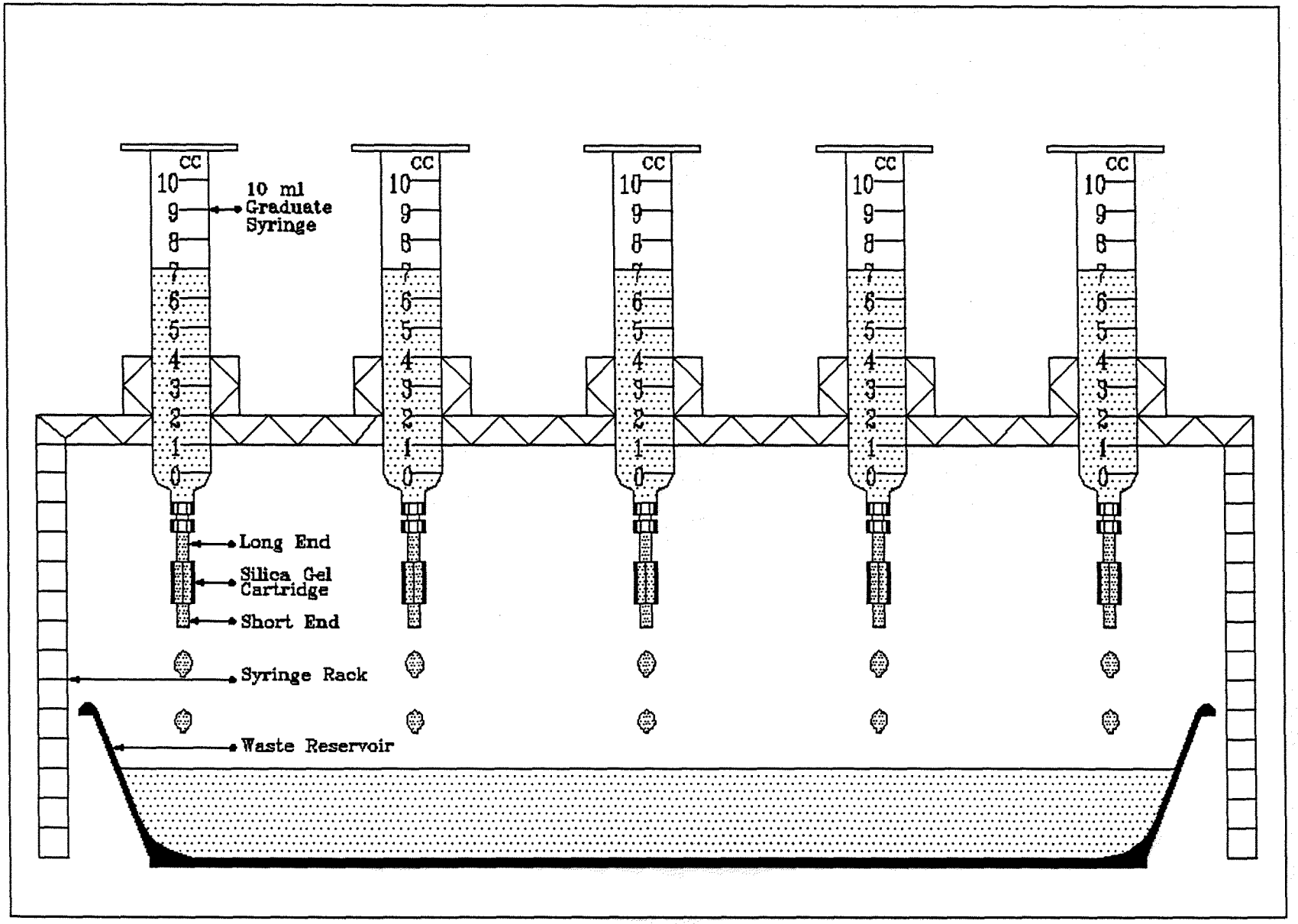
RUN # 11 FEB/02/89 14:56:58

AREA%

RT	AREA	TYPE	AR/HT	AREA%
2.18	12841	PB	0.141	0.106
2.53	0	D VB	0.000	0.000
3.59	82768	BB	0.158	0.685
4.39	691	PB	0.127	0.006
5.02	0	PB	0.000	0.000
5.45	1.1615E+07	BB	0.188	96.135
6.95	1891	PB	0.158	0.016
7.37	16600	BB	0.193	0.137
7.86	18799	BB	0.172	0.156
8.31	1594	BB	0.175	0.013
9.22	133180	PB	0.190	1.102
10.23	0	PB	0.000	0.000
10.63	90053	BB	0.180	0.745
10.96	985	BB	0.107	0.008
11.19	629	BB	0.126	0.005
11.59	3389	BB	0.104	0.028
11.80	440	BB	0.102	0.004
12.05	1787	BB	0.092	0.015
12.30	46767	BB	0.149	0.387
13.42	22691	BB	0.307	0.188
13.85	3570	BB	0.144	0.030

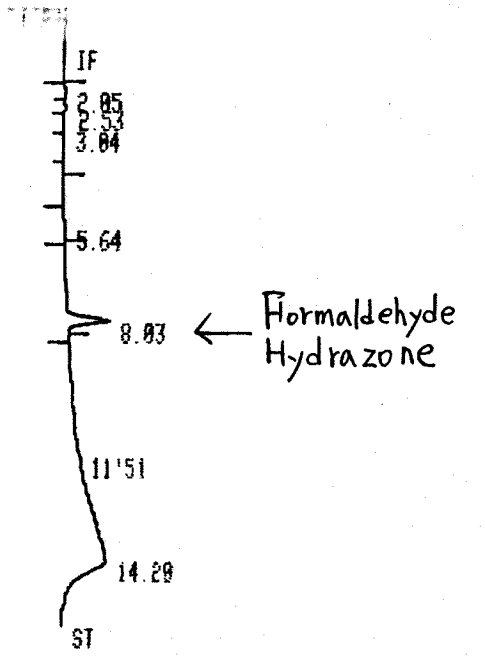
Figure 4. The Impurity Level of An Acceptable Acidified DNPH Coating Solution

Figure 5 : Coating Sep-PAK Silica Cartridges



01/19/89

Set Absorbance Range at 0.05



RUN # 6 JAN/19/89 1

AREA%

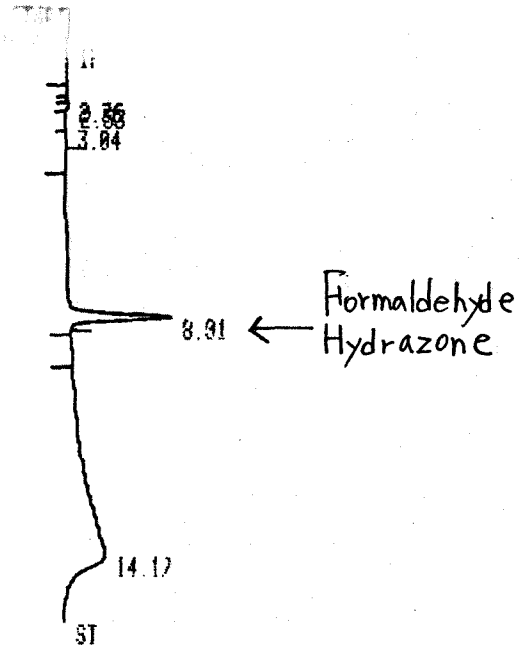
RT	AREA	TYPE	AR/HT	AREA%
2.05	2514	PB	0.162	0.14
2.53	8806	BB	0.150	0.51
3.04	4653	BB	0.410	0.27
5.64	784	PB	0.053	0.04
→ 8.03	95445	PB	0.161	5.55
14.20	1605900	I BP	2.613	93.46

TOTAL AREA=

Figure 6. The HPLC Chromatogram of Free DNPH Formaldehyde Hydrazone Standard Solution (Conc. = 0.0005 g/1000 ml ACN)

01/19/89

Set Absorbance Range at 0.05



RUN # 7 JAN/19/89 13:17:57

AREA%

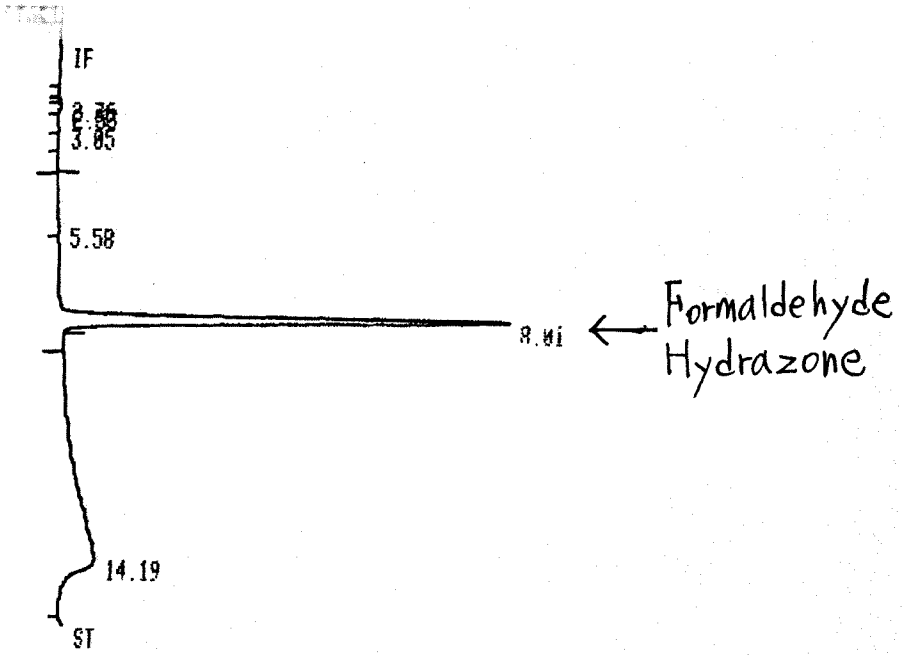
	RT	AREA	TYPE	AR/HT	AREA%
	2.36	603	PB	0.083	0.038
	2.53	6163	BB	0.111	0.388
	3.04	5354	BB	0.446	0.337
→	8.01	216560	PB	0.149	13.617
	14.17	1361700	I BP	2.445	85.621

TOTAL AREA= 1590300

Figure 7. The HPLC Chromatogram of Free DNPH Formaldehyde Hydrazone Standard Solution (Conc. = 0.0010 g/1000 ml ACN)

01/19/89

Set Absorbance Range at 0.05



RUN # 8 JAN/19/89 13:34:15

AREA%

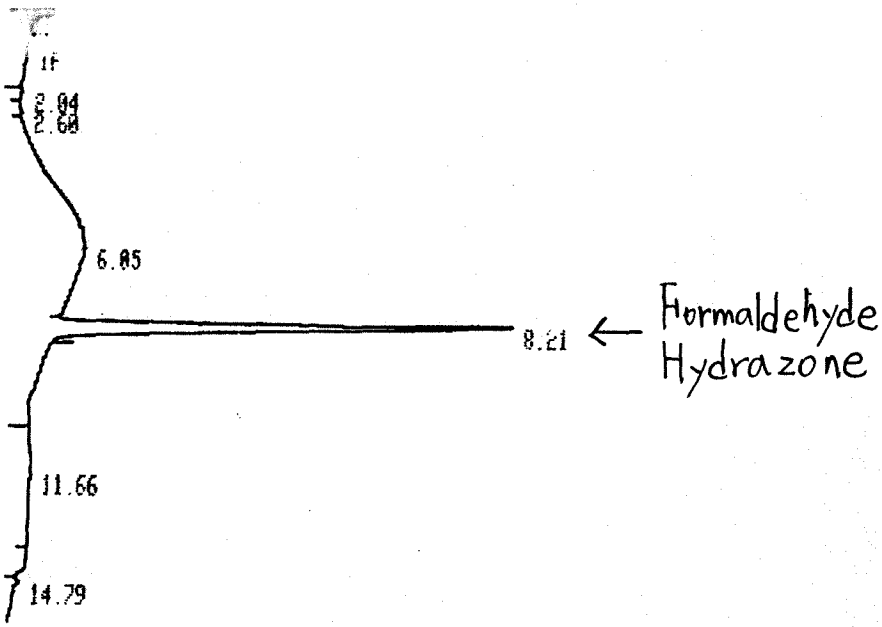
	RT	AREA	TYPE	AR/HT	AREA%
	2.36	432	PB	0.074	0.018
	2.53	5892	BB	0.120	0.246
	3.05	4803	BB	0.400	0.200
	5.58	0	PB	0.000	0.000
→	8.01	1137900	BB	0.178	47.433
	14.19	1249900	BB	2.467	52.103

TOTAL AREA= 2399000

Figure 8. The HPLC Chromatogram of Free DNPH Formaldehyde Hydrazone Standard Solution (Conc. = 0.0052 g/1000 ml ACN)

01/19/89

Set Absorbance Range at 0.1



RUN # 9 JAN/19/89 13:54:49

AREA%

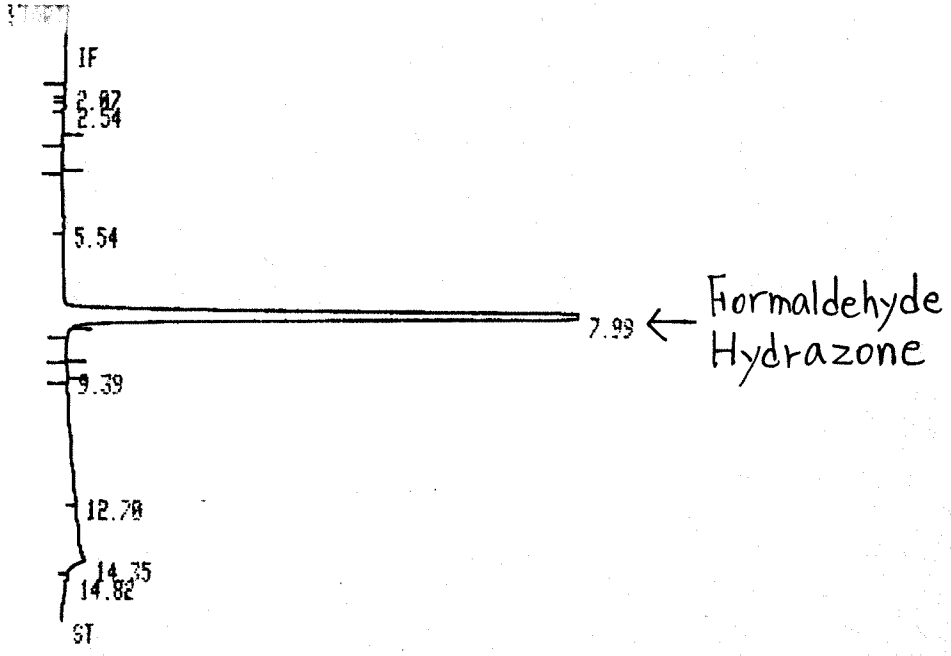
	RT	AREA	TYPE	AR/HT	AREA%
	2.04	2225	D BB	0.124	0.082
	2.60	931	BB	0.081	0.035
	6.05	1463000	BB	2.677	54.134
→	8.21	1173800	BB	0.180	43.433
	11.66	58648	BB	1.404	2.170
	14.79	3959	I PP	0.067	0.147

TOTAL AREA= 2702500

Figure 9. The HPLC Chromatogram of Free DNPH Formaldehyde Hydrazone Standard Solution (Conc. = 0.0104 g/1000 ml ACN)

01/19/89

Set Absorbance Range at 0.1



RUN # 10 JAN/19/89 14:11:01

AREA%

RT	AREA	TYPE	AR/HT	AREA%
2.07	1722	PB	0.142	0.068
2.54	4935	VB	0.132	0.194
5.54	0	PB	0.000	0.000
→ 7.99	2361200	BB	0.176	92.637
9.39	1786	PB	0.186	0.070
12.70	0	PB	0.000	0.000
14.35	179220	BB	0.776	7.031
14.82	0 I	BP	0.000	0.000

TOTAL AREA= 2548800

Figure 10. The HPLC Chromatogram of Free DNPH Formaldehyde Hydrazone Standard Solution (Conc. = 0.0208 g/1000 ml ACN)

STD Solution Calibration Curve (01/19/89)

POINT	X	Y
1	.0005	95445
2	.001	216560
3	.0052	1137900
4	.0104	2347600
5	.0208	4722400

Slope = 2.279617E+08 +/- 952836.1
Intercept = -23969 +/- 15995.39
Correlation = .9999739
Calculated on points 1 TO 5

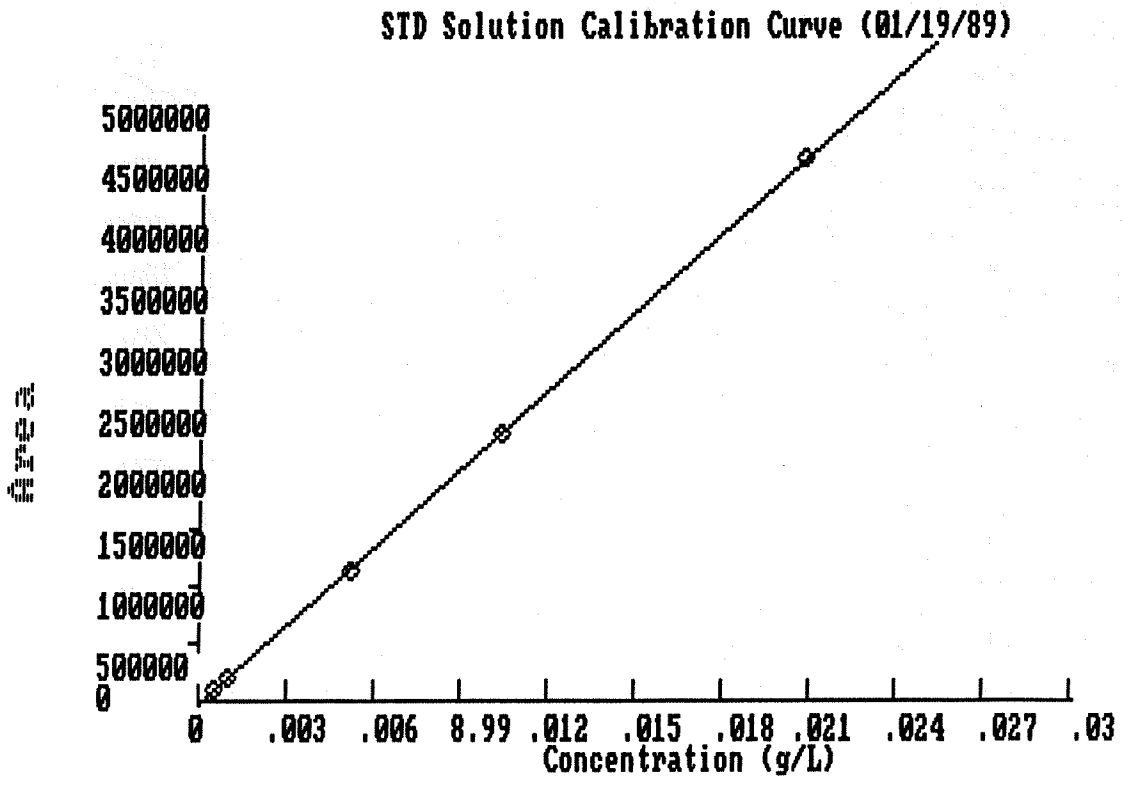


Figure 11. Standard Solution Calibration Curve of Free DNPH Formaldehyde Hydrazone

Figure 12 : Sampling System

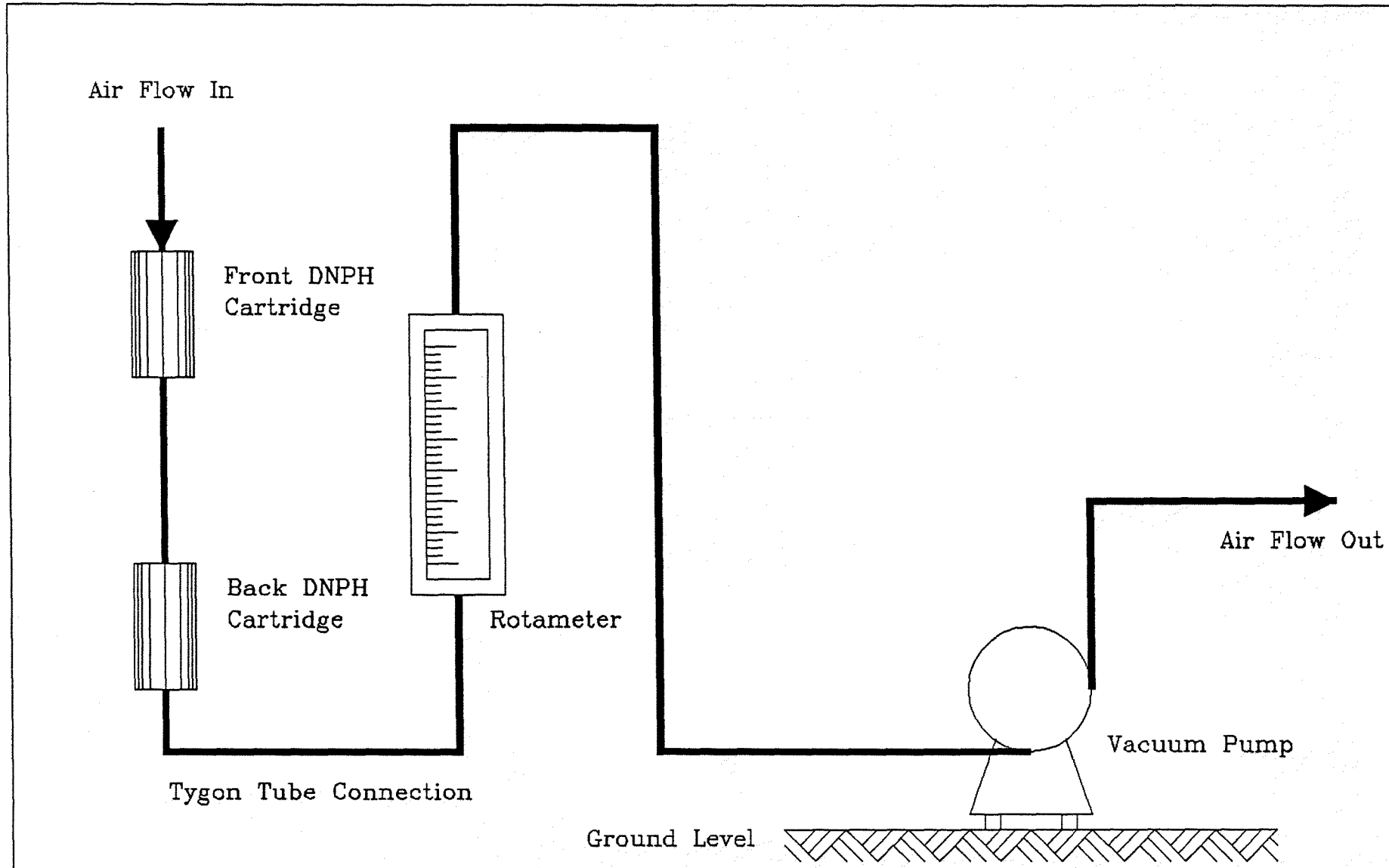
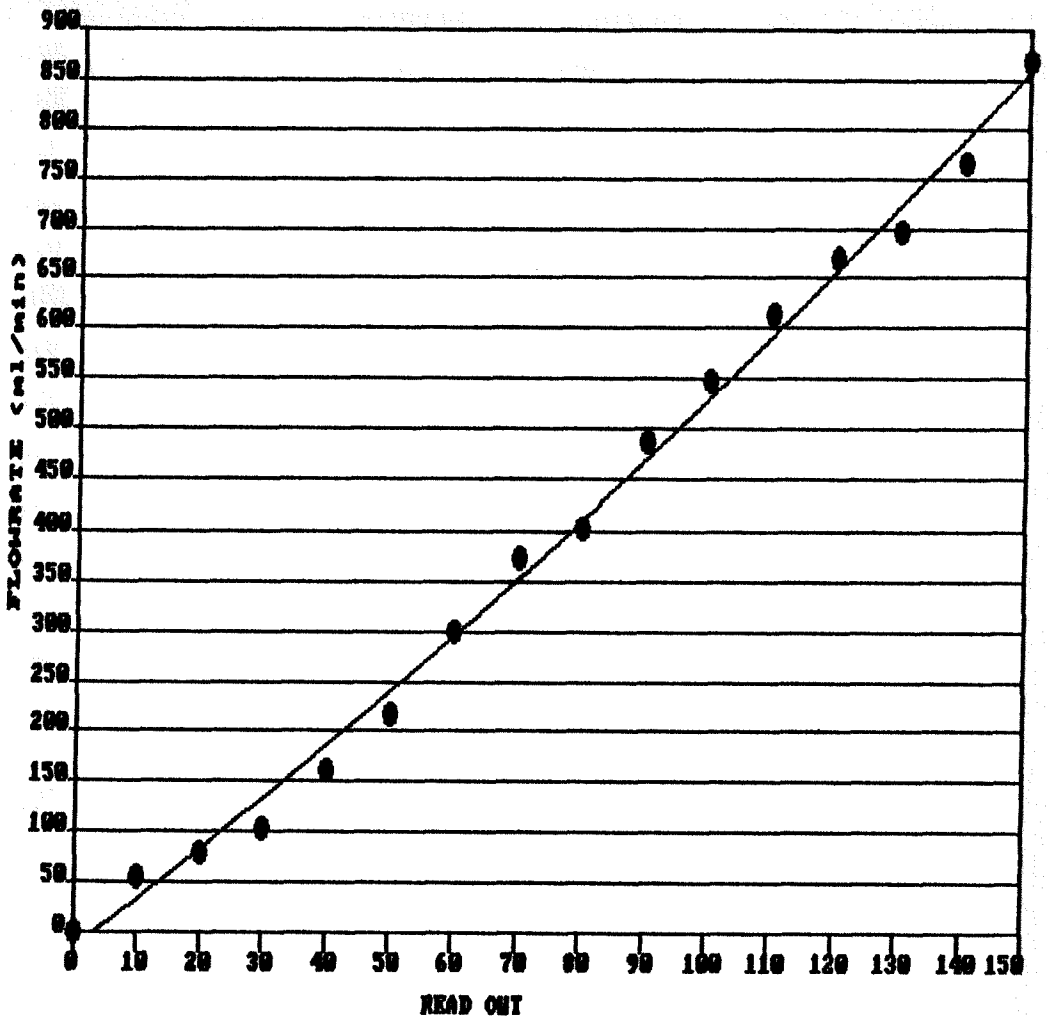


Figure 13. MMSH Calibration Curve (01-20-89)



THE REGRESSION POLYNOMIAL OF LINE 1 -

(-1.494E+01) + (7.116E+02)*X + (1.606E+02)*X^ 2
THE VARIANCE - 3.677E+02

Point	Read Out	Flow Rate
1	0	0.00
2	10	55.07
3	20	78.74
4	30	102.88
5	40	162.25
6	50	217.39
7	60	299.70
8	70	372.21
9	80	403.63
10	90	486.06
11	100	549.08
12	110	615.26
13	120	668.60
14	130	695.01
15	140	765.11
16	150	867.93

Set Read Out at 96 for 506.02 ml/min

Figure 14: Schematic of LDC/Milton Roy HPLC Apparatus

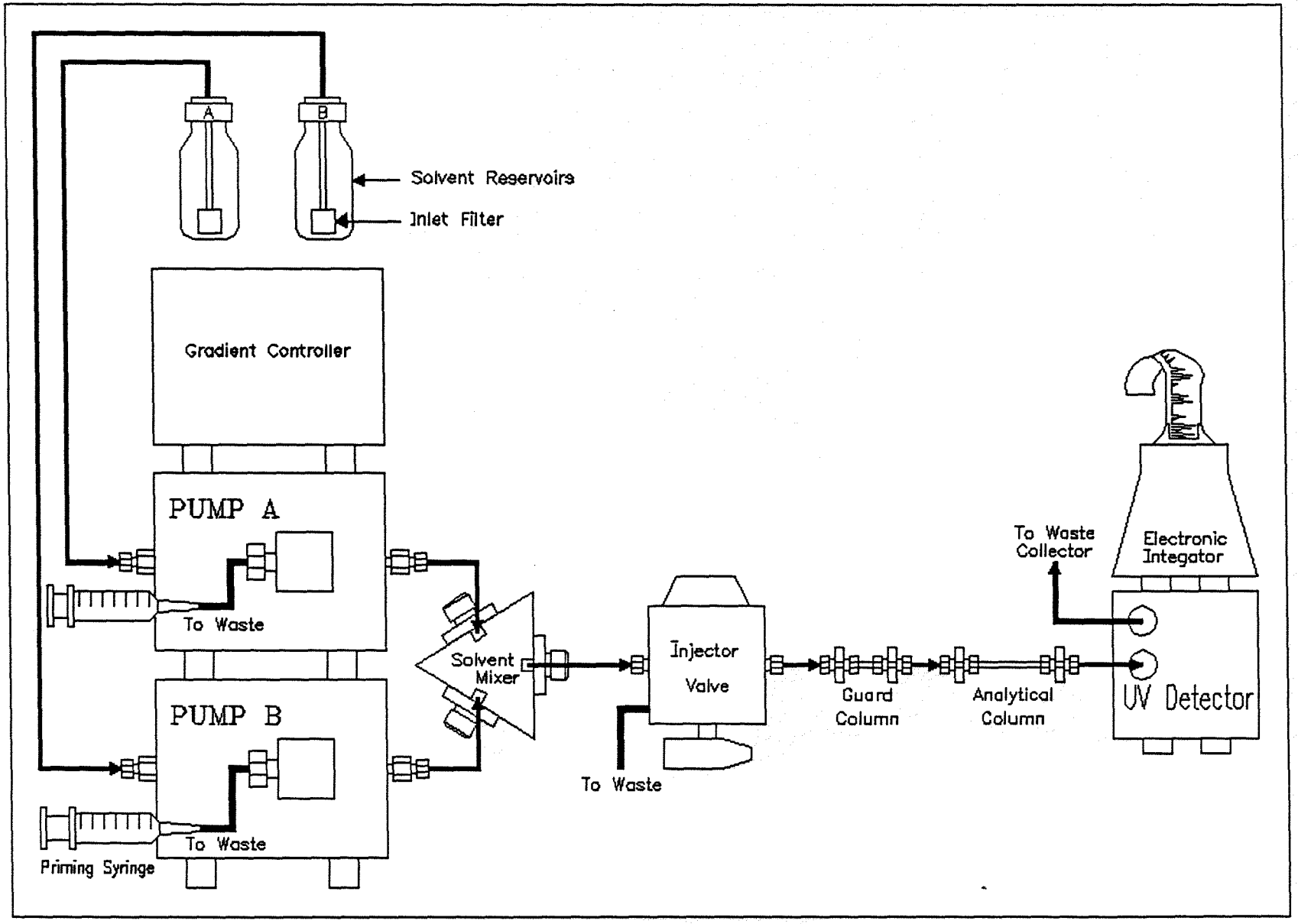


Figure 15: Elution from Silica Gel Cartridge by Gravity Feeding of Acetonitrile

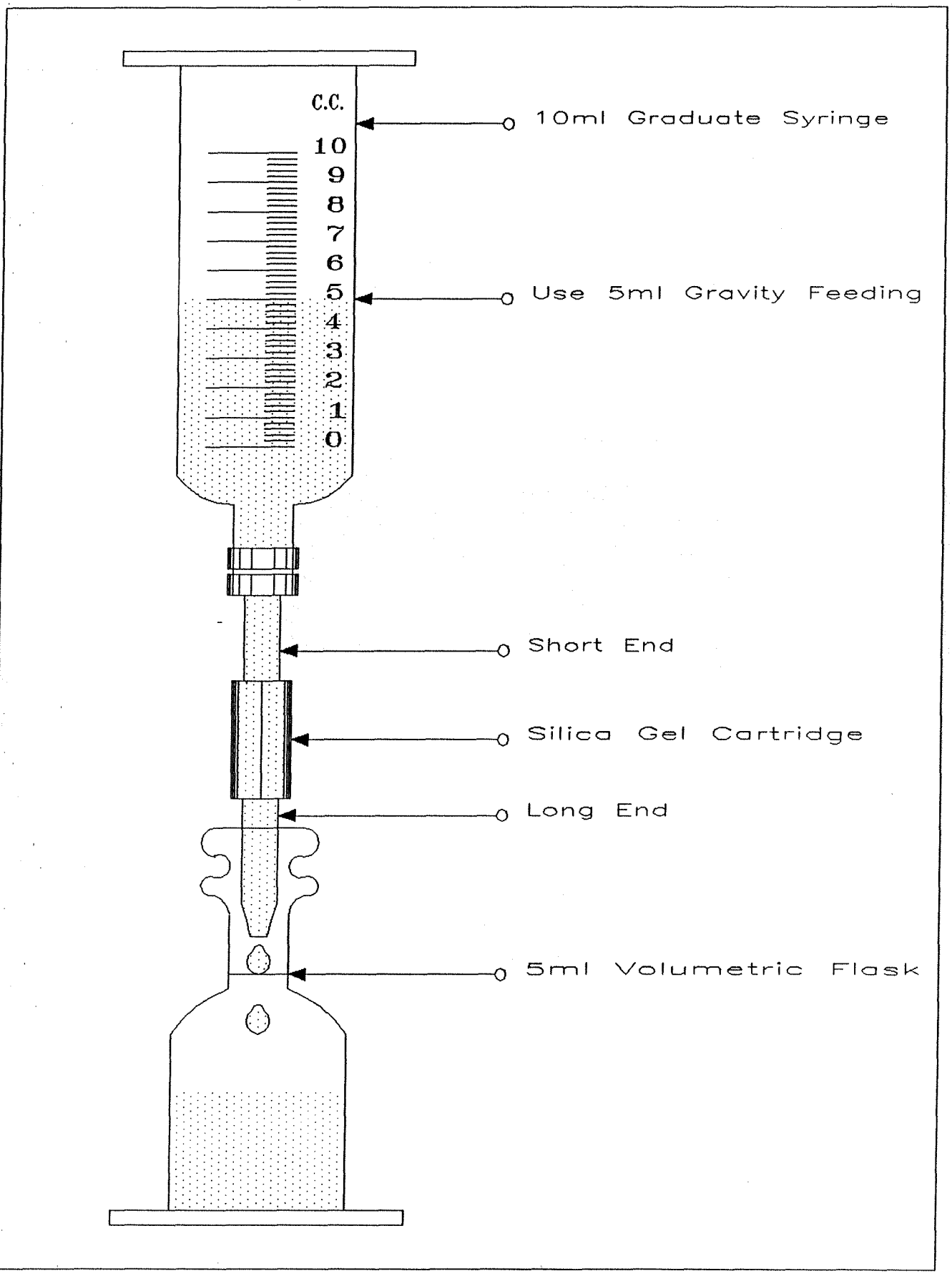


Figure 16. Retention Time Control Chart

of Formaldehyde Hydrazone STD Solution

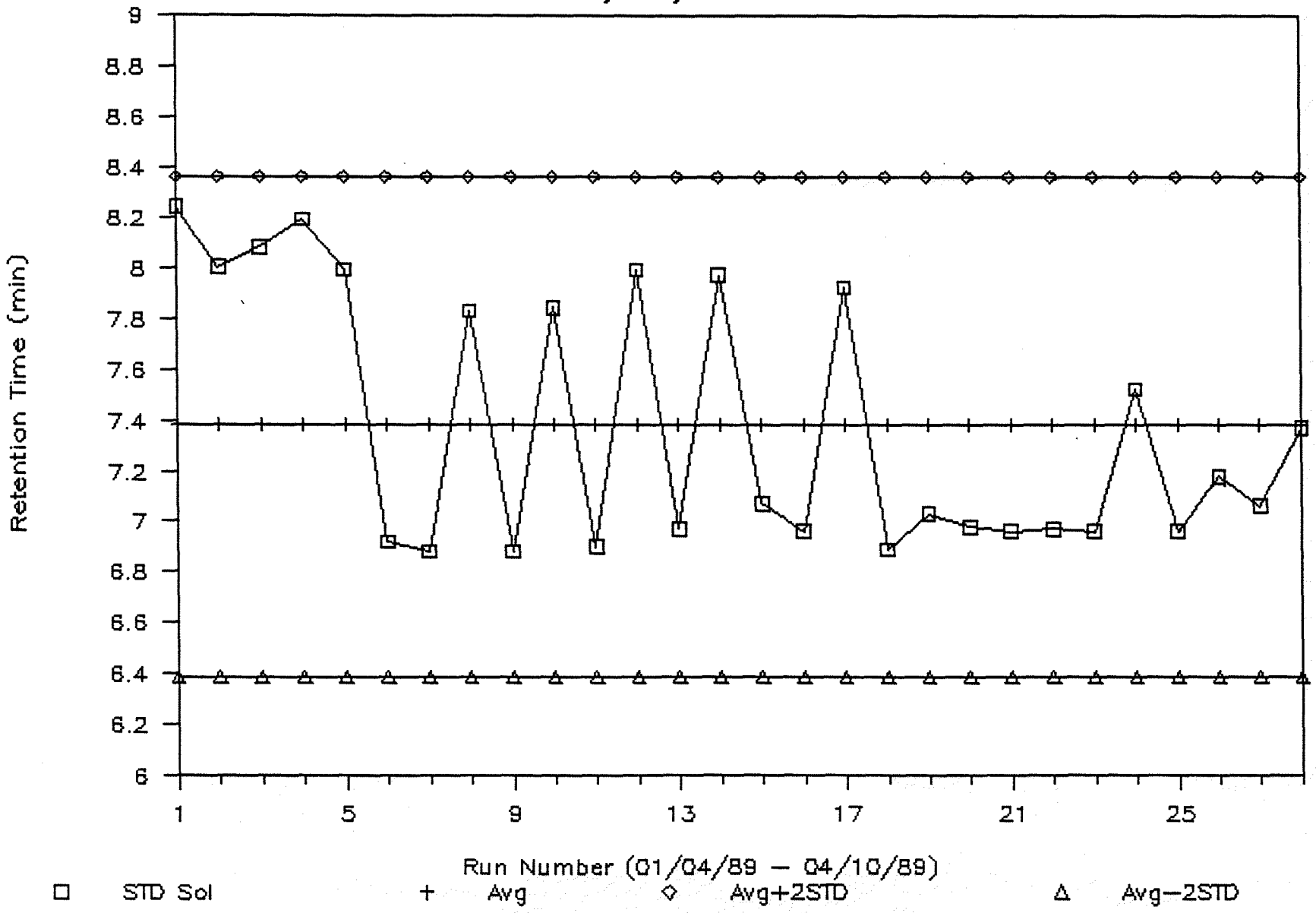
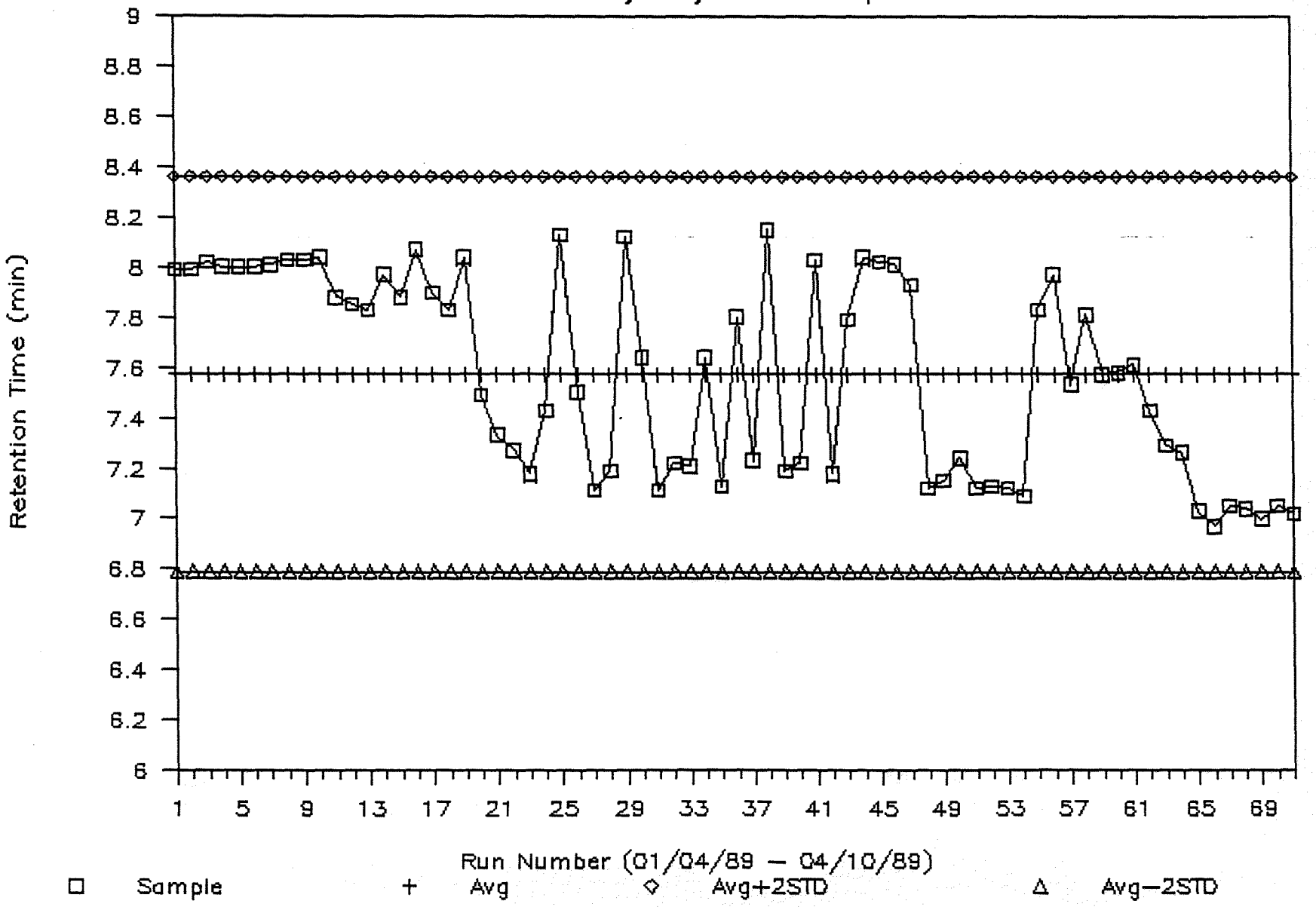
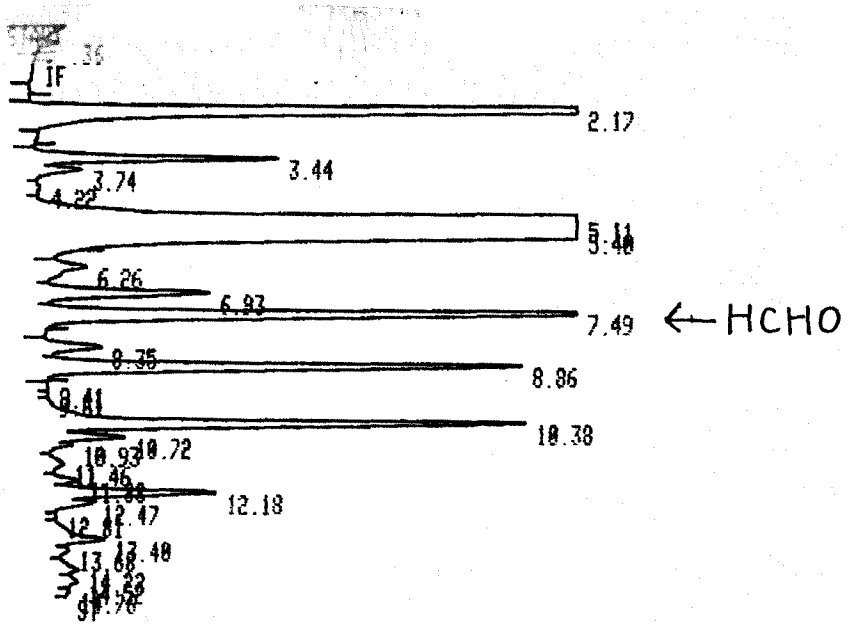


Figure 17. Retention Time Control Chart

of Formaldehyde Hydrazone Samples



01/22/89 Set Absorbance Range at 0.05



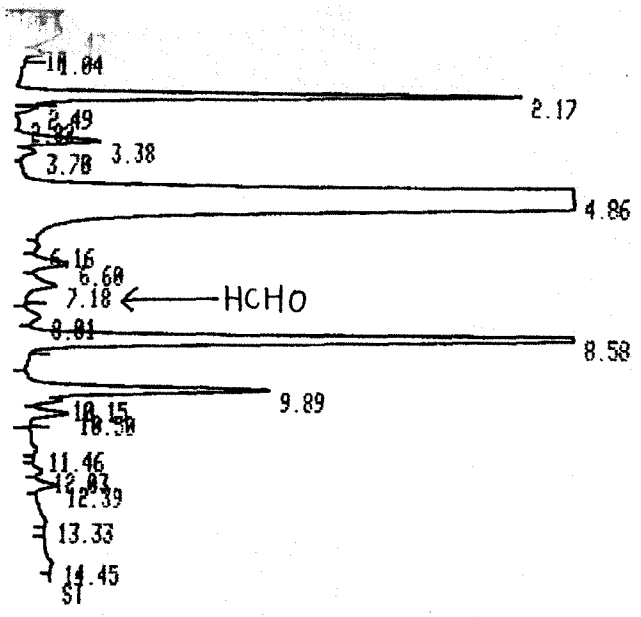
RUN # 25 16:01:22

AREA%

	RT	AREA	TYPE	AR/HT	AREA%
	0.36	26307	D BB	0.109	0.09
	2.17	4512600	PB	0.150	16.79
	3.44	481870	PB	0.144	1.794
	3.74	71024	BB	0.150	0.264
	4.22	6978	BB	0.152	0.026
	5.11	1.5532E+07	SPB	0.137	57.80
	5.40	541130	BB	0.033	2.014
	6.26	122670	BB	0.244	0.457
	6.93	455870	BB	0.196	1.697
→	7.49	1763100	BB	0.195	6.562
	8.35	147720	PB	0.195	0.550
	8.86	1322200	BB	0.195	4.921
	9.41	1420	PB	0.131	0.005
	9.61	419	BB	0.101	0.002
	10.38	1156400	BB	0.177	4.304
	10.72	99919	BB	0.136	0.372
	10.93	6410	D BB	0.059	0.024
	11.46	36348	BB	0.215	0.135
	11.88	34176	BB	0.127	0.127
	12.18	336470	BB	0.164	1.252
	12.47	34788	BB	0.138	0.130
	12.81	1344	BB	0.101	0.005
	13.40	118640	BB	0.201	0.442
	13.68	9642	BB	0.163	0.036

Figure 18. The Chromatogram of the Front Trap of KUSU Sampler in Carteret

01/22/89 Set Absorbance Range at 0.05



RUN # 26 16:17:00

AREA%

	RT	AREA	TYPE	AR/HT	AREA%
	0.47	99497	BP	0.461	0.188
	1.04	28414 D	PB	0.110	0.054
	2.17	1109900	PB	0.156	2.102
	2.49	18218 D	BB	0.209	0.035
	2.82	14148	BB	0.234	0.027
	3.38	194440	BB	0.175	0.368
	3.70	21414	BB	0.136	0.041
	4.86	4.8070E+07	SPB	0.223	91.016
	6.16	9648	BB	0.172	0.018
	6.60	103740	BB	0.205	0.196
→	7.18	81187	BB	0.228	0.154
	8.01	39324	PB	0.217	0.075
	8.58	2308600	BB	0.204	4.371
	9.89	532060	PB	0.168	1.007
	10.15	13115 D	BB	0.114	0.025
	10.50	84357	BB	0.162	0.160
	11.46	14650	PB	0.196	0.028
	12.03	17383	PB	0.163	0.033
	12.39	46957	BB	0.169	0.089
	13.33	910	BB	0.019	0.002
	14.45	7057	PB	0.128	0.013

TOTAL AREA= 5.2815E+07

Figure 19. The Chromatogram of the Back Trap of KUSU Sampler in Carteret

Figure 20. STD Solution Control Chart

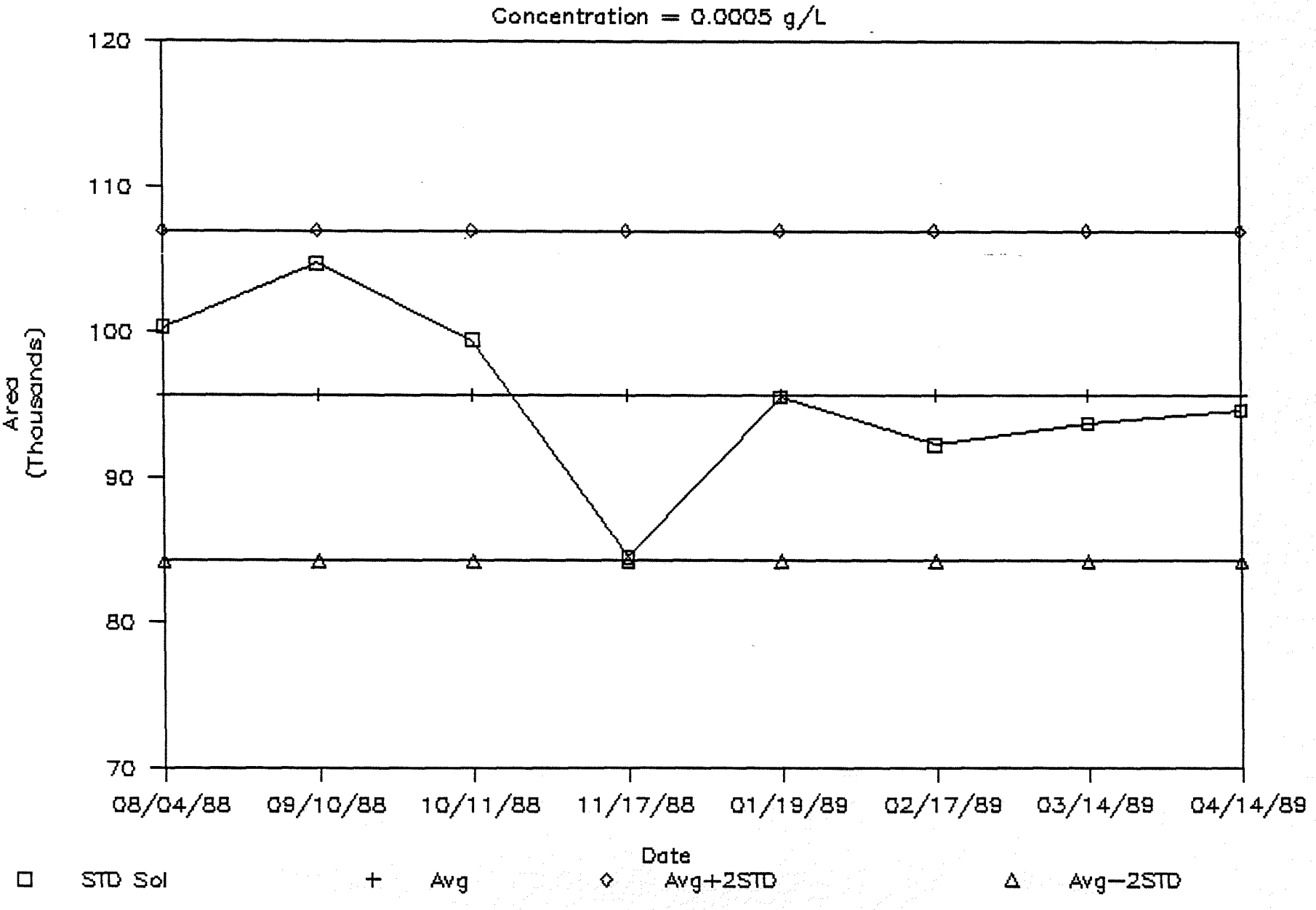


Figure 21. STD Solution Control Chart

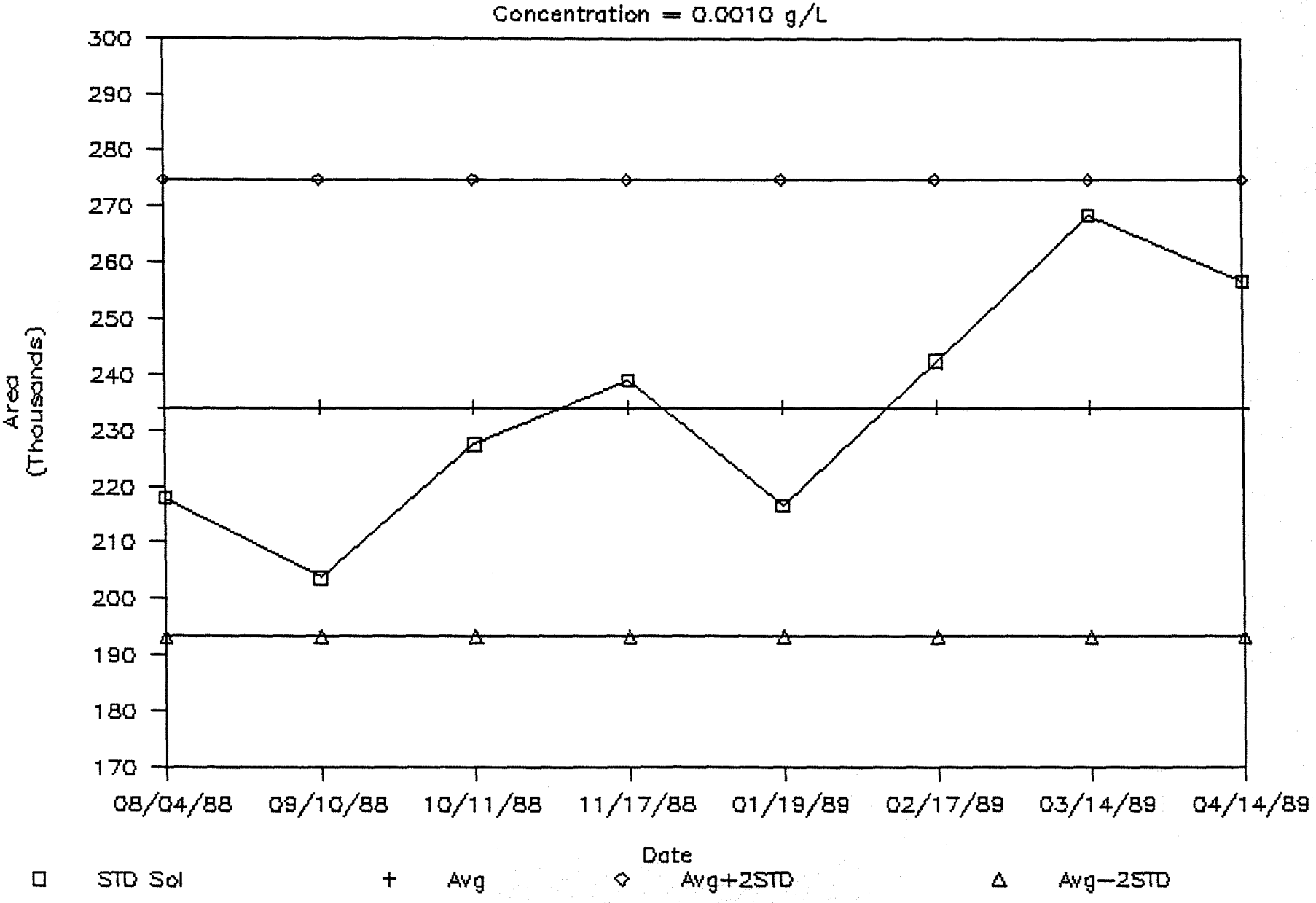


Figure 22. STD Solution Control Chart

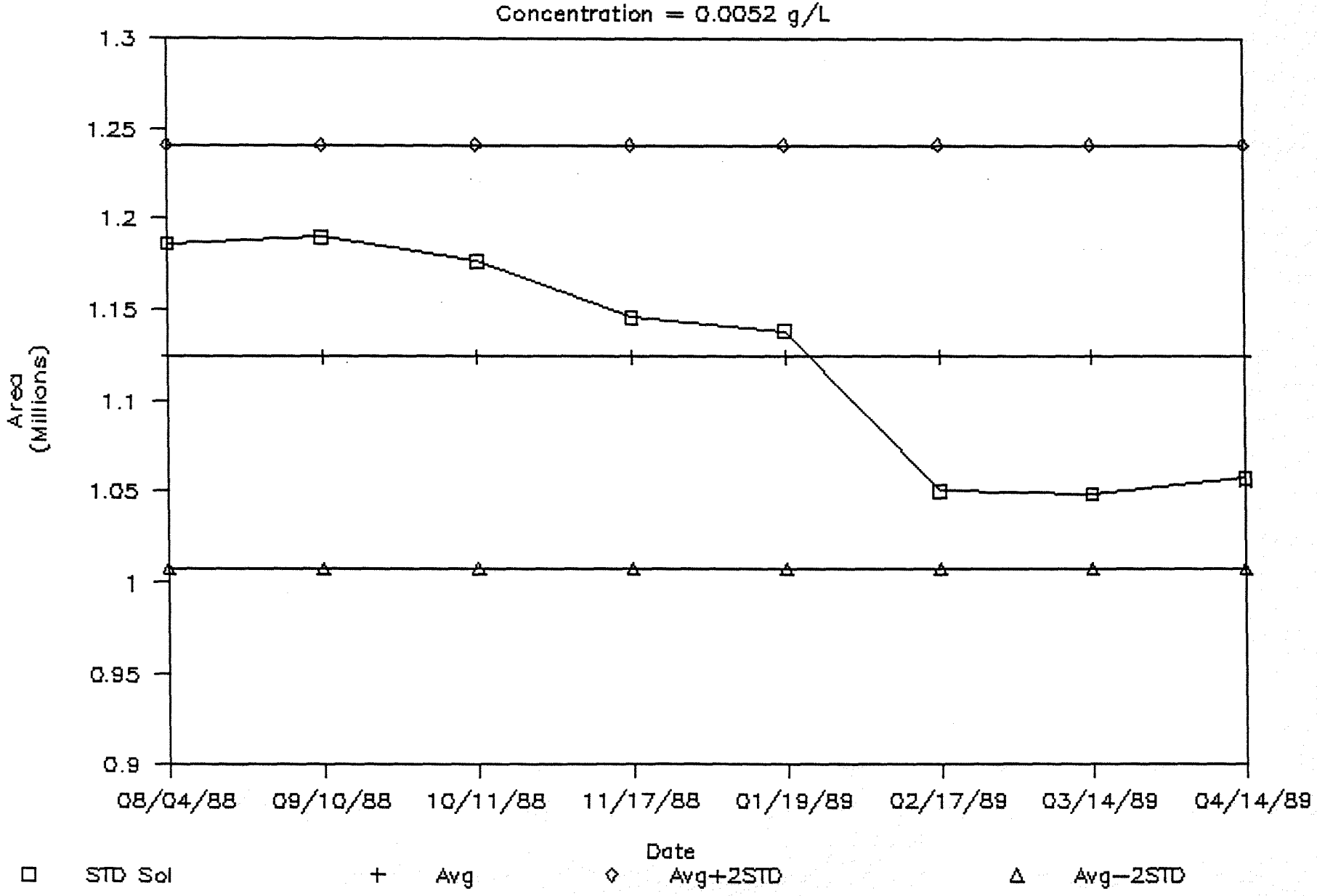


Figure 23. STD Solution Control Chart

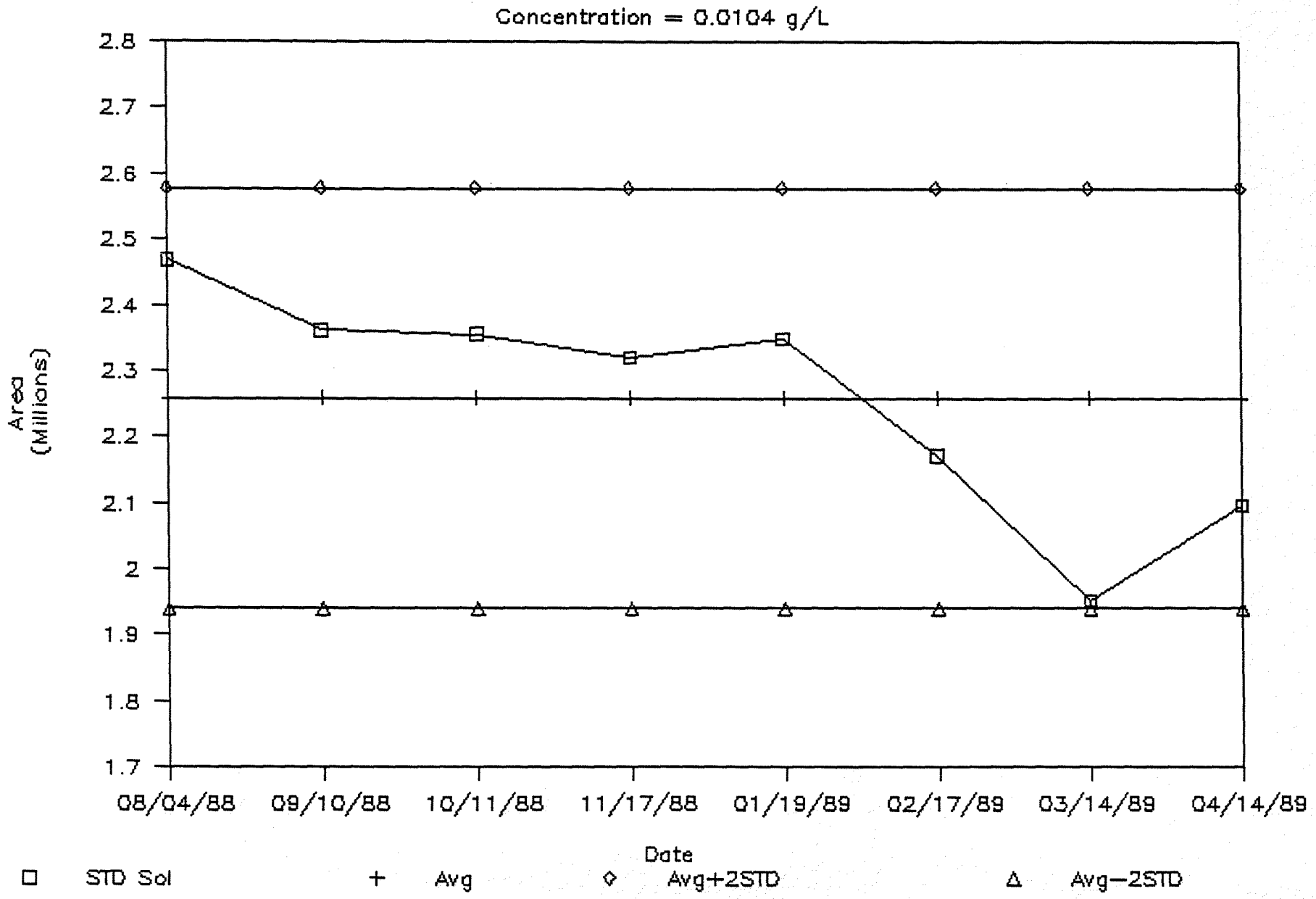
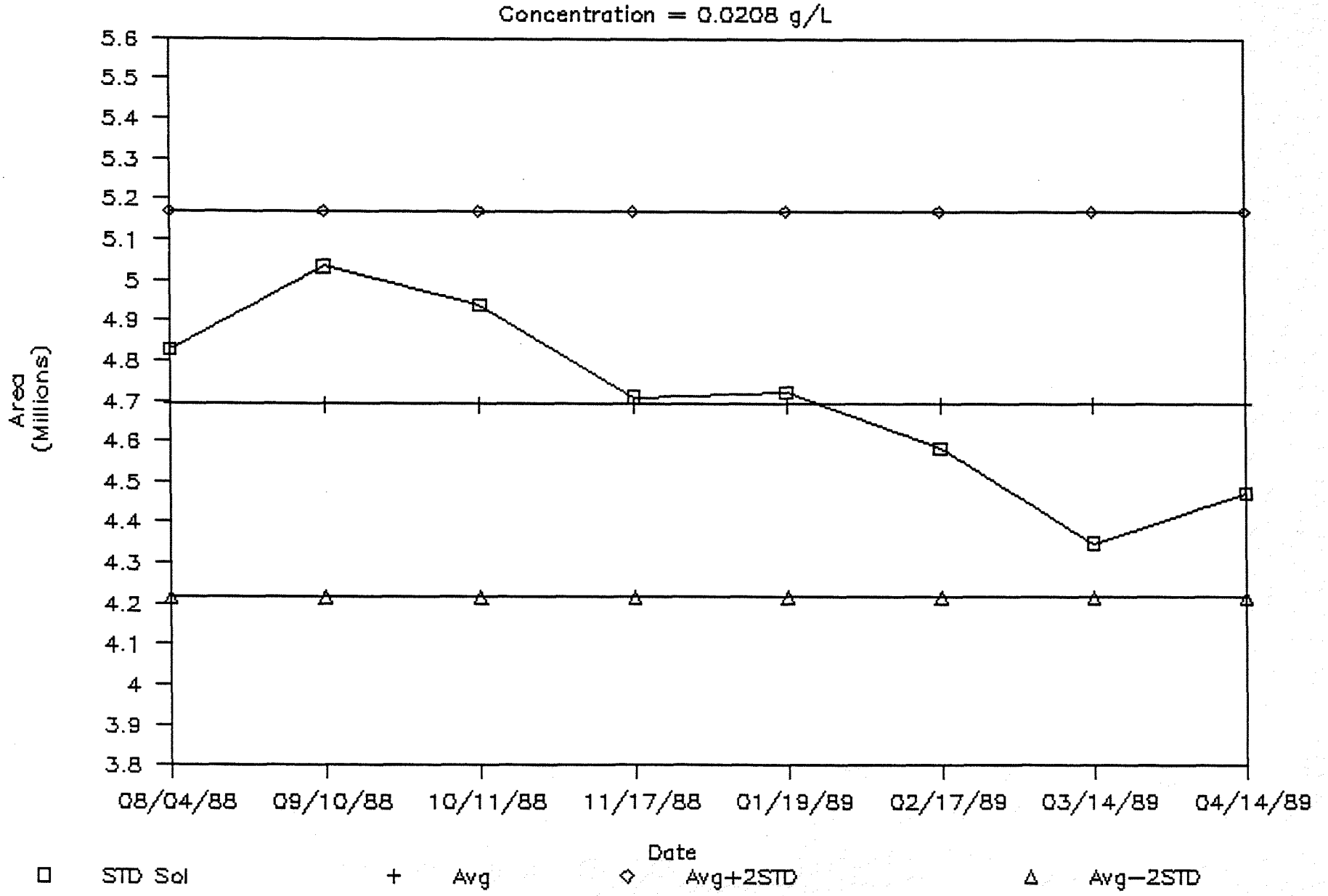
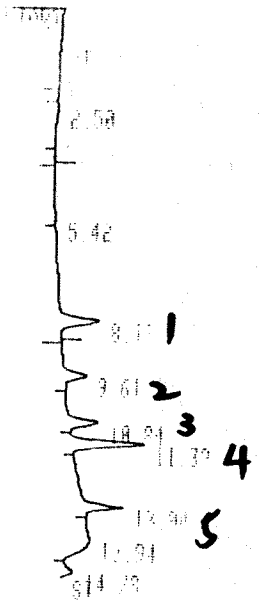


Figure 24. STD Solution Control Chart



Set Absorbance Range at 0.05



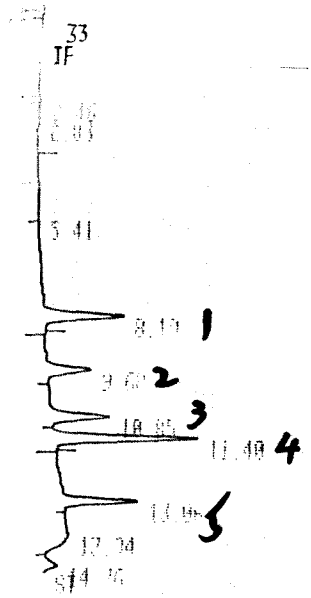
N # 2 NOV/03/88 09:16:49

	AREA% RT	AREA	TYPE	AREA/HT	AREA%
	2.50	7313	VB	0.301	1.019
	5.42	4137	PB	0.444	0.602
1	8.18	1[illegible]380	BB	0.224	16.983
2	9.61	59650	PB	0.194	8.228
3	10.84	73843	BB	0.121	10.242
4	11.39	183350	BB	0.109	25.721
5	[illegible]	83882	BB	0.151	11.640
	13.94	147250	BB	0.699	20.531
	14.78	35882	I BP	0.223	4.579

TOTAL AREA= 720670

Figure 25. The HPLC Chromatogram of Aldehyde Hydrazone Standard Mixtures Concentration 1
1. Formaldehyde Hydrazone
2. Acetaldehyde Hydrazone
3. Acrolein Hydrazone
4. Propionaldehyde Hydrazone
5. Benzaldehyde Hydrazone

Set Absorbance Range at 0.05



JN # 2 NOV-03-88 10:42:47

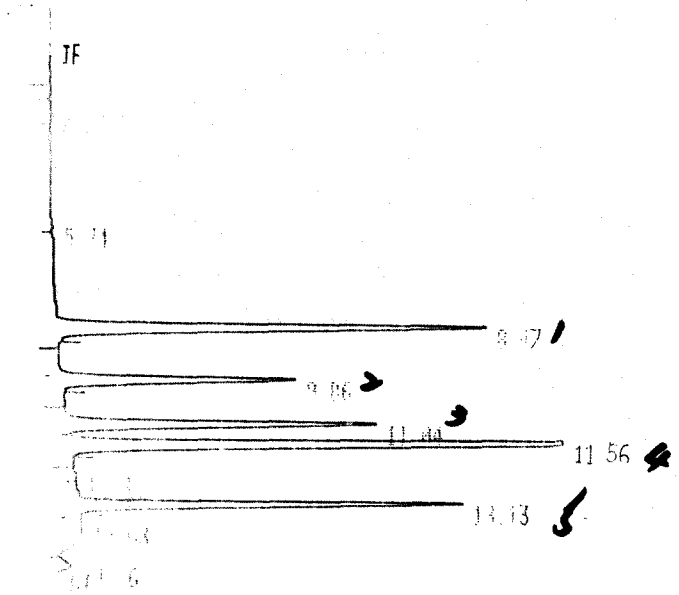
AREA%

	RT	AREA	TYPE	AK/HT	AREA%
	0.33	5663	PB	0.432	0.508
	2.46	652	PB	0.052	0.055
	2.83	946	PB	0.140	0.071
	5.41	5233	PB	0.585	0.439
1	8.19	236760	BB	0.206	19.843
2	9.62	115530	PB	0.185	9.683
3	10.85	149120	BB	0.178	12.497
4	11.40	354870	BB	0.174	29.909
5	13.06	161900	PB	0.153	13.560
	13.94	123020	BB	0.666	10.332
	14.76	36436	I BP	0.211	3.054

OTAL AREA= 1193200
UL. FACTOR= 1.0000E+00

Figure 26. The HPLC Chromatogram of Aldehyde Hydrazone Standard Mixtures Concentration 2
1. Formaldehyde Hydrazone
2. Acetaldehyde Hydrazone
3. Acrolein Hydrazone
4. Propionaldehyde Hydrazone
5. Benzaldehyde Hydrazone

Set Absorbance Range at 0.05



UN # 6 NOV/03/88 10:27:23

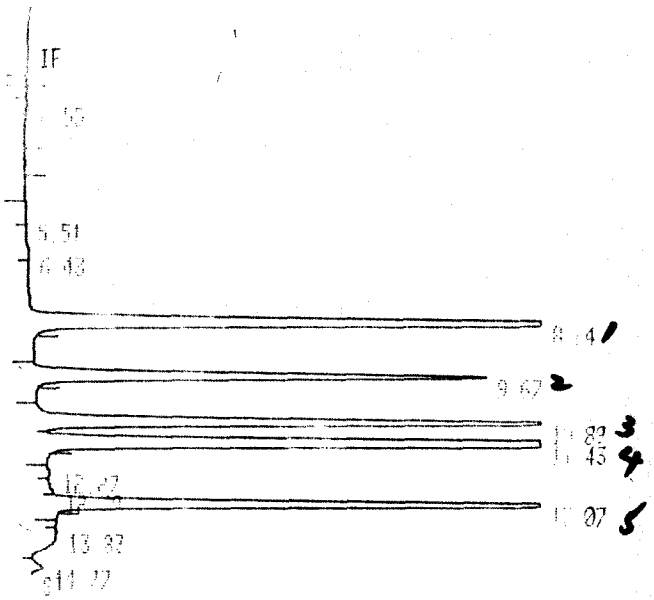
REA%

	RT	AREA	TYPE	AR/HT	AREA%
	2.77	10776	PB	0.322	0.206
	5.74	13716	PB	1.236	0.262
1	8.47	1160600	BB	0.190	22.178
2	9.86	603020	PB	0.189	11.529
3	11.04	774030	PB	0.175	14.791
4	11.56	1793200	BB	0.169	34.267
	12.37	2129	PB	0.133	0.041
	12.87	0	BB	0.000	0.000
5	13.13	837060	BB	0.153	15.996
	13.63	656	PB	0.103	0.013
	14.76	37110 I	PP	0.209	0.709

TOTAL AREA= 5233100

Figure 27. The HPLC Chromatogram of Aldehyde Hydrazone Standard Mixtures Concentration 3
1. Formaldehyde Hydrazone
2. Acetaldehyde Hydrazone
3. Acrolein Hydrazone
4. Propionaldehyde Hydrazone
5. Benzaldehyde Hydrazone

Set Absorbance Range at 0.05



RUN # 9 NOV-03/88 11:13:56

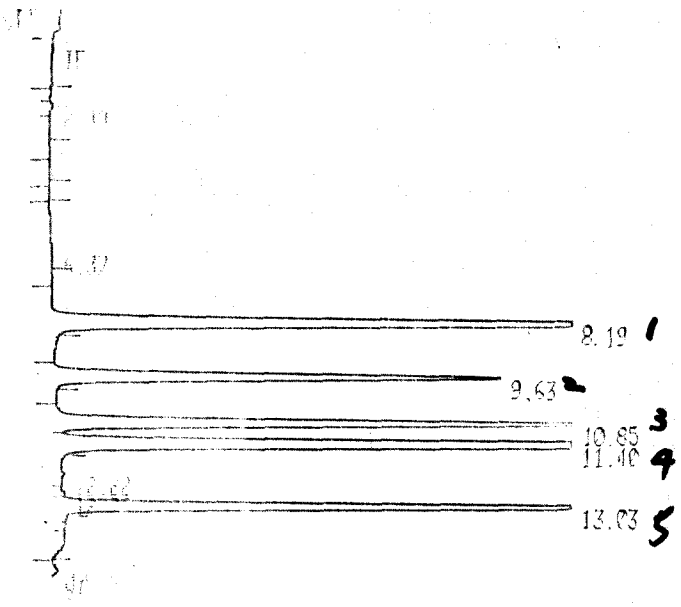
AREA%

	RT	AREA	TYPE	AR/HT	AREA%
	2.55	5382	PB	0.164	0.051
	5.51	1632	PB	0.306	0.016
	6.43	4137	BB	0.327	0.040
1	8.24	2277300	BB	0.195	21.751
2	9.67	1244100	PB	0.193	11.883
3	10.89	1556500	PB	0.100	14.867
4	11.43	3607600	BB	0.173	34.458
	12.27	6408	PB	0.164	0.061
	12.79	0	BB	0.000	0.000
5	13.07	1655100	BB	0.155	15.808
	13.83	79261	VB	0.695	0.757
	14.27	32307 I	BP	0.204	0.309

TOTAL AREA= 1.0470E+07

Figure 28. The HPLC Chromatogram of Aldehyde Hydrazone Standard Mixtures Concentration 4
1. Formaldehyde Hydrazone
2. Acetaldehyde Hydrazone
3. Acrolein Hydrazone
4. Propionaldehyde Hydrazone
5. Benzaldehyde Hydrazone

Set Absorbance Range at 0.1



RUN # 10 NOV/03/88 11:29:21

AREA%

	RT	AREA	TYPE	AR/HT	AREA%
	2.49	3624	PB	0.205	0.035
	6.32	1577	PB	0.172	0.015
1	8.19	2261200	PB	0.197	21.998
2	9.63	1231700	PB	0.194	11.979
3	10.85	1544100	PB	0.179	15.017
4	11.40	3571300	BB	0.173	34.732
	12.22	6554	BB	0.164	0.064
	12.75	0	BB	0.000	0.000
5	13.03	1645600	BB	0.154	16.004
	14.76	15890	I PP	0.209	0.155

TOTAL AREA= 1.0282E+07

MU FACTOR= 1.0000E+00

Figure 29. The HPLC Chromatogram of Aldehyde Hydrazone Standard Mixtures Concentration 5
1. Formaldehyde Hydrazone
2. Acetaldehyde Hydrazone
3. Acrolein Hydrazone
4. Propionaldehyde Hydrazone
5. Benzaldehyde Hydrazone

Formaldehyde Hydrazone Standard Curve

POINT	X	Y
1	.0005	122380
2	.001	236760
3	.0052	1160600
4	.0104	2277300
5	.0208	4523800

Slope = 2.166016E+08 +/- 530610.2
Intercept = 22328 +/- 8907.427
Correlation = .9999909
Calculated on points 1 TO 5

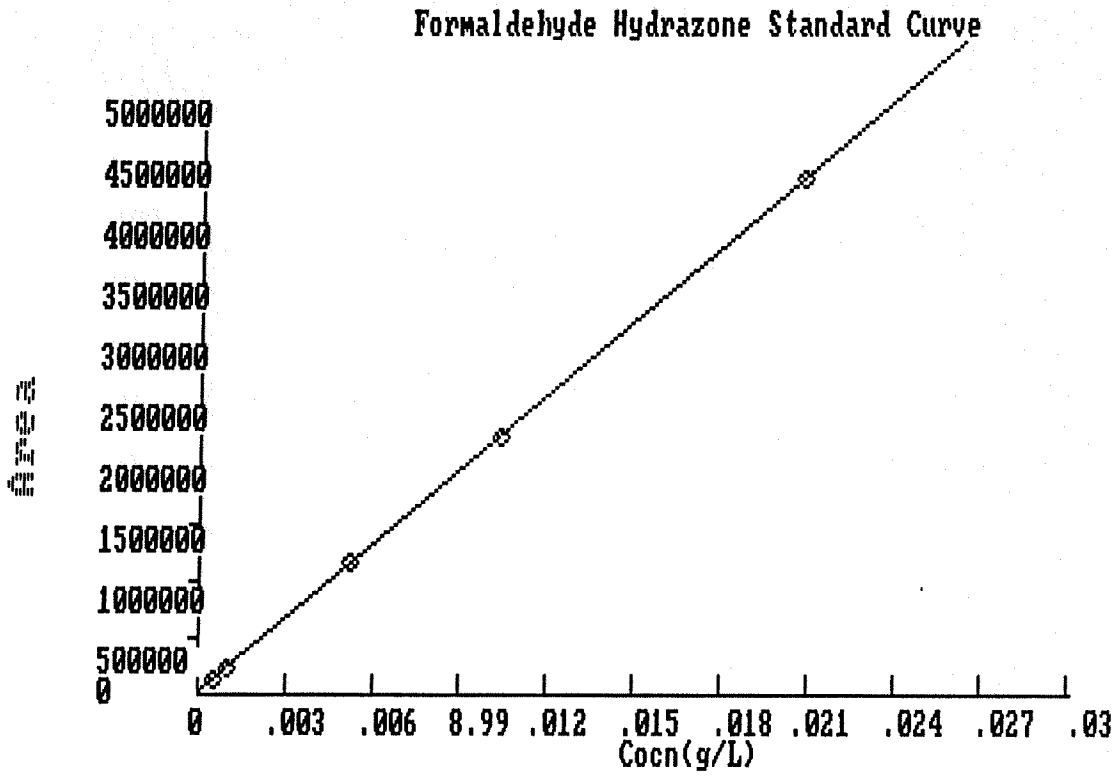


Figure 30. Calibration of Formaldehyde Hydrazone Standards

Acetaldehyde Hydrazone Standard Curve

POINT	X	Y
1	.2925	59650
2	.585	115530
3	2.925	603820
4	5.85	1244100
5	11.7	2463400

Slope = 211352.7 +/- 1034.066
Intercept = -5281.6 +/- 9750.43
Correlation = .9999642
Calculated on points 1 TO 5

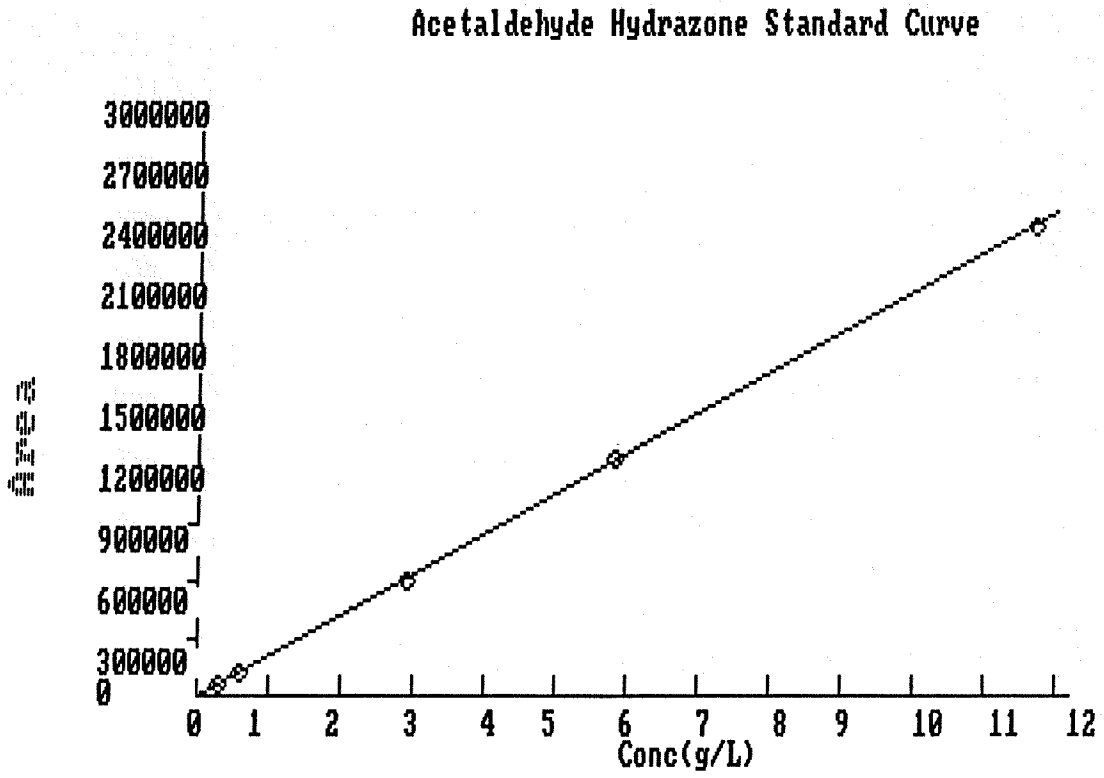


Figure 31. Calibration of Acetaldehyde Hydrazone Standards

Acrolein Hydrazone Standard Curve

POINT	X	Y
1	.3525	73843
2	.705	149120
3	3.525	774030
4	7.05	1556500
5	14.1	3088200

Slope = 219486 +/- 649.8198
Intercept = -1245.9 +/- 7384.169
Correlation = .9999869
Calculated on points 1 TO 5

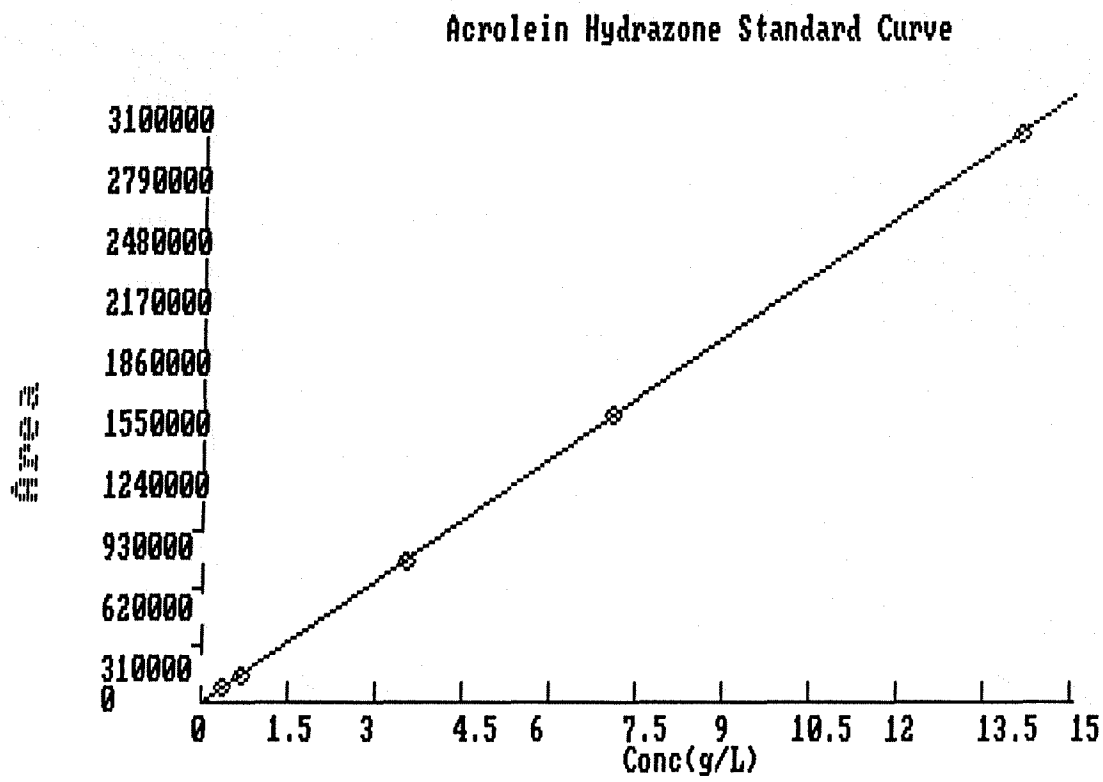


Figure 32. Calibration of Acrolein Hydrazone Standards

Propionaldehyde Hydrazone Standard Curve

POINT	X	Y
1	.935	185350
2	1.87	356870
3	9.350001	1793200
4	18.7	3607600
5	37.4	7142600

Slope = 191053 +/- 577.8805
Intercept = 9059.401 +/- 17418.04
Correlation = .9999864
Calculated on points 1 TO 5

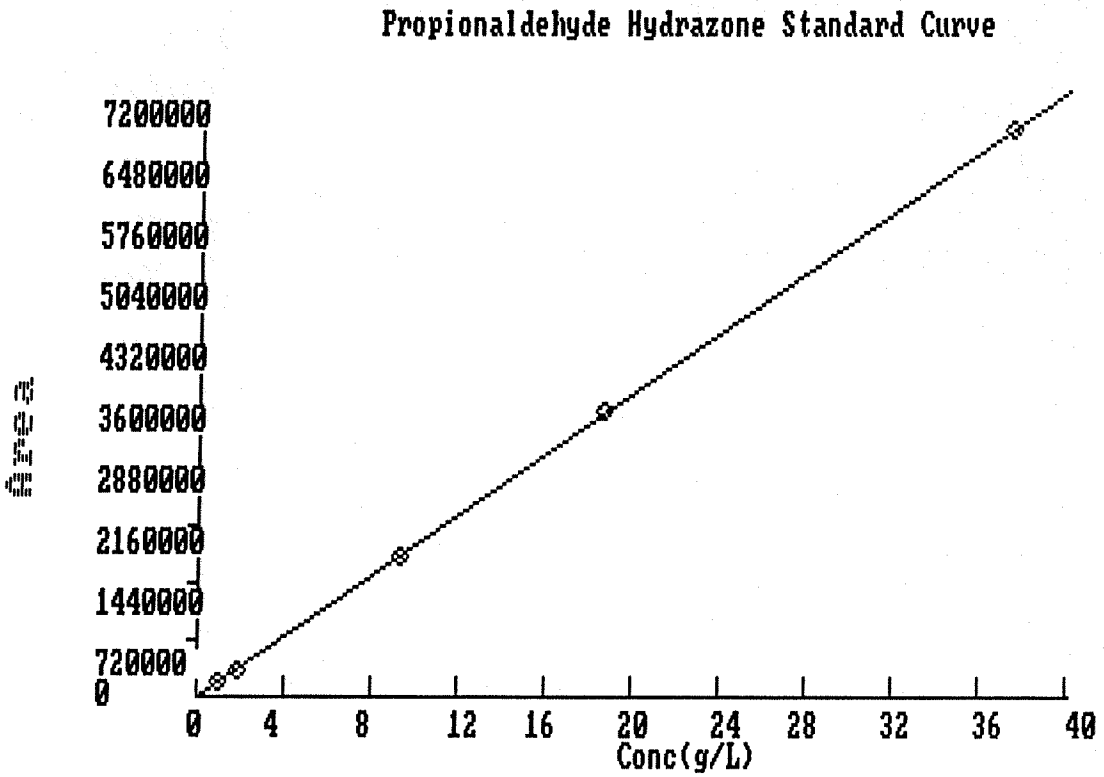


Figure 33. Calibration of Propionaldehyde Hydrazone Standards

Benzaldehyde Hydrazone Standard Curve

POINT	X	Y
1	.475	83882
2	.95	161800
3	4.75	837060
4	9.5	1655100
5	19	3291200

Slope = 173218.4 +/- 532.1976
Intercept = 4538.7 +/- 8149.222
Correlation = .9999858
Calculated on points 1 TO 5

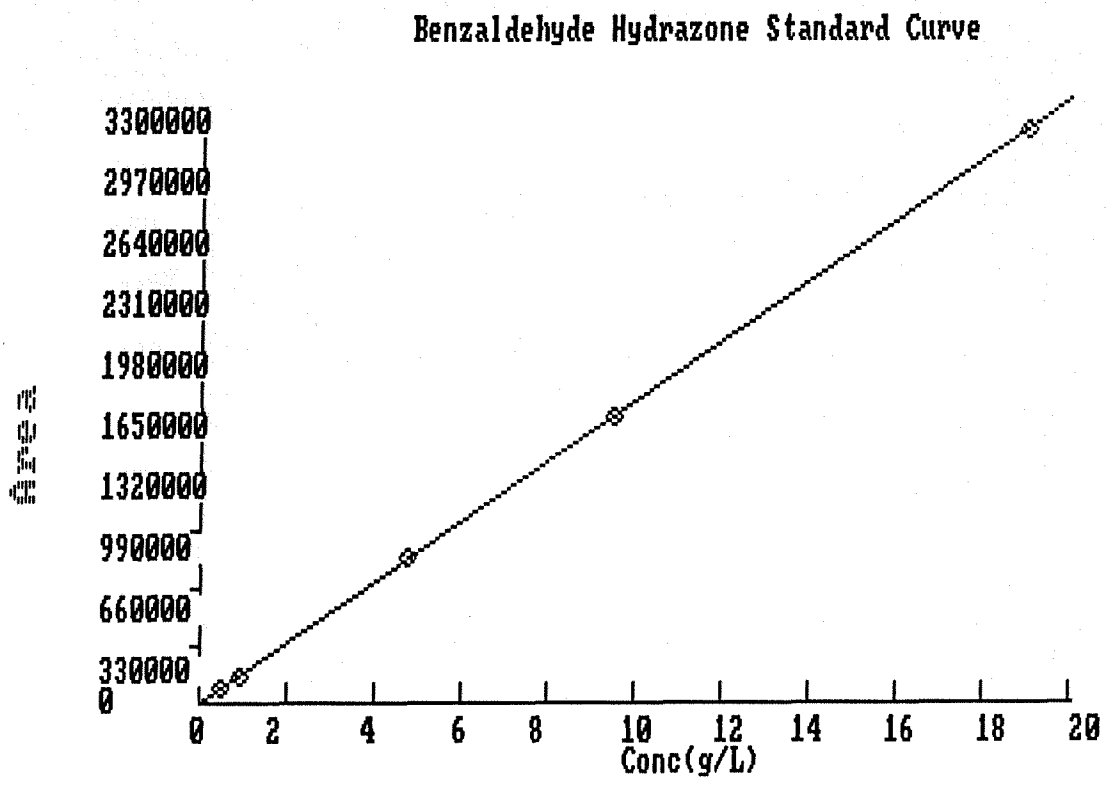


Figure 34. Calibration of Benzaldehyde Hydrazone Standards

Figure 35.

Cartridge blank. Letters along the X-axes are ID codes of the participating laboratories. Numbers along the Y-axes are derivative concentrations in micrograms per cartridge.

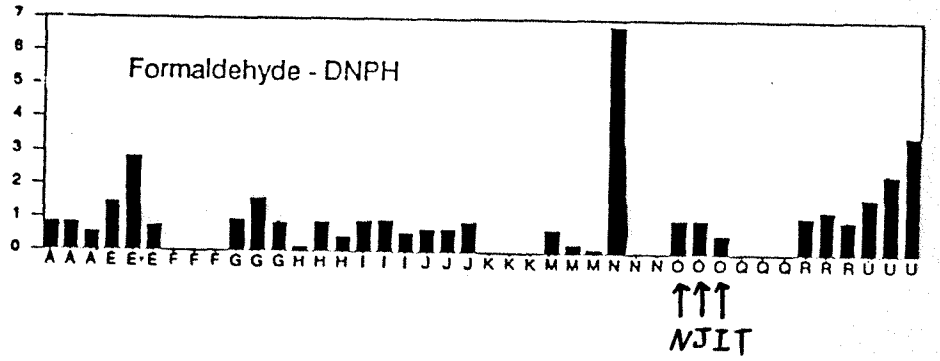


Figure 36.

Formaldehyde-DNPH in spiked cartridges. The fourth A bar is the average of the first three.

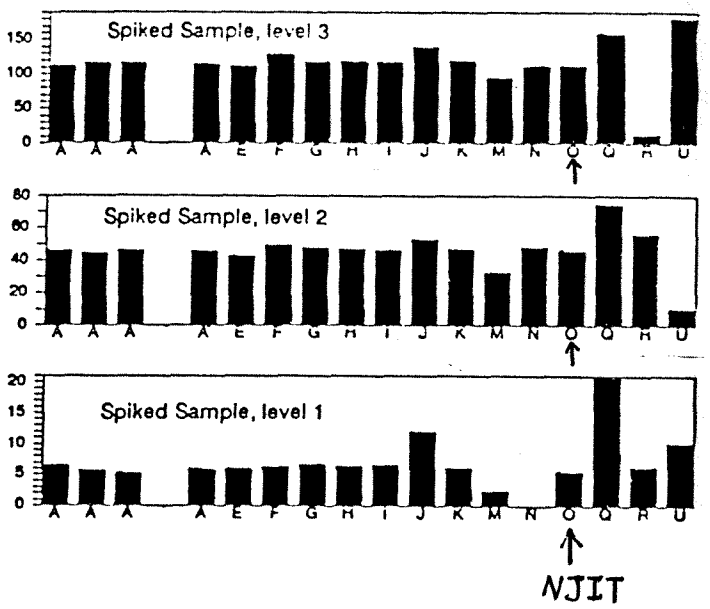


Figure 37.

The exhaust sample set analytical results for formaldehyde - DNPH. Each set of 4 var positions represent a sampling episode. The samples are arranged in increasing order by run number and sampling port position. Lab codes are in the X-axes. values in the Y-axes are in micrograms per cartridge. The Figure also shows how the samples were distributed.

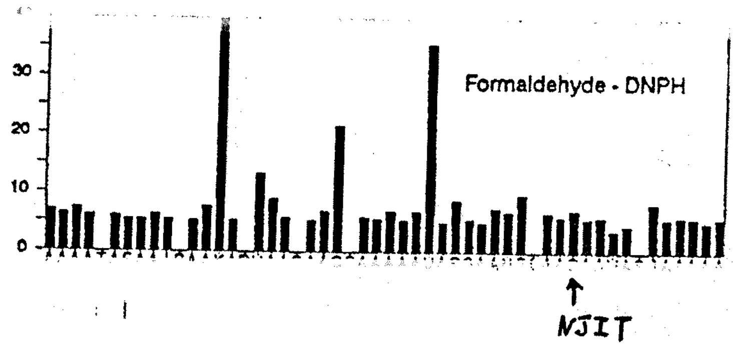


Figure 38.

The exhaust data set with control samples randomly sorted out. The isolated A bar represents the average of the control samples.

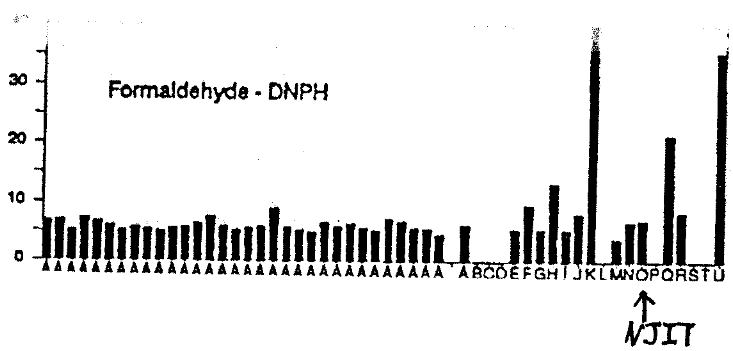


Figure 39. HCHO Conc. Distribution

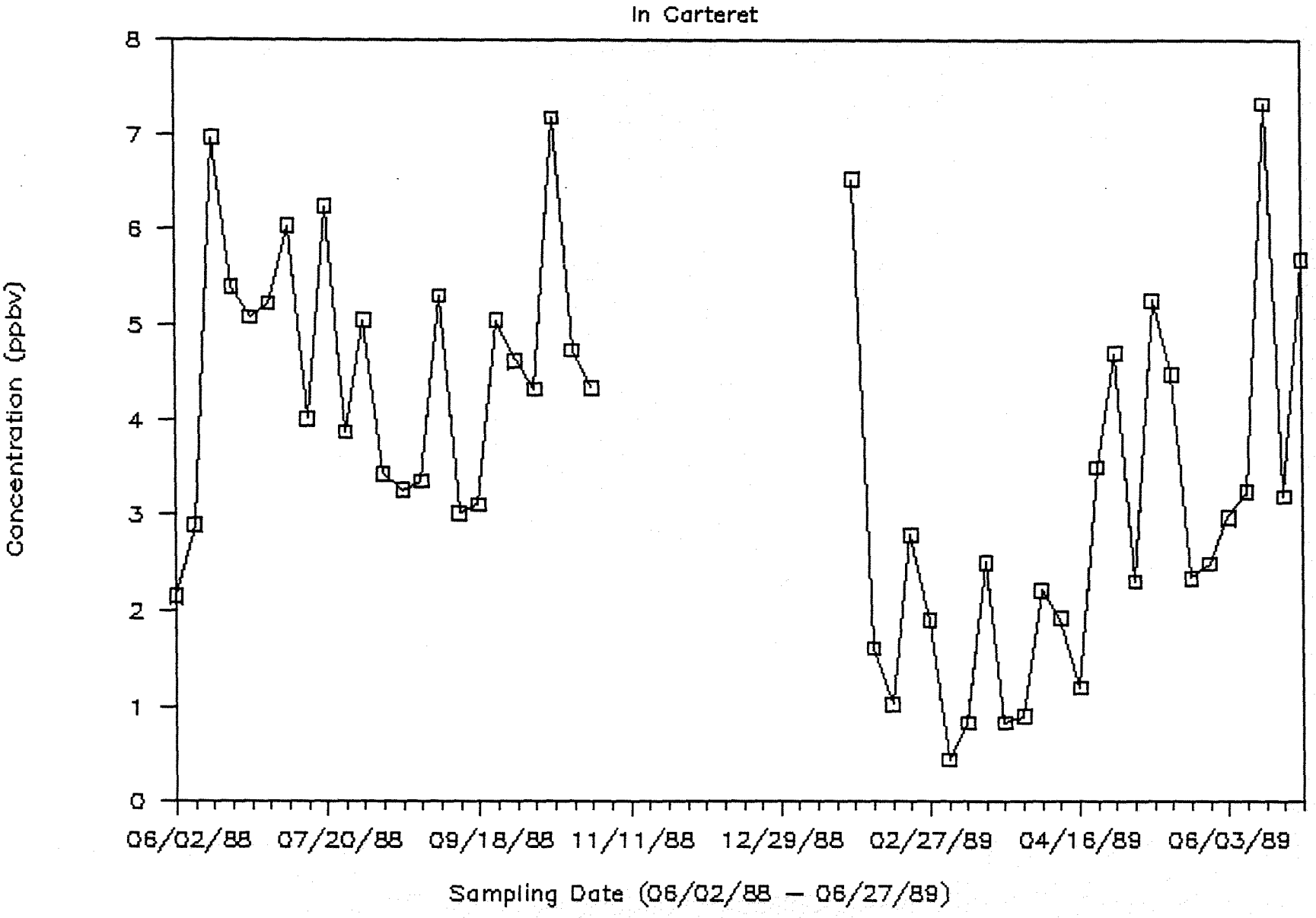


Figure 40. HCHO Conc. Distribution

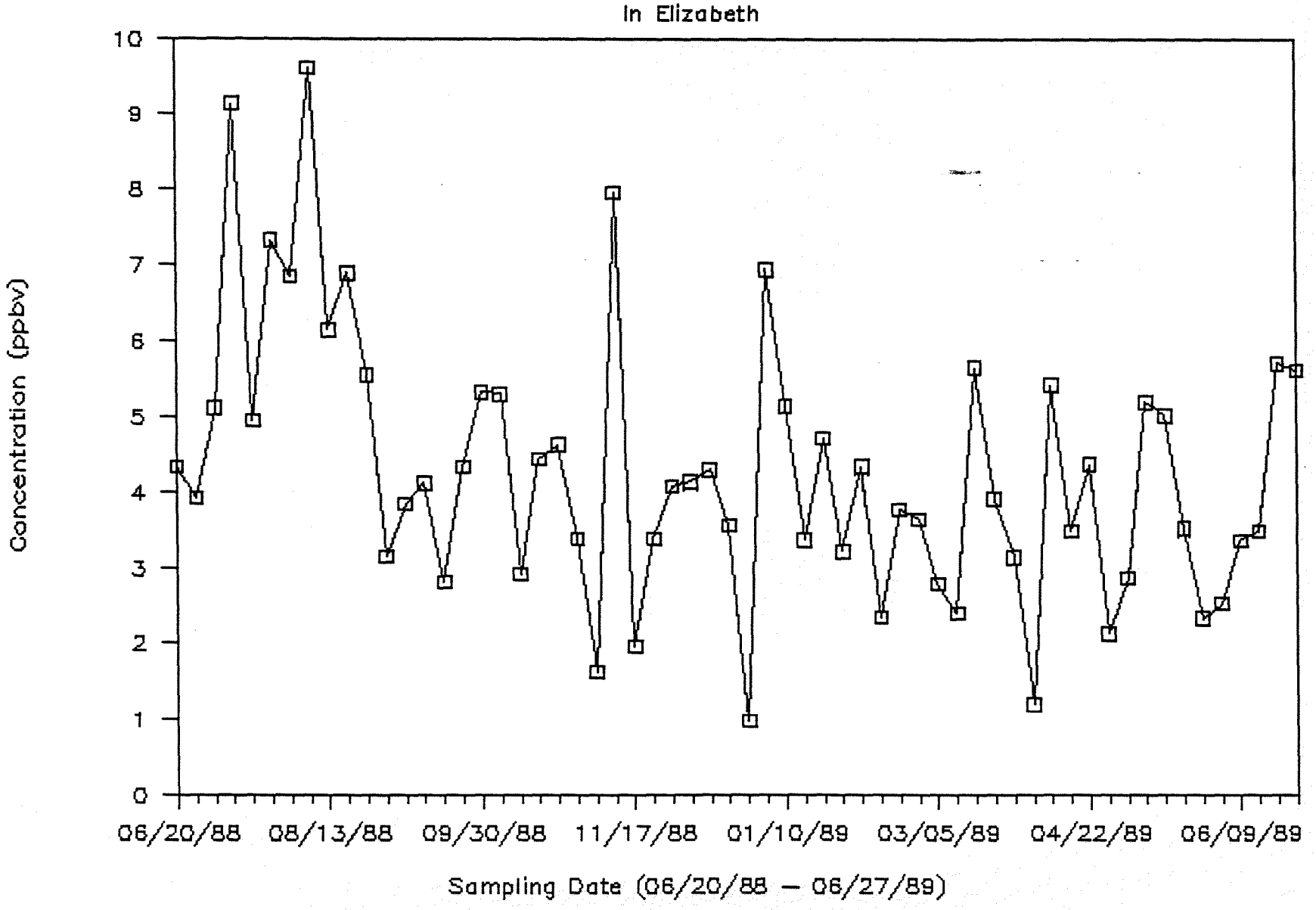


Figure 41. HCHO Statistical Average

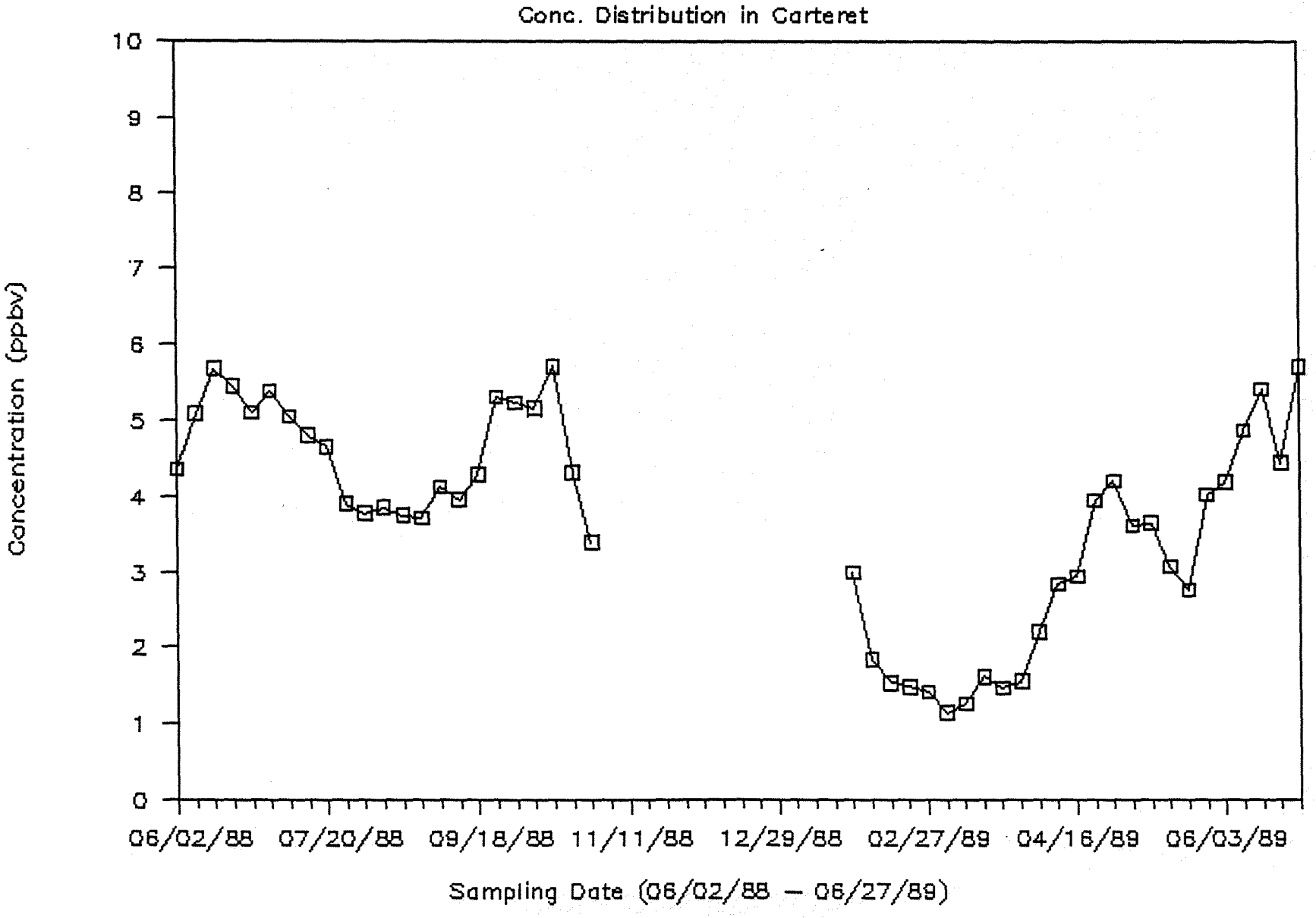
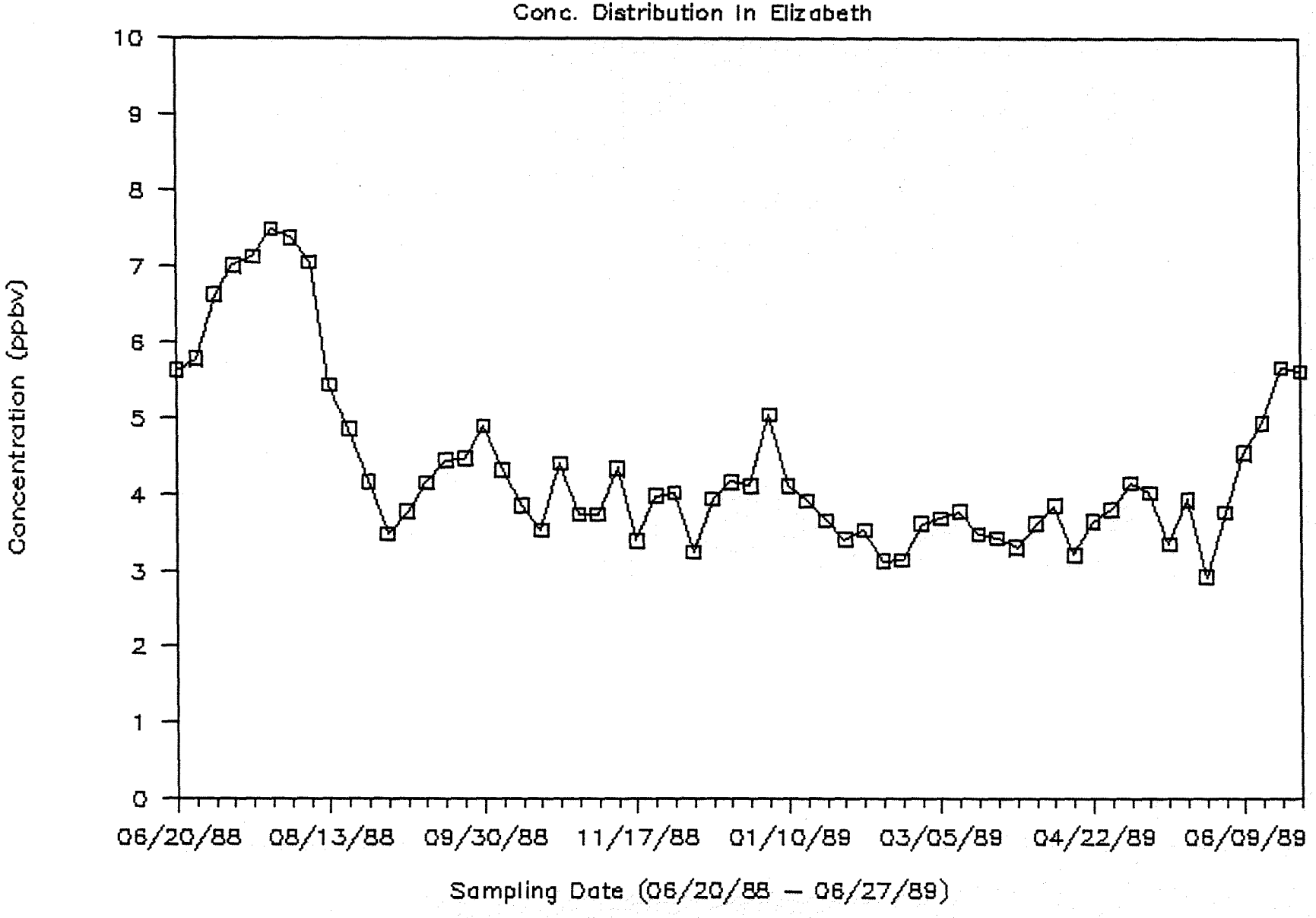
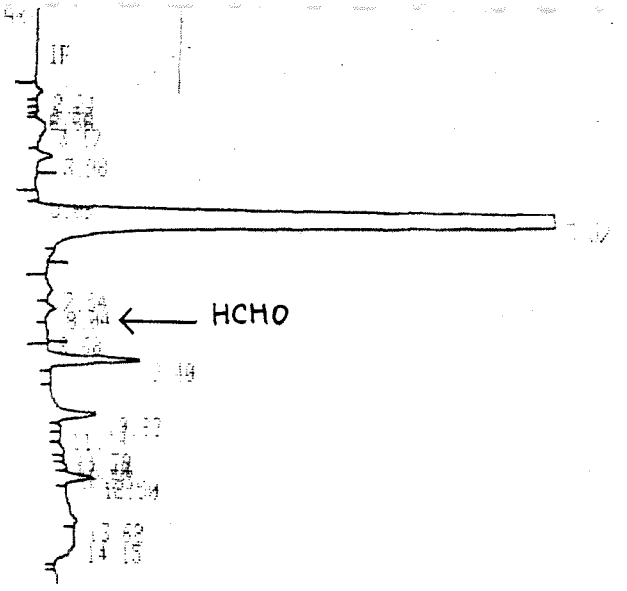
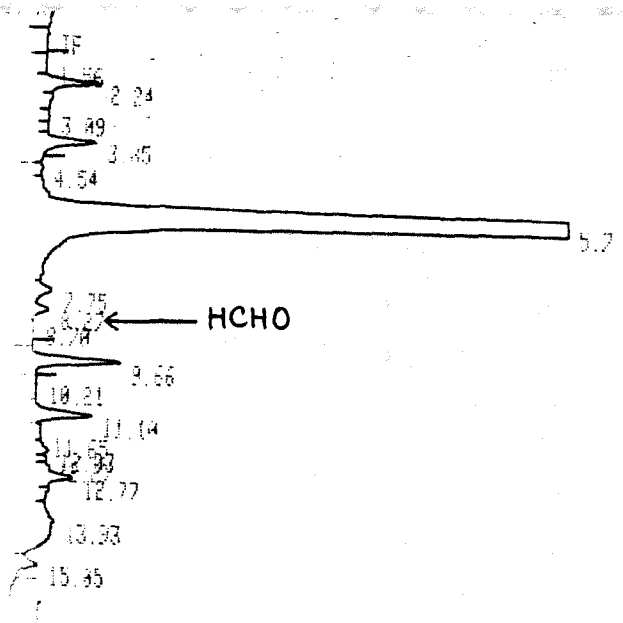
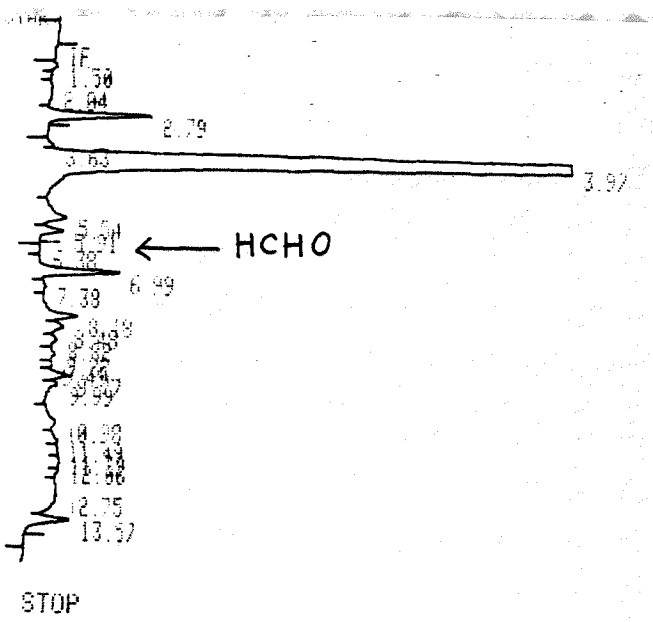


Figure 42. HCHO Statistical Average









80

26

RT	AREA	TYPE	AR/HT	AREA%
2.21	10365	PB	0.160	0.052
2.52	900	V BB	0.029	0.005
2.68	1420	BB	0.084	0.006
3.17	57046	PB	0.411	0.222
3.98	29789	BB	0.177	0.154
4.09	3797	PB	0.150	0.015
5.57	2.5019E+07	SPB	0.189	97.141
7.94	20408	PB	0.247	0.080
8.04	21125	BP	0.171	0.082
9.66	836	BB	0.148	0.003
9.40	2	V	0.185	0.246
10.83		PB	0.169	0.367
11.19	891	BB	0.104	0.004
11.79	6098	PB	0.169	0.024
12.00	962	BB	0.087	0.004
12.23	4007	BB	0.1	0.016
12.50	58552	BB	0.156	0.228
13.62	13039	BB	0.1263	0.05
14.15	27459	BB	0.259	0.10

TOTAL AREA= 2.5760E+07
AUL FACTOR= 1.0000E+00

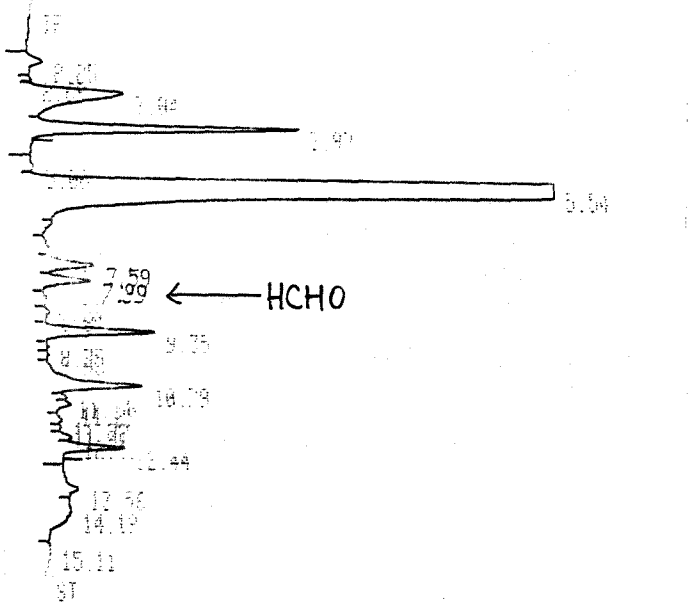
13 DEC-01-98

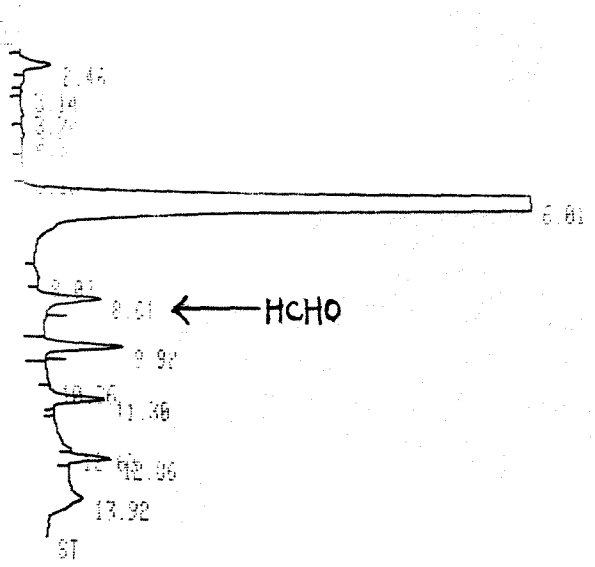
RT	AREA	TYPE	AR/HT	AREA%
1.56	3785	BB	0.345	0.014
2.24	107570	BB	0.151	0.405
3.09	3332	PB	0.168	0.013
3.85	140500	VB	0.194	0.528
4.54	1936	PB	0.129	0.007
5.74	2.5512E+07	SPB	0.207	95.943
[illegible]	43774	BB	0.220	0.165
[illegible]	32932	BB	0.171	0.124
8.70	2079	BB	0.114	0.008
9.66	238100	PB	0.194	0.895
10.21	9270	BB	0.429	0.035
11.10	151880	BB	0.195	0.571
11.65	4388	BB	0.301	0.017
12.03	8909	BB	0.143	0.034
12.27	1103	BB	0.107	0.004
12.72	66543	BB	0.105	0.250
13.93	222340	VB	0.904	0.836

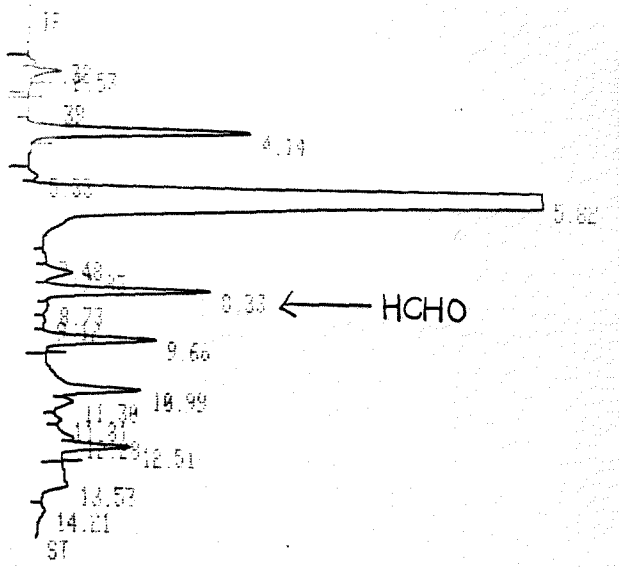
RUN # 11 DEC-15/98 13:46:01

RT	AREA	TYPE	AR/HT	AREA%
1.50	6836	BB	0.120	0.043
2.04	13968	PB	0.444	0.089
2.79	211670	BB	0.143	1.345
3.63	1179	PB	0.038	0.008
3.97	1.4928E+07	SPB	0.149	94.821
5.54	78537	BB	0.252	0.499
5.91	39697	BB	0.136	0.252
6.38	4195	BB	0.134	0.027
6.99	172780	BB	0.153	1.098
7.38	5320	BB	0.145	0.034
8.10	33428	BB	0.093	0.212
8.48	21148	BB	0.177	0.134
8.82	9710	BB	0.149	0.062
9.22	9551	BB	0.153	0.061
9.49	2582	BB	0.105	0.016
9.77	27870	BB	0.121	0.177
9.99	8600	V BB	0.382	0.355
10.98	13829	BB	0.208	0.088
11.49	1487	BB	0.062	0.010
11.79	1912	BB	0.193	0.012
12.06	1502	BB	0.168	0.010
12.75	84108	VB	1.006	0.534
[illegible]	63994	[illegible]	[illegible]	0.407

Figure 43. The Impurity Level of Acceptable DNPH-Coated Silica Blank Cartridges







\# 15

AREA%

RT	AREA	TYPE	AR/HT	AREA%
2.25	449[illegible]	PB	0.208	[illegible]21
2.69	207[illegible]	BB	0.082	006
3.04	483920	BB	0.366	.307
3.97	[illegible]4[illegible]00	BB	0.181	1.866
5.06	7079	PB	0.175	0.021
5.54	3 4705E+07	SPB	0.193	93.695
7.22	3781	PB	0.178	0.010
7.58	140160	BB	0.209	0.378
7.99	112350	BB	0.171	0.303
8.53	9048	BB	0.213	0.024
8.81	12037	BB	0.161	0.033
9.35	293480	BB	0.186	0.792
9.75	2642	BB	0.121	0.007
9.98	1894	BB	0.121	0.005
10.79	248600	BB	0.202	0.671
11.11	4245	BB	0.100	0.012
11.29	13365	BB	0.122	0.036
11.72	4995	BB	0.126	0.014
11.91	1911 D	BB	0.098	0.005
12.18	10276	BB	0.111	0.028
12.44	133600	BB	0.158	0.361
[illegible].56	34661	PB	0.204	0.094
.12	59419	BB	0.467	0.160
11	19368 I	BP	0.693	0.052

RUN # 1 NOV/09/88 11:02:05

AREA%

RT	AREA	TYPE	AR/HT	AREA%
2.46	93375	PB	0.203	0.259
3.14	1813 D	VB	0.091	0.006
3.74	8691	BB	0.368	0.027
4.33	6114	BB	0.251	0.019
5.16	426	BB	0.073	0.001
6.01	3.1347E+07	SPB	0.195	97.183
8.03	5378	BB	0.172	0.017
8.61	192500	BB	0.208	0.597
[illegible].92	210690	PB	0.188	0.653
10.86	0	PB	0.000	0.000
11.30	133930	BB	0.182	0.415
12.63	0	PB	0.000	0.000
12.86	89582	BB	0.151	0.278
13.92	176210 I	BP	0.508	0.546

TOTAL AREA= 3.2255E+07

RUN # 6 NOV/09/88 12:33:47

AREA%

RT	AREA	TYPE	AR/HT	AREA%
2.32	8034	PB	0.112	0.021
2.53	54733	BB	0.127	0.139
3.39	1858	PB	0.176	0.005
4.14	570290	BB	0.178	1.454
5.33	11612	PB	0.136	0.030
5.82	3.7250E+07	SPB	0.195	94.999
7.48	3413	BB	0.187	0.009
7.83	77168	BB	0.211	0.197
8.33	431500	BB	0.182	1.101
8.73	4498	BB	0.183	0.012
9.12	2554	BB	0.172	0.007
9.66	296060	BB	0.184	0.755
10.99	192550	PB	0.167	0.491
11.30	30321	BB	0.189	0.077
11.81	10367	BB	0.136	0.026
12.28	4089	BB	0.058	0.010
12.51	122380	BB	0.137	0.312
13.53	115210	BB	0.401	0.294
14.21	24796 I	BP	0.324	0.063

Figure 44. The High Impurity Level of DNPH-Coated Silica Blank Cartridges

Table 1. Retention Times of Formaldehyde Hydrazone Standard Solutions and Samples (01/04/89 - 04/10/89)

Analysis Number	Retention Time of STD Solution	Retention Time of Sample
1	8.24	7.99
2	8.00	7.99
3	8.08	8.02
4	8.19	8.00
5	7.99	8.00
6	6.92	8.00
7	6.88	8.01
8	7.83	8.03
9	6.88	8.03
10	7.84	8.04
11	6.90	7.88
12	7.99	7.85
13	6.97	7.83
14	7.97	7.97
15	7.07	7.88
16	6.96	8.07
17	7.92	7.90
18	6.89	7.83
19	7.03	8.04
20	6.98	7.49
21	6.96	7.33
22	6.97	7.27
23	6.96	7.18
24	7.52	7.43
25	6.96	8.13
26	7.18	7.50
27	7.06	7.11
28	7.37	7.19
29		8.12
30		7.64
31		7.11
32		7.22
33		7.21
34		7.64
35		7.13
36		7.80
37		7.23
38		8.15
39		7.19
40		7.22
41		8.03
42		7.18
43		7.79
44		8.04
45		8.02

Table 1. (Continued)

Analysis Number	Retention Time of STD Solution	Retention Time of Sample
46		8.01
47		7.93
48		7.12
49		7.15
50		7.24
51		7.12
52		7.13
53		7.12
54		7.09
55		7.83
56		7.97
57		7.53
58		7.81
59		7.57
60		7.58
61		7.61
62		7.43
63		7.29
64		7.26
65		7.03
66		6.97
67		7.05
68		7.04
69		7.00
70		7.05
71		7.02
Average	7.38	7.57
Max	8.24	8.15
Min	6.88	6.97
STD Dev.	0.49	0.39
Average + 2* STD	8.36	0.36
Average - 2* STD	6.39	6.79
RSD%	6.70	5.17

Table 2. An Example of a Completed Formaldehyde Analytical Result Entry Form

Formaldehyde Data of KUSU Sampler in Carteret

Sampling Date	Flow on Reading	Flow off Reading	Average Reading	Flow rate (ml/min)
01/22/89	96.0	94.0	95.0	500.16

Sampling Date	Sampling Time(Min)	Volume (liter)	Front Trap Area	Back Trap Area
01/22/89	1454	727.23	1763100	81187

Sampling Date	Blank Trap Area	True Area	STD Slope	STD Intercept
01/22/89	21126	1741974	2.27962E+08	-2.39690E+04

Sampling Date	Conc. ppb(ug/L)
01/22/89	6.21

Table 3. Analytical Data of NJIT Formaldehyde Hydrazone STDs

(Conc. Unit = g / 1000 ml ACN)

Analyzed Date	Conc.1 0.0005	Conc.2 0.0010	Conc.3 0.0052	Conc.4 0.0104	Conc.5 0.0208
08/04/88	100240	217930	1186000	2468800	4827900
09/10/88	104650	203750	1189600	2361200	5034800
10/11/88	99375	227430	1176500	2354200	4938700
11/17/88	84495	238970	1145700	2319700	4708600
01/19/89	95445	216560	1137900	2347600	4722400
02/17/89	92220	242350	1050200	2171000	4583200
03/14/89	93667	268280	1048000	1952900	4349000
04/14/89	94573	256570	1057100	2096000	4472100
# of Obs.	8	8	8	8	8
Maximium	104650	268280	1189600	2468800	5034800
Minimium	84495	203750	1048000	1952900	4349000
Average	95583	233980	1123875	2258925	4704588
STD Dev.	5671	20309	58380	159322	216396
%RSD	5.93	8.68	5.19	7.05	4.60

Table 4. Formaldehyde Indoor Comparison

Sampling Number	Formaldehyde Conc.(ppb) HEMA	KUSU	Difference	% Difference
1	3.51	3.02	0.49	16.23
2	2.52	2.23	0.29	13.00
3	3.35	3.45	0.10	2.90
4	3.48	3.35	0.13	3.88
Total			1.01	36.01
Average			0.20	7.20
STD Dev.			0.15	5.74

Table 5. Formaldehyde Shootout #2

Date	EPA Formaldehyde Conc.(ppb)	NJIT Formaldehyde Conc.(ppb)	% Difference
07/25/88	3.64	3.84	5.2
07/26/88	0.76	NA	___
07/27/88	1.85	1.69	9.5
07/28/88	4.04	4.90	17.6

NA : NJIT sampling failure due to electric power off

Table 6. Analytical Data of EPA Formaldehyde Hydrazone STDs

(Conc. Unit = g / 1000 ml ACN)

Run Number	Conc.1 0.0005	Conc.2 0.0010	Conc.3 0.0052	Conc.4 0.0104	Conc.5 0.0208
1	122380	236760	1160600	2277300	4523800
2	116130	170160	1045000	2229900	4521900
3	103020	189250	1136900	2352000	4746400
4	103130	228360	1163200	2070200	4421200
5	113102	212350	1048500	2082800	4228800
# of Obs.	5	5	5	5	5
Maximium	122380	236760	1163200	2352000	4746400
Minimium	103020	170160	1045000	2070200	4228800
Average	111552	207376	1110840	2202440	4488420
STD Dev.	7541	24666	53137	110025	167838
%RSD	6.76	11.89	4.78	5.00	3.74

Table 7. Comparsions of NJIT's and EPA's Standard Value

(Conc. Unit = g/1000 mL ACN)

Conc. of HCHO STD	Conc. 1 0.005	Conc.2 0.001	Conc.3 0.0052	Conc.4 0.0104	Conc.5 0.0208
NJIT	95583	233980	1123875	2258925	4704588
EPA	111552	207376	1110840	2202440	4488420
% Diff	16.7	11.4	1.2	2.5	4.8

Table 8. Analytical Data for the Blank Cartridges

Values are in ug/cartridge.

Formaldehyde

	Lab A	Lab O
	0.84	1
	0.82	1.01
	0.55	0.56
Mean	0.74	0.86
Sigma	0.16	0.26
n	3	3
%RSD	21.91	3
Minimum	0.55	0.56
Maximum	0.84	1.01

Table 9. Level 1, Level 2 and Level 3

Spiked Cartridge Data

Formaldehyde

	Lab A	Lab O
Level 1	5.78	5.44
Level 2	45.67	45.92
Level 3	113.53	112.07

Table 10. The Exhaust Sample Data

Values are in ug/cartridge.

Formaldehyde

	Lab A	Lab O
Mean	6.02	6.98
Sigma	0.91	
%RSD	15.04	
n	32	
Minimum	4.48	
Maximum	8.91	

Table 11. Data of Formaldehyde Concentration

Sampling Site	Sampling Date	Conc.(ppb) (ug/m3)	Sampling Site	Sampling Date	Conc.(ppb) (ug/m3)
Carteret	06/02/88	2.16	Elizabeth	06/20/88	4.33
Carteret	06/08/88	2.89	Elizabeth	06/26/88	3.91
Carteret	06/14/88	6.96	Elizabeth	07/02/88	5.10
Carteret	06/20/88	5.40	Elizabeth	07/08/88	9.13
Carteret	06/26/88	5.08	Elizabeth	07/14/88	4.94
Carteret	07/02/88	5.22	Elizabeth	07/20/88	7.31
Carteret	07/08/88	6.04	Elizabeth	08/01/88	6.84
Carteret	07/14/88	4.01	Elizabeth	08/07/88	9.61
Carteret	07/20/88	6.24	Elizabeth	08/13/88	6.14
Carteret	08/01/88	3.87	Elizabeth	08/19/88	6.88
Carteret	08/07/88	5.05	Elizabeth	08/25/88	5.55
Carteret	08/13/88	3.43	Elizabeth	08/31/88	3.14
Carteret	08/19/88	3.26	Elizabeth	09/06/88	3.83
Carteret	08/25/88	3.35	Elizabeth	09/12/88	4.11
Carteret	08/31/88	5.31	Elizabeth	09/18/88	2.80
Carteret	09/06/88	3.02	Elizabeth	09/24/88	4.33
Carteret	09/18/88	3.11	Elizabeth	09/30/88	5.31
Carteret	09/30/88	5.05	Elizabeth	10/06/88	5.29
Carteret	10/06/88	4.62	Elizabeth	10/12/88	2.91
Carteret	10/12/88	4.32	Elizabeth	10/18/88	4.43
Carteret	10/18/88	7.18	Elizabeth	10/24/88	4.62
Carteret	10/24/88	4.74	Elizabeth	10/30/88	3.38
Carteret	10/30/88	4.34	Elizabeth	11/05/08	1.63
Carteret	11/05/08	SP	Elizabeth	11/11/88	7.95
Carteret	11/11/88	SP	Elizabeth	11/17/88	1.97
Carteret	11/17/88	SP	Elizabeth	11/23/88	3.37
Carteret	11/23/88	SP	Elizabeth	11/29/88	4.07
Carteret	11/29/88	SP	Elizabeth	12/05/88	4.13
Carteret	12/05/88	SP	Elizabeth	12/11/88	4.29
Carteret	12/11/88	SP	Elizabeth	12/17/88	3.56
Carteret	12/17/88	SP	Elizabeth	12/23/88	0.99
Carteret	12/23/88	SP	Elizabeth	12/29/88	6.93
Carteret	12/29/88	SP	Elizabeth	01/10/89	5.14
Carteret	01/10/89	SP	Elizabeth	01/16/89	3.36
Carteret	01/16/89	SP	Elizabeth	01/22/89	4.72
Carteret	01/22/89	SP			

SP : Personnel not available or causes loss of valid sample

Table 11. Data of Formaldehyde Concentration

(continued)

Sampling Site	Sampling Date	Conc.(ppb) (ug/m3)	Sampling Site	Sampling Date	Conc.(ppb) (ug/m3)
Carteret	02/03/89	6.53	Elizabeth	02/03/89	3.21
Carteret	02/09/89	1.61	Elizabeth	02/09/89	4.33
Carteret	02/15/89	1.03	Elizabeth	02/15/89	2.34
Carteret	02/21/89	2.79	Elizabeth	02/21/89	3.76
Carteret	02/27/89	1.91	Elizabeth	02/27/89	3.63
Carteret	03/05/89	0.44	Elizabeth	03/05/89	2.79
Carteret	03/11/89	0.83	Elizabeth	03/11/89	2.39
Carteret	03/17/89	2.51	Elizabeth	03/17/89	5.64
Carteret	03/23/89	0.83	Elizabeth	03/23/89	3.90
Carteret	03/29/89	0.09	Elizabeth	03/29/89	3.14
Carteret	04/04/89	2.22	Elizabeth	04/04/89	1.21
Carteret	04/10/89	1.93	Elizabeth	04/10/89	2.83
Carteret	04/16/89	1.20	Elizabeth	04/16/89	3.47
Carteret	04/22/89	3.50	Elizabeth	04/22/89	4.36
Carteret	04/28/89	4.70	Elizabeth	04/28/89	2.13
Carteret	05/04/89	2.31	Elizabeth	05/04/89	2.86
Carteret	05/10/89	5.26	Elizabeth	05/10/89	5.19
Carteret	05/16/89	4.48	Elizabeth	05/16/89	5.01
Carteret	05/22/89	2.34	Elizabeth	05/22/89	3.51
Carteret	05/28/89	2.49	Elizabeth	05/28/89	2.33
Carteret	06/03/89	2.98	Elizabeth	06/03/89	2.52
Carteret	06/09/89	3.24	Elizabeth	06/09/89	3.35
Carteret	06/15/89	7.32	Elizabeth	06/15/89	3.48
Carteret	06/21/89	3.19	Elizabeth	06/21/89	5.70
Carteret	06/27/89	5.69	Elizabeth	06/27/89	5.61

Carteret	Total #	48	Elizabeth	Total #	60
	Average	3.68		Average	4.29
	Maximum	7.32		Maximum	9.61
	Minimum	0.44		Minimum	0.99

Table 12. Data of Formaldehyde Statistic Average Concentration

Sampling Site	Sampling Date	Conc.(ppb) (ug/m3)	Sampling Site	Sampling Date	Conc.(ppb) (ug/m3)
Carteret	06/02/88	4.35	Elizabeth	06/20/88	5.62
Carteret	06/08/88	5.08	Elizabeth	06/26/88	5.77
Carteret	06/14/88	5.67	Elizabeth	07/02/88	6.62
Carteret	06/20/88	5.44	Elizabeth	07/08/88	7.01
Carteret	06/26/88	5.09	Elizabeth	07/14/88	7.12
Carteret	07/02/88	5.38	Elizabeth	07/20/88	7.48
Carteret	07/08/88	5.04	Elizabeth	08/01/88	7.37
Carteret	07/14/88	4.79	Elizabeth	08/07/88	7.05
Carteret	07/20/88	4.65	Elizabeth	08/13/88	5.43
Carteret	08/01/88	3.90	Elizabeth	08/19/88	4.85
Carteret	08/07/88	3.77	Elizabeth	08/25/88	4.16
Carteret	08/13/88	3.84	Elizabeth	08/31/88	3.47
Carteret	08/19/88	3.74	Elizabeth	09/06/88	3.77
Carteret	08/25/88	3.70	Elizabeth	09/12/88	4.14
Carteret	08/31/88	4.12	Elizabeth	09/18/88	4.43
Carteret	09/06/88	3.95	Elizabeth	09/24/88	4.46
Carteret	09/18/88	4.28	Elizabeth	09/30/88	4.89
Carteret	09/30/88	5.30	Elizabeth	10/06/88	4.31
Carteret	10/06/88	5.22	Elizabeth	10/12/88	3.84
Carteret	10/12/88	5.15	Elizabeth	10/18/88	3.52
Carteret	10/18/88	5.70	Elizabeth	10/24/88	4.40
Carteret	10/24/88	4.31	Elizabeth	10/30/88	3.73
Carteret	10/30/88	3.38	Elizabeth	11/05/08	3.73
Carteret	11/05/08	SP	Elizabeth	11/11/88	4.34
Carteret	11/11/88	SP	Elizabeth	11/17/88	3.39
Carteret	11/17/88	SP	Elizabeth	11/23/88	3.97
Carteret	11/23/88	SP	Elizabeth	11/29/88	4.01
Carteret	11/29/88	SP	Elizabeth	12/05/88	3.24
Carteret	12/05/88	SP	Elizabeth	12/11/88	3.94
Carteret	12/11/88	SP	Elizabeth	12/17/88	4.16
Carteret	12/17/88	SP	Elizabeth	12/23/88	4.11
Carteret	12/23/88	SP	Elizabeth	12/29/88	5.04
Carteret	12/29/88	SP	Elizabeth	01/10/89	4.11
Carteret	01/10/89	SP	Elizabeth	01/16/89	3.91
Carteret	01/16/89	SP	Elizabeth	01/22/89	3.65
Carteret	01/22/89	SP			

SP : Personnel not available or causes loss of valid sample

Table 12. Data of Formaldehyde Statistic Average Concentration

(continued)

Sampling Site	Sampling Date	Conc.(ppb) (ug/m3)	Sampling Site	Sampling Date	Conc.(ppb) (ug/m3)
Carteret	02/03/89	2.99	Elizabeth	02/03/89	3.41
Carteret	02/09/89	1.84	Elizabeth	02/09/89	3.52
Carteret	02/15/89	1.54	Elizabeth	02/15/89	3.13
Carteret	02/21/89	1.49	Elizabeth	02/21/89	3.14
Carteret	02/27/89	1.42	Elizabeth	02/27/89	3.61
Carteret	03/05/89	1.15	Elizabeth	03/05/89	3.68
Carteret	03/11/89	1.27	Elizabeth	03/11/89	3.77
Carteret	03/17/89	1.62	Elizabeth	03/17/89	3.48
Carteret	03/23/89	1.47	Elizabeth	03/23/89	3.42
Carteret	03/29/89	1.56	Elizabeth	03/29/89	3.31
Carteret	04/04/89	2.21	Elizabeth	04/04/89	3.61
Carteret	04/10/89	2.83	Elizabeth	04/10/89	3.84
Carteret	04/16/89	2.93	Elizabeth	04/16/89	3.21
Carteret	04/22/89	3.94	Elizabeth	04/22/89	3.64
Carteret	04/28/89	4.19	Elizabeth	04/28/89	3.80
Carteret	05/04/89	3.60	Elizabeth	05/04/89	4.14
Carteret	05/10/89	3.64	Elizabeth	05/10/89	4.01
Carteret	05/16/89	3.07	Elizabeth	05/16/89	3.34
Carteret	05/22/89	2.76	Elizabeth	05/22/89	3.93
Carteret	05/28/89	4.01	Elizabeth	05/28/89	2.92
Carteret	06/03/89	4.18	Elizabeth	06/03/89	3.76
Carteret	06/09/89	4.86	Elizabeth	06/09/89	4.54
Carteret	06/15/89	5.40	Elizabeth	06/15/89	4.93
Carteret	06/21/89	4.44	Elizabeth	06/21/89	5.66
Carteret	06/27/89	5.10	Elizabeth	06/27/89	5.61
Carteret	Total #	48	Elizabeth	Total #	60
	Average	3.74		Average	4.34
	Maximum	5.70		Maximum	7.48
	Minimum	1.15		Minimum	2.92

Table 13. Investigation of Ozone Interference

Date	Ozone (ppb)	Formaldehyde detected conc.(ppb) Method #1	Method #2	Method #3	(#3-#1)/#1
06/29/89	25	18.18	6.79	14.85	-18.32
06/30/89	47	19.29	17.51	15.95	-17.31
07/03/89	85	27.08	23.54	24.33	-10.16
07/26/89	71	66.62	48.34	62.82	-5.70
07/27/89	62	58.51	40.73	40.28	-31.16

Method #1 : using KI coated copper tubing in front of cartridge

Method #2 : using $NaHSO_3$ coated copper tubing in front of cartridge

Method #3 : only copper tubing in front of cartridge