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Correlation of Remote and Wet Chemical Sampling Techniques for Hydrogen Fluoride from Gypsum Ponds

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Division of Stationary Source Enforcement
Washington, D.C.

Contract No. 68-01-4143
Technical Service Area 2
Task Order No. 59

CORRELATION OF REMOTE AND WET CHEMICAL SAMPLING TECHNIQUES FOR HYDROGEN FLUORIDE FROM GYPSUM PONDS

Headquarters DSSE

Final Report

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DISCLAIMER

ABSTRACT

For several years, the Environmental Protection Agency (EPA) has used the Remote Optical Sensing of Emissions (ROSE) system to characterize the gaseous pollutants emitted by a variety of point and extended area sources. The purpose of this program was to extend the data base of this versatile and promising pollutant sensor by comparing the data generated by the ROSE system with data generated by standard techniques for the sampling and analysis of hydrogen fluoride. The program was divided into five phases including a literature review, pretest survey, sampling and analytical trials in the laboratory, preliminary field phase, and the final, collaborative field phase. The field sampling efforts were conducted along gypsum ponds at two phosphate fertilizer facilities. For the formal sampling phase, both the double filter cassette and sodium bicarbonate-coated tube were used for the point sampling. The point sampling effort was conducted simultaneously with the operation of the ROSE system. A sampling period of 15 minutes was compatible with the sensitivity requirements of the analytical methods. The fluoride collected by the wet chemical methods was analyzed colorimetrically using a semiautomated method with lanthanum-alizarin complexone for the colorimetric reagent. Two data reduction methods, a peak area and peak height procedure, were used to compute the HF concentrations from the spectra obtained by the ROSE system. In 32 independent tests of comparable ambient HF concentrations, the overall average HF concentration was 37.6 ppb (ROSE system, peak area method), 36.1 ppb (ROSE system, peak height method) and 36.4 ppb (wet chemical techniques). The standard deviation between the ROSE system data and the manual sampling results was 11.9 ppb and 9.7 ppb for the peak area and peak height computation procedures, respectively.

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SECTION 1

INTRODUCTION

STATEMENT OF THE PROBLEM

For several years the Environmental Protection Agency (EPA) has used the Remote Optical Sensing of Emissions (ROSE) system to characterize the gaseous pollutants emitted by a variety of point and extended area sources.[1] The ROSE system consists of a Fourier transform infrared (FTIR) interferometer with telescopic optics and has been installed in a van. The system is used either with a remotely located infrared light source to make long path (up to 1.5 km) atmospheric absorption measurements or in a single-ended mode to measure the infrared emission signal from gases exiting industrial stacks at elevated temperatures.

For the purpose of developing a technical basis for enforcement action to abate human health hazards, it may be necessary to determine concentrations of toxic gaseous pollutants in the vicinity of sources. The ROSE system used in the "active long path mode" is conceptually capable of evaluating the breathing zone pollutant concentrations. The purpose of this task was to extend the data base of this versatile and promising pollutant sensor by comparison of data generated by the ROSE system with data generated by standard techniques for the measurement of hydrogen fluoride (HF). This work will enhance the ability of the EPA to rely, in enforcement actions, upon data generated by the ROSE system.

PROJECT PHASES

A phased approach was adopted for conducting the project. The five phases are indicated below and will be presented in more detail in the subsequent sections.

- Literature Review

- Pretest Survey

- Sampling and Analytical Trials in Laboratory

- Preliminary Field Phase

- Collaborative Field Sampling and Analytical Phase

The purpose of the literature review was to determine which techniques for the sampling and analysis of HF would facilitate the collaborative sampling program. Three possible sampling procedures (i.e., the double filter cassette, the sodium bicarbonate-coated glass tube, and the prefilter and impinger system) were selected for further investigation.

The Pretest Survey was conducted to accomplish the following:

● Locate two phosphate chemical plants with a geography compatible with the ROSE system and chemical sampling methods.

● Determine sites at each plant which are adjacent to gypsum ponds and have an unobstructed path length of about 400 meters. This would provide a high signal to noise ratio for the ROSE system.

● Determine the feasibility of using the proposed wet chemical sampling methods at the sites.

● Determine the availability of onsite laboratory space and instrumentation for the fluoride analysis.

The facilities at both CF Industries and Agrico Chemical Company, located in the Bartow, Florida phosphate complex, were found to meet the physical criteria above.

A protocol for the Laboratory Phase utilizing the three proposed manual sampling trains was developed and implemented. The Laboratory Phase was designed to determine the reproducibility and sensitivity of each sampling method under controlled conditions of hydrogen fluoride concentrations. The results of the Laboratory Phase were evaluated and sampling and analytical methods were selected.

A Test Plan was developed for the Preliminary Field Phase based upon the results of the Pretest Survey and preliminary laboratory work. The objectives of this phase were to evaluate the compatibility of the selected sampling procedures with the sites; to determine the range of ambient HF concentrations at each site; and to determine whether a minimum sampling period of 16 minutes for each method was compatible with the sensitivity requirements of the analytical methods.

A Test Plan for the Formal Collaborative Sampling Phase was then developed to measure the ambient HF concentrations at the two sites, using both the double filter cassette and sodium bicarbonate-coated tube and sampling simultaneously with the EPA ROSE system. The fluoride collected by the wet chemical methods was analyzed spectrophotometrically with a Technicon Autoanalyzer. Some samples were also analyzed by ion chromatography (IC).

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SECTION 2

SUMMARY AND CONCLUSIONS

The three methods (the ROSE system and the two manual sampling methods) utilized for the sampling and analysis of HF along the edge of a gypsum pond gave good agreement. Two data reduction methods were used to compute the HF concentrations from the spectra obtained by the ROSE system. One method for determining the HF concentration is based upon elimination of the H_2O interference and determination of the area under the HF absorption line. In the peak height method, the sample and background spectra were plotted, and the net peak absorbance of the line center due to HF was measured by subtracting the H_2O absorbance found at the peak maximum for HF. Most of the HF concentrations changed by ± 3 ppb or less when the peak area and peak height data were compared. However, the HF concentrations that were apparently higher at Agrico using the peak area method were found to be within the range of the point sampling values when the peak height method was used for data reduction. In 32 independent tests of comparable ambient HF concentrations, the overall average HF concentration was 37.6 ppb (ROSE system, peak area method), 36.1 ppb (ROSE system, peak height method), and 36.4 ppb (manual techniques). The standard deviation between the ROSE system (peak area method) and the manual sampling methods (for any single measurement) was 11.9 ppb, while the standard deviation based on the ROSE data computed from the peak height was 9.7 ppb.

Both manual sampling methods used in this study, the filter cassette with the citrate-treated and sodium-hydroxide-treated filters, and the bicarbonate-coated glass tubes, were effective for the collection of gaseous HF. Laboratory results indicated that the two methods collected 100 percent of the HF generated for each run. The precision, as measured by the relative standard deviation for replicate experiments, was less than 8 percent for each manual sampling method. Replicate measurements in the field (preliminary experiments) showed more variation with a between-method relative standard deviation of 37.4 percent. This increased variability is ascribed to increased random error.

An analysis of the sources of error for the ROSE method revealed that the maximum error on any single HF measurement (average of 100 interferograms) is ± 25 percent. This analysis is based, in part, upon the variation in the peak absorption for the spectra of CO_2 and N_2O, since these gases should have essentially constant concentrations. The error in the ROSE measurement is also consistent with the observation that on multiple reduction of the same HF data, the maximum variation on HF concentration or identical runs was never greater than 25 percent.

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SECTION 3

LITERATURE REVIEW FOR MANUAL SAMPLING
AND ANALYSIS OF HF

Prior to the commencement of the collaborative sampling program, it was necessary to determine the chemical techniques to be used for sampling and analysis, which would facilitate the comparison of the ROSE system with standard, wet chemical methods. Ambient sampling for HF is complicated by the low concentrations and the reactivity of the compound, as well as the presence of substances which interfere with the analysis. The selection of the methods to be utilized was based on the compatibility with the sampling program, including sensitivity (minimum sampling time), reproducibility, ease of handling, and freedom from interferences.

The literature has been reviewed with respect to the above sampling and analytical requirements of the program. An extensive review of sampling and analytical procedures for fluorida was published by Jacobson and Weinstein in 1977.[2] This review, coupled with the NERAC computer searches of the post-1976 literature, formed the basis of the literatrue review.

Sampling procedures published by ASTM[3] or ISC[4] were selected, since they have been subjected to extensive laboratory and field evaluation. In addition, consultations with Dr. Jay Jacobson and Mr. Richard Mandl of the Boyce Thompson Institute for Plant Research were very helpful in the determination of the sampling procedures to be used. Brief descriptions of the selected procedures are given below.

DESCRIPTION OF HF SAMPLING METHODS

In addition to the manual sampling methods, automated methods which combined sampling and analysis were also reviewed. These automated methods were eliminated since the cost of multiple units was relatively high and the units would be used only for this study.

Prefilter and Impinger Method—ASTM No. D3267

Air is drawn through a short Teflon probe and a citric acid-treated prefilter to remove particulate. Two impingers, a standard and a modified Greenburg-Smith, both containing a sodium hydroxide solution or water, follow to remove gaseous fluorides. Sampling trains without a prefilter do not separate gaseous and particulate components. These may contribute additional fluoride ions or complex with collected gaseous fluoride ions and make analysis difficult. This technique is not readily conductive to short sampling periods for

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low hydrogen fluoride concentrations. To overcome this problem, the impinger solutions must be evaporated to a smaller volume, risking the loss of collected fluoride.

Double Tape Sampler—ASTM No. D3266

This method automatically separates and collects acidic, gaseous, and particulate fluoride forms by means of a double paper tape system. Air is drawn across a citric acid-treated prefilter tape for particulate removal and then an alkali (sodium hydroxide)-treated filter to remove gaseous acidic fluoride. The instrument may be programmed for sampling times varying from a few minutes to several hours. After sampling, the tapes are stored in a compartment which is protected from fluoride contaminated ambient air. The advantages are automated collection and ease of sample recovery. The main disadvantage is cost.

Prefilter and Alkali-Treated Filter (Double Filter Cassette)

This method is a modification of the preceding ASTM procedure. The modification was necessitated by the lack of availability of the automatic double paper tape sampler. A citric acid-treated prefilter is followed by an alkali-treated (sodium-hydroxide) filter. The first filter will remove particulate and the second will remove acidic fluoride gases. Advantages of this method include ease of sample handling and recovery. Elution of the fluoride content from the dry filter requires small amounts of water.

Bicarbonate-Coated Glass Tube and Particulate Filter—ASTM No. D3268

A 4-ft borosilicate glass tube, the inside of which is coated with sodium-bicarbonate, is held vertically above a 47 mm citric acid-treated Whatman 42 filter. Gaseous fluorides are removed by chemical absorption on the wall of the tube while particulates are drawn through and collected on the filter. An advantage of this technique is the relative ease of recovery. Collection of fluoride requires a small volume of eluent which results in a concentrated solution for analysis. In this way, a minimum sampling time, necessary for comparison with the ROSE system, can be achieved. The method is also low in cost. Since the filter follows the gaseous collection device, this technique is recommended for use in the presence of particulate which may react with and remove HF on a prefilter. Difficulty in handling seems to be the major drawback.

Quartz Tube with Carbonate-Coated Silver Beads

This system works on the same principle as the bicarbonate-coated glass tube. A quartz tube containing sodium bicarbonate-coated silver beads follows a separator (a Herpetz cap or heated membrane filter) to exclude large particles. Advantages are ease of handling and concentration of gaseous fluoride. The method, however, does not provide complete separation of particulate and gaseous fluorides. It is also relatively expensive.

The previously described sampling methods have been utilized in the field for the collection of gaseous fluoride,[5-8]

DESCRIPTION OF LABORATORY PROCEDURES FOR HYDROGEN FLUORIDE ANALYSIS

Ion Exchange--ASTM No. D3269

The ion exchange column is ASTM[3] and Intersociety Committee[4] approved as a method for the isolation and concentration of fluoride in a sample. The fluoride ion is preferentially sorbed on an anion exchange resin while interfering substances and the solvent pass through. A small volume of eluent is then required to desorb the fluoride. An automated ion chromatograph incorporates the isolating capabilities of the ion exchange column with a conductimetric detection system. Low concentrations of fluoride ions can be measured with a minimum amount of sample preparation. This reduces the risk of sample contamination or loss of fluoride during evaporation. The ion chromatograph, however, is not portable. Samples must be brought back from the field to the laboratory and risk fluoride loss due to prolonged storage. Fluoride complexed with other species will not be detected unless the fluoride is converted to the ionic form.

Willard-Winter Distillation--ASTM No. D3269

This technique employs steam distillation from a strong acid, sulfuric or perchloric, in the presence of silica to separate interfering substances. Fluoride is collected as fluosilicic acid. This method is used only for separation, not for measurement. If complexing of the fluoride ion; i.e., CaF, Ca_2FPO_4, etc., is suspected, a NaOH fusion is required prior to the distillation and subsequent analysis.

Spectrophotometric Procedures--ASTM No. D3269

A reagent, composed of an element such as aluminum, iron, thorium, zirconium, lanthanum, or cerium, which reacts with inorganic fluoride to produce a compound or complex with a low dissociation constant, and an indicator dye, undergoes a shift in absorption spectrum in the presence of fluoride. Zirconium-Eriochrome Cyanine R, Zirconium-SPADNS, and Lanthanum-Alizarin Complexone are the three commonly used reagents. The first two experience fading when complexed with fluoride and obey Beer's law over the range from 0 to 1.4 µg F/ml with a detection limit of the order of 0.02 µg F/ml. The Lanthanum-Alizarin Complexone reagent differs from the above reagents since there is an increase in absorbance of the solution proportional to the amount of fluoride present. This is more sensitive and covers a lower range, 0 to 0.5 µg F/ml, with a detection limit of approximately 0.015 µg F/ml.

Semiautomated Method with Microdistillation--ASTM No. D3270

The sample solution is mixed with sulfuric acid and pumped into the polytetrafluoroethylene coil of a microdistillation device maintained at 170°C. The acidified sample is carried to a fractionation column by a stream of air. The fluoride and water vapor are condensed and pumped continuously from the distillate collector, while the solids and spent acids are removed from the system. The distillate is mixed continuously with a colorimetric reagent and passed through the flow cell of a spectrophotometer. The equipment required for this procedure is commercially available, and this system was employed at Agrico Chemical Co. for the fluoride analyses.

Titrimetric Procedures--ASTM No. D3269

The sample solution containing an indicator dye; e.g., - Alizarin Red S, Eriochrome Cynanine R, or SPADNS is buffered at pH 3.0. Upon addition of thorium nitrate, insoluble thorium fluoride is formed. When the end point is reached, the excess thorium reacts with the indicator dye causing a change in color which can be detected visually or by instrumental techniques. The method is capable of high sensitivity; but it is slow and tedious and the results are highly dependent on the analyst.

Potentiometric Method--ASTM No. D3269

The method requires the use of an ion specific electrode for the measurement of fluoride. Ionic strength and pH must be controlled, and the sample must be free from agents which complex fluoride. The potential of the sample in millivolts is recorded and converted to µg/ml of fluoride using a calibration curve. The detection range is 0.019 µg F/ml to 19,000 µg F/ml. Slow response time and nonlinearity of the calibration curve cause measurements below 0.1 µg F/ml to be less accurate. Care must be exercised because ion specific electrodes have a limited life span.

CONCLUSIONS

Three sampling and two analytical techniques were chosen, based on the literature review. The manual sampling methods using a prefilter and impinger, the double filter cassette, and the bicarbonate-coated glass tube were investigated in more detail in the laboratory phase. Fluoride analysis for the laboratory phase was accomplished primarily by ion chromatography, although some solutions were also analyzed by a spectrophotometric method using Lanthanum-Alizarin Complexone as the chromotropic reagent. For the preliminary field phase all of the fluoride analyses were done by IC, with some of the solutions also analyzed at Agrico Chemical Co. using the semiautomated method described previously. All of the fluoride samples were analyzed at Agrico Chemical Co. for the collaborative field phase with some samples also being analyzed by IC.

SECTION 4

PRETEST SITE SURVEYS

INTRODUCTION

The Task Manager, Mr. Mark Antell, had contacted two sites in the Bartow, Florida phosphate complex at which the program could be conducted. The two phosphate fertilizer facilities included CF Industries, Inc., Bartow, Florida, and Agrico Chemical Co., South Pierce, Florida. To determine the feasibility of utilizing each facility, site surveys were conducted and the following criteria were evaluated:

- Physical layout of the gypsum ponds

- Access roads for the ROSE van

- Longest unobstructed line of sight available for ROSE system

- Fluoride concentrations in the ponds

- Meteorological patterns which could affect results

- Availability of laboratory facilities for sample recovery

- Possibility of fluoride analyses being done by the facility

- Availability of electrical power.

SITE SURVEYS

CF Industries, Inc.

The layout of the gypsum pond area is illustrated in Figure 1. For the measurement of HF by the ROSE system a path length of at least 400 meters was desirable. Therefore, two of the possible sample lines were located at cooling pond No. 1 (lines A and B) while the third possible line of sight was adjacent to cooling pond No. 2 (line C). Pond No. 2 was eliminated from consideration because there was no electric power available and because there might be interferences in the form of "hot spots" which might be introduced by plumes from the phosphoric acid plant across the pond from the expected southeastern winds. The gypsum stacks on the East side of pond No. 1 would not interfere at either line A or B when the wind was blowing from the

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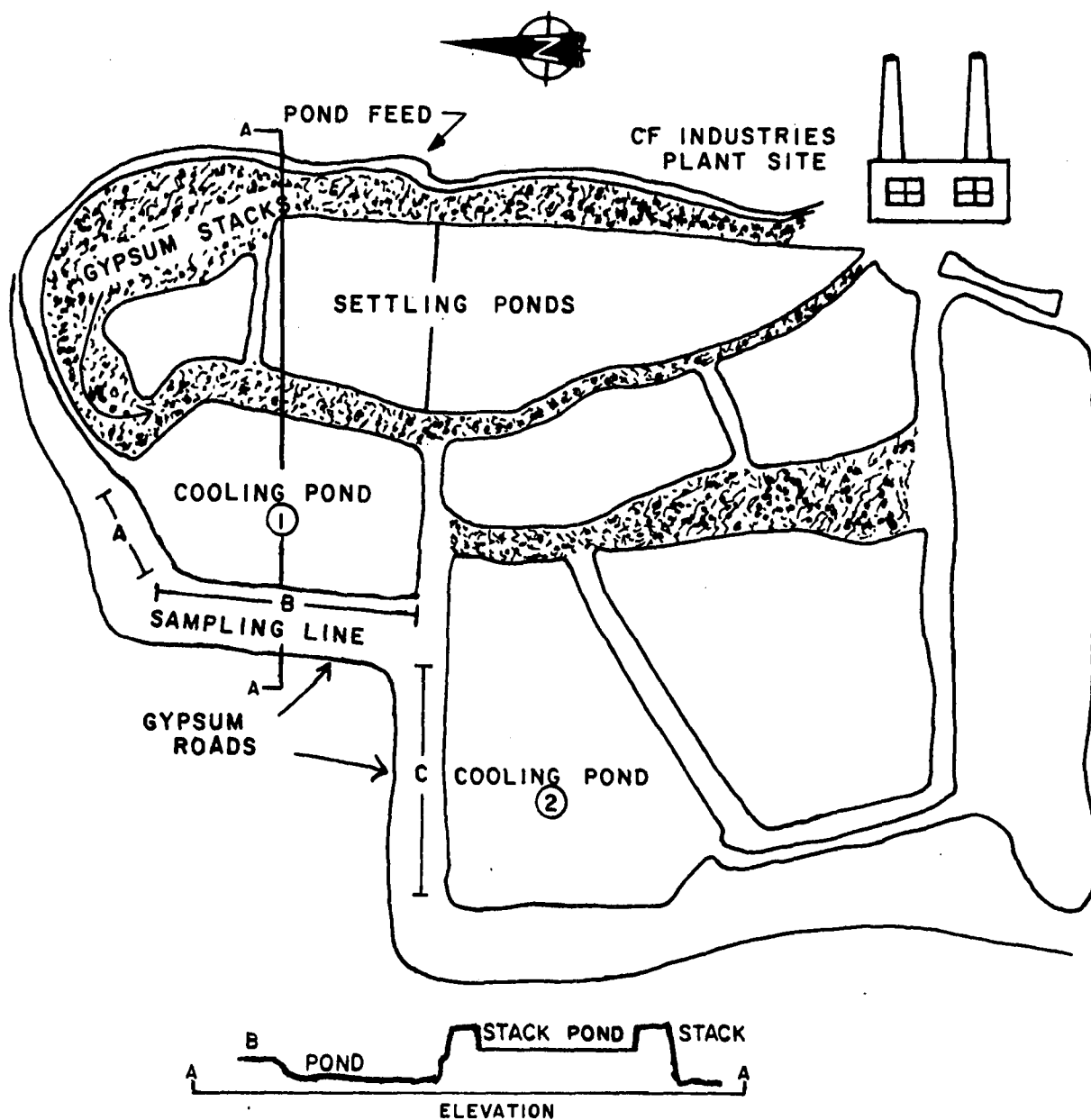
Figure 1. CF Industries gypsum ponds.

southeast across the pond. Of the two lines of sight, B was preferred (Figure 2). This was chosen because the path length for the ROSE system was longer and some onsite electrical power was available. For line B, extra mobile generators would be required to provide the remaining power not accessible onsite.

The F⁻ concentration of pond No. 1, as measured by plant personnel with an Orion ion specific electrode, was usually between 8,000 and 9,000 ppm. The pond has a pH of 1.2, although it is commonly between 1.5 and 1.6. In a previous report by The Research Corporation of New England (TRC), the ambient HF concentration measured at the edge of the pond was 20-30 ppb and was considered high enough for the manual sampling methods and the ROSE system.

Meteorological data (i.e., wind speed and wind direction) are measured at the plant, and this information would be available to GCA. Laboratory facilities were not available to permit the onsite analysis of the collected samples.

Agrico Chemical Co.

The plant geography as shown in Figure 4 is amenable to the use of sampling methods in any of three locations. Both the upper and lower gypsum stacks (B and C) on the east side of the main cooling pond provide a straight and flat span with no topographic interferences. The effect of the gypsum stacks on the ambient HF concentrations was unknown at that time. The accessibility of the upper stack to the ROSE van would be a problem and would prevent its use during the sampling phase. A grassy road (A) on the west side of the pond could also be utilized. There was, however, a great deal of brush in this area which may cause obstructions or alter concentration levels. The road on the lower stock (line C) was chosen for the sampling effort (Figure 3).

The fluoride concentration in the cooling pond ranged from 9,000 to 14,000 ppm. The laboratory did have space available for the recovery of ⁚ samples prior to analysis. In addition, Agrico had offered to analyze the samples for fluoride using ASTM Method D3270, which is an automated colorimetric method using a Technicon Autoanalyzer with a micro-distillation unit.

The wind speed and direction are measured at the plant and were available to GCA personnel. No electrical power could be provided at any of sampling sites and mobile generators are required.

CONCLUSIONS

The physical configurations of the gypsum ponds at both CF Industries and Agrico Chemical Co. were amenable to the testing program. At CF Industries ambient HF concentrations at the pond edge were known to be sufficient for both the ROSE and the wet chemical sampling and analytical methods. The fluoride concentrations in the Agrico gypsum pond also appeared to be high enough to provide sufficient HF concentrations for the ambient measurements.
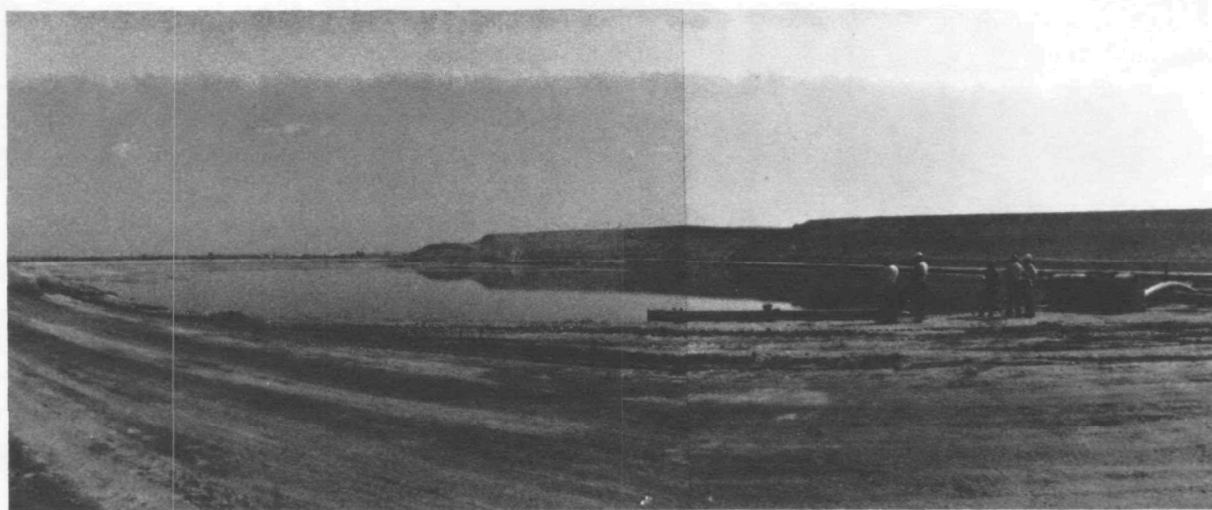
Figure 2. Gypsum pond at CF Industries.

Figure 3. Gypsum pond at Agrico.
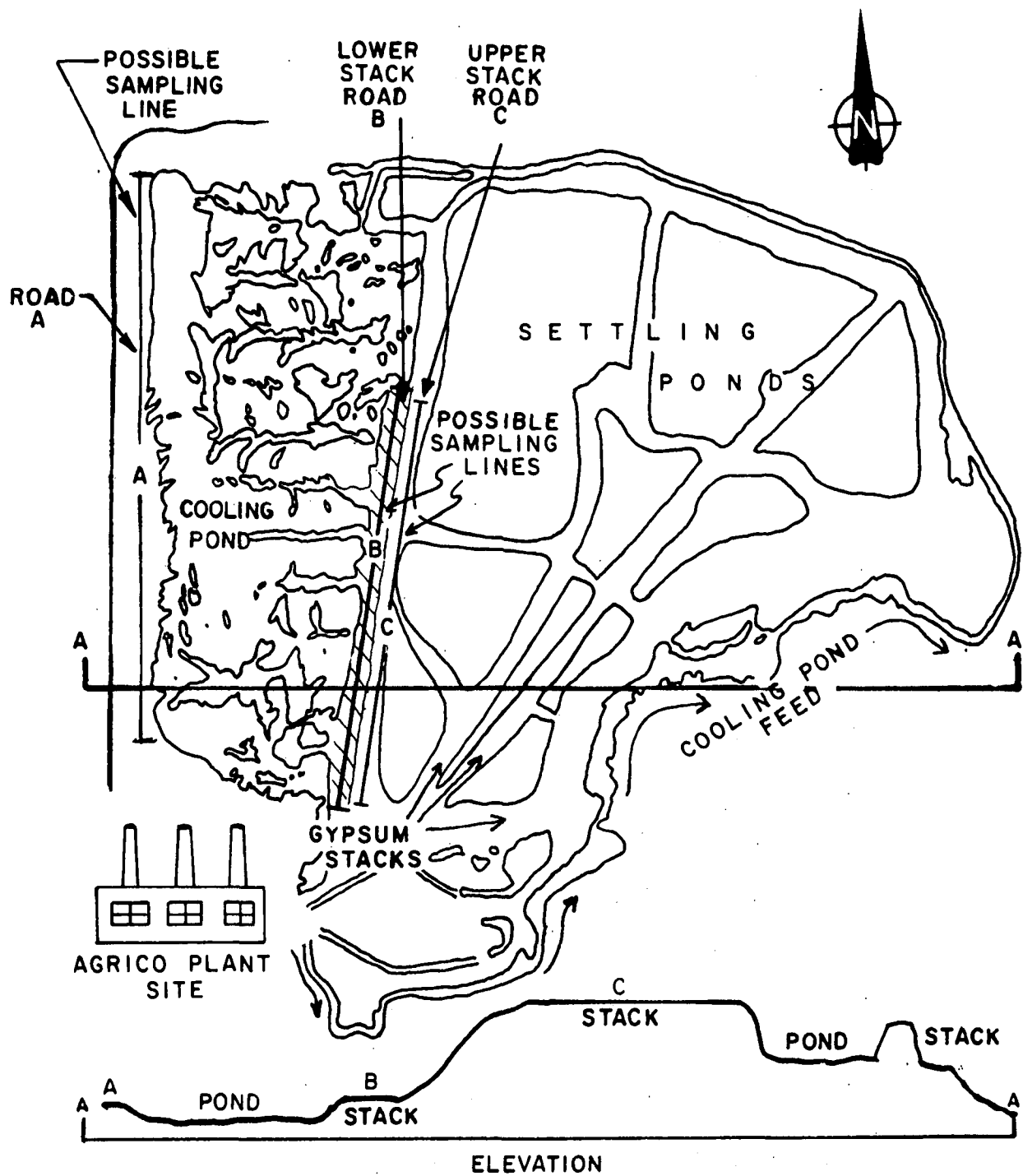
Figure 4. Agrico gypsum ponds.

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It was decided that both gypsum ponds should be tested during the preliminary wet chemical field sampling phase. The bulk of this experimental work should be conducted at CF Industries, where ambient concentrations are known and electricity is available. Representative measurements at Agrico using the wet chemical methods would characterize the HF concentrations at the pond edge.

SECTION 5

LABORATORY PHASE

The purpose of this phase was to select HF collection and analytical methods, which would facilitate the comparison of optical and chemical methods in the final field sampling phase. An HF generator was constructed to investigate the three sampling procedures selected from the literature review. Ion chromatography (IC) was utilized for fluoride analysis to determine the collection efficiencies of the three methods and to identify any interference problems.

HF GENERATION SYSTEM

The design for the HF Generation System and the injection box was supplied by Dr. Jay S. Jacobson of the Boyce Thompson Institute for Plant Research[9] (personal communication of Jacobson and Heller, letter of April 10, 1979). An HF generation system was constructed as illustrated in Figure 5. Air was pumped through an indicating silica gel drying trap, a tube packed with glass wool, and a Whatman 42 filter into heated teflon tubing at a flow rate of 1.5 dscfm. An aqueous HF solution was pumped at 0.05 ml/min into the heated Teflon tubing (located in the injection box) through which the filtered air flowed. The injection box was kept at 175°F. The fluoride-laden air was then cooled to room temperature in an ice bath and divided. Sampling took place at two points downstream of the flow division. The portion of air that was not sampled was exhausted to a laboratory hood.

Originally, the intent had been to pump the air stream into a section of PVC tubing with four sampling ports located 3 feet from the duct inlet and equidistant from each other. The HF analysis yielded values which were lower than expected from the amount of HF introduced into the system. The split stream was used to correct the problem.

The amount of fluoride put into the system is dependent on flow rate and the concentration of the HF solution, i.e., the concentration of solution in the reservoir times the flow rate (μg HF/ml x ml/min = μg HF/min). Adjustments of the air flow rate through the system alters the concentration of fluoride per unit volume of air, but not the amount of fluoride delivered through the system. The latter is controlled by varying the aqueous HF solution concentrations. The concentration of HF in the air stream is determined by the following equations:
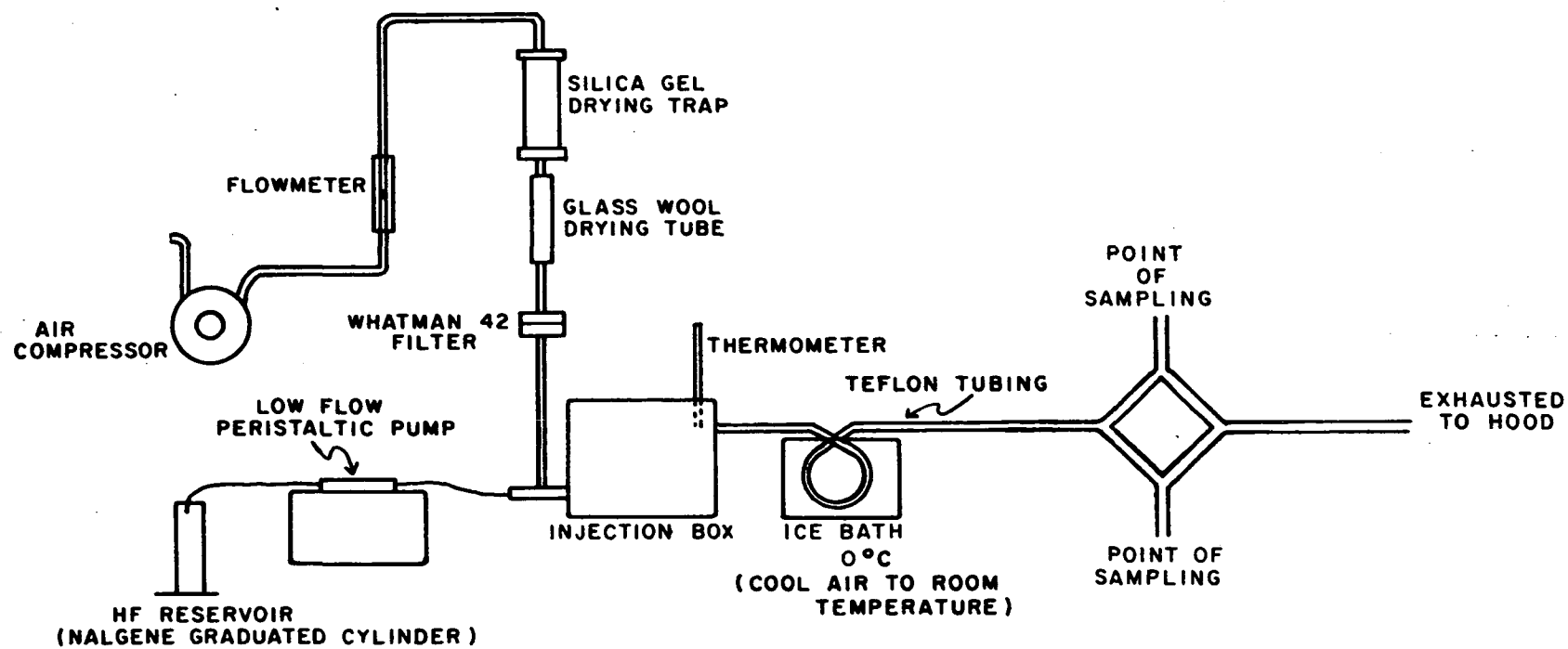
Figure 5. HF generation system.

$$\mu g \ HF/dsft^3 = \frac{\mu g \ HF \ ml^{-1} \ x \ ml \ min^{-1}}{Vm \ (dsft^3)}$$

where Vm dsft^3 is at 77°F and 29.92 in.Hg.

$$\mu g \ HF/dsm^3 = \frac{\mu g \ HF \ dsft^{-3}}{0.02832 \ ft^3 \ m^{-3}}$$

$$HF \ (ppb) = \frac{\mu g \ HF \ dsm^{-3}}{0.818 \ \mu g \ dsm^{-3} \ ppb^{-1}}$$

PRESAMPLING PREPARATION

All impingers, related glassware, and polyethylene sampling bottles utilized in the laboratory phase were cleaned with an Alconox solution and rinsed with tapwater and distilled, deionized water. The glassware was air-dried and capped with parafilm.

The sodium bicarbonate-coated tubes were prepared as outlined in ASTM D3268. The tubes were cleaned with detergent, alcoholic KOH solution, and distilled water. While the inner surface was still wet, a 5 percent (by weight) NaHCO$_3$ solution was poured through the tube to coat the internal surface. Hot, fluoride-free air (prepared by passing air through coiled copper tubing heated by a heating tape) was blown through the tube to dry the sodium bicarbonate on the inner wall.

The prefilter and filters were treated with citric acid or sodium hydroxide respectively, according to ASTM D3266. The filters were immersed in the appropriate solution (either 0.1 m citric acid in 95 percent ethanol or 0.5 N NaOH in 95 percent ethanol and 5 percent glycerin) and dried under an infrared lamp.

All filters and tubes were sealed until sampling occurred. At the completion of each sampling run, the filters or tubes were resealed until recovery.

The dry gas meters were calibrated according to procedures in APTD 0576.

SAMPLING PROCEDURES

The three wet chemical sampling procedures, found to be applicable to this program, are described below. The collection methods are illustrated in Figure 6.

Double Filter Cassette

The double filter cassette sampling train is a modification of ASTM D3266, i.e., a double filter cassette is used in place of the AISA Automatic Tape Sampler. The constituents of the train were a 37 mm Millipore filter cassette containing a Whatman 42 filter pretreated with a citric acid solution
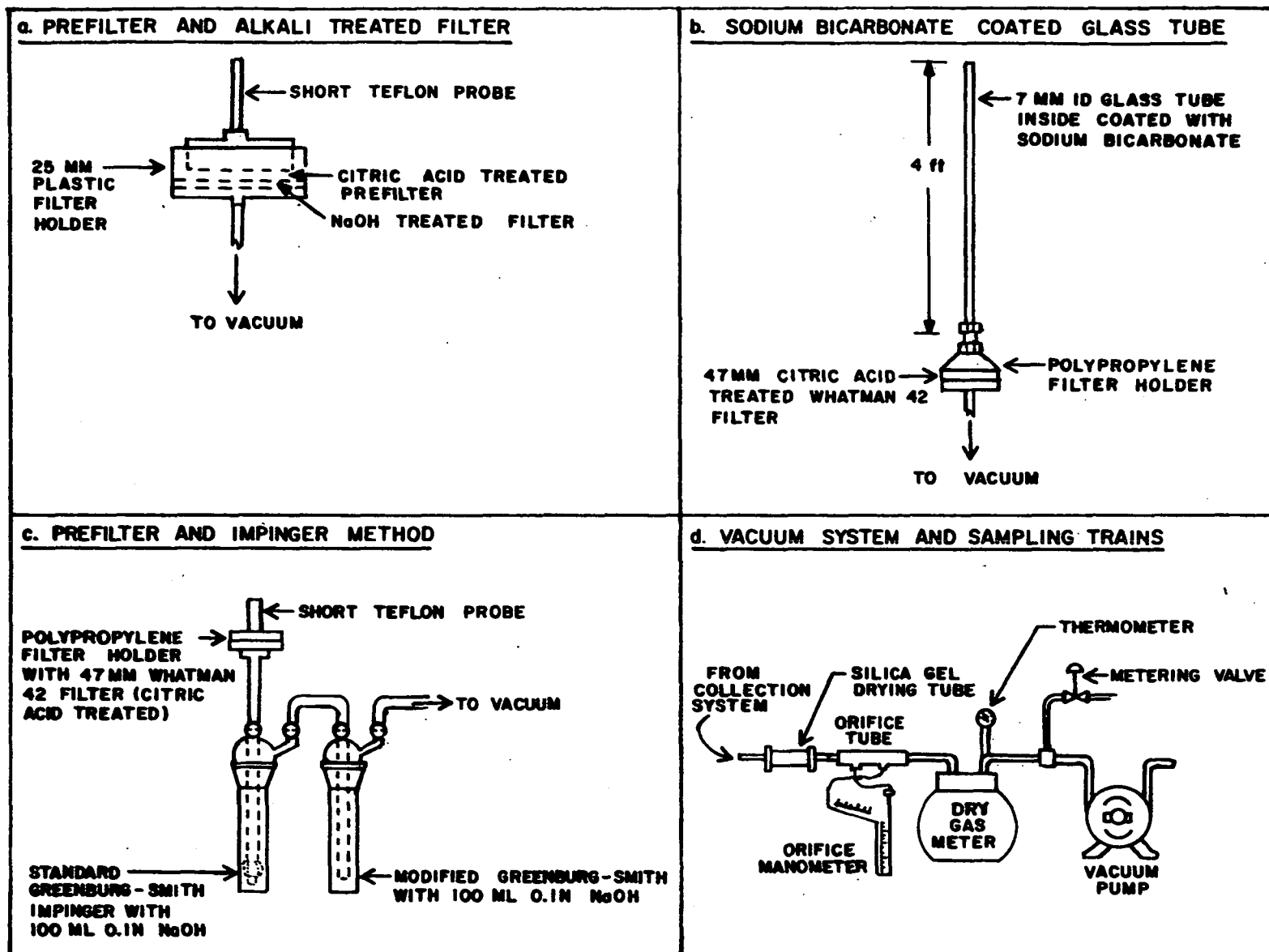
Figure 6. HF collection methods and sampling train.

back to back with a Whatman 4 filter pretreated with a sodium hydroxide solution; a modified Greenburg-Smith impinger containing indicating-silica gel; dry gas meter and an orifice meter; and a leakless lubricating vane pump.

The sampling rate was 0.5 cfm. Leak checks of all sampling trains were conducted prior to and after each sampling run to determine that a leak rate of not greater than 0.02 cfm existed. The cassettes were capped to prevent exposure to the ambient air. After sampling the inlet and outlet were again plugged. The used filters were placed in clean sample bottles and 10.0 ml of distilled deionized water and 0.1 ml of 1.0N NaOH were added. The bottles were sealed tightly until analysis.

Sodium Bicarbonate-Coated Tube

Sampling with the sodium bicarbonate-coated tube was performed as described in ASTM D3268. The train consists of a 4-ft glass tube (7 mm ID) evenly coated with sodium bicarbonate, connected directly to a 47 mm polypropylene filter holder containing a citric acid treated Whatman 42 filter. The tube was followed by the same drying, vacuum and metering equipment as described for the double filter cassette sampling train.

Both ends of the collecting tube were sealed until sampling took place. After sampling, the ends were capped until recovery. The air to be sampled was drawn through the tube at a rate of 0.5 cfm. Each sampling train was leak checked before and after the sampling run to determine that no leak greater than 0.02 cfm existed. The collected fluorides were eluted with 8-9 ml of distilled deionized water. One drop of 1.0N NaOH was added and the solution was diluted to 10.0 ml. The samples were stored in clean bottles and sealed until analysis.

Prefilter and Impinger

Sampling with the prefilter and impinger was performed according to ASTM D3267. The constituents of the train, as shown in Figure 4, were a short Teflon probe, a 47 mm Whatman 42 citric acid-treated filter in a polypropylene holder, a standard and modified Greenburg-Smith impinger with 100 ml of 0.1N NaOH, a modified Greenburg-Smith impinger with indicating silica gel, a dry gas meter, and a leakless lubricated vane pump.

The sampling rate was 1.0 cfm. Leak checks were performed prior to and after testing to prove that the leak rate was less than 0.02 cfm. At the completion of each test, the collecting solution was measured and transferred to a clean sample bottle.

ANALYTICAL PROCEDURES

The samples from the laboratory phase were analyzed for F^- on a Dionex Model 14 Ion Chromatograph. This automated ion chromatograph incorporates the ion-separating capabilities of the ion exchange column with a conductimetric detection system.

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Ion chromatography (IC) is used to identify and quantitate cations and anions in solution. Conductimetric detection enables the analyst to monitor the ion separations, but, until recently, the eluent background conductance prevented its use. The conductance of the eluent is removed by the appropriate combination of separator and background suppressor columns. The IC flow scheme for anion analysis is illustrated in Figure 7.

The principles of IC can be illustrated using anion analysis as an example. A sample is injected into the separator column, which consists of a strong base anion exchange resin in the bicarbonate form. The anions are distributed between the resin and the $NaHCO_3$-Na_2CO_3 eluent. Separation of the anions depends upon the degree of affinity of the anion for the anionic exchange groups on the resin. The anions are eluted from the separator column in the Na^+ form. This solution passes through the suppressor column, which contains a cation exchange resin in the H^+ form. The suppressor column converts the sodium salts of the anions to their corresponding acids. It also converts the eluent to H_2CO_3, which has a low conductance. The conductivity of the anions is measured via the peak height, and the anions are identified by their retention times. The peak heights are converted to concentrations by comparison with a calibration curve.

The column system employed for the fluoride analyses consisted of a pre-column (3 x 150 mm) to remove particulates, strongly retained anions, and organic species; a separator column (3 x 250 mm) in the HCO_3^- form; and a supressor column (6 x 250 mm) in the H^+ form to remove the background conductivity of the eluent. The eluent, which was a solution of 0.003 M $NaHCO_3$ and 0.0024 M Na_2CO_3 was pumped through the column at a rate of 150 ml/hr. The injection loop had a capacity of 100 µl and the sample was introduced from a 5 ml disposable syringe fitted with a 0.22 µm Millipore filter to remove particulate matter. A 1N H_2SO_4 solution regenerated the suppressor column after an 8-hr period.

RESULTS

A series of tests were conducted with each procedure (Table 1). The sampling period and the approximate HF concentration to be introduced into the generating system is listed for each trial. The actual HF concentration is given in Table 2. Sampling runs 1-16 were designed to examine the reproducibility of the results of each type of sampling device and to provide information on the sampling period required by each method. Two sampling trains containing the same sampling method were run simultaneously. Runs 1-6 consisted of two double filter cassette samplers, runs 7-11 utilized two bicarbonate-coated glass tube trains, and runs 12-16 used two pre-filter and impinger sampling trains.

A second series of tests were designed to facilitate intercomparisons of the three methods. Five double filter cassette/sodium bicarbonate-coated tube runs at 50.1 ppb HF, four runs at 30.8 ppb HF, and three trials at 18.2 ppb HF were completed. The sampling period was 15 minutes. In addition, experiments with impinger/bicarbonate-coated tubes and impinger/double filter cassettes were conducted using 50.1 ppb HF with a sampling time of 30 minutes.
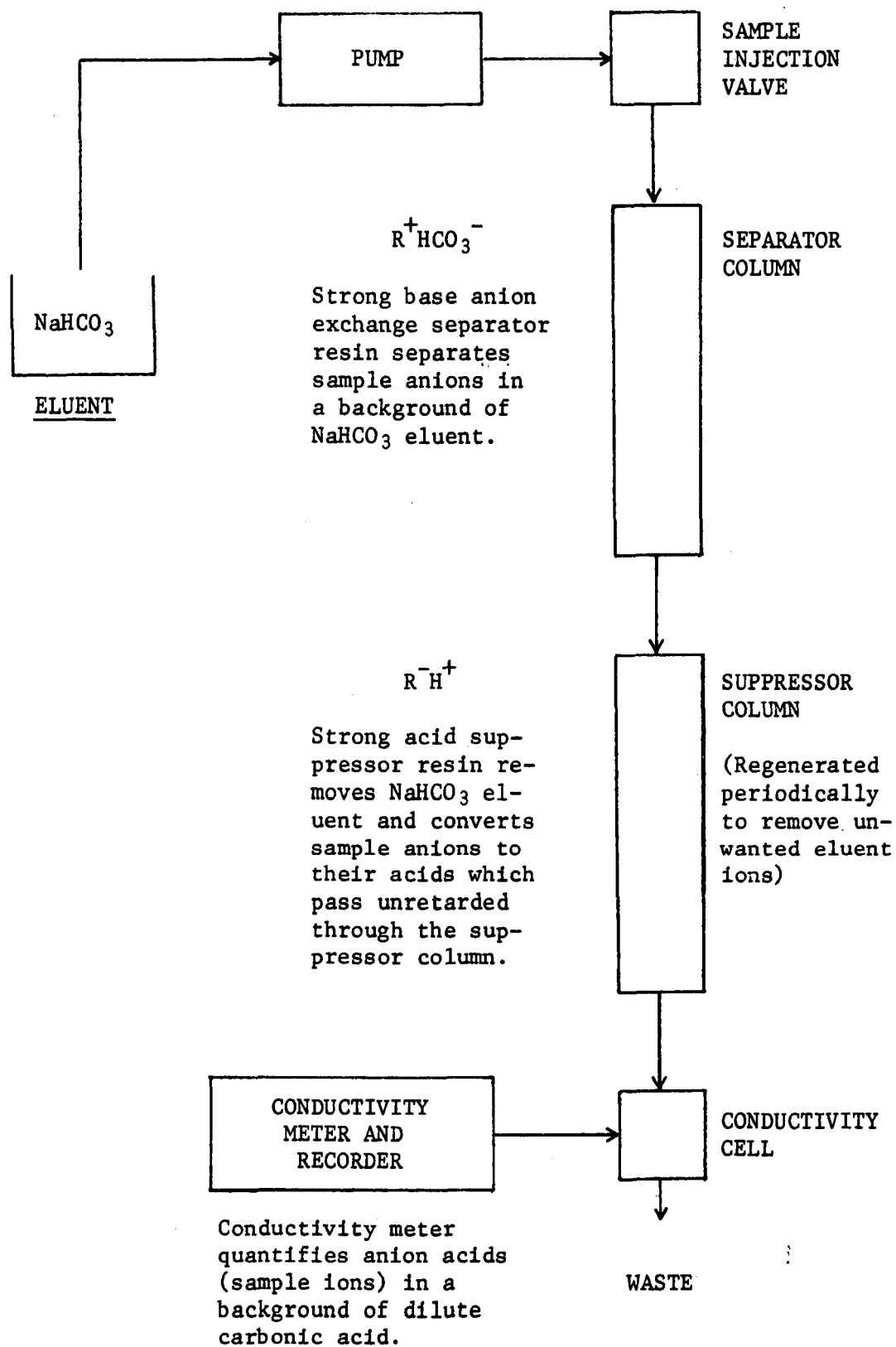
Figure 7.   Ion chromatography flow scheme (anion analysis illustrated).

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TABLE 1. TESTING SCHEDULE FOR LABORATORY PHASE

Run No.	Sampling methods	Sampling period (min)	HF range concentration (ppb)
1-6	Double filter--double filter	15	50
7-11	$NaHCO_3$-coated--$NaHCO_3$-coated tube	15	50
12-16	Impinger--impinger	30	50
17-21	Double filter--$NaHCO_3$-coated tube	15	50
22-30	Impinger--$NaHCO_3$-coated tube	30	50
31-36	Impinger--double filter	30	50
37-40	Double filter--$NaHCO_3$-coated tube	15	30
41-43	Double filter--$NaHCO_3$-coated tube	30	20

The results of the laboratory sampling phase are presented in Table 2 for each run. The recovery of the generated HF by each of the three sampling devices is summarized in Table 3. For each amount of HF generated the mean standard deviation(σ) and percent recovery are given for the corresponding sampling method. The double filter cassette and bicarbonate-coated tube methods collected 100 percent of the HF generated for each experiment. Replicate experiments indicated that the precision as measured by the relative standard deviation (RSD, RSD = $\sigma/\bar{x}$) was usually less than 8 percent (Table 4) for the double filter cassettes and bicarbonate-coated tubes.

The impinger solutions, however, yielded HF concentrations which were much higher than the amount of HF generated. It appears that the impinger solutions or the impinger glassware were contaminated with high concentrations of fluoride. In these experiments, the impingers were rinsed with deionized water between runs. To investigate the contamination problem, the impingers were subjected to a complete washing procedure (including acid rinsing) between experiements. The HF concentrations found in the impinger solutions were still higher than the amount of HF generated. This discrepancy between HF concentrations indicates that some problems exists when the HF is collected in 0.1N NaOH.

CONCLUSION

The double filter cassettes and sodium bicarbonate-coated tubes were the most efficient and reproducible of the collection methods which were tested. It was recommended that these two collection devices be tested further in the preliminary field phase.

TABLE 2. RESULTS OF THE LABORATORY SAMPLING PHASE[a]

HF, ppb generated	HF, ppb determined					
	Filter-Filter	Tube-Tube	Filter-Tube	Impinger-Tube	Impinger-Filter	Impinger-Impinger
57.5	54 58					
57.5	58 58					
57.3	54 52					
57.3	54 57					
57.3	55 60					
57.3	58 57					
50.1			50 48	337 48	35 47	
50.1			51 53	210 55	165 48	
50.1			50 42	791 49	953 52	
50.1			51 49	1705 49	1612 50	
50.1			50 52	1055 50	37 49	
50.1				134 48	617 50	
50.1				374 49		
50.1				27 50		
30.8			32 28			
30.8			30 32			
30.8			31 31			
30.8			30 29			
18.2			19 19			
18.2			17 19			
18.2			25 18			
61.5		59 60				
61.5		67 63				
61.5		82 72				
61.5		62 61				
61.5		63 70				
57.0[b]					56[b]	157[b]
57.0					276[b]	

[a] Analyses by Ion Chromatography.

[b] New cleaning process for glasswsare.

TABLE 3. RECOVERY OF HF BY THREE SAMPLING DEVICES

Level of HF generated (ppb)		Sampling device		
		Filter[a]	Tube[a]	Impinger[a]
18.2	$\bar{x}$, ppb measured σ % recovered	20.3 4.0 111.5	18.7 0.66 102.6	
30.8	$\bar{x}$, ppb measured σ % recovered	30.8 0.96 100.0	30.0 2.05 97.4	
50.1	$\bar{x}$, ppb measured σ % recovered	49.8 1.43 99.4	48.8 2.15 97.4	575 1148
57.4	$\bar{x}$, ppb measured σ % recovered	56.3 2.59 98.1		163 286
61.5	$\bar{x}$, ppb measured σ % recovered		63.1 3.95 102.6	

[a]Analysis by Ion Chromatography.

TABLE 4. PRECISION - LABORATORY PHASE

Group	Parameter	ppb HF generated														
		18.2			30.8			50.1			57.3			61.5		
		$\bar{x}$	σ	RSD	$\bar{x}$	σ	RSD	$\bar{x}$	σ	RSD	$\bar{x}$	σ	RSD	$\bar{x}$	σ	RSD
Filter-filter	Within F_1										55.5	1.97	3.55			
	Within F_2										57	2.68	4.71			
	All filters together										56.3	2.61	4.64			
	Between F_1 and F_2										56.3	3.3	5.86			
Tube-tube	Within T_1													62.8	3.30	5.25
	Within T_2													63.5	4.50	7.08
	All tubes together													63.1	3.66	5.80
	Between T_1-T_2													63.1	4.73	7.50
Filter-tube	Within F	20.33	4.16	20.4	30.8	0.96	3.11	50.4	0.55	1.09						
	Within T	18.7	0.57	3.04	30.0	1.85	6.08	48.8	4.32	8.85						
	Between F-T	19.5	5.14	27.6	30.0	2.65	8.67	49.6	4.4	8.06						
Filter	All filters							49.80	1.40	2.81						
Tube	All tubes							49.4	3.07	6.2						

SECTION 6

PRELIMINARY FIELD SAMPLING PHASE

The preliminary field phase was conducted June 13-20, 1979. It was designed to determine:

1. The compatibility of the selected manual sampling procedures with the sampling location, i.e., the presence or lack of interfering substances, sensitivity levels, etc.

2. The range of ambient HF concentrations at the two ponds.

3. If a sampling period of 15 minutes is compatible with the sensitivity requirements of the analytical techniques.

PRESAMPLING PREPARATION

The impingers, related glassware and polyethylene sampling bottles were treated as follows:

1. Washed with Alconox solution, rinsed with tap water followed by distilled deionized water.

2. Scrubbed and rinsed with a 10 percent potassium hydroxide solution in methanol (alcoholic KOH solution).

3. Rinsed with distilled deionized water.

4. Rinsed with 0.1N HCl.

5. Rinsed with distilled deionized water.

The glassware was then air-dried and capped with parafilm. The required treated filters and coated glass tubes were prepared as described in the laboratory phase.

The dry gas meters were calibrated according to procedures in APTD 0576. The Climatronics Wind Mark III Wind Measuring System was electrically calibrated and aligned prior to and after the sampling.

SAMPLING LOCATIONS

The line of sight and associated sampling sites selected for the gypsum pond at CF Industries are shown in Figure 8. This line of sight was
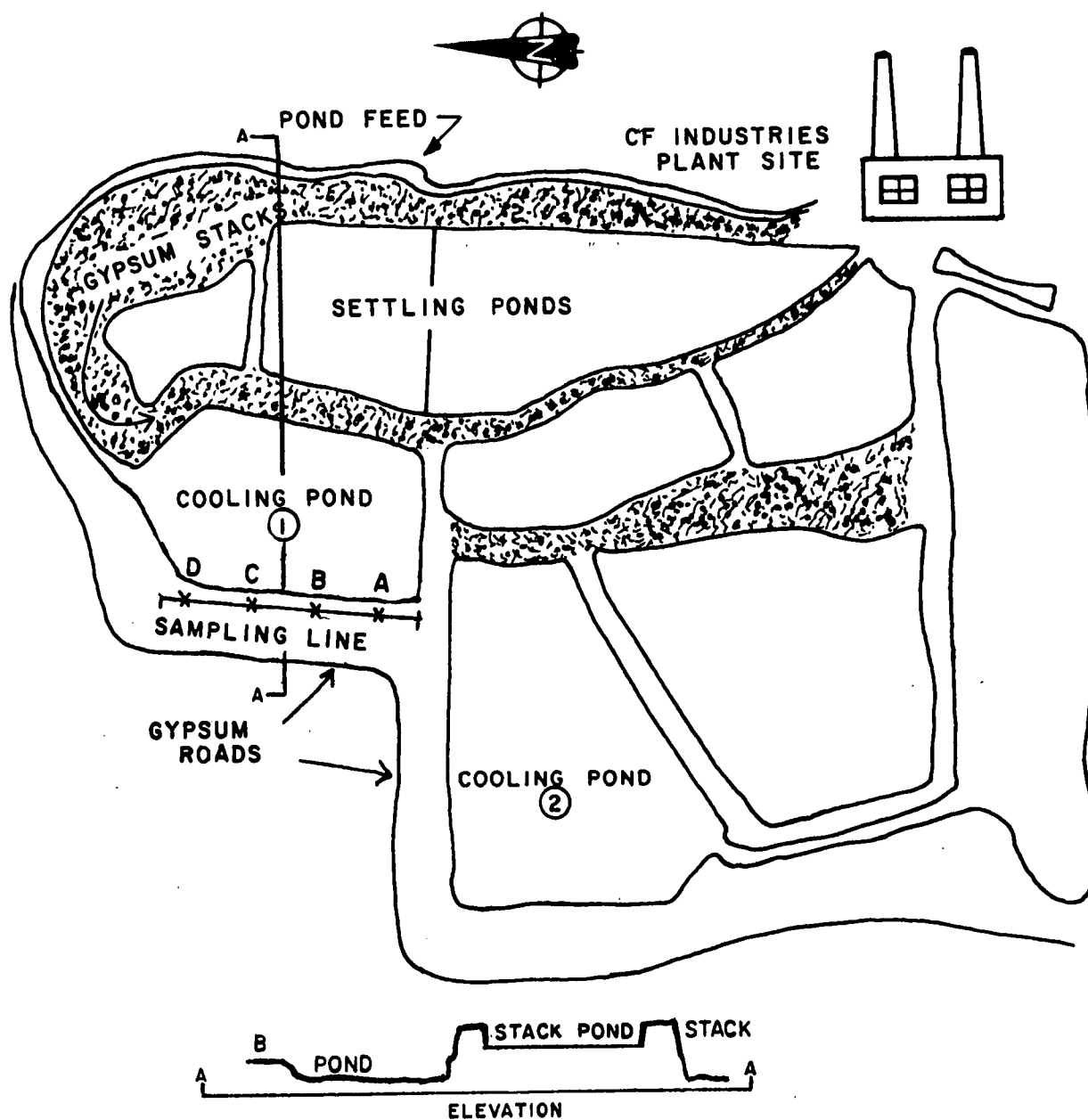
Figure 8. Sampling points at CF Industries gypsum ponds.

approximately 465 meters in length and was divided into four equal segments. The sampling sites were situated at the center of each segment.

The line of sight selected for the Agrico gypsum pond was on the east side lower stack roadway (Figure 9). The line of sight was approximately 600 meters long. It was divided into four equal segments and a sampling site was situated at the center of each segment. The proposed line of sight on the western edge of the pond could not be used due to relatively tall shrubbery growing in the area between the roadway and the pond. This would interfere with the air flow pattern. The wet chemical sampling probes could have been elevated above the tops of the shrubbery, however, the ROSE equipment could not. The wind flow pattern for both sites in past years showed winds blowing from the southeast.

Sampling Protocol

CF Industries, Inc.--

On the first day, the double filter cassette was utilized at the four sampling sites to determine the ambient HF concentration. All four sites were sampled simultaneously. The sampling rate was 0.5 cfm, for a duration of 15 minutes. Four sets of samples were obtained. The filters were treated as described in the laboratory phase and were sent to the GCA laboratory for analysis by IC. The samples were analyzed the next day, and the results were transmitted to the field team. The results of these samples (designated Nos. 1-4) are given in Table 5. The values obtained showed that the ambient HF concentration was at a satisfactory level for the sampling and analytical methods. Successive samples showed good reproducibility. A gradient along the line of sight was also shown to be present. The wind was blowing from the northeast with a speed of 7-10 mph.

The original plan was to sample two sites concurrently with the three methods, the double filter cassette, bicarbonate-coated tube, and impingers with the prefilter, being operated simultaneously at each site. Five replicates were to be run. The sampling trains were then to be moved to the next two sites, and five runs were to be conducted. However, due to electrical power and equipment constraints, the plan was modified as discussed below.

At each site, the impinger train was operated for 30 minutes at a sampling rate of 1 cfm. Either the double filter cassette or bicarbonate-coated tube was started simultaneously with the impinger and operated for 15 minutes with a sampling rate of 0.5 cfm. After 15 minutes, the run was terminated and the other sampling train was started, and was operated for 15 minutes with a flow rate of 0.5 cfm. Five replicates were run for each site. The samples were recovered as described in the laboratory phase, and were returned to GCA for analysis by IC. An aliquot of the impinger solution was given to CF Industries staff.

The windspeed and direction were also obtained (Table 6).

Agrico Chemical Co.--

The revised sampling protocol described for CFI was conducted at the Agrico Pond. Some samples were analyzed by the Agrico Environmental


27
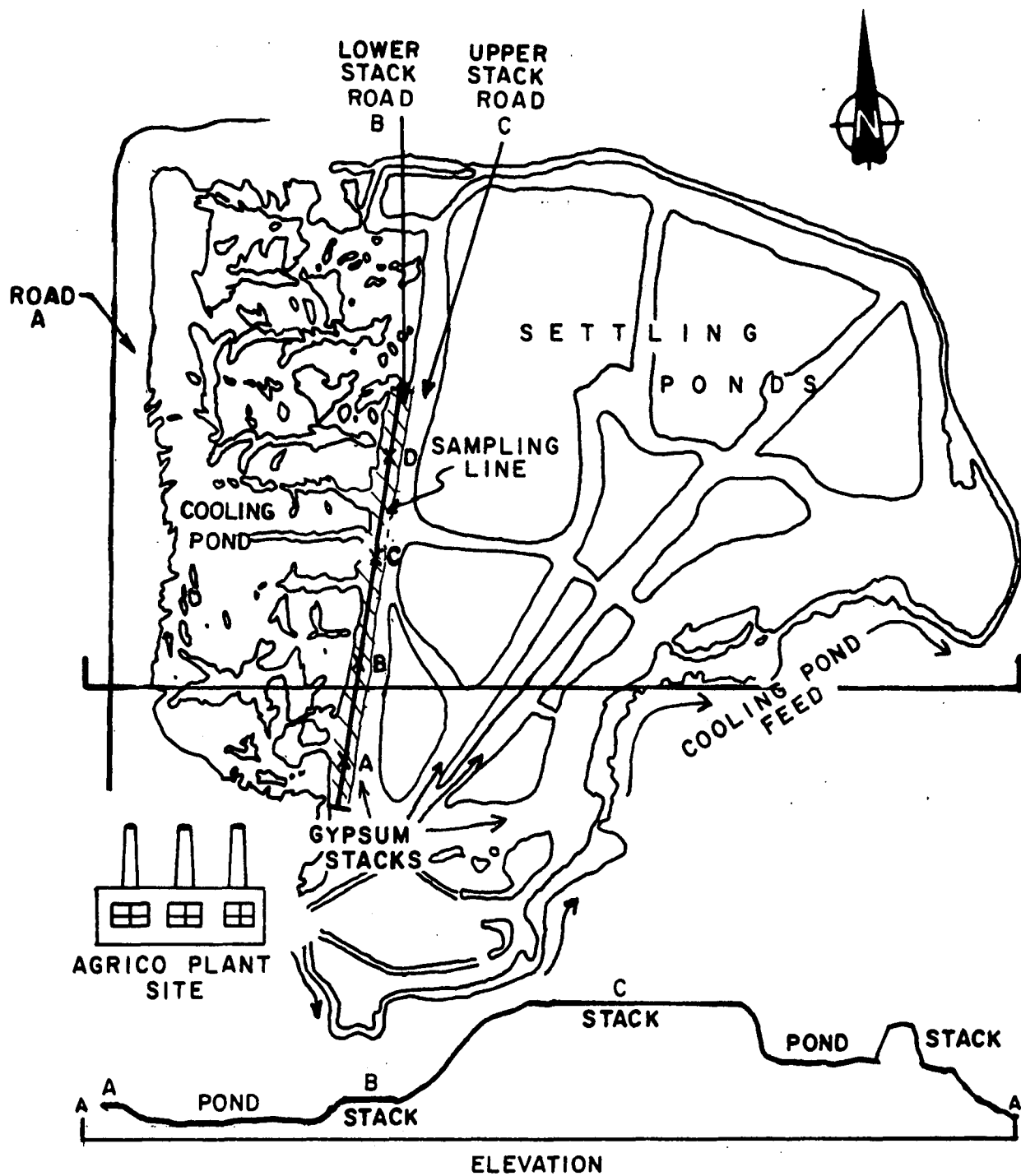
Figure 9. Sampling points at Agrico Chemical Co.'s gypsum ponds.

TABLE 5. PRELIMINARY FIELD PHASE: HF CONCENTRATIONS

| | | | PPB HF[a] | | | | | | | | | | | |
| | | | Site A | | | Site B | | | Site C | | | Site D | | |
Run No.	Date	Time	F	T	I	F	T	I	F	T	I	F	T	I
CFI														
1	6/12/79	1345	50			29			71			95		
2	6/12/79	1500	53			35			74			73		
3	6/12/79	1530	65			36			76			79		
4	6/12/79	1600							81					
5	6/13/79	1415	59	41	258 (60)	43	42	611 (82)						
6	6/13/79	1500	50	24 (21)		19	19	67 (69)						
7	6/13/79	1530	28	23	476 (60)	37	36	96 (93)						
8	6/13/79	1605	17 (38)	25		18	15							
9	6/14/79	1000	21	24	(54)	18	17	318			8 (103)			
10	6/14/79	1100							14	17		57	30	
11	6/14/79	1200							32	27		36	17	0 (57)
12 rain	6/14/79	1250							35	30	208 (51)	17	36 (34)	154 (64)
13	6/14/79	1530							14	21	(2)	36	17	
14	6/14/79	1610							21	18	(8) (103)	42	17	0 (54)
Agrico														
1	6/18/79	1115	23	21	0 (39)	54	32 (35)	9 (48)						
2	6/18/79	1200	29 (27)	24	0 (27)	24	24 (30)	194 (50)						
3	6/18/79	1230	38 (26)		0 (52)	32	23							
4	6/18/79	1511	27	28	0 (54)	39	29							
5	6/18/79	1545	23	20	22 (33)	36	38	29 (55)						
6	6/19/79	1030							35	32	0 (30)	19	16	17 (23)
7	6/19/79	1100							35	25	174 (28)	37	24	
8	6/19/79	1145							39	31		43	39	
9	6/19/79	1345							40	42		46	38	
10	6/19/79	1430							40	37		47	45	409 (50)

[a] Analysis by ion chromatograph unless noted otherwise, i.e., ( ) = auto analyzer.

TABLE 6. WINDSPEED AND WIND DIRECTION

Date	Runs	Time	WS (Mph)	WD (°)	WS Mps
Agrico					
6/18	A1+B1	11:15	3	360	1.3
	A2+B2	12:00	3.5	Variable	1.6
	A3+B3	12:30	4	345	1.8
	A4+B4	15:11	6	360	2.7
	A5+B5	15:45	5	350	2.2
6/19	C+D1	10:30	3	Variable	1.3
	C+D2	11:00	2.5	Variable	1.1
	C+D3	11:45	2.0	Variable	0.9
	C+D4	13:45	5	10	2.2
	C+D5	14:30	3.5	35	1.6
CFI					
6/12	F1	13:50	10	50	4.5
	F2	15:00	10	45	4.5
	F3	15:30	7	95	3.1
	F4	16:00	8	95	3.6
		Rain			
6/13	A+B1	14:15	10	40	4.5
	A+B2	15:00	15	40	6.7
	A+B3	15:30	10	40	4.5
	A+B4	16:05	11	40	4.9
6/14	A+B5	10:00	10	40° gusty	4.5
6/14	C+D1	11:00	9	40	4.0
	C+D2	12:00	10	40	4.5
	C+D3	12:50	10	40	4.5
		Rain			
	C+D4	15:30	14	25	6.3
	C+D5	16:10	14	25	6.3

Laboratory using a Technicon Autoanalyzer and the semiautomated spectrophoto-metric procedure (ASTM D 3270). All samples were returned to GCA for analysis by IC.

RESULTS AND CONCLUSIONS

The results of the preliminary field phase tests are presented in Table 5. The data indicate that for a majority of runs the filter and tube results are comparable when the solutions were analyzed by both the IC and the spectrophotometric method. Some of the data for the impinger runs, however, were not comparable to the other results. As demonstrated in Table 5, the ambient HF concentrations determined by the IC and autoanalyzer vary widely, and results for the impinger solutions are inconclusive. Since there appears to be some problem with impinger solutions, this method for the collection of HF was not considered further.

Several conclusions can be drawn from the results of the preliminary field phase:

1. A sampling period of 15 minutes was adequate for both the filter and tube collection methods for measuring the HF concentration at each of the gypsum ponds.

2. The double filter cassette and the bicarbonate-coated tubes give more consistent results than the impinger solutions and were selected for use in the formal field phase.

3. No interferences were observed when either filter or tube samples were analyzed by either the IC or autoanalyzer methods. A previous ROSE study has found that a possible interferent, SiF_4, was not present in the atmosphere above the gypsum ponds.[10]

4. The citrate-treated prefilters, used in the double filter cassette, were analyzed for fluoride, and the results are presented in Table 7. The prefilter was intended to remove particulate matter and was not supposed to remove any HF. The results indicate that no fluoride was collected on the citrate prefilter.

TABLE 7. ANALYSIS OF CITRATE FILTERS FOR FLUORIDE

Sample	F^- (µg/mL)	Blank (µg/mL)	net F^- (µg/mL)
1	0.37	0.36	0.01
2	0.38	0.36	0.02
3	0.36	0.36	0
4	0.35	0.36	0

5. The precision between the two manual sampling devices is shown in Table 8. In most of the runs the quantity of ppb collected by each method is comparable. The data in Table 8 indicate that both methods can be used for HF sampling since the quantities of HF collected are similar for samples collected simultaneously.

TABLE 8.   PRELIMINARY FIELD PHASE: INTERSAMPLING DEVICE PRECISION AT SAME SITE

Group	Filter ppb HF	Tube ppb HF	d (F-T)	σ
	59	41	18	
	50	24	26	14.8
	28	23	5	
CFI Site A	17	25	-8	
	21	24	-3	
	Σ 175	137	38	
	x̄ 35	27.5	7.6	
	23	21	2	
	29	24	5	
Agrico Site A	27	28	-1	4.4
	23	30	-7	
	Σ 102	103	-1	
	x̄ 25.5	25.8	-0.3	
	43	42	1	
	19	19	0	
CFI Site B	37	36	1	1.6
	18	15	3	
	18	17	1	
	Σ 135	129	6	
	x̄ 27.0	25.8	1.4	
	54	32	22	
	24	24	0	
Agrico Site B	32	23	9	11.6
	39	29	10	
	36	38	-2	
	Σ 185	146	39	
	x̄ 37.0	29.2	7.8	
	14	17	-3	
	32	27	5	
CFI Site C	35	30	5	4.8
	14	21	-7	
	21	18	3	
	Σ 116	113	3	
	x̄ 23.2	22.6	0.6	
	35	32	3	
	35	25	10	
Agrico Site C	39	31	8	6.1
	40	42	-2	
	40	37	3	
	Σ 189	167	22	
	x̄ 37.8	33.4	4.4	
	57	30	27	
	36	17	19	
CFI Site D	17	36	-19	22.1
	36	17	19	
	42	17	25	
	Σ 188	117	71	
	x̄ 37.6	23.4	14.2	
	19	16	3	
	37	24	13	
Agrico Site D	43	39	4	7.1
	46	38	8	
	47	45	2	
	Σ 192	162	30	
	x̄ 38.4	32.4	6.0	
Grand	Σ 1282	1074	208	11.3
	x̄ 32.9	27.5	5.3	

SECTION 7

FORMAL FIELD PHASE

INTRODUCTION

The objective of the formal field phase of the project was to compare the results of the simultaneous measurement of ambient HF levels as obtained by manual wet chemical sampling methods with the EPA ROSE system. Both sampling systems were located along the edge of the gypsum ponds at CF Industries and Agrico Chemical Co.

The protocol for this phase was determined by the combined results of the preceding phases. The constraints of the ROSE van and onsite electrical power were also considered. Sampling at CF Industries was conducted on July 24th and 25th, 1979 while samples were obtained at Agrico on July 26, 1979.

SAMPLING LOCATIONS

The sampling line of sight was adjacent to each pond as shown in Figures 10 and 12. The ROSE van and light source were aligned visually and the distance between them was measured with a laser rangefinder. The line of sight established at each pond was divided into four equal segments. One manual sample was situated at or as close as possible to the center of each segment. The locations designated A, B, C and D, were determined by the restraints of the terrain and positions of the electrical generators.

AT CF Industries, the line of sight for the ROSE system was 3 feet east of the wet chemical sampling line (Figure 11). At Agrico, the line of sight for the ROSE system is shown in Figure 13. The positions of the sampling sites were determined by the configuration of the road. The height of the inlet of each of the manual sampling devices was at the midpoint of the light beam but did not interfere with the beam.

SAMPLING AND ANALYTICAL PROCEDURES

Manual Wet Chemical Methods

Two collection devices were used with the manual sampling grains; i.e., (1) a filter cassette containing a citric acid-treated prefilter followed by a sodium hydroxide-treated filter (designated F) (Figure 14), and (2) a sodium bicarbonate-coated pyrex tube (designated T) (Figure 15). The vacuum/metering system was a Research Appliance Corporation (RAC) meter control console, which was calibrated according to procedures delineated in EPA publication APTD 0576.

COOLING POND

LIGHT SOURCE AND TELESCOPE

RECEIVER
TELESCOPE

SITE D — 47m — SITE D — 104m — SITE C — 109m — SITE B — 96m — SITE A — 57m —

ROSE VAN

413m

OPTICAL SAMPLING PATH

GENERATOR

CF INDUSTRIES

N
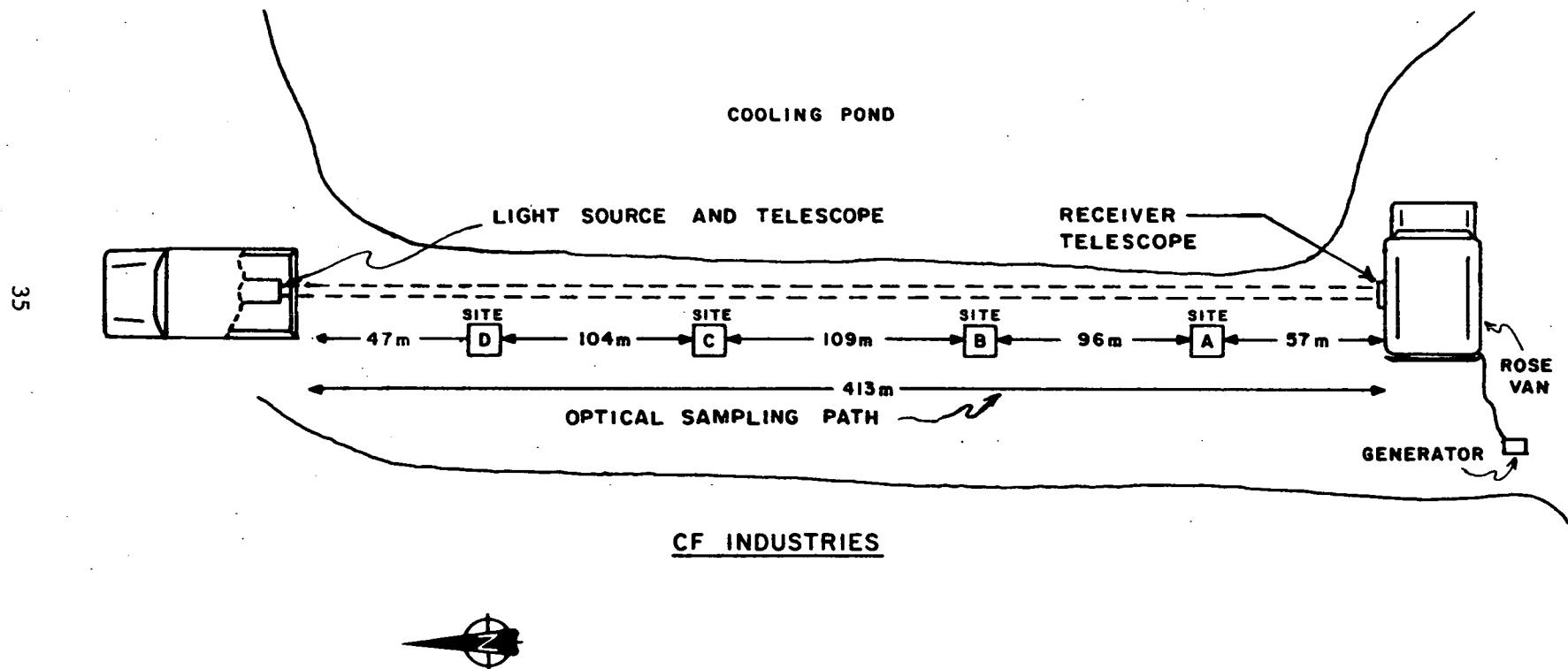
Figure 10. Line of sight at CF Industries.

Figure 11. Sampling line at CF Industries (with light source for ROSE system in background).
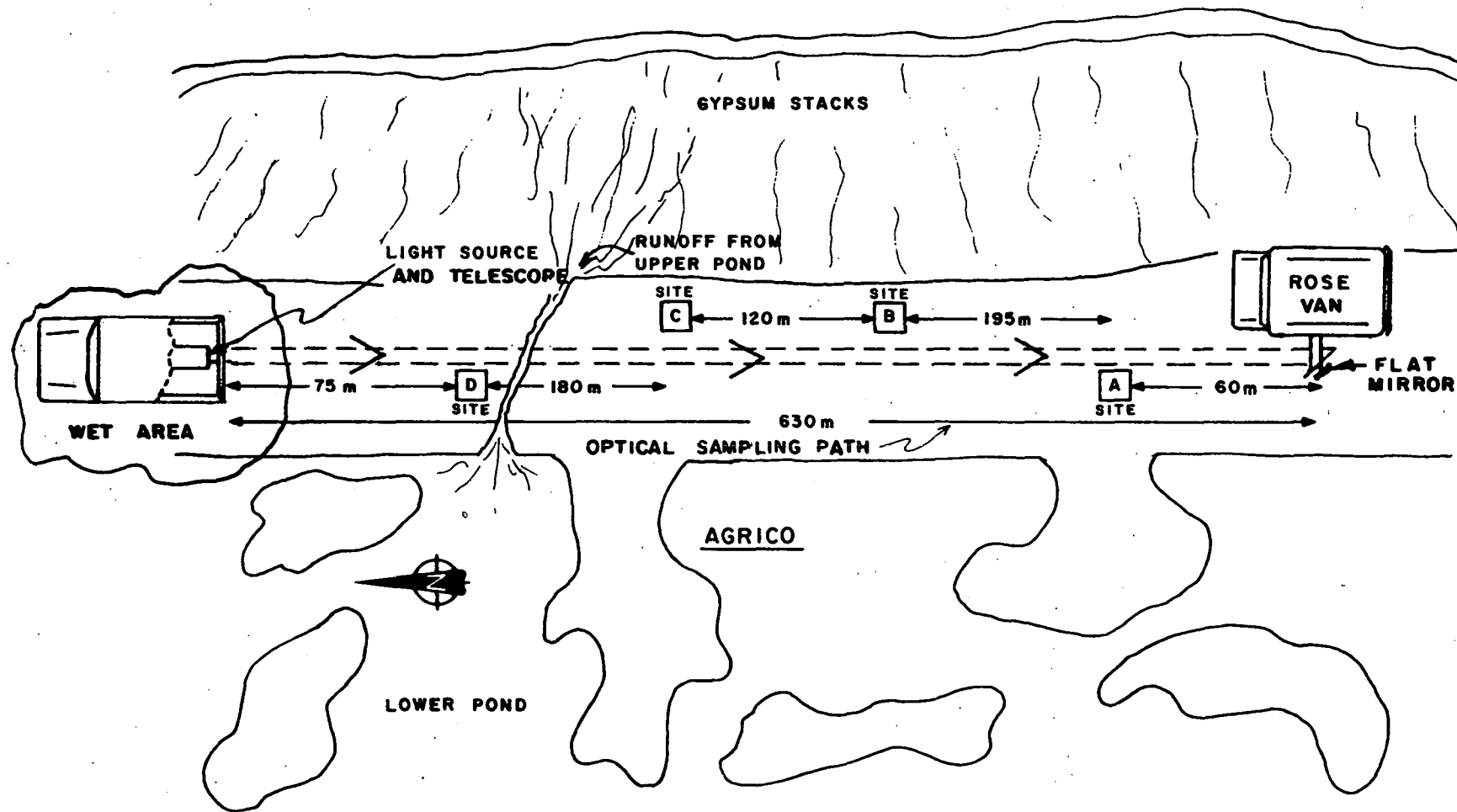
Figure 12. Line of sight at Agrico.

Figure 13. Sampling line at Agrico (with ROSE van in foreground).

Figure 14.   Sampling train and filter cassette.
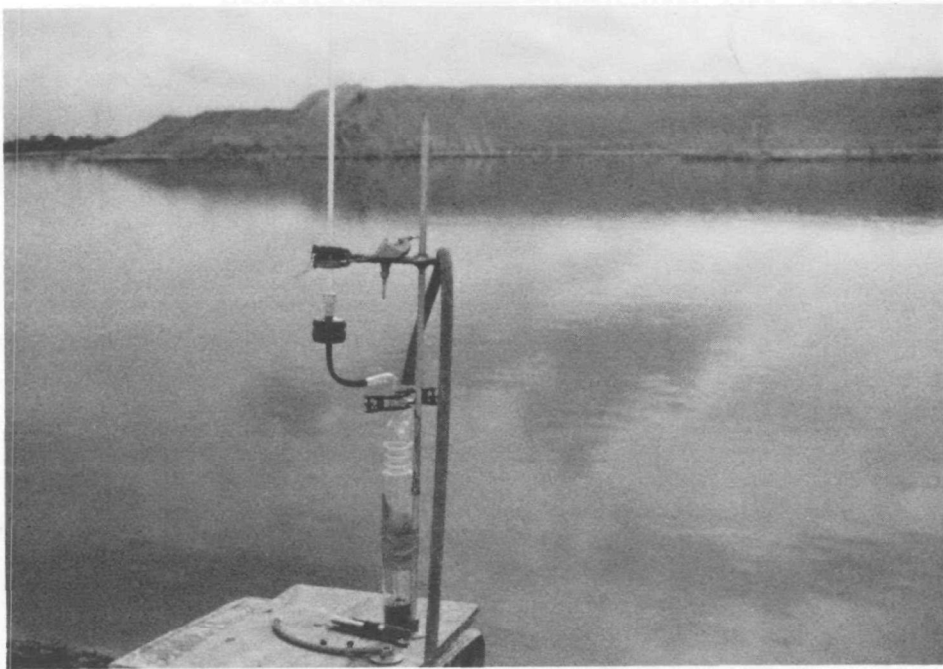
Figure 15.   Sodium bicarbonate-coated tube.

The filters and tubes were prepared as described in Section 4. The sampling trains are shown in Figure 16. Regardless of the collection device (filter or tube), the sampling train was used at all four sample locations. The air was sampled at a rate of 0.5-0.6 acfm for a sampling period of 16 minutes. Twenty runs were conducted at CF Industries. All odd numbered runs were executed with the filter cassettes, and the even numbered runs used tubes for sample collection. The initial 10 runs were conducted on July 24, 1979 while the remainder of the samples at CF Industries were collected the next day. Test samples for 18 runs (No. 21-38) were collected at the Agrico gypsum pond on July 26, 1979. Two sets of samples were collected with the filter cassette, followed by one run with the bicarbonate-coated tube. This sequence was repeated six times. The sampling rate and duration was the same as for the CFI runs.

After completion of the sampling runs the collection devices were removed and the samples were recovered as follows:

Filter – The sodium hydroxide filter was placed in a 125 ml LPE bottle, 10 ml of distilled deionized water and 0.1 ml of 1N NaOH were added. The bottle was capped and swirled.

Tube – Two 5 ml portions of distilled deionized water were poured onto the inner surface of the tube; the tube was swirled and the liquid collected in a 125 ml LPE bottled. To preserve the sample, 0.1 ml of 1N NaOH was added. The bottle was capped and swirled.

Blank filters and tubes were also subjected to the above procedure.

All samples were analyzed the day after they were collected. Analyses were done at the Agrico Analytical Laboratory using a semi-automated spectro-photometric procedure with a Technicon autoanalyzer system. The remaining aliquots of the CFI samples were brought back to the GCA Laboratory for analysis by IC.

Remote Optical Sensing of Emissions (ROSE) System

A schematic of the ROSE optical system is shown in Figure 17. The light source-telescope system used for the long-path absorption measurements is shown in Figure 18. The f/5 scope is of Dall-Kirkham configuration with a 30 cm diameter primary mirror. The light source is a 1000 watt quartz-iodine lamp (in wavelength regions where the quartz envelope is opaque, its thermal emission provides sufficient energy). The light source and telescope system is transported to the measurement site in the ROSE van (Figure 19) and installed in a locally obtained truck which is driven to a desired location (Figure 20); a small generator powers the light source if local power is not available.

The remainder of the ROSE system is permanently installed in an 8.5 meter van. A telescope identical to that described above collects energy from the remote light source directly through a port in the side of the van, as indicated in Figure 17. The receiver telescope focuses energy at the interferometer aperture, which is adjustable for compatibility with desired spectral resoltuion. The interferometer and peripheral equipment comprise

40
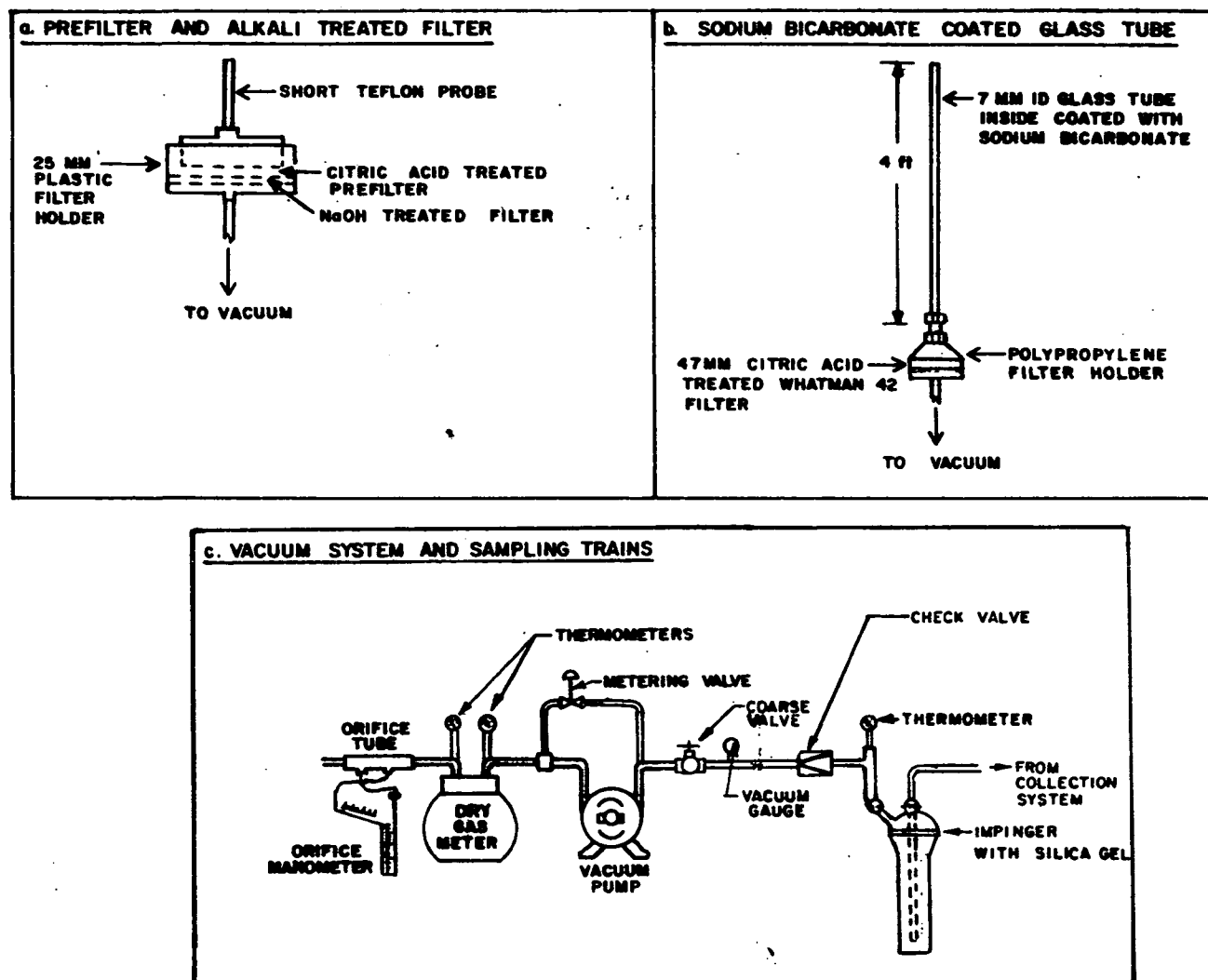
Figure 16. HF sampling trains utilized in the final field phase (a) prefilter and alkali treated filter (b) sodium bicarbonate coated glass tube (c) vacuum system for sampling trains.
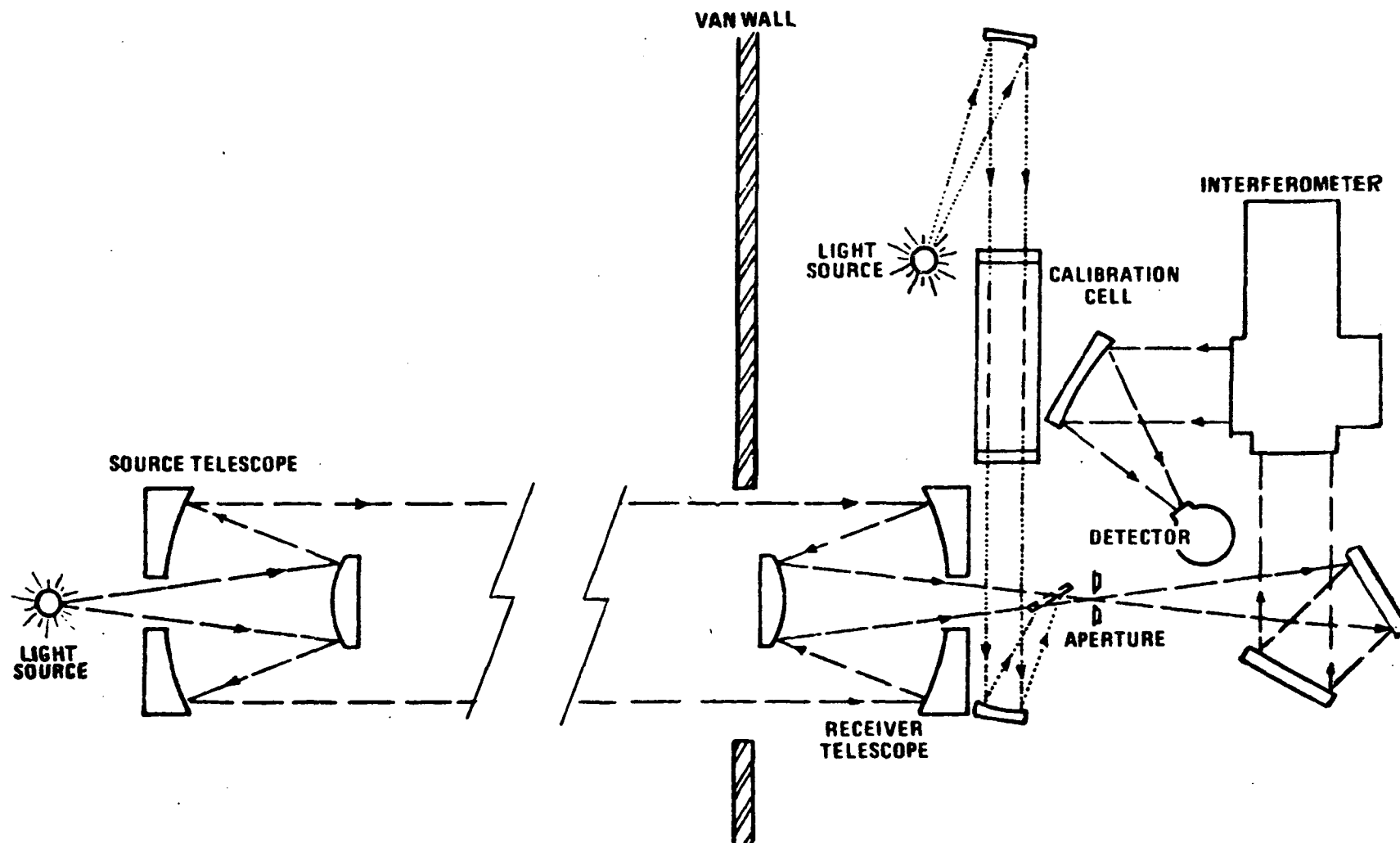
Figure 17. The ROSE optical system.
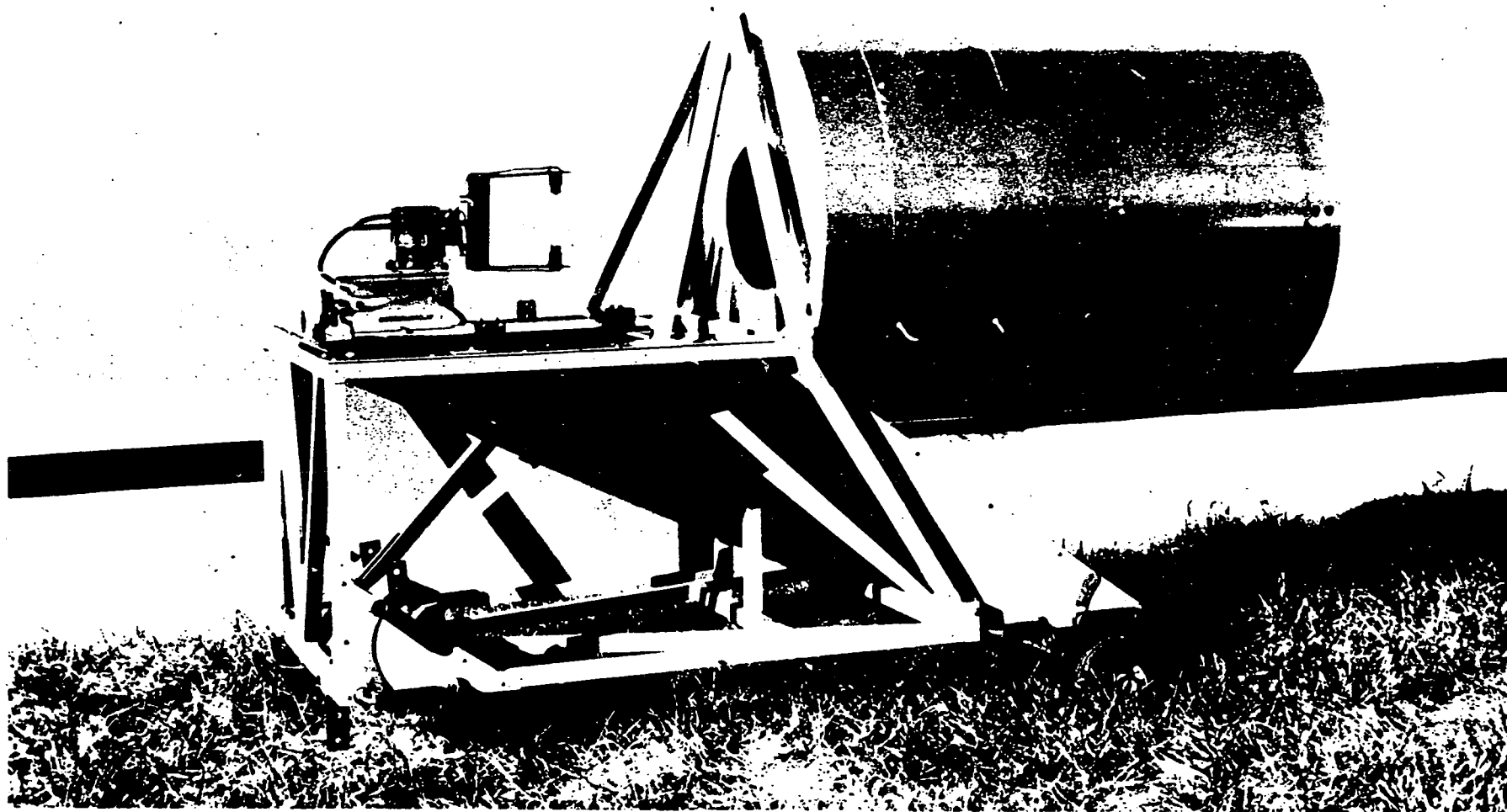
Figure 18.   The ROSE system light source and telescope.

Figure 19. ROSE van and receiver telescope.

Figure 20. Quartz-iodine light source and telescope.

a standard Nicolet Instrument Corporation Model 7199 FT-IR system configured
to fit into the van. Major components of this system consist of a computer
with 40K memory, dual-density disk with 4.8 million, 20-bit word capacity,
teletype, paper tape reader, oscilloscope interactive display unit, and a
high-speed digital plotter. Maximum spectral resolution achievable with this
system is 0.06 cm^{-1}.

The interferometer itself is mounted on the telescope support structure.
All other systems (except the plotter) are arranged in two 19-inch relay racks.
The general layout of the van is shown in Figure 21. Two beamsplitters,
BaF$_2$ and ZnSe, are available for use in the interferometer. A dual-element,
sandwich-type detector is mounted in a liquid nitrogen dewar. For the 1800
to 6000 cm^{-1} region InSb is used, and HgCdTe is used from 600 to 1800 cm^{-1};
the two regions are scanned separately. During data collection single inter-
ferograms are collected and stored on disk and then averaged at the end of the
data collection period. The inverse Fourier transform of the averaged inter-
ferograms is then calculated by the computer to produce a single spectrum. It
has been found practical to average about 100 interferograms; this requires a
data collection time of 16 minutes. (The signal-to-noise of the spectrum is
improved by the square root of the number of interferograms collected.)

Sampling Protocol

The manual collection devices were set into the four sampling trains
and initial system readings obtained. The four samplers and the ROSE
system were then started simultaneously. The sampling and spectral ac-
cumulation proceeded for 16 minutes. All systems were stopped simultaneously.
The final readings for the manual samplers were obtained and the spectra
obtained by the ROSE were checked.

CALCULATIONS

Manual Methods

1. The volume of dry gas sampled is converted to standard conditions,
   77°F and 29.92 "Hg. (25°C and 760 mm Hg).

$$\text{Vmstd} = \text{dry std ft}^3 = \frac{537 \, (Y) \, (VM) \, (PB + \frac{PM}{13.6})}{(29.92)(TM)}$$

Where: Y = dry gas meter calibration factor

VM = sample gas volume, ft^3

PB = Barometric pressure "Hg

PM = ΔH, pressure at DGM "H$_2$O

TM = Temperature at dry gas meter, °R (°R = °F + 460)

537°R = 77°F + 460

2. Vmstd, dry std. m^3 = Vmstd (dry std. ft^3) x 0.02832
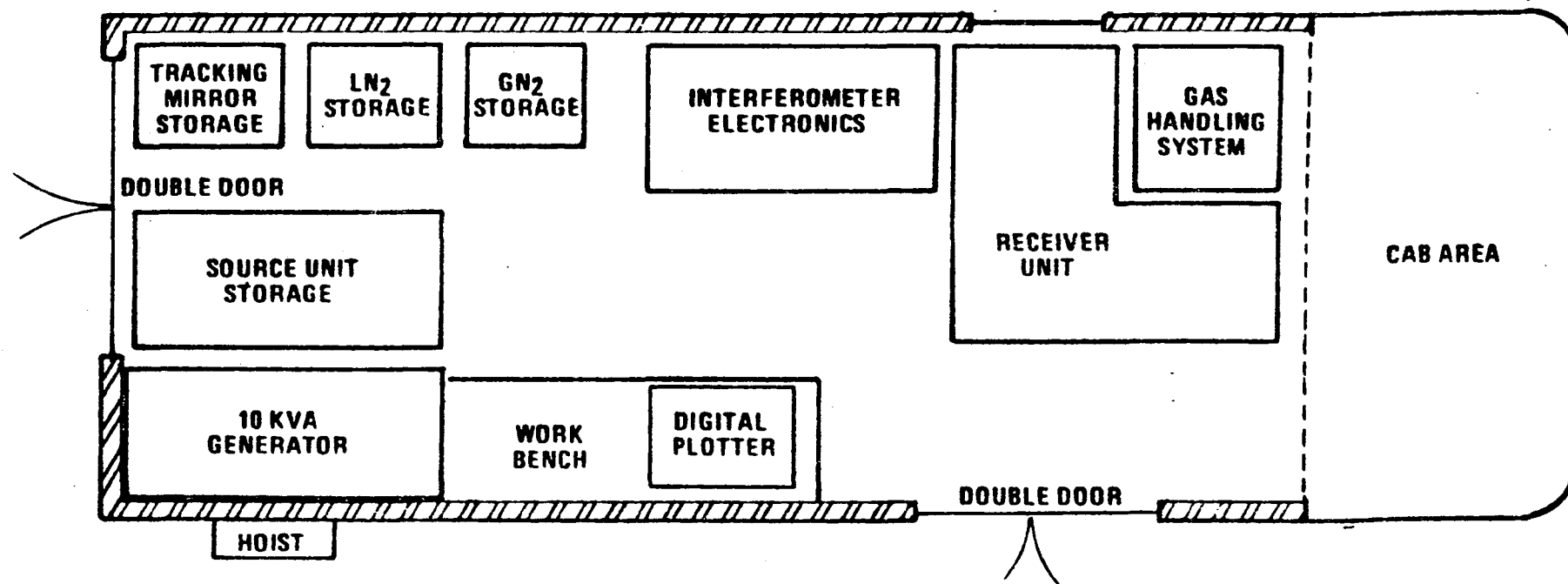
Figure 21.   Layout of ROSE system in van.

3. The concentration of HF in the ambient air is determined by:

$$\mu g\ HF/_{m}3 = \frac{\mu g\ F^{-}/_{ml} \times V_{L} \times \dfrac{20.006\,(HF)}{18.998\,(F)}}{Vmstd\ (m^3)}$$

Where: V_L = volume of sample, ml

4. The concentration in ppb is:

$$ppb\ HF = \frac{\mu g\ HF/m^3}{0.818\ \mu g/m^3/ppb}$$

Where: $0.818 = \dfrac{20.006\ \mu g/\mu mole \times 10^9\ \mu L/m^3}{24.45\ \mu L/\mu mole \times 10^9\ ppb}$

5. The four results from each manual sampling run were averaged arithmetically and geometrically.

$$\overline{X}\ Arithmetic = \frac{\sum\limits_{n=1}^{4} X_i}{4}$$

$$\overline{X}\ Geometric = \{(X_A)(X_B)(X_C)(X_D)\}^{\frac{1}{4}}$$

ROSE Method

Calibration of the ROSE system field data is normally done by recording spectra of known amounts of the gas in question (contained in the calibration cell shown in Figure 17). The transmittance of the gas sample is related to the cell length and gas concentration by Beer's Law:

where $\tau(\nu) = e^{-K(\nu)CL}$

ν = wavenumber (cm^{-1})

C = concentration (ppm)

L = path length (meters)

and $K(\nu)$ = spectral absorption coefficient (ppm meters)$^{-1}$.

The quantity $K(\nu)$ is determined from the calibration spectra and then used with the field data to determine the average concentration between the light source and the receiver unit (again using Beer's Law). In filling the calibration cell either a few torr of the pure gas are admitted to the evacuated cell and then the total pressure is brought to one atmosphere with the addition of air or nitrogen, or a premixed sample is admitted to the cell to a total pressure of one atmosphere. (A total pressure of one atmosphere is used so that the spectral lines of the gas sample are pressure broadened to the same extent as in the field data.)

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Because of its high reactivity, HF requires a special gas handling system for filling calibration cells. Such a system was not available at the EPA laboratory. Therefore another method, which is based on measuring the area under the absorption curve of the spectral line in question, was used. The particular advantage of this method is that the area under the absorption curve is independent of the spectral resolution used, which thus allows the use of HF data obtained at low resolution[11,12] to be used as calibration data. From the low resolution data, the relationship between the area under an absorption line and the gas optical depth (product C x L) was determined (private communication of D. E. Burch and D. A. Gryvnak, Aeronautic Division of Ford Aerospace and Communications Corporation), and the resulting calibration curve is shown in Figure 22.

The R(5) line of HF at 4174 cm^{-1} was selected for the concentration calculation because it provides the most suitable compromise between maximum line strength and minimum water vapor interference. The signatures of pure H_2O, "clean air," and the gypsum pond (typical) are shown in the 4168 to 4178 cm^{-1} region in Figure 23. It is seen that there are weak H_2O lines at approximately 4173.6 and 4173.9 cm^{-1}. The methods used to eliminate the H_2O interference and determine the area under the HF absorption line are described below.

First, the clean air and a gypsum pond spectra were expressed in units of absorbance [Log τ (ν)] so that the spectra could be manipulated arithmetically. The ROSE system software contains an interactive subtraction program that allows the difference between two spectra (expressed in absorbance) to be displayed on an oscilloscope and allows the optical depth of the background spectrum to be varied until the desired amount of water vapor interference is subtracted from the gypsum pond spectrum. In using this method, it was found that the selection of the amount of water vapor to be subtracted was subjective and not reliably reproducible. An objective and reliably reproducible method was achieved simply by multiplying the background spectrum by a factor that would make the maximum absorbance of the water vapor line at 4176.4 cm^{-1} equal in both spectra (Figures 24 and 25). In this way, the optical depth (C x L) of H_2O was made equal in each spectrum. The background spectrum was then subtracted from the pond spectrum and the result converted back to transmittance (Figure 26). (Similar sets of data are shown in Figures 27 to 29). All of these data manipulations were carried out using standard system software.

This substraction method is effective in eliminating H_2O interference, but does increase the noise level in the spectra and makes the determination of the base line (line of 100% HF transmittance) a potential major source of error. This problem was handled by taking a laboratory spectrum of the R(5) line of HF (which was essentially noise-free), expressing the line in assorbance, and then multiplying the line by series of factors chosen so that when the laboratory line was converted back to transmittance, a series of absorption lines were obtained that spanned the range of transmittances observed in the field data. A preliminary estimate of the baseline was determined by measuring the maximum HF absorption (difference between pond and clean air spectra at the center of the R(5) line in Figures 24 and 25) for each spectrum. Then a laboratory-generated line was selected that gave the best fit between the general shape of the field line and the estimated baseline. The final result is indicated in Figures 26 and 29. The area under the absorption curve was

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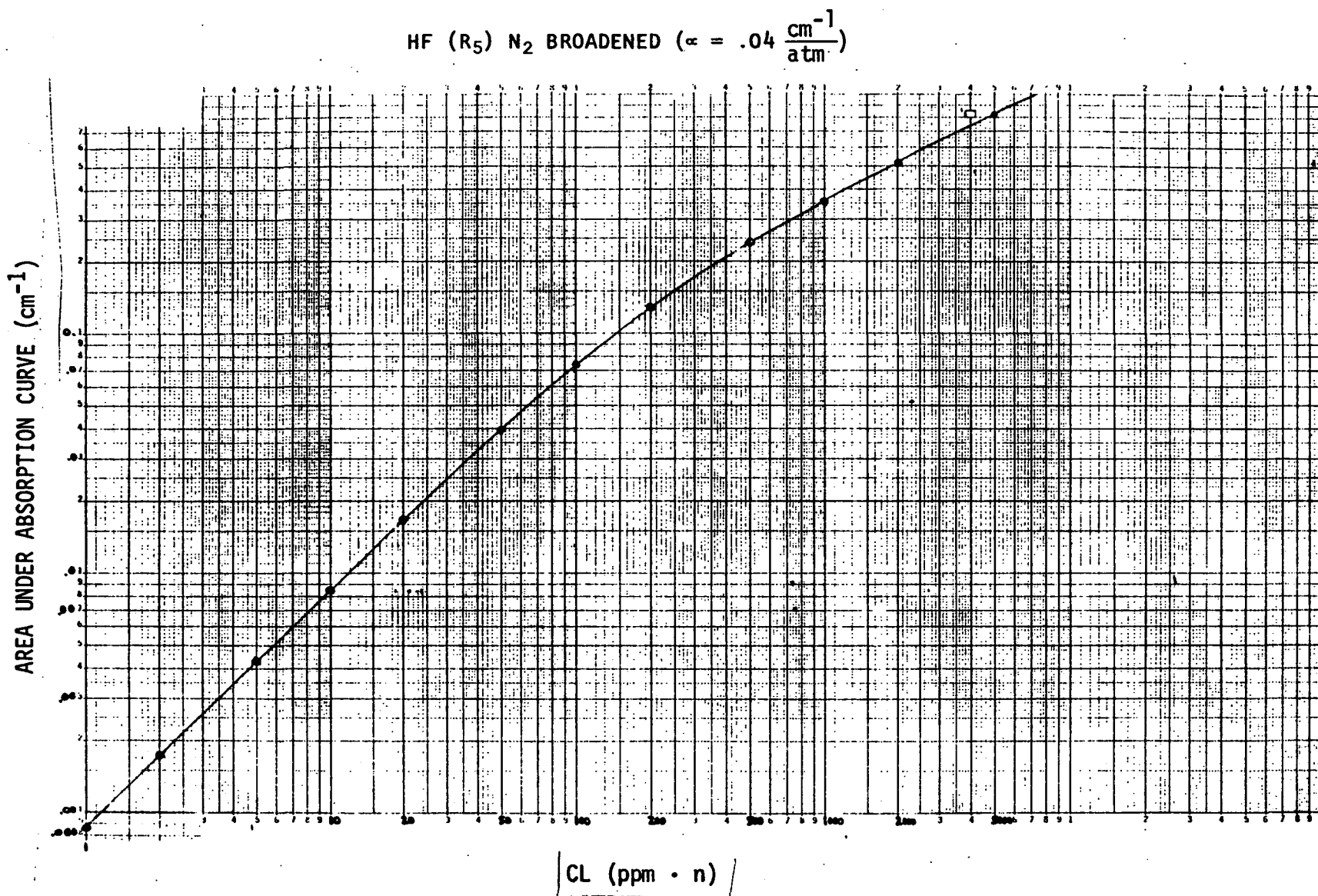
Figure 22. Concentration calibration curve for the R(5) line of HF.
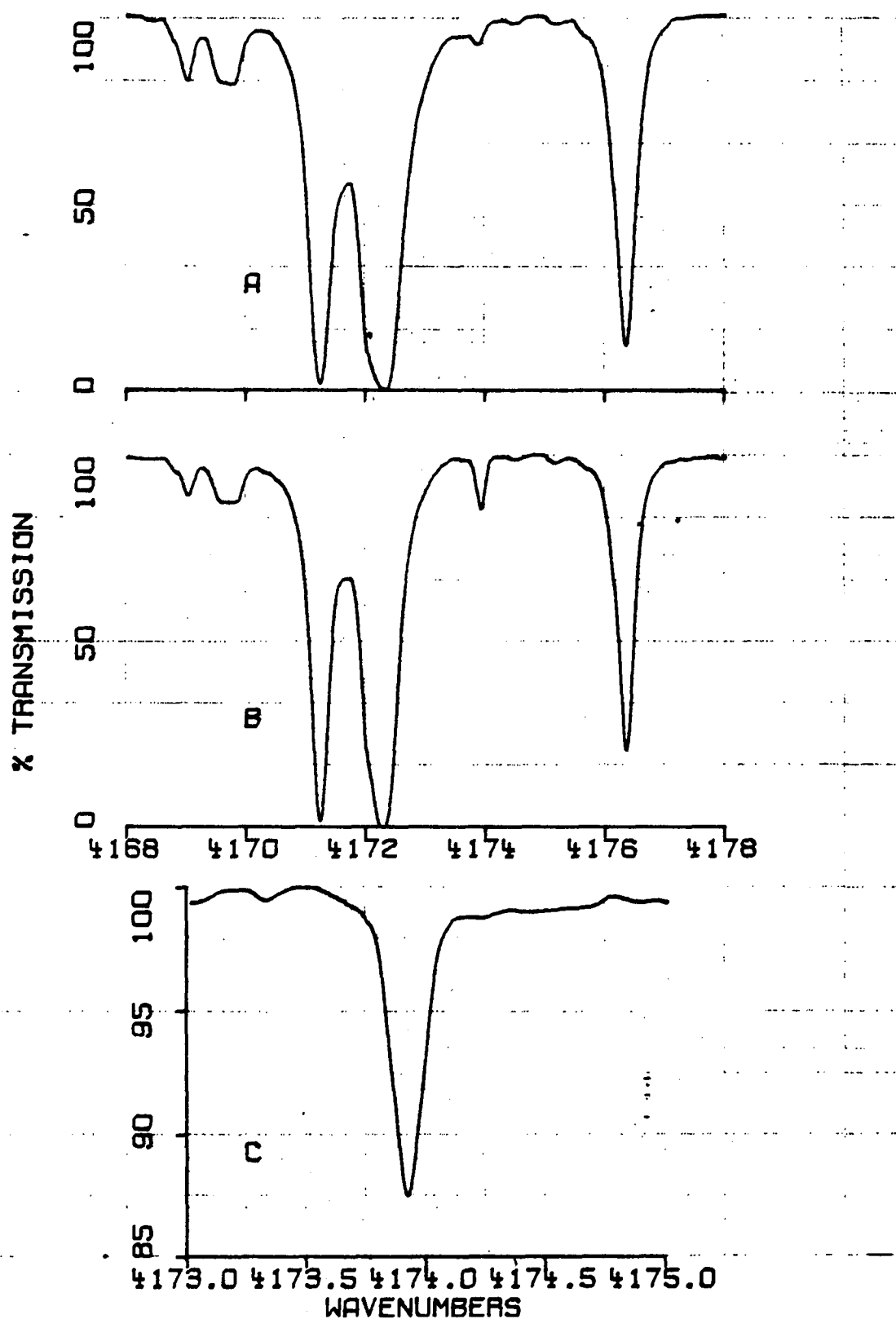
Figure 23. (A) Background spectrum, 900-meter path; (B) gypsum pond spectrum, AGRICO, 630-meter path; and (C) subtracted spectrum.
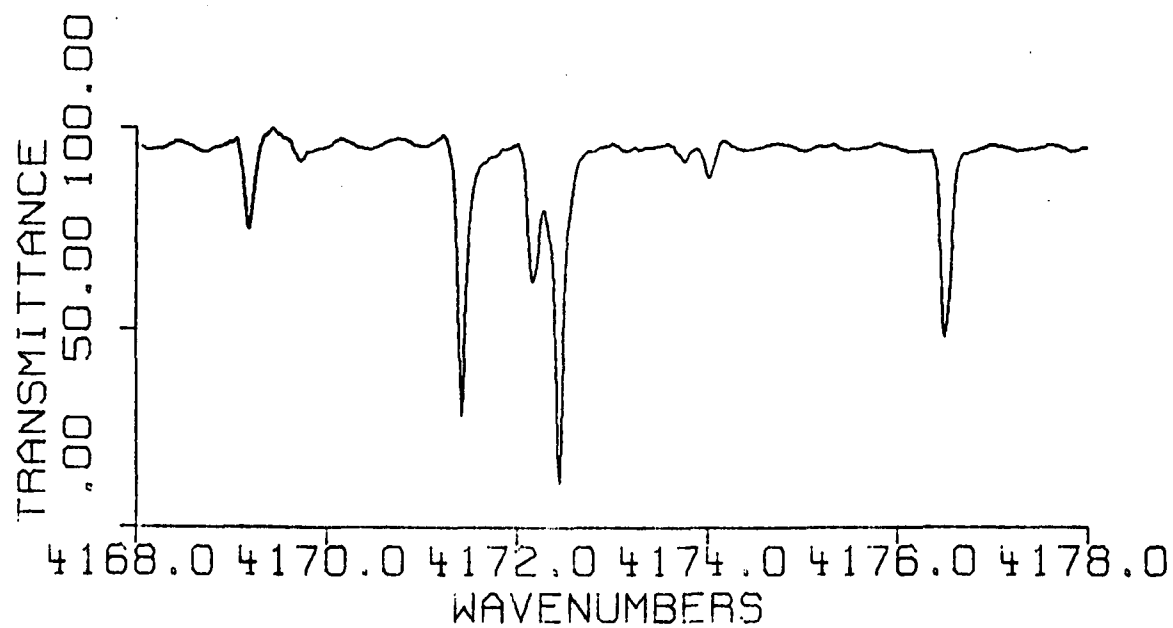
Figure 23D. Pure H_2O (not broadened to atmospheric pressure).
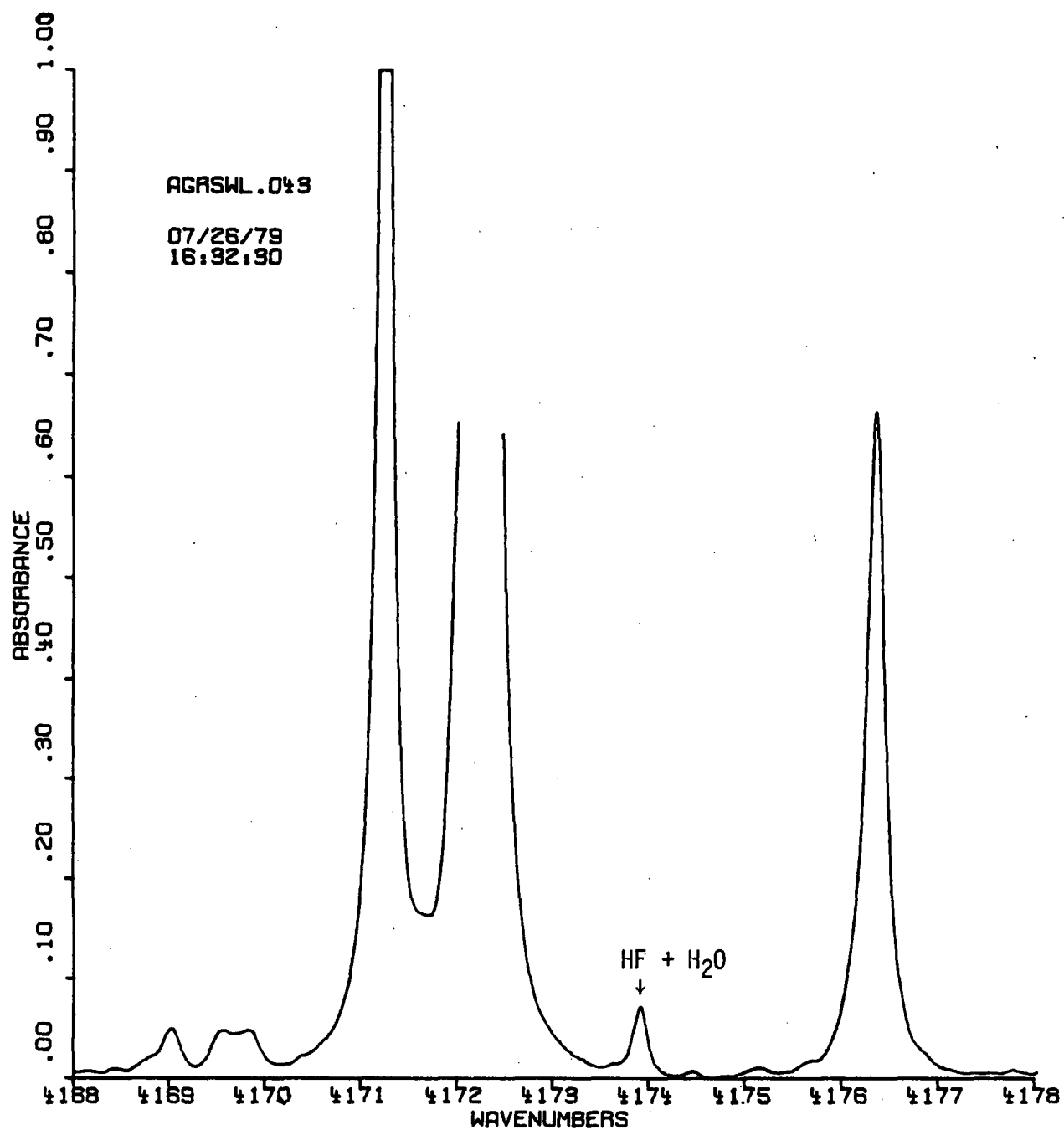
Figure 24. Original spectrum run--ROSE 43, GCA 32.
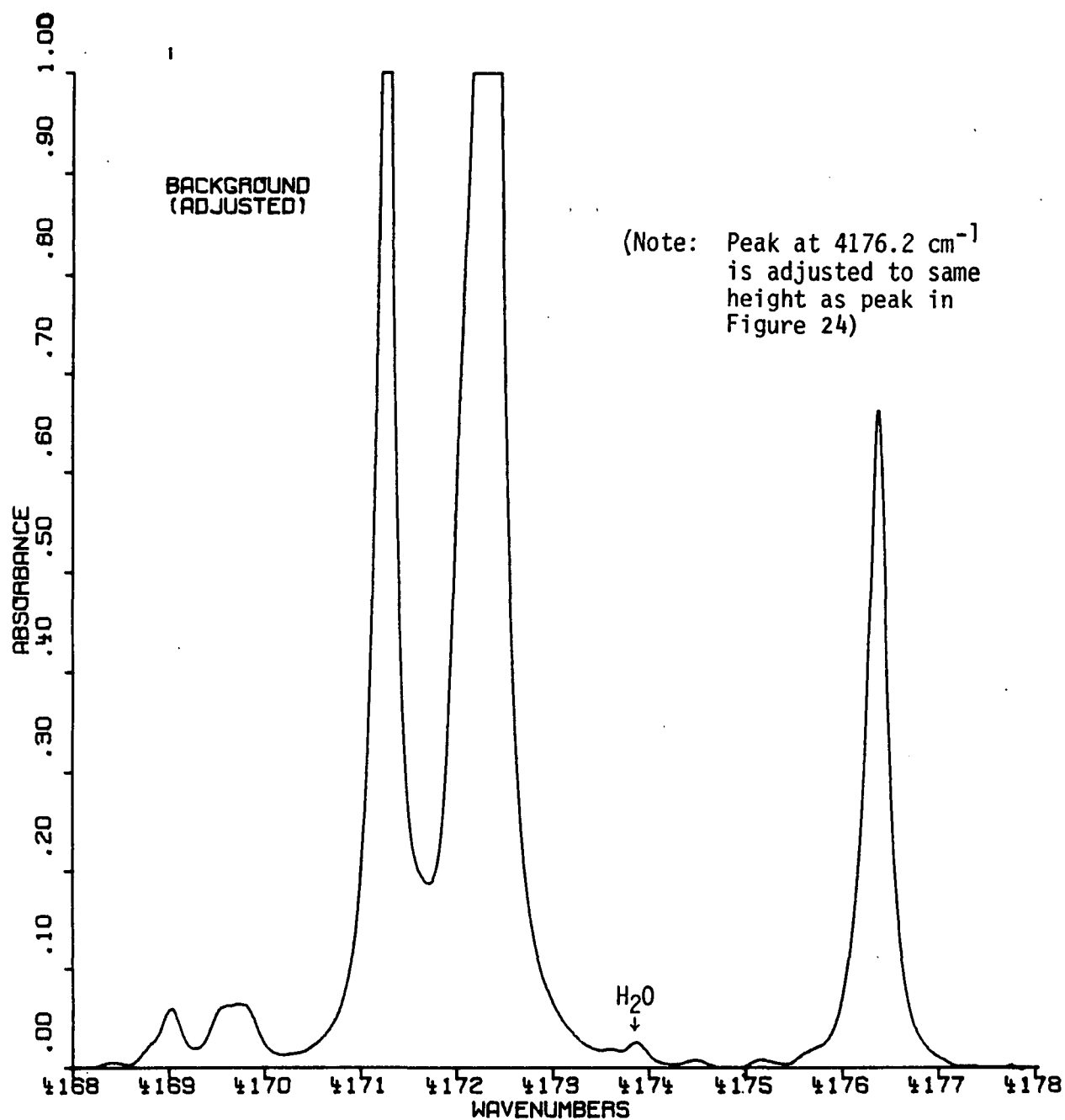
Figure 25. Background spectrum adjusted for constant water vapor; used to correct run – ROSE 43, GCA 32.
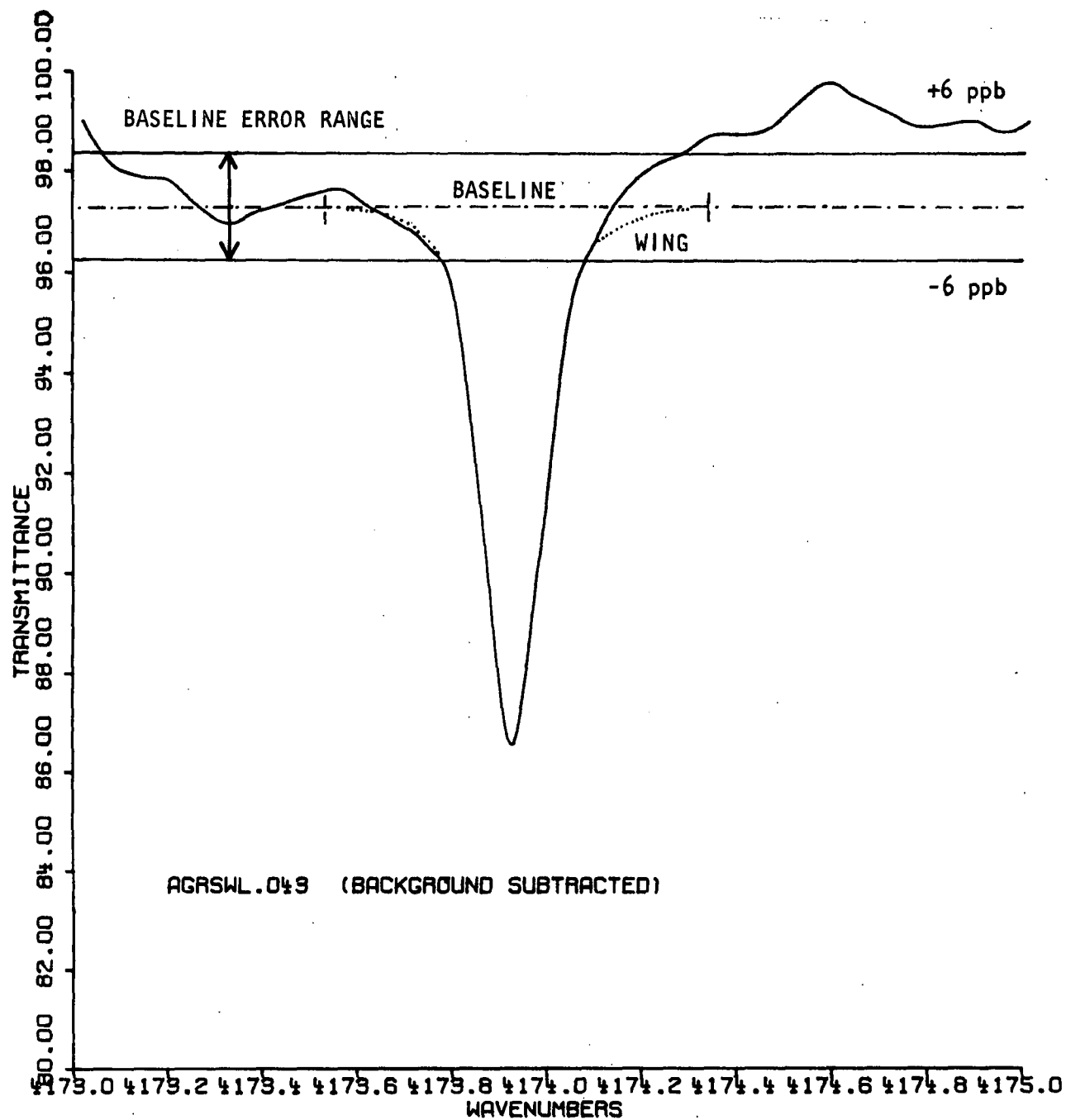
Figure 26. Subtracted spectrum; run number ROSE 43, GCA 32.
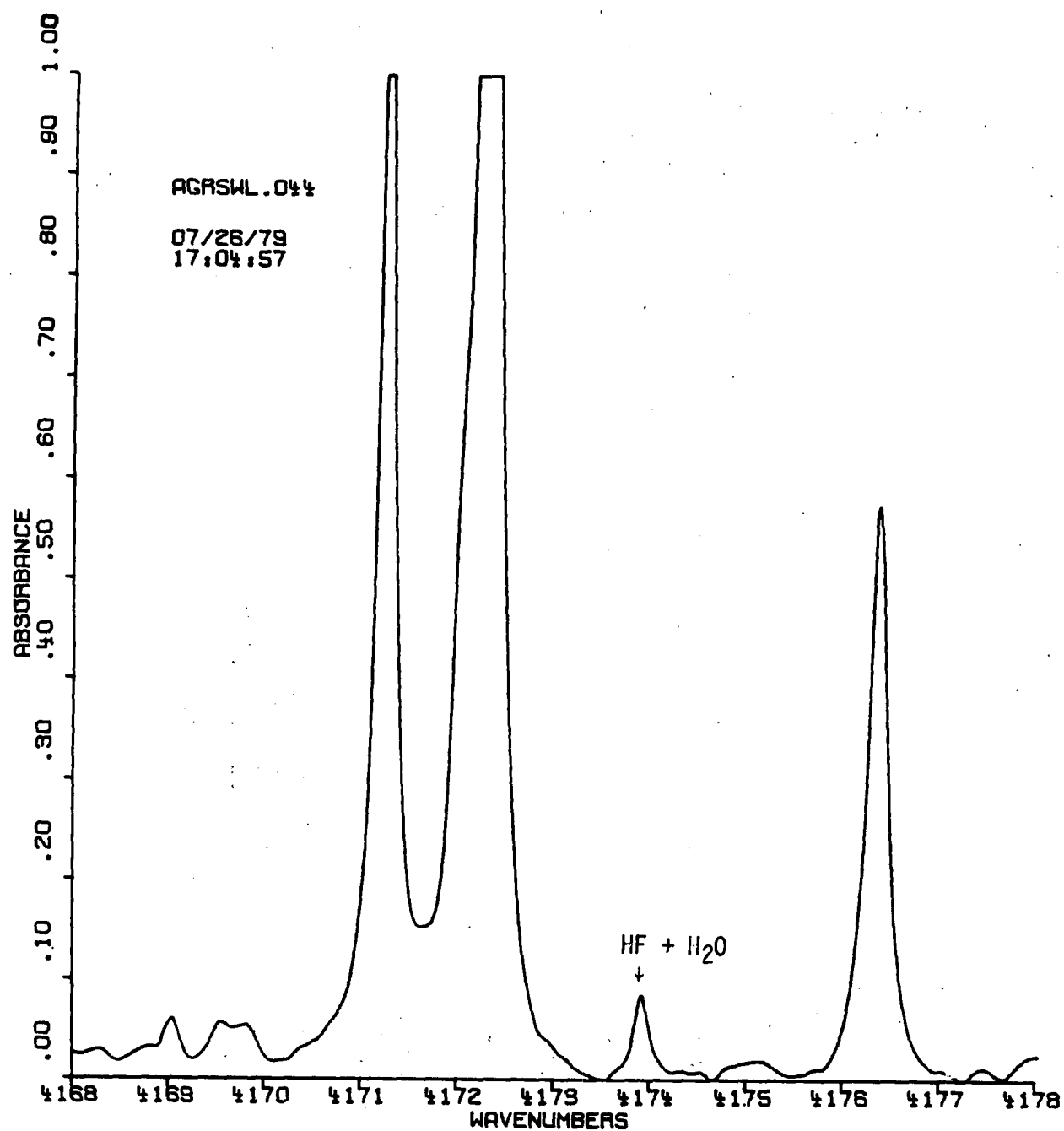
Figure 27. Original spectrum; run number ROSE 44, GCA 33.
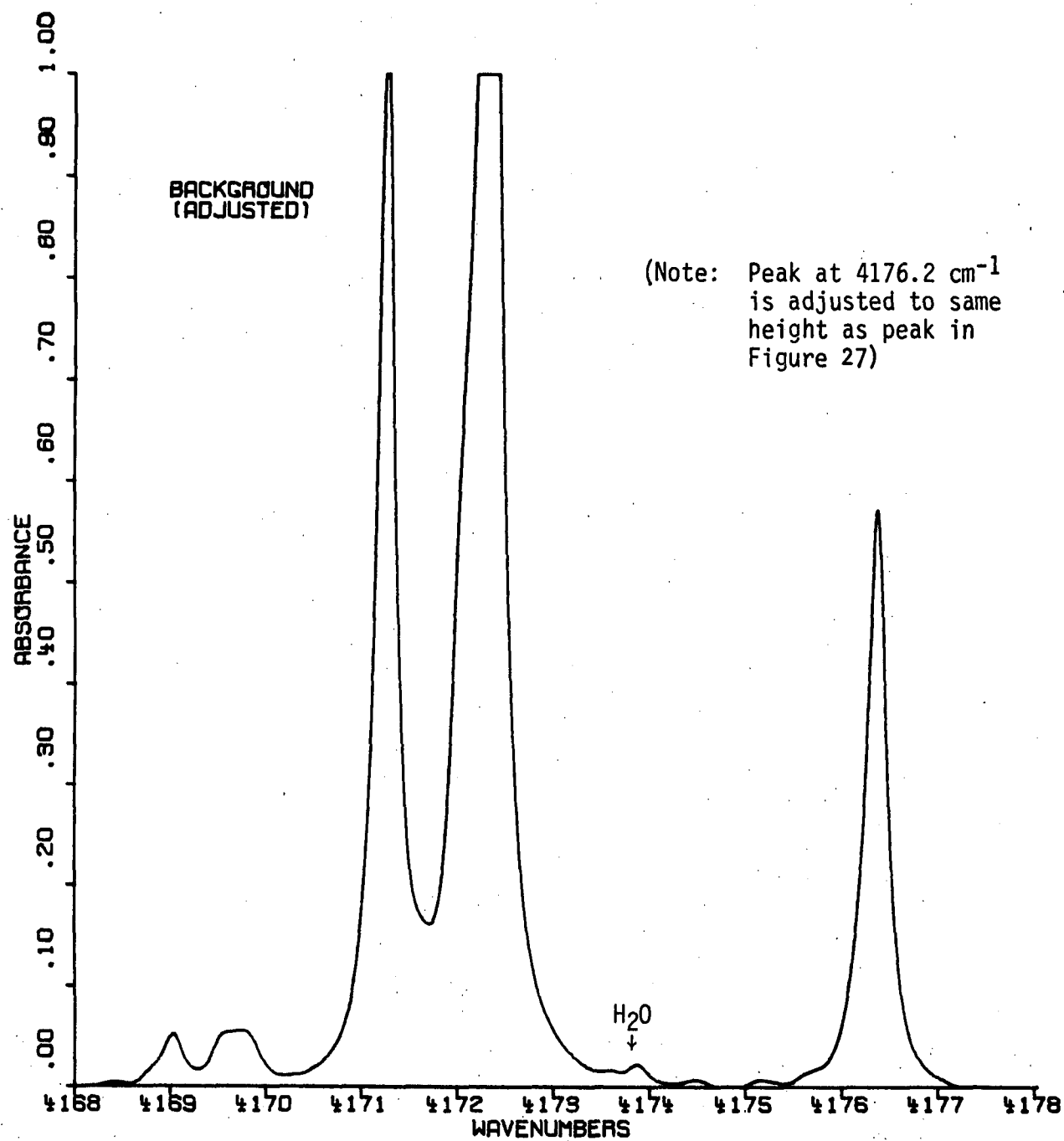
Figure 28. Adjusted background spectrum; run--ROSE 44, GCA 33.
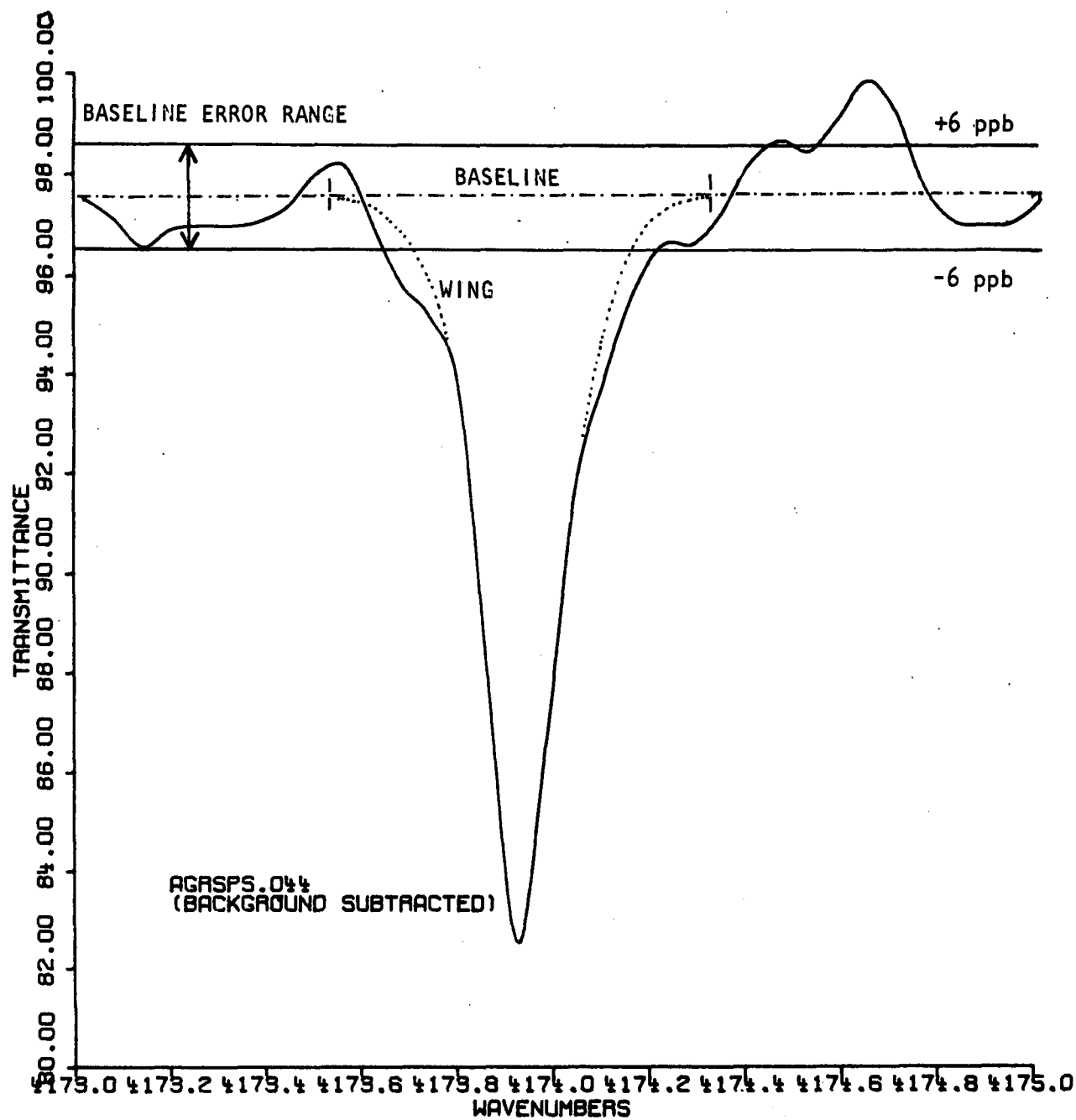
Figure 29. Subtracted spectrum; run—ROSE 44, GCA 33.

then measured directly and the concentration determined from the calibration curve (Figure 22) and the path length. This procedure was carried out for each field spectrum. A base line error range is indicated in Figures 26 and 29; the magnitude of this error is discussed elsewhere.

Comparison of the HF concentrations measured by the ROSE system (as described above) with those measured by point sampling methods indicated general agreement except for the last set of measurements at Agrico. Here, four of the last five ROSE measurements were significantly higher than the highest of the point measurements. The point measurements were generally consistent from site to site, with site D (closest to the van) having the highest value. The ROSE measurements for these data sets could only be correct if very high ($\sim$400 ppb) HF concentrations existed in the vicinity of the van. A close inspection of the ROSE spectra for these last five data sets were appreciably noisier than previous data.

A slightly different data reduction procedure was therefore tried. First, the ROSE data for each set (two mornings at CFI and a morning and afternoon at Agrico) were averaged. This had the effect of improving the S/N ratio by a factor of three. These average data were then reduced as described previously. The peak transmittance of each of the four averaged spectra was measured, and using the "known" HF concentrations, an absorption coefficient was calculated. The four values obtained were 5.14, 5.04, 5.29, and 5.09 x 10^{-3} (ppm x meters)$^{-1}$. The average of these averages was 5.14 x 10^{-3} (ppm x meters)$^{-1}$, and this taken as the value of K for the R(5) line of HF.

Then, all data were reprocessed as above up to the step requiring computer subtraction of pond and background spectra expressed in absorbance. Instead, the two spectra were plotted and the peak absorbance of the line center due to HF was measured by subtracting off the H_2O interference (Figure 30). The lines of zero HF absorption were determined visually. The HF concentration for each line was then calculated from the abosrbance using the average K value. The results were that the four HF concentrations that were apparently high were now within the range of the point values. All other HF concentrations changed by ±3 ppb or less from the previous values.

Sources of Error

ROSE Method--
Potential sources of error in ROSE system measurements have been studied extensively under both laboratory and field conditions. The laboratory studies have addressed system reproducibility and calibration error. The reproducibility of the system was tested by collecting separate sets of interferograms (50 in each set) on the same gas sample in a cell. Each set was transformed to give a single spectrum. It was found that for gas samples whose line widths are comparable ($\sim$0.2 cm^{-1}--gases like CO and HF) with the instrument resolution (0.125 cm^{-1}), a variation in line intensity of approximately ±1 percent occurred between the sets of spectra. Calibration accuracy was tested by filling a gas cell to the same nominal pressure several times and collecting a set of interferograms after each fill. The error in this case was determined by the accuracy to which the pressure gauge in the gas handling system could be read--about ±5 percent.

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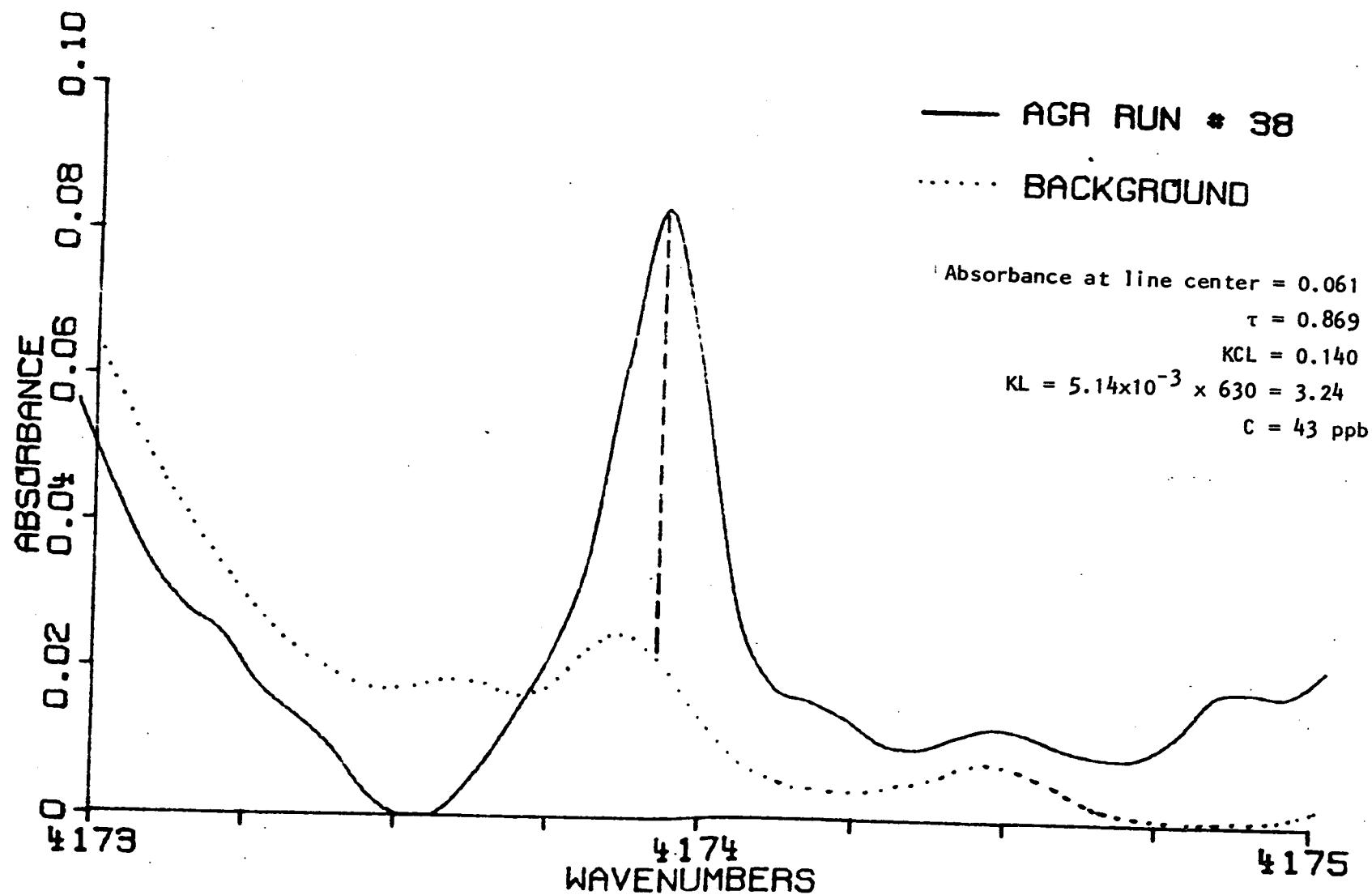
Figure 30. Data reduction method – subtracting peak height of background.

Error in field measurements tends to be greater than in laboratory measurements simply because as the light source is moved further and further from the van, less energy is collected, and the S/N ratio decreases. The most reliable test of the system for field measurements is to compare from run to run the spectra obtained for the gases CO_2 and N_2O. Since these species have essentially constant concentrations, comparison of spectra from different runs gives a measure of the overall instrument performance. Figures 31 and 32 compare eight runs from Agrico. The variation in peak absorption of all runs (strongest and weakest) is 4.6 percent. Figure 33 shows the results for N_2O, where the variation is 5.4 percent. Because of the fall-off in detector sensitivity toward shorter wavelength, the S/N ratio is about four times less at the region of HF absorption than at the regions of CO_2 and N_2O absorption. This is evidenced in Figures 34 and 35, where another CO_2 band (located where the S/N ratio is the same as for HF) is shown. Here the maximum variation is 14.2 percent. For the HF measurements the noise is further increased due to the subtraction of two spectra. These considerations lead to a maximum error on any single HF measurement (average of 100 interferograms) of ±30 percent. This error is consistent with the observation that on multiple reductions of the same HF data, the maximum variation in HF concentration on identical runs was never greater than 30 percent.

Manual Sampling Methods--

The two manual sampling methods for the collection of HF have been studied in the laboratory and field and the results of these experiments were presented in Sections 5 and 6, respectively. The percent recovery of HF for each method was shown to be about 100 percent (Table 3). The precision for each sampling device for the laboratory phase is given in Table 4. For both sampling devices the relative standard deviation was less than 10 percent for HF concentrations above 18 ppb. The percent recovery and precision shown in Tables 3 and 4, respectively, are a reflection of the sources of error in both the sampling devices and the analytical method. In the laboratory phase, ion chromatography was used to analyze the samples for HF.

The precision obtained in the preliminary field phase is presented in Table 8. Again, ion chromatography was used to determine HF in the samples.

For the formal field phase, the samples were analyzed by the colorimetric method using a Technicon Autoanalyzer. The precision and accuracy of the semi-automated method have been documented by ASTM-Method D3270. A collaborative study by nine laboratories using the method for the determination of HF in vegetation gave relative standard deviations ranging from 4 to 13.4 percent for different types of vegetation. Replicate analyses of standard NaF solutions by four laboratories had relative standard deviations of 11.4, 3.9, and 3.0 percent for solutions containing 0.28, 1.41 and 2.81 µg F/ml, respectively. Replicate analyses of standard NaF solutions by four laboratories showed average recoveries of 101.8, 101.4, and 100.7 percent for solutions containing 0.28, 1.41, and 2.81 µg F/ml, respectively.
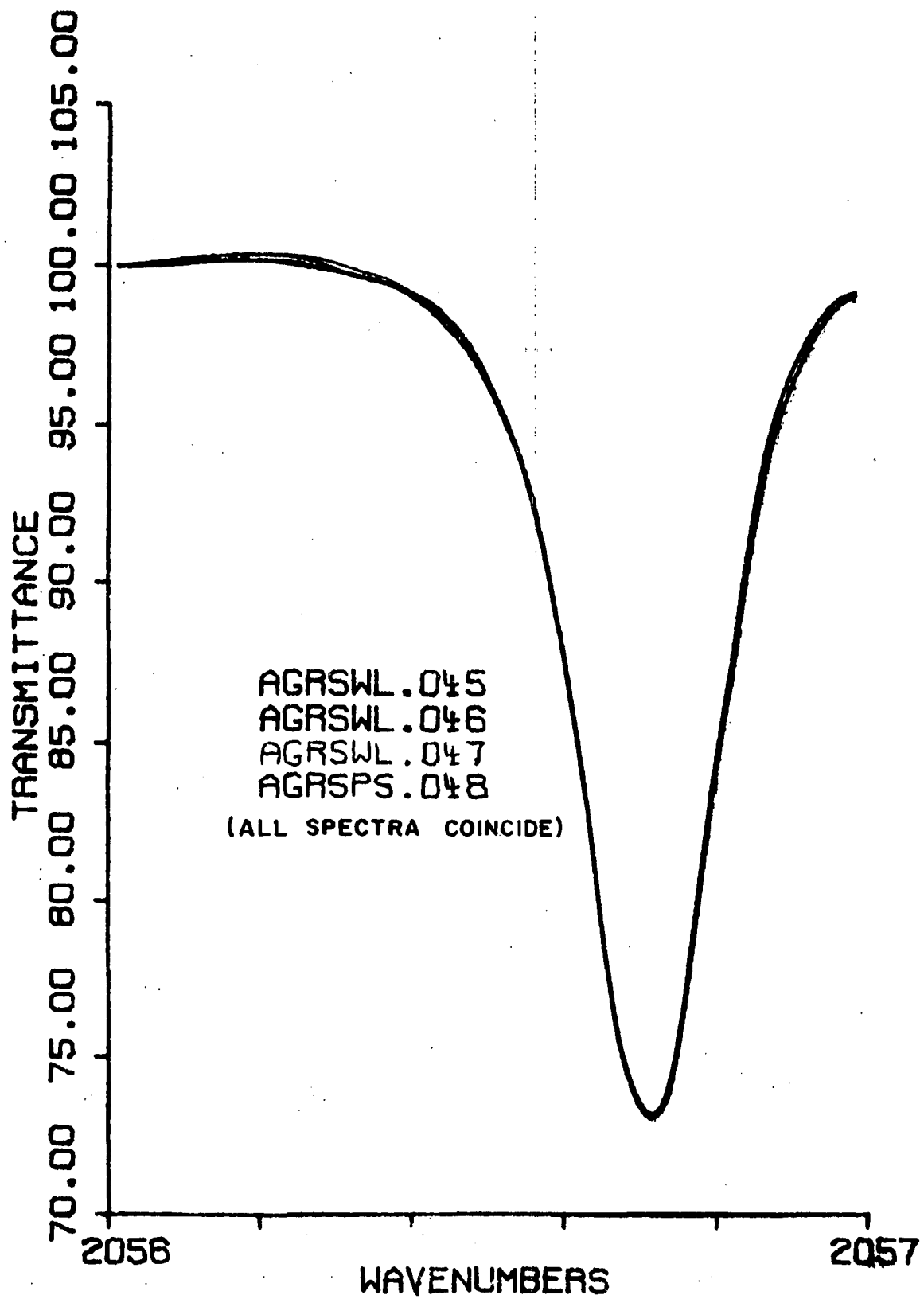
Figure 31. Spectra of CO_2 at Agrico (absorption at 2056.7 cm^{-1})
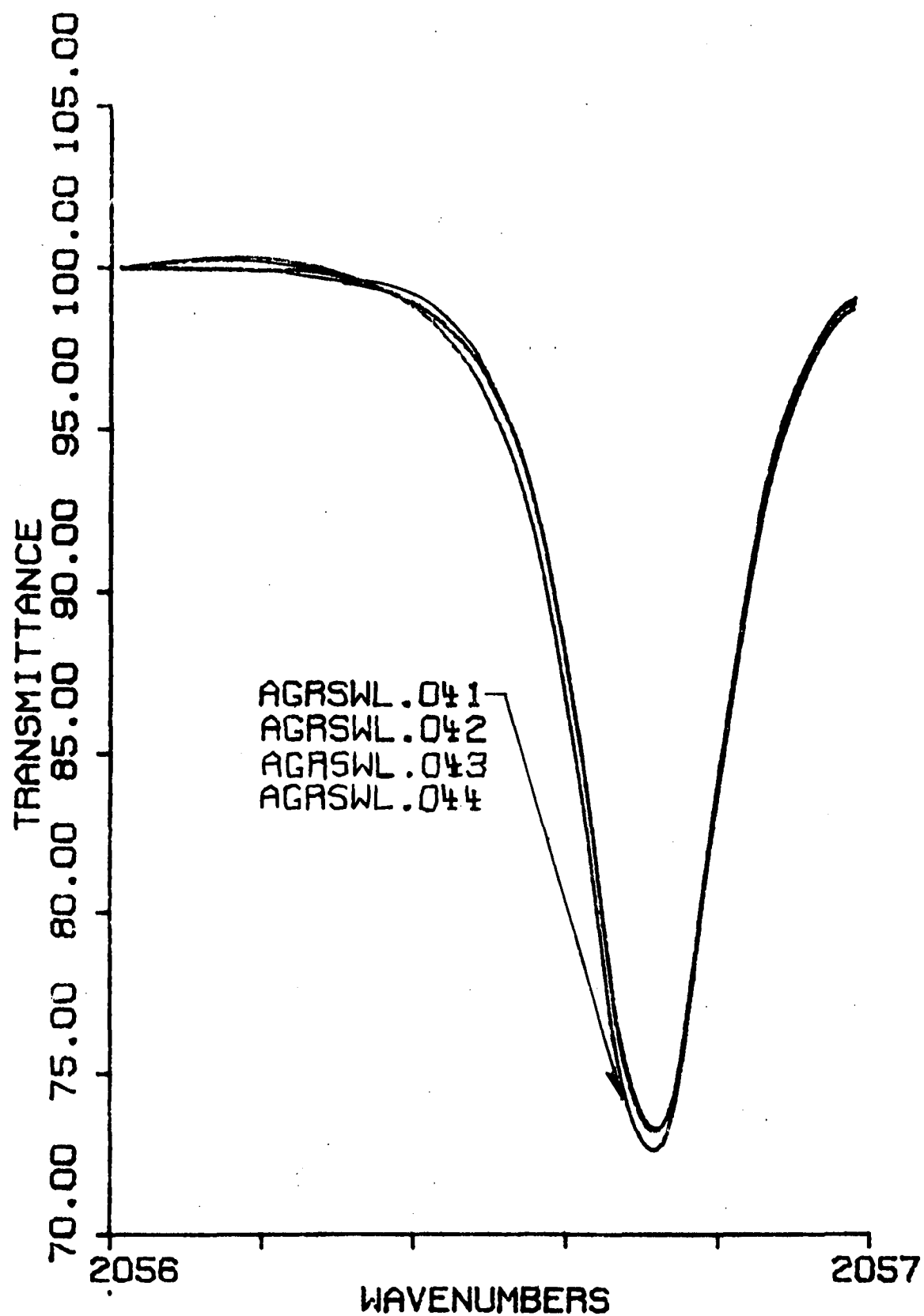
Figure 32. Spectra of CO_2 at Agrico (absorption at 2056.7 cm^{-1}).
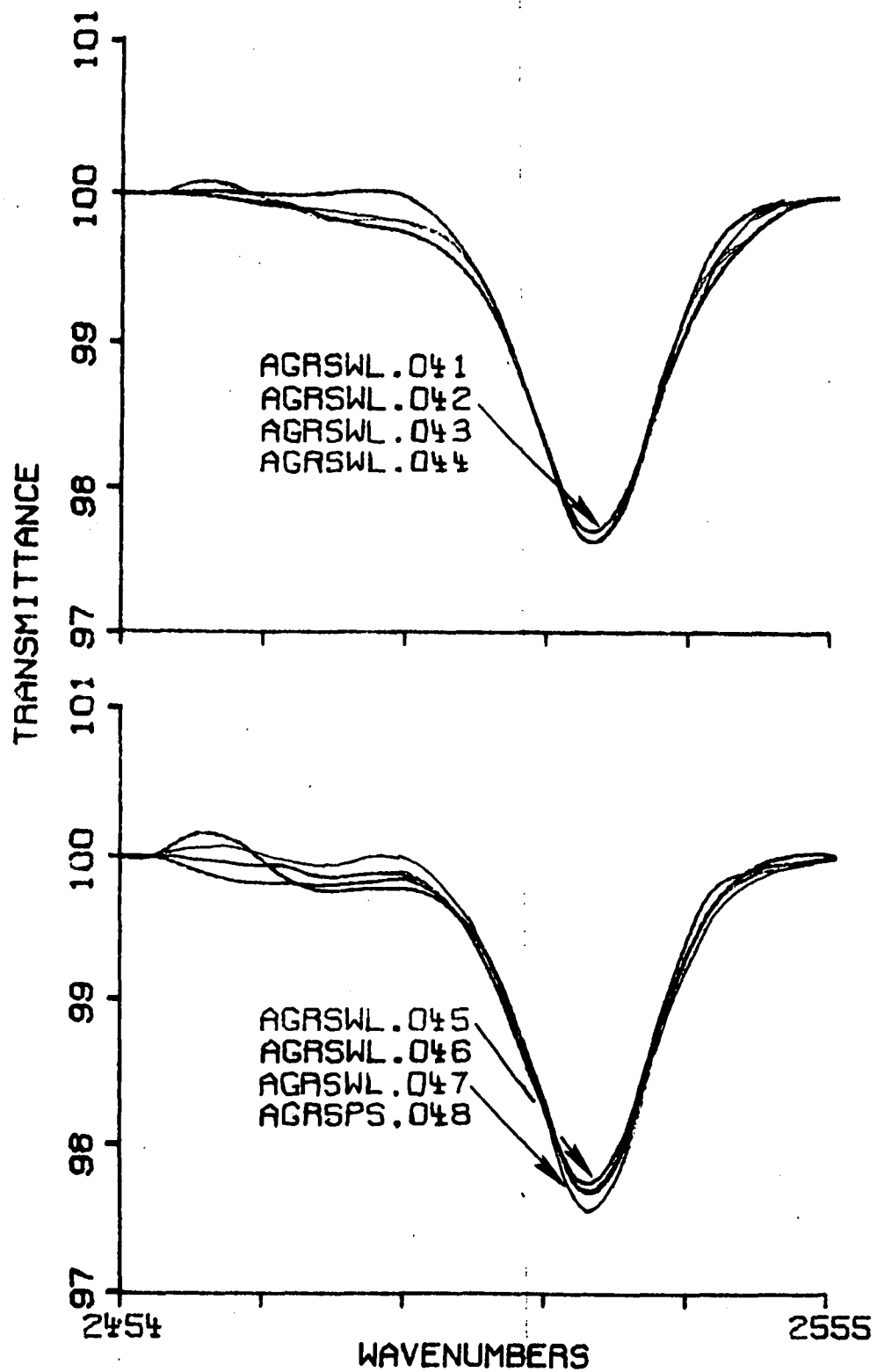
Figure 33. Spectra of N_2O at Agrico.
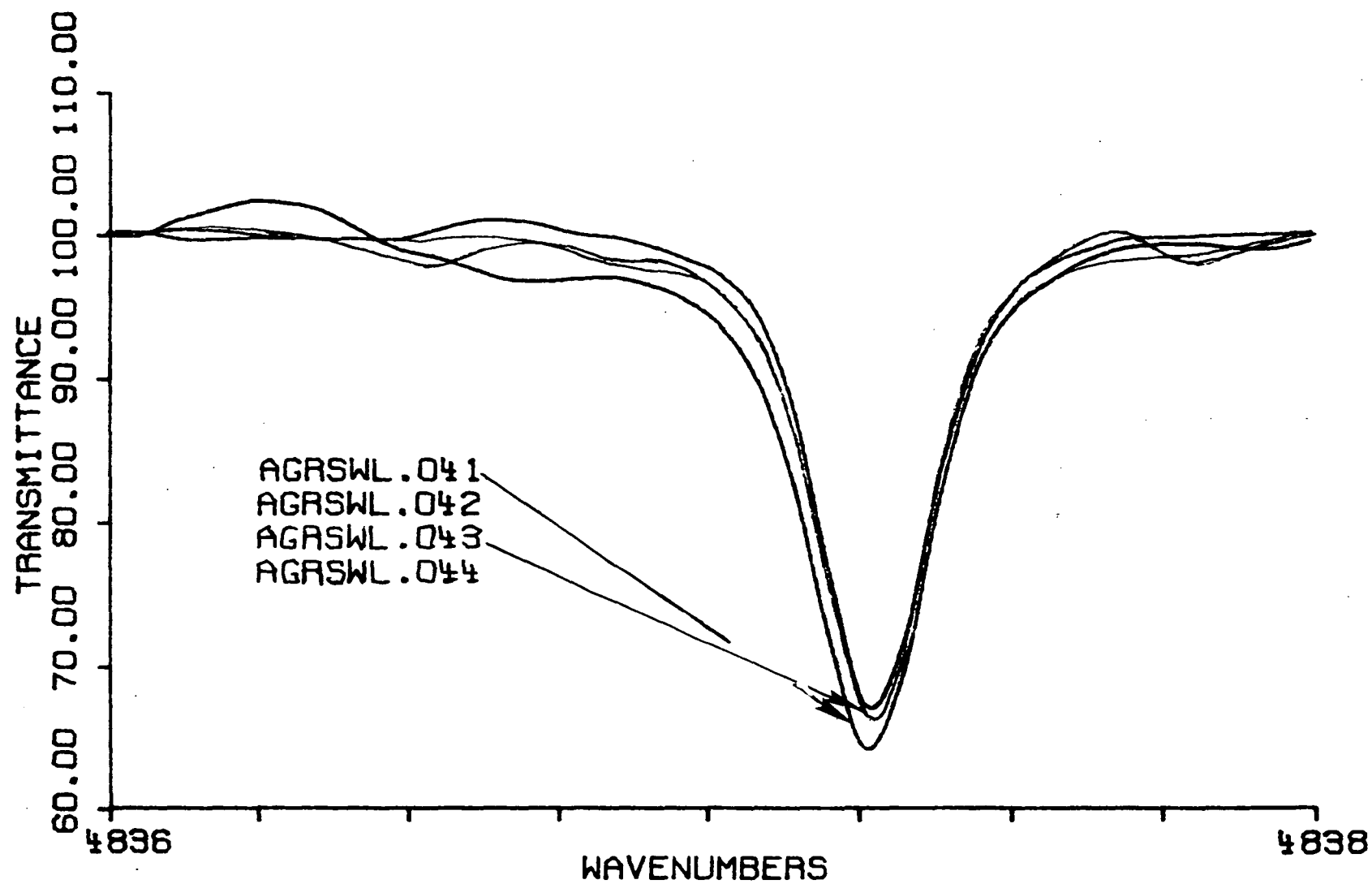
Figure 34. Spectra of CO_2 – absorption at 4837.25 cm^{-1} (Agrico runs 41-44).
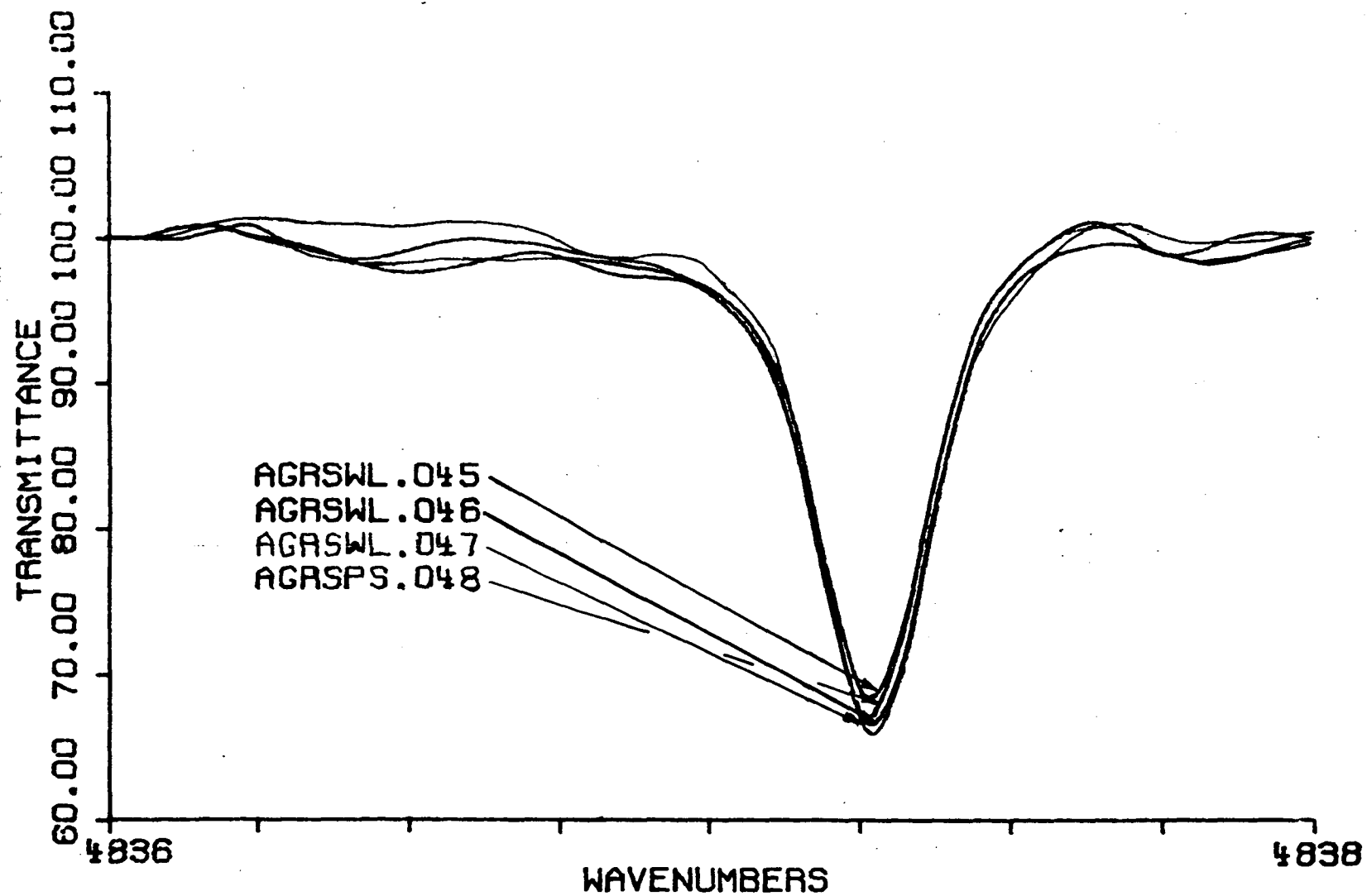
Figure 35. Spectra of CO_2 – absorption at 4837.25 cm^{-1} (Agrico runs 45-48).

RESULTS

Manual Methods

The results of the sampling program are presented in Table 9, for the autoanalyzer analyses; and in Table 10 for the IC analyses. The calculations corresponding to these tables are presented in Appendix B. The samples were stored for several weeks prior to the IC analysis because there were some instrumental problems with the ion chromatograph. Since the holding time for fluoride in solution is about 7 days, the IC data were not compared with the data from the ROSE method. Instead, the data from the autoanalyzer analyses were used in the statistical analysis.

ROSE Method

The results of the data reduction of the ROSE spectra are given in Tables 11 and 12 for CFI and Agrico, respectively. These tables include the data based on both the peak area and peak height methods.

Weather Conditions

A summary of the wind speed, wind direction, and ambient temperature is given in Table 13. The relative humidity for the 3 days was 95 percent.

Statistical Analysis and Discussion of the Data

The final data set, tabulated in the sequence in which the samples were collected, is presented in Table 14. Five data points have been deleted from the manual sampling data. These data correspond with the ROSE data which were omitted because the spectra were either obtained at lower resolution or the baseline was too noisy.

Graphical representations of the data are presented in the following Figures:

- Figures 36 to 39 depict the change in the HF concentration with time at CFI, as measured by the ROSE and manual methods. For the ROSE method, the data based on peak area (Figures 36 and 38) and peak height (Figures 37 and 39) are presented. Figures 36 and 37 indicate the concentrations for each sampling site, while Figures 38 and 39 present the average concentrations of the sampling sites.

- Figures 40 to 43 illustrate the change in the HF concentration with time at Agrico, as measured by the ROSE and the manual methods. Figures 40 and 42 are based upon the calculation of the ROSE data by the peak area method, while Figures 41 and 43 represent the peak height method for computing the ROSE data. Figures 40 and 41 indicate the concentration for each sampling site while Figures 42 and 43 present the average concentrations of the sampling points.

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TABLE 9. HF CONCENTRATION DATA FOR MANUAL SAMPLING AND ANALYSIS BY SPECTROPHOTOMETRIC METHOD

Date	GCA run no.	Sampling start time	Concentration (ppb)				Arithmetic mean	Geometric mean	Collection device [a]
			Site						
			A	B	C	D			
7/24/79	1	0905	26	36	37	40	35	34	F
(CFI)	2	0936	26	27	27	52	33	32	T
	3	1008	16	46	52	53	42	38	F
	4	1043	27	44	52	27	38	36	T
	5	1124	32	32	35	32	33	33	F
	6	1200	44	36	–	36	39	39	T
	7	1224	35	57	50	50	48	47	F
	8	1246	46	24	40	30	35	34	T
	9	1307	44	48	43	45	45	45	F
	10	1330	42	40	30	40	38	38	T
Mean			33.8	39.0	40.7	40.5	38.6	37.2	
7/25/79	11	0805	30	27	36	44	34	34	F
(CFI)	12	0830	19	15	22	51	27	24	T
	13	0940	34	58	43	48	46	45	F
	14	1005	14	98	25	29	42	32	T
	15	1027	32	34	51	75	48	45	F
	16	1050	22	106	–	24	51	38	T
	17	1115	52	37	47	42	45	44	F
	18	1145	17	7	44	24	23	19	T
	19	1205	43	54	60	53	53	52	F
	20	1225	27	31	17	24	25	24	T
Mean			29.0	46.7	38.3	41.4	39.4	34.1	
7/26/79	21	1040	20	19	–	31	23	23	F
(Agrico)	22	1106	21	29	29	40	30	29	T
	23	1131	22	27	27	42	29	29	F
	24	1150	34	29	32	43	35	34	F
	25	1210	34	26	36	45	35	35	T
	26	1230	31	29	34	42	34	34	F
	27	1252	35	34	35	46	37	37	F
	28	1311	37	–	–	45	41	41	T
	29	1528	26	33	37	59	39	37	F
	30	1550	30	36	32	50	37	36	F
	31	1608	31	27	46	43	37	36	T
	32	1630	23	–	27	38	29	29	F
	33	1655	32	33	32	52	37	36	F
	34	1721	34	30	33	47	36	36	T
	35	1742	26	30	30	39	31	31	F
	36	1807	25	22	29	34	28	27	F
	37	1827	26	26	30	35	29	29	T
Mean			28.6	28.6	32.6	43.0	33.3	32.6	

[a] F = filter cassette
T = bicarbonate-treated tube

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TABLE 10. HF CONCENTRATION DATA FOR MANUAL SAMPLING AND
ANALYSIS BY IC

Date	GCA run No.	Site A	B	C	D	Arithmetic average	Geometric average	Collection device[a]
7/24/79	1	17	37	25	50	32	30	F
	2	31	30	24	47	39	32	T
	3	-	3	11	-	7	6	F
	4	17	52	46	43	40	36	T
	5	9	5	-	-	7	7	F
	6	43	26	-	25	31	30	T
	7	15	28	9	29	20	18	F
	8	35	11	25	24	24	22	T
	9	22	-	22	10	18	17	F
	10	36	36	23	37	33	32	T
Mean		25	25.3	21	33.1	25	23	
7/25/79	11	31	44	74	27	44	41	F
	12	13	10	19	75	29	21	T
	13	26	45	57	31	40	38	F
	14	25	92	21	36	43	36	T
	15	26	26	6	66	31	23	F
	16	17	96	-	30	48	37	T
	17	48	37	35	39	40	40	F
	18	60	2	46	30	34	20	T
	19	19	23	30	43	35	27	F
	20	28	24	16	24	24	23	T
Mean		29.3	39.9	33.8	40.1	37	31	

[a]F = filter cassette
T = bicarbonate-treated tube

TABLE 11. RESULTS OF ROSE MEASUREMENTS—CFI

GCA run No.	ROSE run No.	HF concentration (ppb)	
		Peak area	Peak height
1	4	$-^a$	$-^a$
2	6	$-^a$	$-^a$
3	7	$-^a$	$-^a$
4	9	43	42
5	10	40	39
6	11	41	40
7	13	39	43
8	14	30	30
9	15	43	43
10	16	34	32
11	17	$-^b$	$-^b$
12	18	30	27
13	19	28	28
14	20	27	32
15	21	39	39
16	22	27	28
17	23	30	29
18	24	39	38
19	25	36	38
20	26	41	43

[a] Omitted; spectrum obtained at lower resolution than rest of data.

[b] Spectrum too noisy; cannot define baseline.

TABLE 12. RESULTS OF ROSE MEASUREMENTS--AGRICO

| GCA run No. | ROSE run No. | HF concentration (ppb) | |
		Peak area	Peak height
21	30	21	21
22	31	25	23
23	32	37	32
24	33	33	35
25	34	35	36
26	35	40	41
27	36 & 37	35	34
28	38	41	38
29	40	$-^a$	$-^a$
30	41	40	39
31	42	43	41
32	43	38	37
33	44	62	46
34	45	59	46
35	46	37	37
36	47	46	41
37	48	46	38

[a]Noisy spectrum; cannot define baseline.

TABLE 13. WINDSPEED AND WIND DIRECTION DATA AND
AMBIENT TEMPERATURE

Date	GCA run No.	Sampling period (EDT)	Wind direction (DEG)	Wind speed (MPH)	Ambient Temp. (°F)
7/24/79	1	0905-0921	125	11	79
(CFI)	2	0936-0956	120	11	82
	3	1008-1024	135	10	83
	4	1043-1056	150	11	83
	5	1124-1140	145	16	83
	6	1200-1216	150	13	85
	7	1224-1240	150	12	89
	8	1246-1302	135	12	89
	9	1307-1323	125	12	91
	10	1330-1346	135	14	89
Mean			137	12.2	85
7/25/79	11	0805-0821	295	12	81
(CFI)	12	0830-0846	125	12	81
	13	0940-0956	140	13	82
	14	1005-1021	155	14	82
	15	1027-1042	140	13	83
	16	1050-1106	145	12	84
	17	1115-1131	145	12	84
	18	1145-1201	140	12	84
	19	1205-1221	140	12	85
	20	1225-1241	130	12	86
Mean			140	12.4	83
7/26/79	21	1040-1056	140	9	85
(Agrico)	22	1106-1122	135	11	88
	23	1131-1147	120	11	89
	24	1150-1206	125	10	89
	25	1210-1226	130	10	90
	26	1231-1247	125	11	91
	27	1252-1380	125	10	92
	28	1311-1327	120	9	93
	30	1550-1606	105	7	95
	31	1608-1624	125	7	95
	32	1630-1646	105	8	95
	33	1655-1711	110	7	95
	34	1721-1737	110	8	95
	35	1742-1758	130	5	95
	36	1807-1823	140	5	93
	37	1827-1843	145	7	93
Mean			124.3	8.4	92

TABLE 14. HF CONCENTRATION DATA GROUPED IN SEQUENCE OBTAINED

Date	GCA run No.	Sampling start time	A	B	C	D	Arithmetic mean	Geometric mean	Collection device[a]	Peak area	Peak height
			Concentration (ppb)								
			Manual sampling							ROSE method	
			Site								
7/24/79	4	1043	27	44	52	27	38	36	T	43	42
(CFI)	5	1124	32	32	35	32	33	33	F	40	39
	6	1200	44	36	-	36	39	39	T	41	40
	7	1224	35	57	50	50	48	47	F	39	43
	8	1246	46	24	40	30	35	34	T	30	30
	9	1307	44	48	43	45	45	45	F	43	43
	10	1330	42	40	30	40	38	38	T	34	32
Mean			38.6	40.1	41.7	37.1	39.4	38.0		38.6	38.4
7/25/79	12	0830	19	15	22	51	27	24	T	30	27
(CFI)	13	0940	34	58	43	48	46	45	F	28	28
	14	1005	14	98	25	29	42	32	T	27	32
	15	1027	32	34	51	75	48	45	F	39	39
	16	1050	22	106	-	24	51	38	T	27	28
	17	1115	52	37	47	42	45	44	F	30	29
	18	1145	17	7	44	24	23	19	T	39	38
	19	1205	43	54	60	53	53	52	F	36	38
	20	1225	27	31	17	24	25	24	T	41	43
Mean			28.9	48.8	38.6	41.1	40.0	34.1		33.0	33.6
7/26	21	1040	20	19	-	31	23	23	F	21	21
(Agrico)	22	1106	21	29	29	40	30	29	T	25	23
	23	1131	22	27	27	42	29	29	F	37	32
	24	1150	34	29	32	43	35	34	F	33	35
	25	1210	34	26	36	45	35	35	T	35	36
	26	1231	31	29	34	42	34	34	F	40	41
	27	1252	35	34	35	46	37	37	F	35	34
	28	1311	37	-	-	45	41	41	T	41	38
	30	1550	30	36	32	50	37	36	F	40	39
	31	1608	31	27	46	43	37	36	T	43	41
	32	1630	23	-	27	38	29	29	F	38	37
	33	1635	32	33	32	52	37	36	F	62	46
	34	1722	34	30	33	47	36	36	T	59	46
	35	1742	26	30	30	39	31	31	F	37	37
	36	1809	25	22	29	34	28	27	F	46	41
	37	1827	26	26	30	35	29	29	T	46	38
Mean			28.8	28.4	32.3	42.0	33.0	32.3		39.9	36.6
Grand mean			31.0	39.1	36.1	40.7	36.4	34.0		37.6	36.1

[a] F = Filter cassette.

T = Bicarbonate - treated tube.
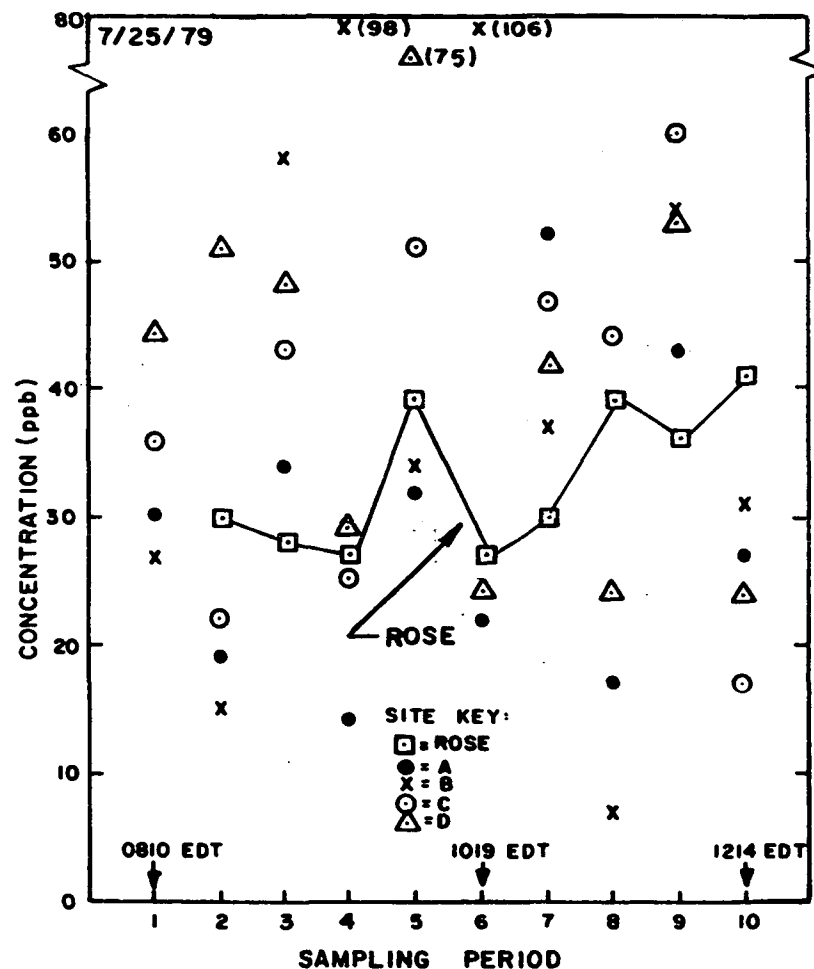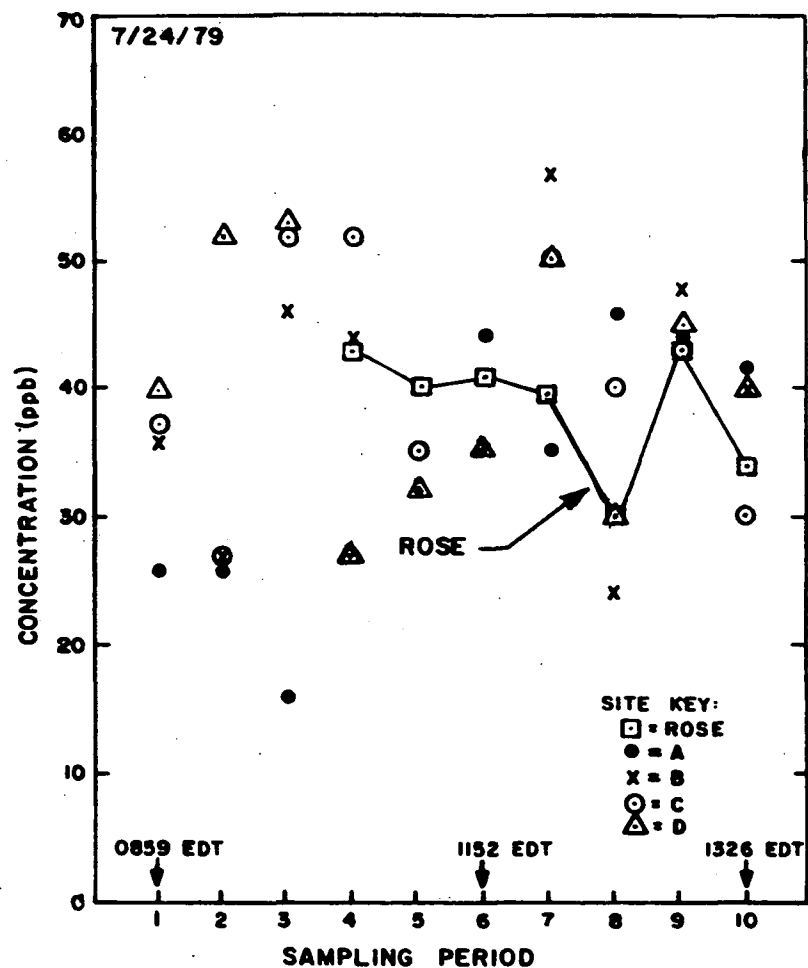
Figure 36. Changes in concentration with time at CFI for each manual sampling site and for the ROSE data based on peak area.
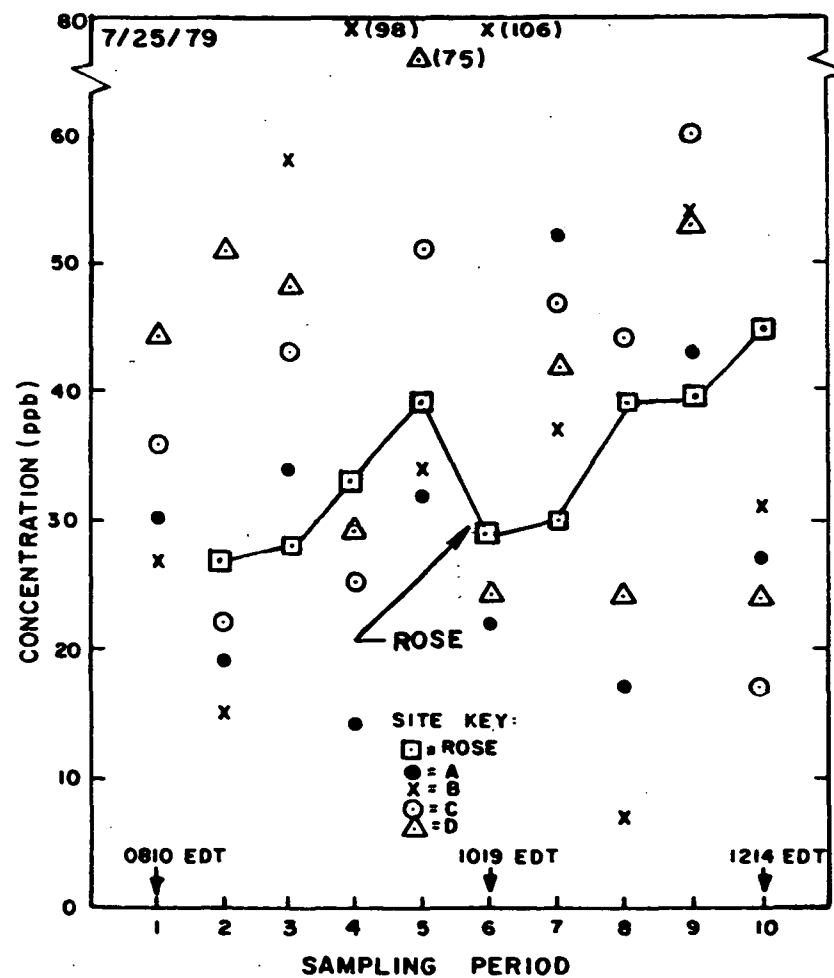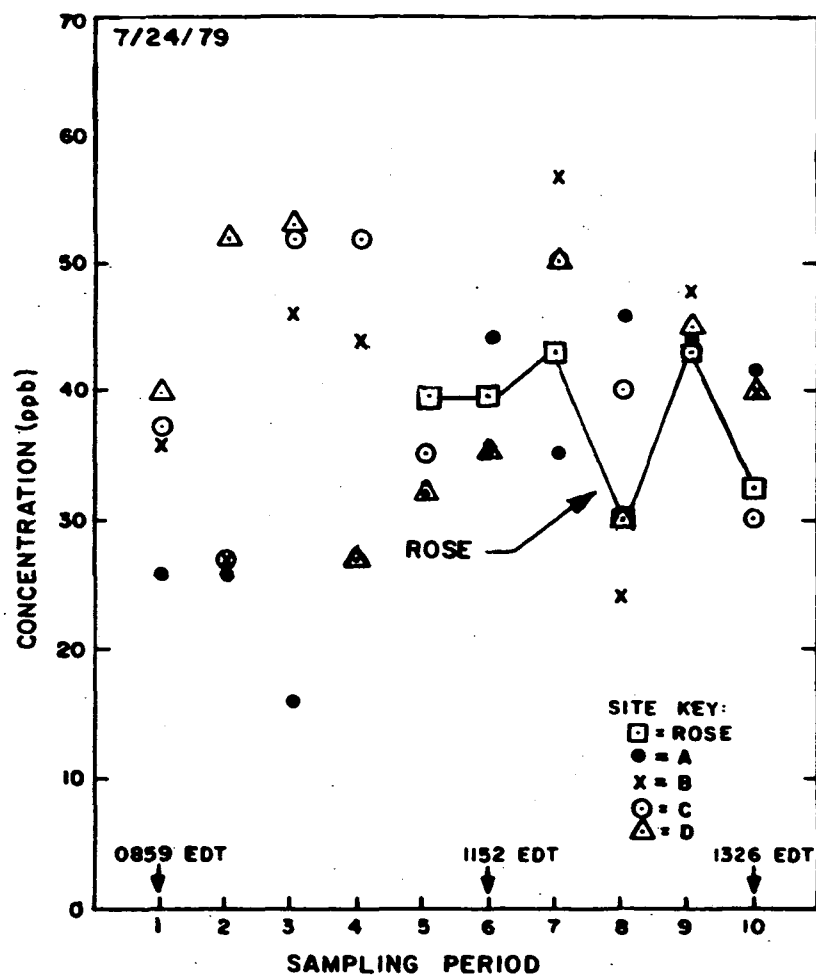
Figure 37. Changes in concentration with time at CFI for each manual sampling site and for the ROSE data, based on peak height.
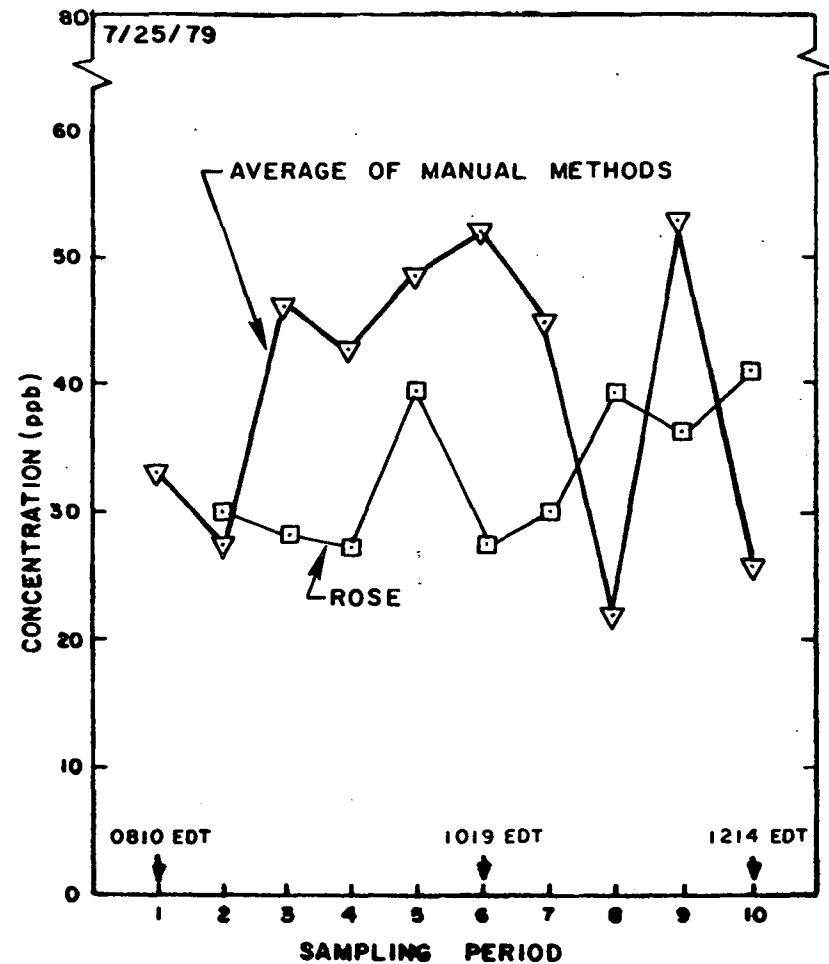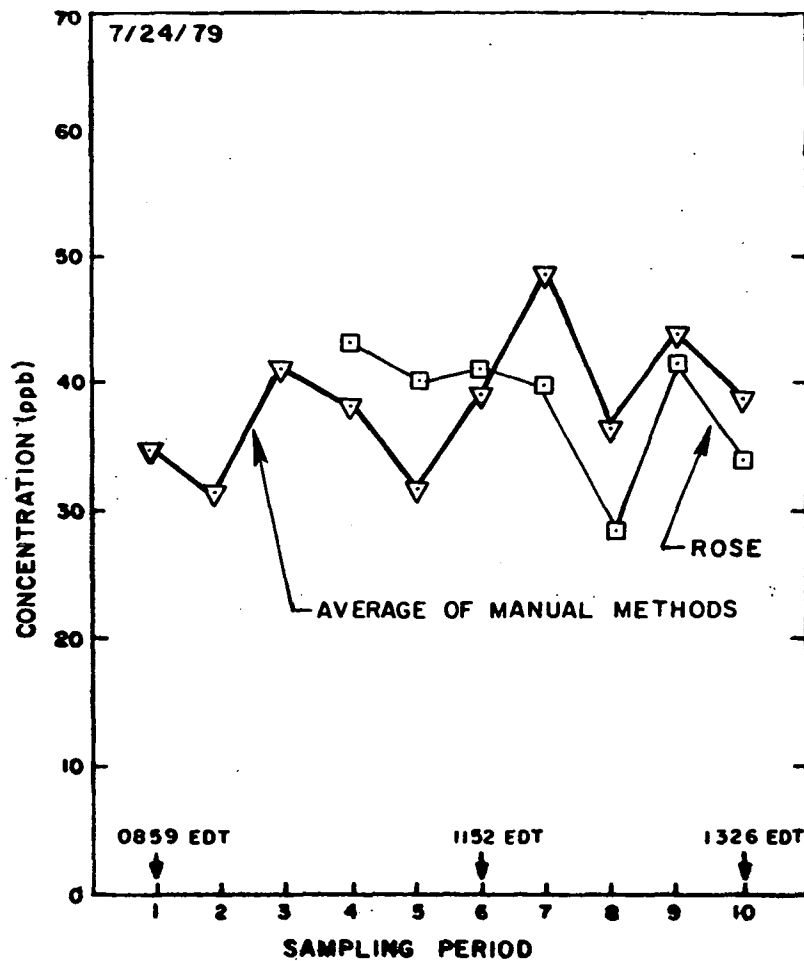
Figure 38. Changes in concentration with time at CFI for the average of the manual sampling sites and for the ROSE data (peak area method).
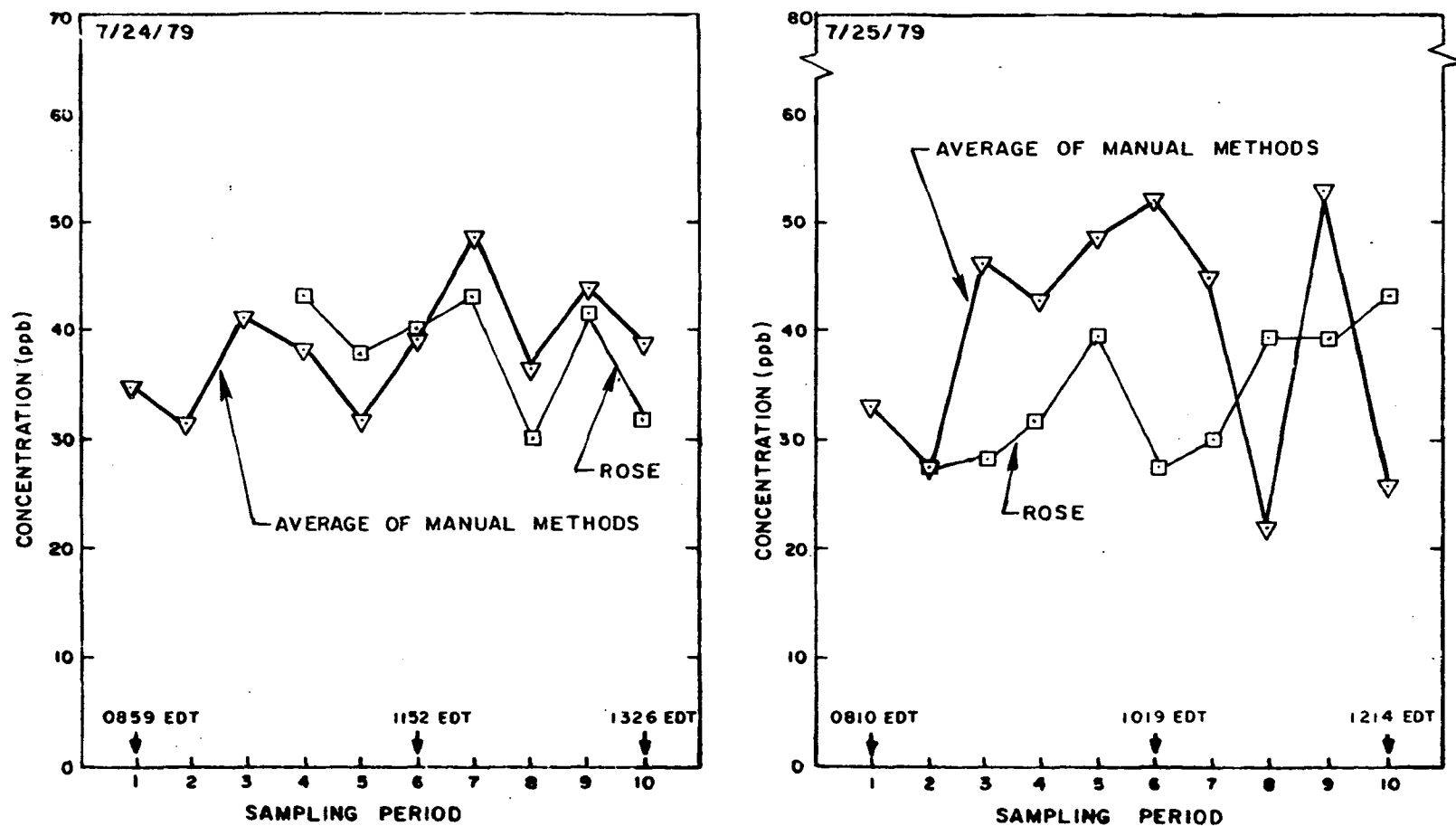
CHANGES IN CONCENTRATION WITH TIME AT CFI

Figure 39. Changes in concentration with time at CFI for the averages of the manual sampling sites and for the ROSE data (peak height method).
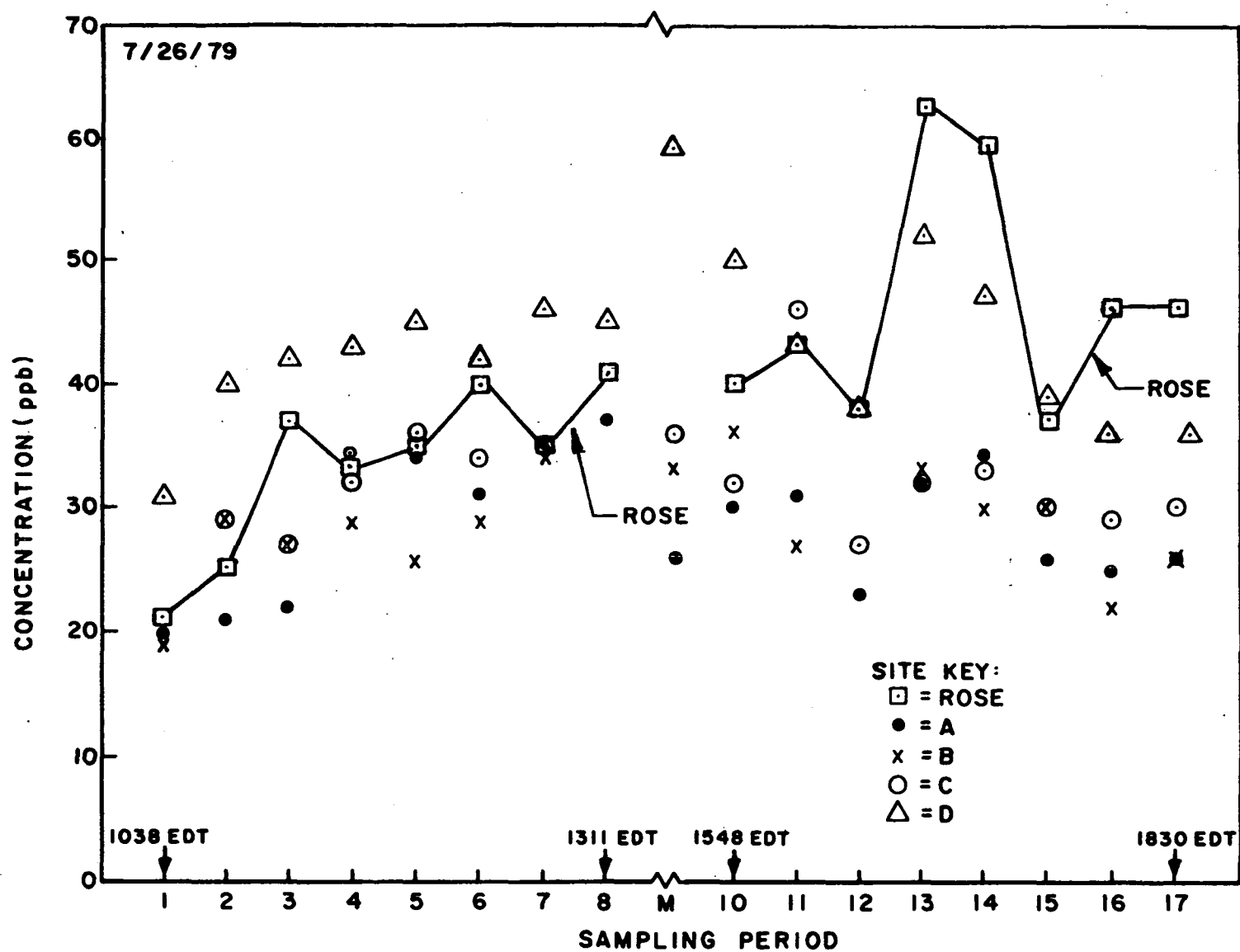
Figure 40. Changes in concentration with time at Agrico for each manual sampling site and for the ROSE data (peak area method).
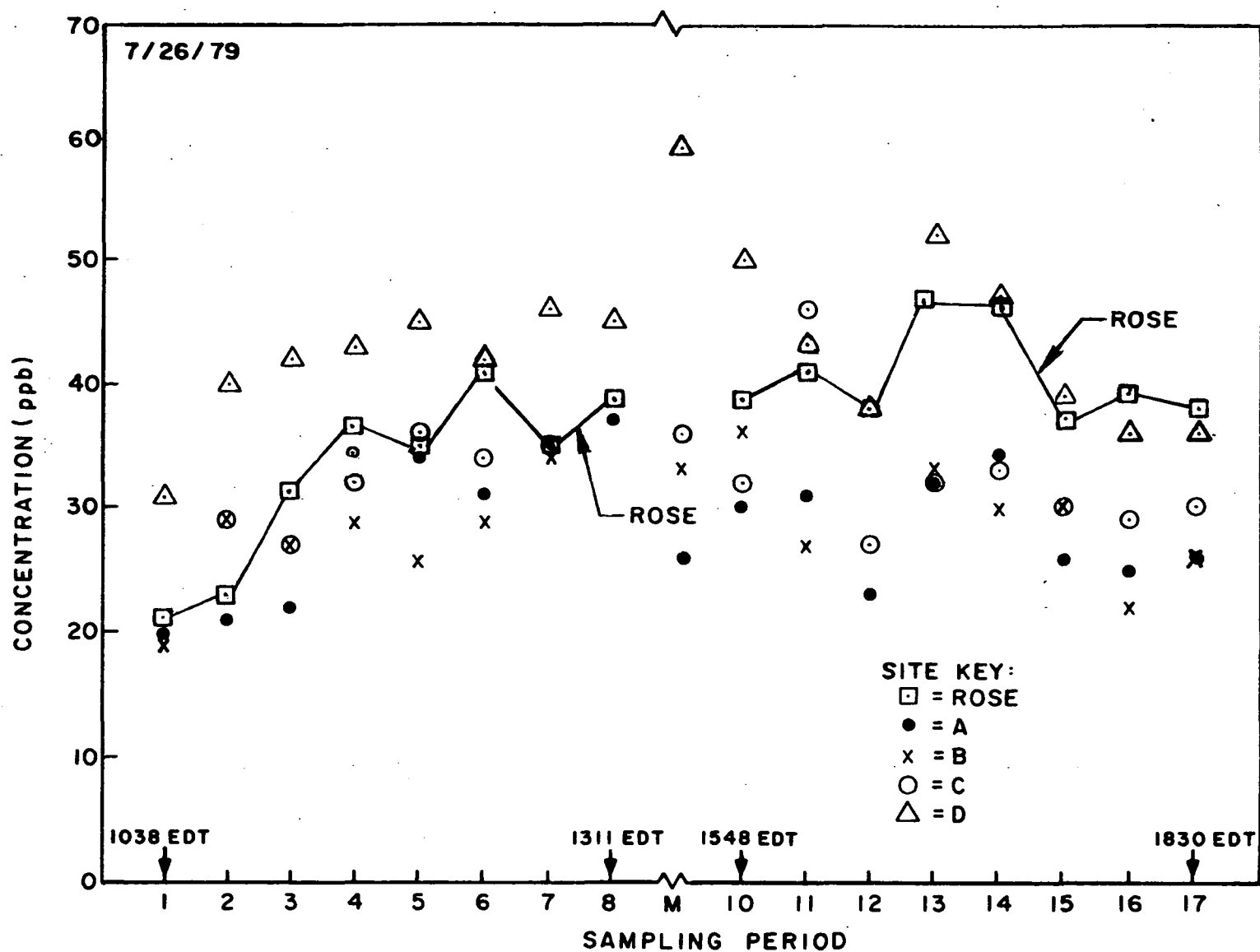
Figure 41. Changes in concentration with time at Agrico for each manual sampling site and for the ROSE data (peak height method).
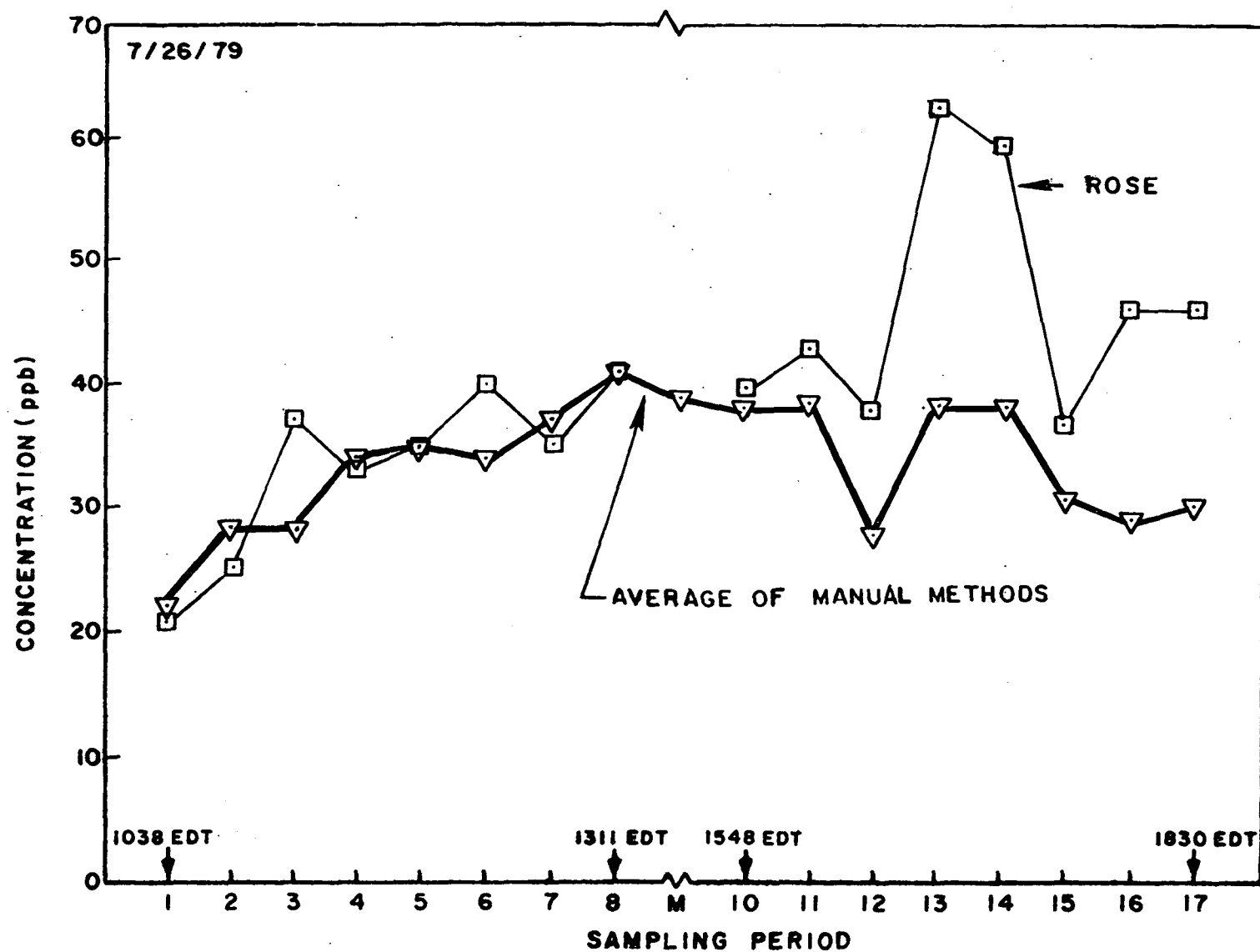
Figure 42. Changes in concentration with time at Agrico for the averages of the manual sampling sites and for the ROSE data (peak area method).
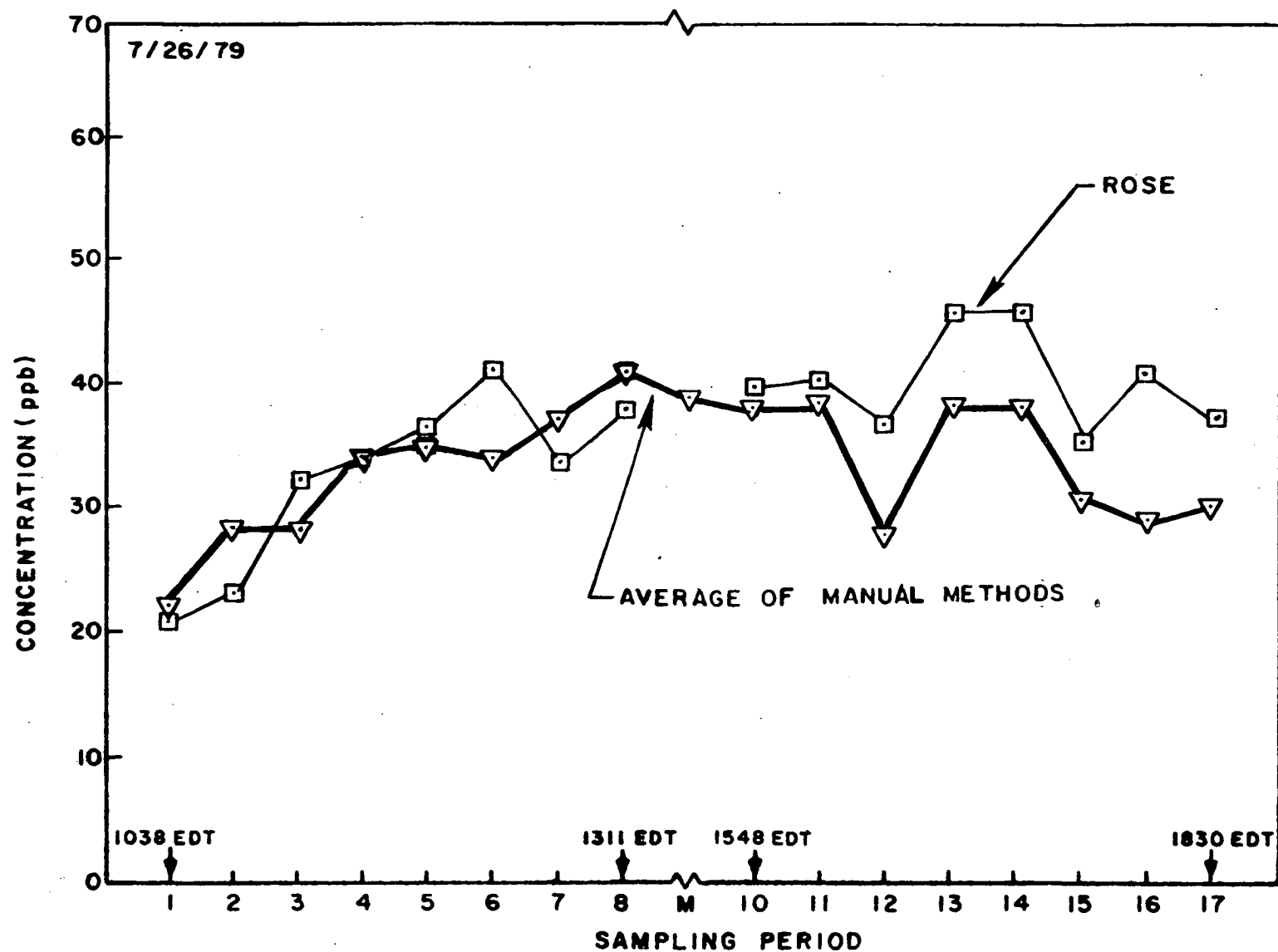
Figure 43. Changes in concentration with time at Agrico for the averages of the manual sampling sites and for the ROSE data (peak height method).

- Figure 44 plots the HF concentration measured by the ROSE method (based on peak area) against the HF concentration obtained by the manual sampling method at CFI (7/24/79). Figure 45 makes a similar comparison, however, the ROSE data is based on the peak height method for calculating the HF concentrations.

- Figures 46 and 47 compare the ROSE data for the peak area and peak height methods, respectively, with the manual sampling results at CFI (7/25/79).

- Figures 48 and 49 plots the ROSE data for the peak area and peak height methods, respectively, against the HF concentrations obtained by the manual sampling efforts at Agrico.

- Figures 50 and 51 compares the overall data sets for both sampling methods at the two gypsum ponds. The ROSE data is based upon the peak area method and peak height method in Figures 50 and 51, respectively.

The ROSE system measures the average concentration of HF molecules in the 30 cm diameter cylinder extending through the atmosphere from the source to the receiver telescope. The point sampling systems measure the point concentrations of HF. Both the optical and point method measurements were averaged over 16-minute time intervals for each sampling period. If the HF concentration were relatively uniform along the sampling path, fairly small differences would be expected between values obtained at the four sampling sites during a given sampling period, and reasonable agreement between an average of the sampling site values and a ROSE measurement would be expected. If, on the other hand, there were appreciable concentration gradients along the path, then the two methods could give widely differeing results without either being "incorrect." The situations that best illustrate this are: (1) a spatially small but high concentration HF pocket could slowly traverse the area of a single point monitor (the result would be a high reading at one site, but no appreciable affect on the ROSE data); and (2) an extended pocket of high HF concentration that slowly passed through the optical path but missed the point monitors (obvious results).

Inspection of data shown in Figures 36 and 37, with the above in mind, show the following:

(1) During the sampling at CFI on 7/24 the HF concentration spread between sampling sites is at maximum about ±35 percent of the average value for a sampling period. The agreement between the ROSE and average point values are all within the estimated ROSE error, and furthermore, each method follows the same up and down trends.

(2) During the sampling at CFI on 7/25 the fluctuations between point measurement sites during a given sampling period were much greater than on 7/24, and the highs and lows vary between sites for different

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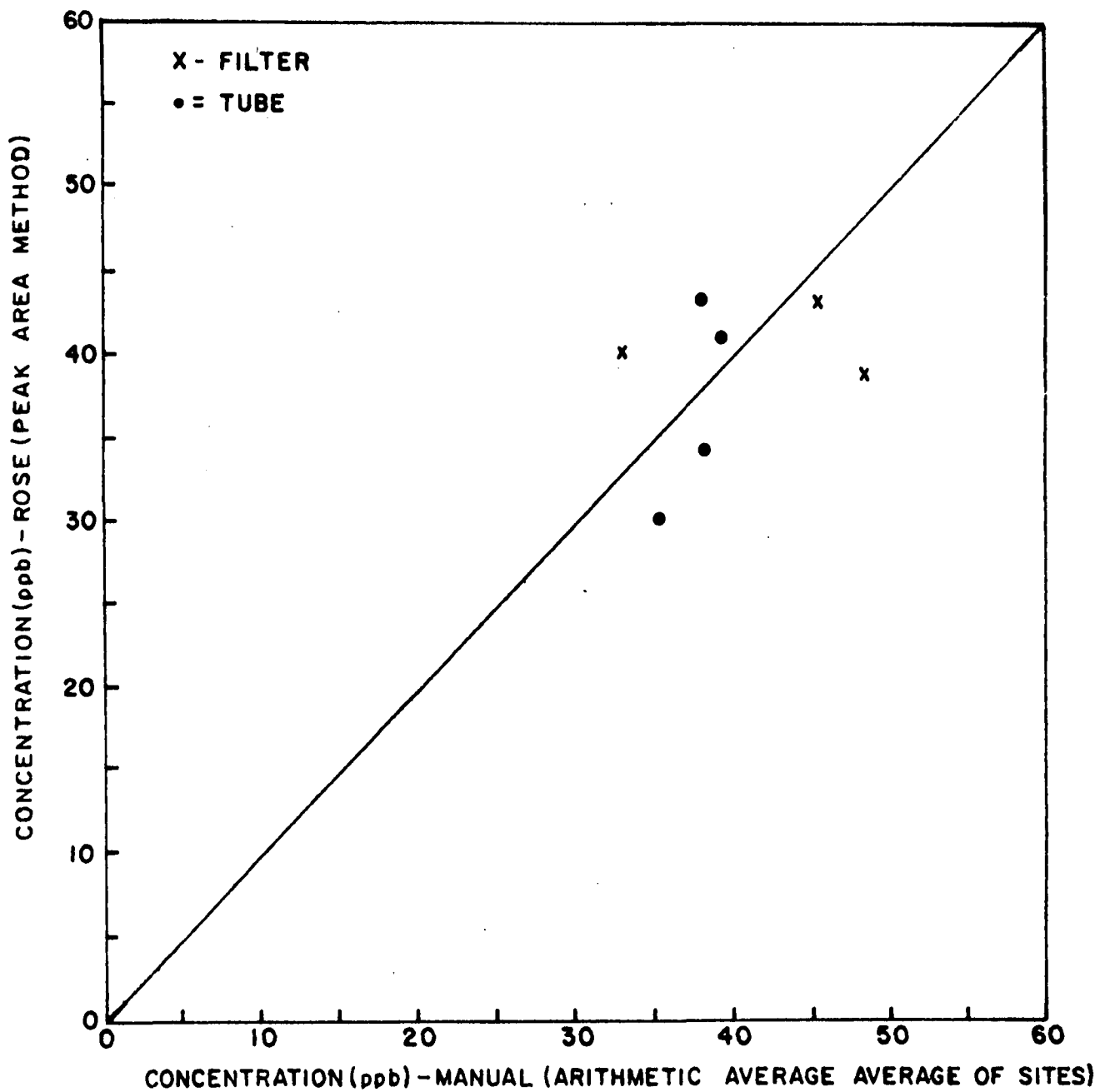
Figure 44. Comparison of HF concentrations measured by two techniques at CFI 7/24/79). (Peak area method for ROSE data).
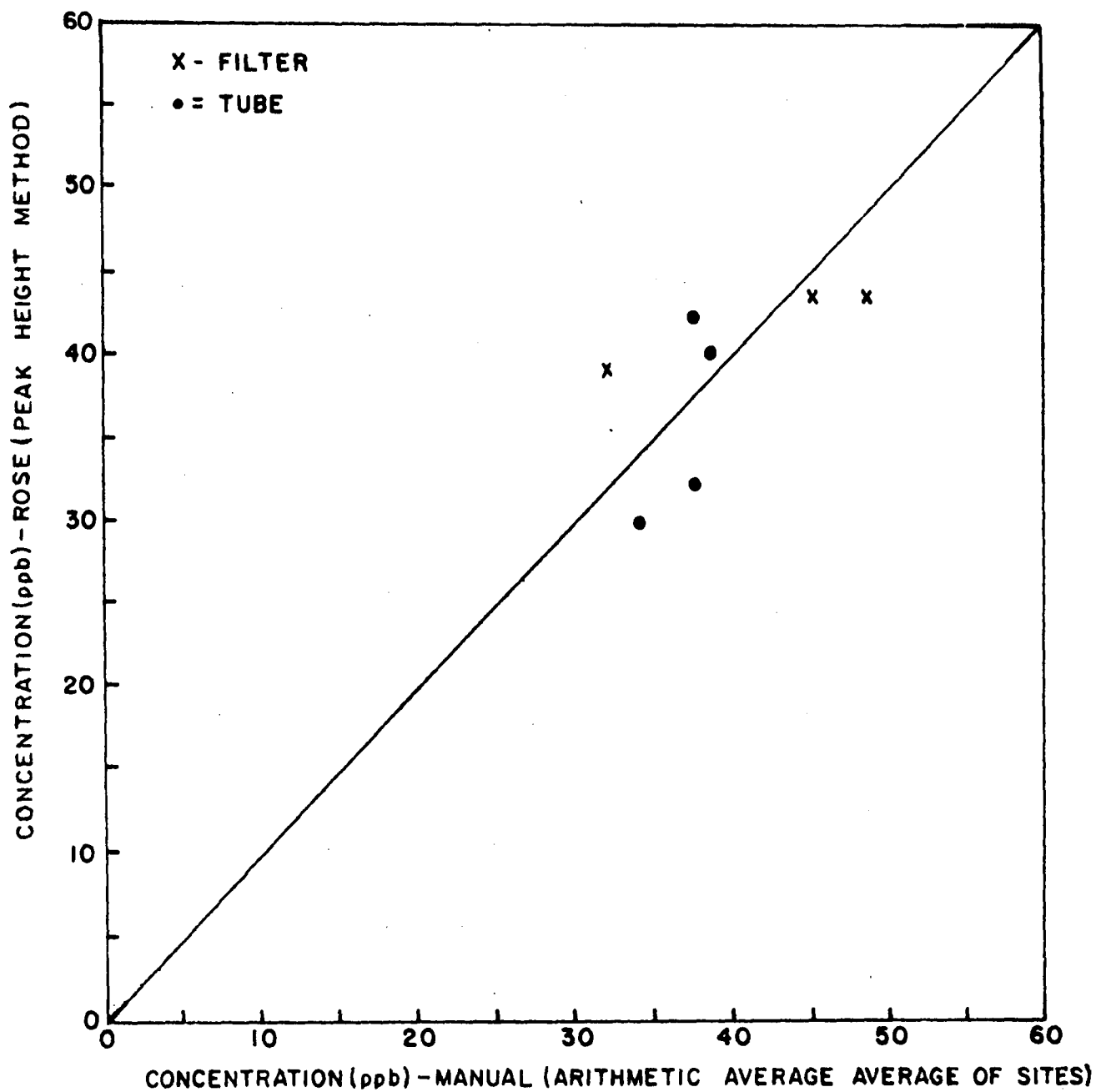
Figure 45. Comparison of HF concentrations measured by two techniques at CFI (7/24/79). (Peak height method for ROSE data).

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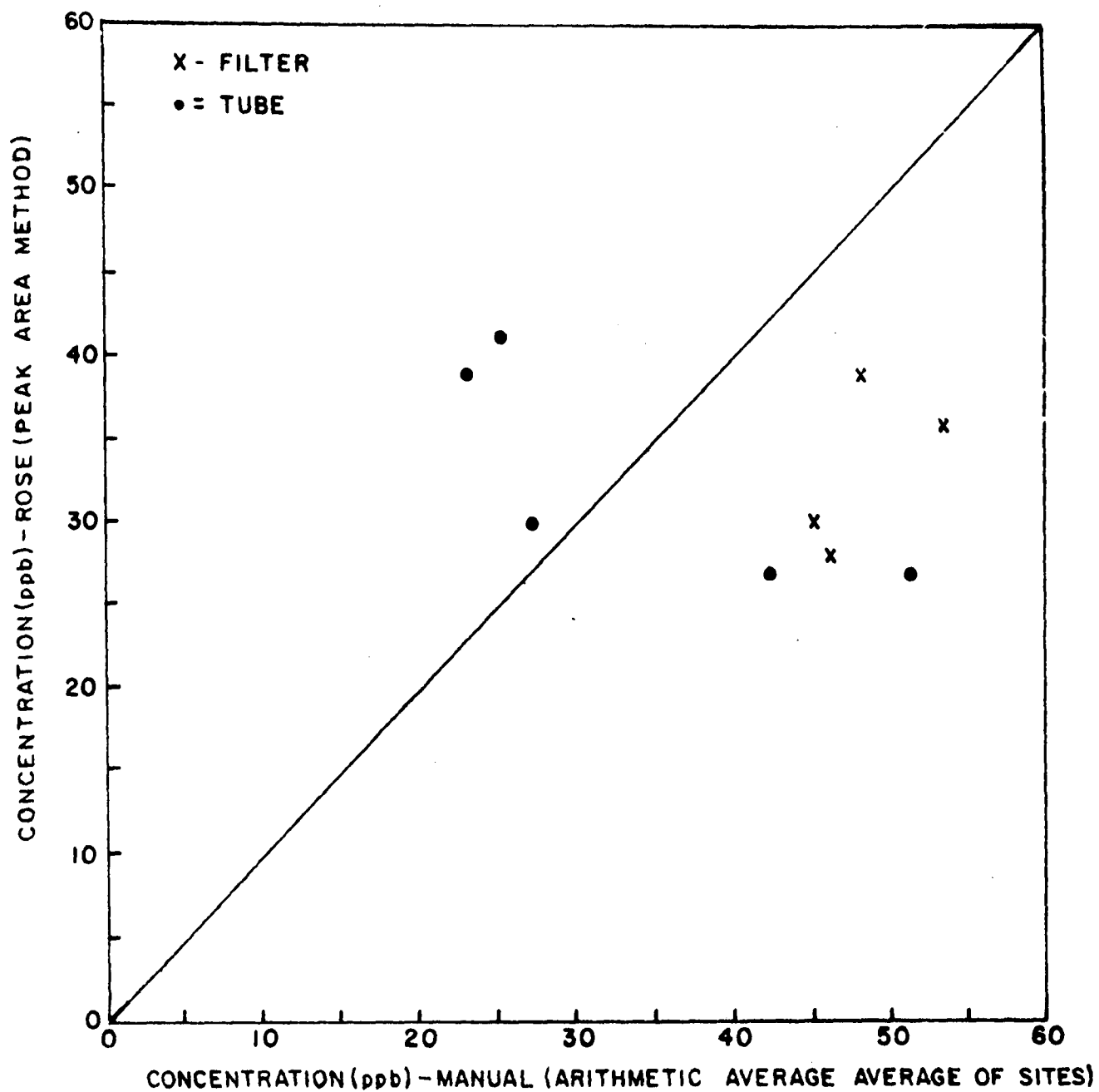
Figure 46. Comparison of HF concentrations measured by two techniques at CFI site (7/25/79). (Peak area method for ROSE data).

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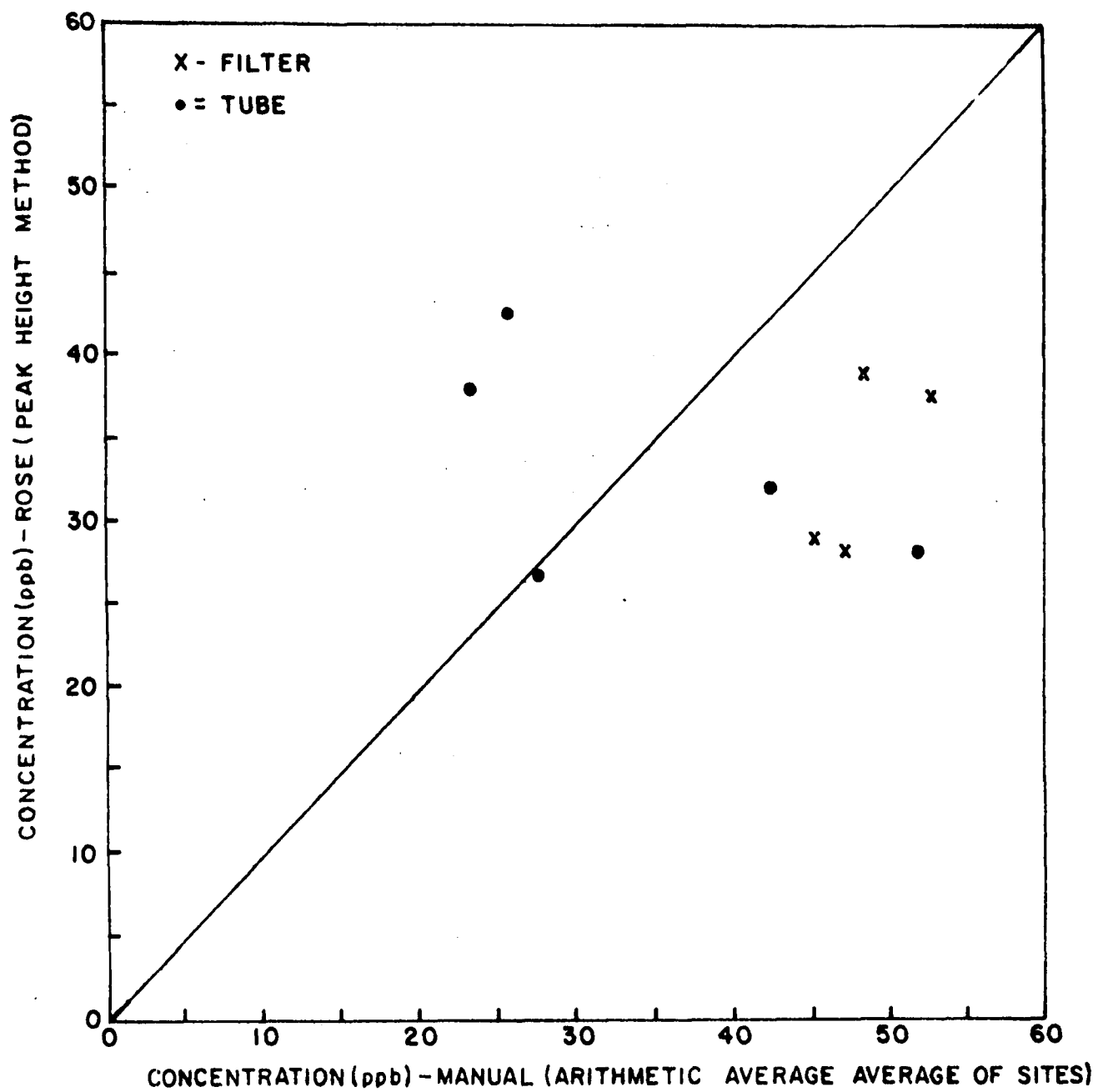
Figure 47. Comparison of HF concentrations measured by two techniques at CFI site (7/25/79). (Peak height method for ROSE data).
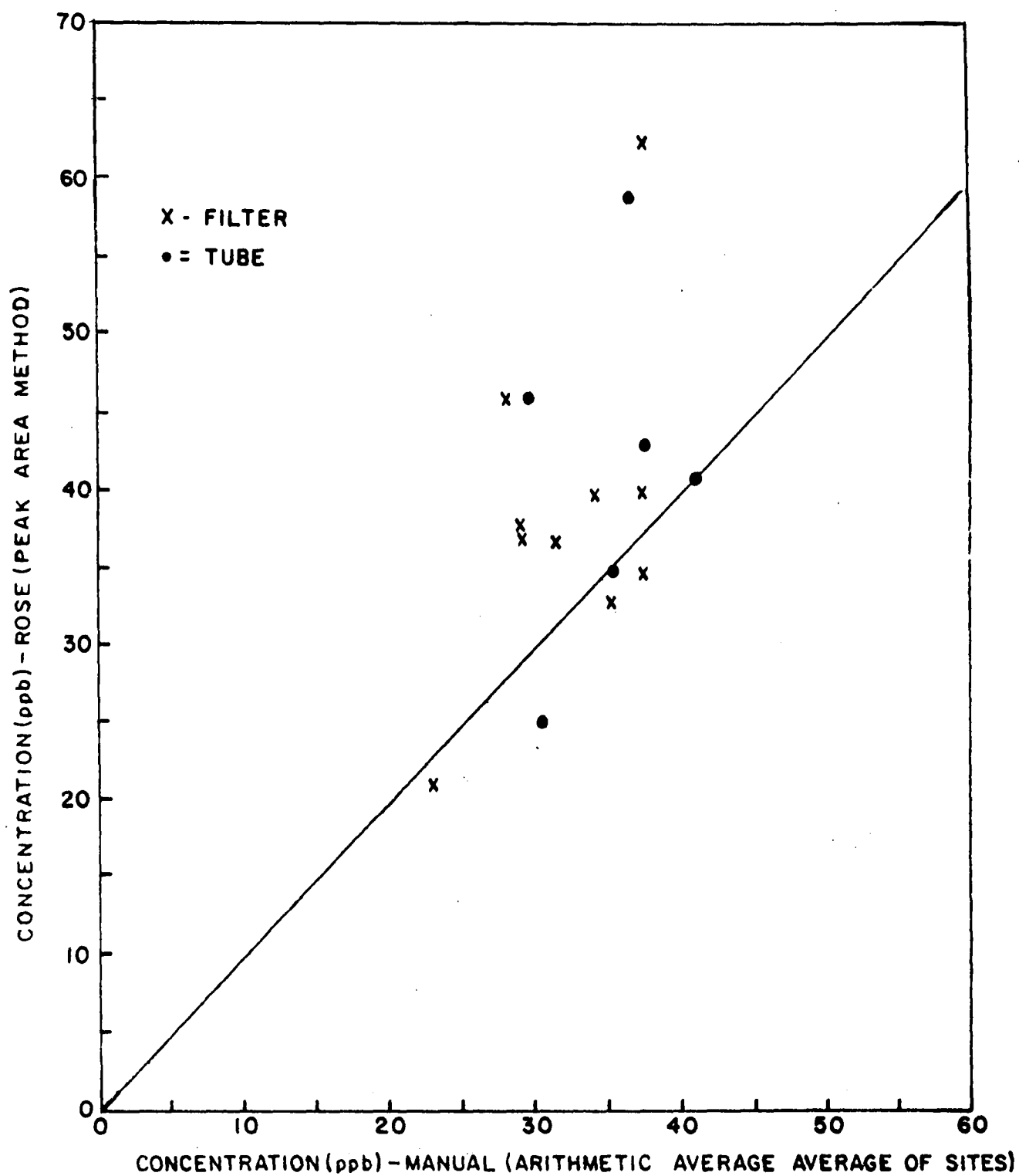
Figure 48. Comparison of HF concentrations measured by two techniques at Agrico site (7/26/79). (Peak area method for ROSE data).
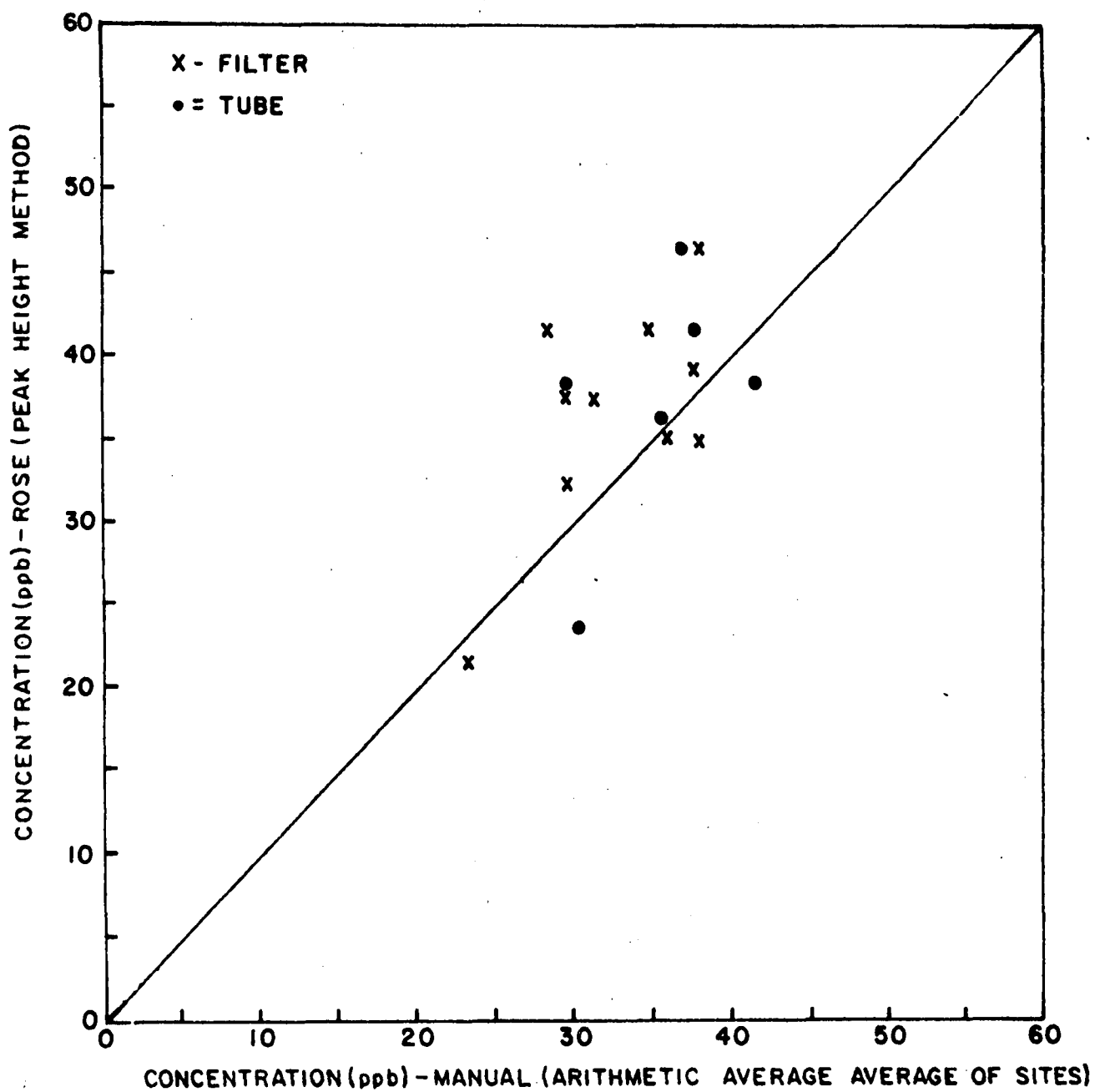
Figure 49. Comparison of HF concentrations measured by two techniques at
Agrico site (7/26/79). (Peak height method for ROSE data).

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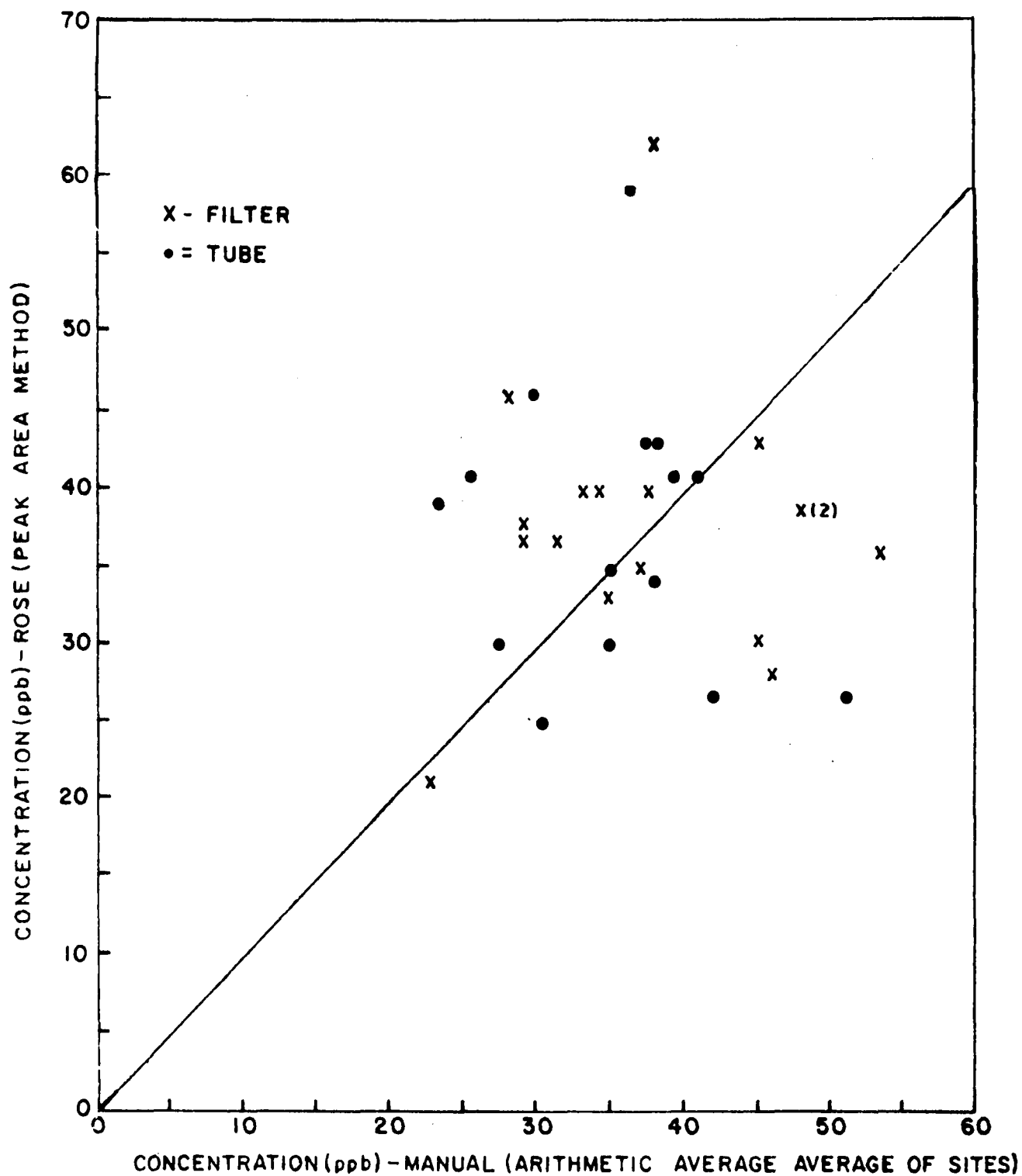
Figure 50. Composite comparison of HF concentrations measured by two techniques. (Peak area method for ROSE data).
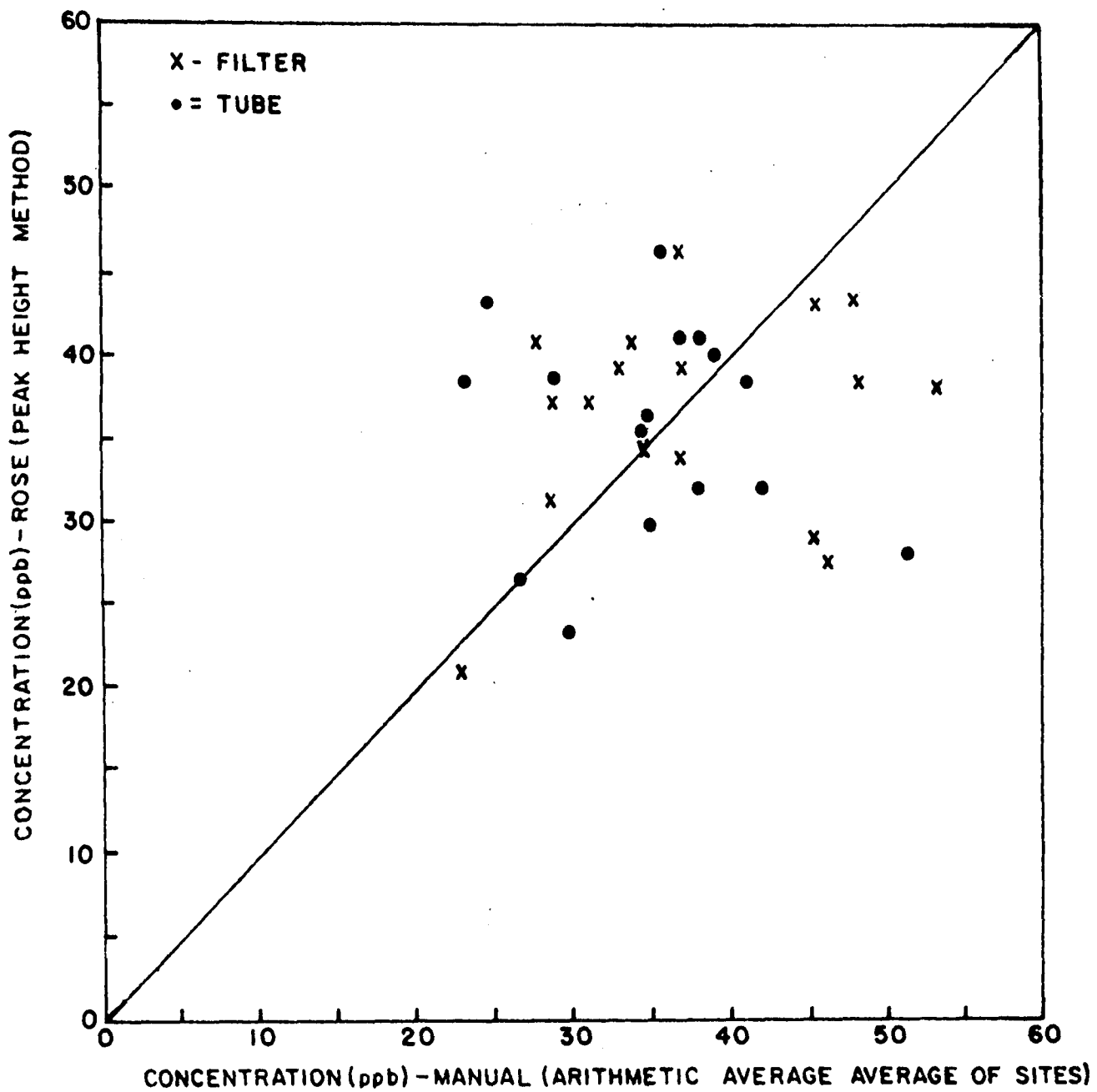
Figure 51. Composite comparison of HF concentrations measured by two
techniques. (Peak height method for ROSE data).

periods. The point measurements thus indicate widely varying HF concentrations. As might be expected, in this case the agreement between the two methods is not as good as on 7/24.

The analysis of the measurements at Agrico shows an appreciable difference from CFI in that a true HF gradient along the sampling path is indicated by the point measurement (Figures 40 and 41). Sites A and B are generally the lowest and Site D always the highest (by an appreciable amount) in HF concentration. The readings at D can be explaiend by the fact that the site was next to a small stream of liquid leaking from an upper gypsum pond. Also, it should be noted that the truck holding the ROSE light source and telescope was in an area surrounded by pond runoff. The data fall into two categories:

(1) During the first eight sampling periods (1038 to 1311 hours) the agreement between the methods is excellent.

(2) In the eight late afternoon sampling periods (1548 to 1830 hours) the ROSE data gave HF concentrations always a slightly higher than the average of the point sampling data.

The original ROSE data for the last six runs at Agrico were reprocessed a number of times to eliminate the possibility that human error could have caused the difference between the point and ROSE values. Also, the CO_2 and N_2O concentrations measured by the ROSE system were compared for the last six runs. No mistakes in data reduction were found for the HF measurements. The CO_2 and N_2O concentrations were all within ±5 percent of each other (respectively) when measured in spectral regions of maximum S/N. In the spectral region where the signal to noise was about the same for CO_2 as for HF, the apparent CO_2 concentration varied about ±15 percent. The internal checks on the spectral data provided by CO_2 and N_2O show that there is nothing abnormal about the spectra measured by the ROSE system during the last six sampling periods at Agrico. The consistently higher values obtained by the ROSE system during the warm afternoon may have been due to the pond runoff in the vicinity of the light source.

To determine whether any statistical differences existed between the sampling sites at CFI and Agrico, and analysis of variance was calculated for the data obtained each sampling day (no data were deleted for this analysis). The analyses are presented in Tables 15 to 17. The results of these analyses indicated no differences among the sites at CFI, however, a significant difference existed among the sampling sites at Agrico.

Statistical analyses based on the differences between the manual sampling data and the ROSE values are presented in Tables 18 and 19 for all of the data and for each day of sampling. The difference between the arithmetic mean of the manual methods ($\bar{A}$) and the ROSE data (R) was computed from the data in Table 14. Tables 18 and 19 represent the statistical analyses based on the ROSE data computed by the peak area and peak height methods, respectively.

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TABLE 15. COMPARISON OF MANUAL SAMPLING DATA AT CFI
(7/24/79)

Date	Start time	Site				Total
		A	B	C	D	
7/24/79 (CFI)	0859	26	36	37	40	139
	0931	26	27	27	52	132
	1007	16	46	52	53	167
	1037	27	44	52	27	150
	1119	32	32	35	32	131
	1152	44	36	–	36	116
	1227	35	57	50	50	192
	1243	46	24	40	30	140
	1304	44	48	43	45	180
	1326	42	40	30	40	152
		338	390	366	405	1499

Source	df	SS	MSV	F
Sites	3	305.5	101.8	1.11
Times	9	935.5	935.7	1.63
Error	26	2374.6	2374.8	
Total	38	3616.0		

F 5%, 3/26 = 2.98
        9/26 = 2.27

Conclusions:

  a. No significant difference among the sampling
      locations.

  b. No significant difference among the sampling
      times.

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TABLE 16.   COMPARISON OF MANUAL SAMPLING DATA AT CFI
             (7/25/79)

Date	Start time	Site A	B	C	D	Total
7/25/79	0830	19	15	22	51	107
(CFI)	0942	34	58	43	48	183
	1010	14	98	25	29	166
	1027	32	34	51	75	192
	1049	22	106	–	24	152
	1115	52	37	47	42	178
	1133	17	7	44	24	92
	1154	43	54	60	53	210
	1214	27	31	17	24	99
		260	440	309	370	1379

Source	df	SS	MSV	F
Sites	3	1,835.8	611.9	1.34
Time	8	4,220.5	527.6	1.15
Error	23	10,548.1	458.6	
Total	34	16,604.4		

F 5%, 3/23 = 3.03
      8/73 = 2.37

Conclusions:

No significant differences among the sampling sites
and among the sampling times.

TABLE 17. COMPARISON OF MANUAL SAMPLING DATA AT
AGRICO (7/26/79)

Date	Start time	Site				Total
		A	B	C	D	
7/25/79 Agrico	1038	20	19	–	31	
	1106	21	29	29	40	
	1130	22	27	27	42	
	1149	34	29	32	43	
	1209	34	26	36	45	
	1230	31	29	34	42	
	1251	35	34	35	46	
	1311	37	–	–	45	
	1548	30	36	32	50	
	1607	31	27	46	43	
	1632	23	–	27	38	
	1704	32	33	32	52	
	1732	34	30	33	47	
	1746	26	30	30	39	
	1809	25	22	29	34	
	1830	26	26	30	35	
		461	397	452	672	1982

Source	df	SS	MSV	F
Sites	3	1885.4	628.5	23.3
Error	56	1506.5	26.90	
Total	59	3391.9		

F 5%, 3/56 = 2.76

Conclusions:

There is a significant difference among the sampling sites.

TABLE 18. STATISTICAL ANALYSES BASED ON DIFFERENCE VALUES FOR MANUAL SAMPLING DATA AND ROSE DATA (PEAK AREA METHOD)

					Concentrations in ppb		
	n	$\bar{d}^{(1)}$	$Sd^{(2)}$	$(\bar{A})^{(3)}$	$\bar{R}^{(4)}$ (peak area)	$\overline{(R/\bar{A})}^{(5)}$	Range of $(R/\bar{A})$
All data	32	-1.2	11.9	36.4	37.6	1.09 ± 0.34	0.53 - 1.70
CFI 7/24	7	+0.8	5.8	39.4	38.6	1.00 ± 0.18	0.86 - 1.33
CFI 7/25	9	+7.0	14.6	40.0	33.0	0.93 ± 0.45	0.53 - 1.70
Agrico 7/26	16	-6.8	9.3	33.0	39.8	1.21 ± 0.29	0.83 - 1.68

(1) $\bar{d}$ (average of differences) = $\Sigma(\bar{A}-R)/n$

(2) Sd (standard deviation of differences) = $[\Sigma(d-\bar{d})^2/n-1]^{\frac{1}{2}}$

(3) $(\bar{A})$ = mean of data for manual methods

(4) $\bar{R}$ = mean of ROSE values (peak area method)

(5) $\overline{(R/\bar{A})}$ = $\Sigma(R/\bar{A})/n$

TABLE 19. STATISTICAL ANALYSES BASED ON DIFFERENCE VALUES FOR MANUAL
SAMPLING DATA AND ROSE DATA (PEAK HEIGHT METHOD)

					Concentrations in ppb		
	n	$\bar{d}^{(1)}$	$Sd^{(2)}$	$\bar{A}^{(3)}$	$\bar{R}^{(4)}$ (peak height)	$\overline{(R/\bar{A})}^{(5)}$	Range of $(R/\bar{A})$
All data	32	+0.3	9.7	36.4	36.1	1.04 ± 0.28	0.55 → 1.72
CFI 7/24	7	+1.0	4.8	39.4	38.4	0.98 ± 0.13	0.84 → 1.18
CFI 7/25	9	+6.4	14.5	40.0	33.6	0.94 ± 0.44	0.55 → 1.72
Agrico 7/26	16	-3.6	5.6	33.0	36.6	1.11 ± 0.18	0.92 → 1.46

(1) $\bar{d}$ (average of differences) $= \Sigma(\bar{A}-R)/n$

(2) Sd (standard deviation of differences) $= [\Sigma(d-\bar{d})^2/n-1]^{\frac{1}{2}}$

(3) $(\bar{A})$ = mean of data for manual methods

(4) $\bar{R}$ = mean of ROSE values (peak height method)

(5) $\overline{(R/\bar{A})} = \Sigma(R/\bar{A})/n$

The mean HF concentration determined by the manual sampling methods for all of the data was 36.4 ppb compared to a concentration of 37.6 ppb calculated by the peak area method of the ROSE system. The peak height method (Table 19) gave an overall average of 36.1 ppb HF. The standard deviation of the difference was 11.9 and 9.7 ppb for Tables 18 and 19, respectively, with the variation at CFI on 7/25/79 contributing significantly to raise the overall standard deviation.

Theoretically, random errors should give an overall $\bar{d}$ that is zero or very close to zero. The small $\bar{d}$, based on both methods for computing the ROSE data, indicates a good correlation between the ROSE system and the manual sampling methods. In addition, the overall average of the quotient $(R/\bar{A})$ should be about one if the data from the manual sampling methods and the ROSE system is comparable for any given run. The values for $(R/\bar{A})$ approach one in both tables.

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    Applications to Chemical Systems Vol. 2, Academic Press, N.Y. 1979.
    Chapter 2, Hanst, Phillip, Trace Gas Analysis; Chapter 3, Herget, William
    R., Air Pollution: Ground Based Sensing of Source Emissions.

APPENDIX A - PROJECT PARTICIPANTS

The following personnel from GCA, EPA, CF Industries and Agrico Chemical Company participated in the performance of this task.

GCA Technology Division

Dan Bause

John Fitzgerald

Mark McCabe

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Verne Shortell

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Mark Antell

EPA-RTP

William F. Herget

CF Industries

Steve Martin

William Schimming

Agrico Chemical Company

Ed Germain

Maurice Johnson

Harold Long

Charles Kinsey

APPENDIX B - LABORATORY RESULTS AND CALCULATIONS

1. PRELIMINARY LABORATORY PHASE

   a. Laboratory Results

   b. Calculations

2. PRELIMINARY FIELD PHASE

   a. Laboratory Results

   b. Calculations

3. FORMAL FIELD PHASE

   a. Laboratory Results

   b. Calculations

APPENDIX B-1

LABORATORY PHASE – LAB RESULTS

Ion Chromatograph –
Fluoride Analysis

GCA No.	Sample ID	µg F/ml	Remarks
3439	T2A	0.5	
3440	T2B	0.35	
3442	T3A	0.5	
3443	T3B	0.5	
3444	T3C	0.3	
3445	T4A	0.3	
3446	T4B	2.0	
3447	T4C	10.0	
3448	T5A	1.0	
3454	std. ~55ppm	~55ppm	must dilute & rerun for better value
3455	F-1-A	0.5	
3463	F3A	0.5	
3464	F3B	0.3	
3465	F3C	0.3	
3466	F3D	<0.3	
3472	F5B	1.4	
3626	F-1-Na	2.0	
3627	F-1-Citric	ND	non detected

Ion Chromatograph - Summary of Data

Contract   1-451-259   Date   5-18-79

Analyst   B. Myatt   Anion(s)/Std. curve(s)   F- (5-14-79 AAS)

GCA No.	Sample ID	Conc. F- (ug/ml)	remarks
3719	R1I1	0.15	
3720	R1I2	<0.04	
3721	R1F	1.20	
3722	R2I1	0.10	
3723	R2I2	2.88	
3724	R2FN	1.28	
3725	R2FC	<0.04	
3726	R2IF	<0.04	
3727	R3I1	0.15	
3728	R3I2	0.88	
3729	R4I1	0.68	

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F⁻ analysis from 1-451-259

(from 5-16-79)   5-17-79

Sample   µg/ml F⁻

Sample	µg/ml F⁻	
I-1-C – GCA 3696	2.31	
I-2-A 1 - GCA 3697	1.95	
I2-A2 – GCA 3698	1.29	
I-2-C1 – GCA 3699	1.03	
I-2-C-2 – GCA #3700	0.62	
I-3-A-1 – GCA #3701	0.62	
I-3-A-2 – GCA #3702	0.40	
I-3-C-1 – GCA #3703	0.49	
I-3-C-2 – GCA #3704	<0.04	too dilute – gave to BMM for further work
I-3-AF – GCA #3705	0.74	
I-3-CF – GCA #3706	<0.04	too dilute – gave to BMM for further work
I1-I3 (.1 N NaOH) GCA #3707	3.02	
I-3-F (blank) – GCA #3708	1.46	
I-4-A-1 – GCA #3709	2.45	
I-4-A-2 – GCA #3710	1.05	
I-4-C-1 – GCA #3711	1.60	
I-4-C-2 – GCA #3712	0.93	
I-5-A-1 – GCA #3713	1.85	
I-5-A-2 – GCA #3714	0.56	
I-5-C-1 GCA #3715	1.23	
I-5-C-2 GCA #3716	8.12	
I-4-5 (.1 N NaOH) GCA #3717	7.00	
HF Soln. E GCA #3718	47.4	

Ion Chromatograph Fluoride Analysis

I-431-___
May 21-22, 1979
B. Myatt

Anal. Date	GCA No.	Sample ID	μg F/ml	Remarks		Anal. Date	GCA No.	Sample ID	μg F/ml	Remarks
5/18	3730	R4I2	1.10			5/22	3755	R-12-T	1.49	
5/21	3707	I1I3	1.25	X			3756	R-13-I1	1.84	
	3717	I4S	0.45	X			3757	R-13-I2	5.23	
	3731	R4T	1.47				3758	R-13-T	2.70	
	3732	R3T	1.47				3759	R-(0.1N NaOH)	0.91	
	3733	R5T	1.00				3760	HF gen soln F	close to 55 ppm	~55 ppm off calibr. curve
	3734	R5TF	3.58				3761	R-14-I1	1.86	
5/21	3735	R5FN	4.8				3762	R-14-I2	5.39	
5/22	3736	R5FC	<0.05				3763	R-14-F	7.34	spots in bottle smell of alcohol
	3737	R6T	1.30				3764	R-15-I1	0.3	
	3738	R6F	0.78			5/22	3765	R-15-I2	<0.05	
	3739	R7F	0.70							
	3740	R7T	0.78							
	3741	R8I1	5.0							
	3742	R8I2	1.25							
	3743	R8F	1.58							
	3744	R9I1	3.85							
	3745	R9I2	3.00							
	3746	R9F	1.68							
	3747	R-10-I1	0.71							
	3748	R-10-I2	1.84							
	3749	R-10-F	4.86	spots in bottle						
	3750	R-11-I-1	3.23 3.23	ran twice						
	3751	R-11-I2	0.63							
	3752	R-11-T	2.60	spots in bottle						
	3753	R-12-I1	3.28							
5/22	3754	R-12-I2	5.05							

Ion Chromatography
Fluoride Analysis

I-451-259
May 23, 1979
B. Myatt

Anal Date	GCA No.	Sample ID	conc. µgF⁻/ml	Remarks			
5/23	3766	R-15-F	0.75		7.575	23.26	31.97
	3767	R-16-I1	1.36				
	3768	R-16-I2	4.26				
	3769	R-16-F	.6.85	6.919			
	3770	R-17-I1	0.91	} run as replicates			
	3770	R-17-I1	0.88				
	3771	R-17-I2	0.67				
	3772	R-17-T	1.00	10.100			
	3773	R-18-I1	1.18				
	3774	R-18-I2	2.02				
	3775	R-18-T	0.85	8.585			
	3776	R-19-I1	0.18	} run as replicates			
	3776	R-19-I1	0.18				
	3777	R-19-I2	ND	—no F⁻ peak			
	3778	R-19-T	0.83	8.3??			
	3789	D(0.1N NaOH)	ND	—no F⁻ peak			
	3791	✓R-20-F	0.64		6.???	27.97	35.41
	3792	✓R-20-T	0.48		???	22.??	28.2?
	3793	✓R-21-F	1.47	} run as replicates	14.???		cont.
	3793	✓R-21-F	1.40				
	3794	✓R-21-T	0.55		?.??	25.47	32.24
	3795	✓R-22-F	0.91			38.?	4?.??
	3796	✓R-22-T	0.56		5.656	23.??	??.?
	3797	✓R-23-F	0.37		3.737	2?.??	27.1?
	3798	✓R-23-T	0.30		3.0??	??.??	24.61
	3799	✓R-24-F	0.37		?.??	2?.??	26.3?
5/23	3800	R-24-T	0.31		?.1??	17.36	32.24

Ion Chromatography
Fluoride Analysis

1-451-259
May 24, 1979
Bmyatt

Anal. Date	GCA No.	Sample ID	ug F-/ml	remarks
5/24	3801	R-25-F	0.45	
	3802	R-25-T	4.11	specks in bottle (AgNO₃)
	3803	R-26-F	0.74	
	3804	R-26-T	0.48	
	3805	R-27-TA	0.84	
	3806	R-27-TC	0.75	
	3807	"50ppb soln"		
	3808	"25ppb soln"		
	3809	"10ppb soln"	9.5	
	3810	R-28-TA	1.36	specks in bottle (AgNO₃)
	3811	R-28-TC	1.18	
	3812	R-29-TA	1.18	former APS/AgNO₃ bottle
	3813	R-29-TC	0.93	
	3814	R-30-TA	1.21	former APS/AgNO₃ bottle
	3815	R-30-TC	0.97	
	3816	R-31-TA		
	3817	R-31-TC	1.00	
	3818	R-32-TBC	3.40	
	3819	R-32-TBA	4.86	

Ion Chromatography

Fluoride Analysis

Anal. Date	GUA No.	Sample ID	Conc. µgF/ml
5/24	3683	F-9-A	1.02
	3685	F-10-A	0.85
	3738	R-6-F	0.78
	3737	R-6-T	0.88
	3687	F-11-A	0.85
	3739	R-7-F	0.81
	3740	R-7-T	0.71

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Ion Chromatography
Fluoride Analysis

BMmyatt
may 29, 1979

Anal. Date	GCA NO.	Sample ID	conc. µgF/ml	remarks
5/29	3807	"50ppb soln"	46.0	required 1:10 dilution
	3808	"25ppb soln"	24.8	
	3818	R-32-TBC	7.7	
	3821	R-33-IA (#1)	0.30	
	3822	R-33-IA (#2)	ND	
	3823	R-33-IC(#1)	0.55	
	3824	R-33-IC(#2)	0.22	
	3825	R-34-IA (#1)	0.30	
	3826	R-34-IA(#2)	1.09	

DATE	RUN #	acf Vm	TM °R	Pb	Vmc	Pb-vac	dscf Vmstd	sample vol (ml)	ug/ml F blank	ug/ml sample	Blank sample ug/ml	total ug	dscm Vmstd	ug/m3	ppb F	g nct total qcbt
5/11	F-7	6.839	532	30.15	4.8	25.35	5.751	5.1	ND	1.39	1.39	6.579	.1629	42.90	54	57.5
	F-8	6.376	538		3.95	26.20	5.479	5.1		1.39	1.39	7.089	.1552	45.68	58	
5/11		6.047	532		4.2	25.95	5.722	5.1		1.46	1.46	7.446	.7620	45.96	58	57.5
5/15	F-9	6.638	538	30.15	3.0	27.15	3.911	5.1	no detectable	1.50	1.50	7.450	.1694	45.70	57	57.3
	F-10	6.856	533	30.14	3.1	27.09	6.138	10.1		.73	.73	7.373	.1738	40.42	52	
		7.096	533		3.4	27.74	6.517			.75	.75	7.375	.1890	41.03	52	
	F-11	6.957	533		6.5	23.64	5.445			.65	.65	6.565	.1542	42.57	54	
		6.150	536		4.75	23.39	5.141			.62	.62	6.565	.1455	43.52	57	
	F-12	8.311	533		10.5	19.64	3.804			.46	.46	6.666	.1530	43.59	55	
		6.703	539		3.4	26.74	3.921			.45	.45	7.979	.1677	47.58	60	
5/15		6.179	533		5.0	24.14	5.153			.45	.65	6.565	.1459	45.61	58	57.13
5/11	R-1 I	8.303	538	30.14	10.4	19.54	13.258	10.1	ND	.66	.46	6.666	.1489	44.7	57	50.1
	E	19.000	533	30.47	8.6	21.77	13.88	10.74	1.05	.56		.890	37.31	47	
	R-2 E	13.735	538		5.0	25.47	11.475	10.1	ND	1.20	1.20	12.12	.325	37.29	47	
	F		533		6.4		11.82	47.48		1.28	1.28	12.928	.335	38.13	48	140
	R-3 I		538		3.9			10.11	ND	.58		.339	37.06	47	218
	E		533		8.3			43.98	.47	.57	115	11.615	.377	37.91	48	
	R-4 I		538		5.4			10.11	.45	.65		.308	42.23	53	157
	E		533		.9			47.49	.43	1.47	1.05	10.605	.242	43.82	55	
5/11	R-5 E	8.824	533	30.47	3.4	29.57	8.339	10.1	ND	.73	.72	7.272	.1823	39.89	50	
	E	7.077	538		4.4	27.47	6.436	10.1		1.00	.50	585d	.1538	36.08	48	
	R-6 E	4.350	533		2.0	26.07	6.682	10.1	ND	.78	.78	7.878	.1970	42.13	53	
	E	4.380	538		1.45	28.47	6.956		.38	1.20	.78	7.878	.1897	42.13	33	
	R-7 F	6.940	538		8.0	29.02	6.606		ND	.70	.70	2016	.1777	39.78	50	
	E	8.452	534		7.2	30.47	6.876		.42	7.8	.36	4026	.1106	41.11	42	LEAK?
	R-8 E	6.458	533		11	18.47	3.905	10.1	ND	1.58		15.958	.388	41.12	52	
			534				11.76	47.46	.456	1.25			.333	110.5	913 140	
5/17	R-9 E	23.114	534	30.47	10.5	20.47	15.23	10.1	ND	1.68	1.68	14.968	.432	39.28	50	
	I		531		8.5		14.76	91.55	.45	3.85	320		.353	876 397	1109 503	
	R-10 F		534		12.0		13.04	50.74	ND	71.18	VOID		.369	VOID		
			534		1.7			10.74	.45	1.70	1.28	12.928	.396	434 360	81 329	
	R-11 I	16.395	539		8.7	21.77	11.79	10.1	.42	3.23 .63	2.76 2.18		.334	38.91	49	
	I		539		9.1		15.02	94.74	.45	1.61	1.21	12.807	.434	895 30.9	753 38	
	R-12 I		534		7.6		11.84	10.74	.45	3.24 5.03	283 1.60		.335	28.91	49	
	I		539		7.2		15.02	89.53	.45	1.75		12.928	.368	889 663	866 839	
	R-13 I		533		6.7		11.84	10.1	.45	189 5.23	139 4.78		.326	89 16.6	50	
5/11			539				12.84	47.50	.45				.365	179 655	226 829	
	R-14 I	15.798	535	30.45	.4	30.15	15.74	49.50	ND	1.16 5.34	1.91 4.94		.449	155 555	196 703	
	F	15.098	535		7.5	22.95	11.420	10.1		VOID			.323	29.92	37	CONTAM VOID
	R-15 I	19.759	535		8.0	20.95	13.682	49.47	.205	13.2			.299	38.73	49	
	F	14.436	540		12.3	17.95	10.591	10.1	ND	1.13	1.15	11.615	.249	38.73	47	
	R-16 I	21.463	535		1.6	17.93	15.468	41.47	.49	1.34 4.26	1.91 3.81		.4439	89 409	106 511	
	F	13.41	532		9.6	28.85	12.764	10.1	ND	1.40	1.40	14.40	.364	39.12	50	
	R-17 I	19.836	533			28.85	13.493	45.98	.43	91.18	46.83	20.7 246	.488	95 53	678 67	
	I	25.929	532			18.85	16.879	10.9	.45	2.23	1.60	18.180	.4780	88.03	48	
	R-18 I	21.089	532		11.6	18.95	13.436	45.49	.45	1.18 2.92	.13 1.57		.3719	88 207	13 262	
	I	15.207	539		7.7	22.95	11.436	10.1	.42	1.65	1.23	12.423	.3236	38.39	49	
5/11	R-19 I	19.172	534		8.1	22.35	13.160	48.47	.42	18.40	5.43	8.64	.400	21.59	27 0	
	I	14.879	539	30.95	5.2	26.25	12.987	10.1	.42	1.85	6.43	19.443	.3621	39.89	50.0	50.1

RUN#	Vm (act)	Tm °R	Pb	Vac ("Hg)	Pb-Vac	acf Vm STD	dscm VM STD	samp vol ml	Blank ug/?	ug F/samp	ug F tot	ug/m3	ppb F v/u rgc	ppb F v/u actual
R-20 F	11.034	532	30.15	7.0	21.5	8.034	.2580	10.1	0	.64	6.404	25.39	32	30.8	
T	9.588	540		5.7	24.45	7.461	.2170			.48	4.848	22.34	28		
R-21 F	12.279	533		9.5	20.05	8.395	.2377			.55	5.555	23.36	30		
T	9.388	539		5.1	25.05	7.700	.8181			.55	5.555	23.49	32		
R-22 F	11.292	534		7.3	22.85	8.527	.2415			.59	5.622	24.13	31		
T	8.428	539		0.4	29.75	8.209	.2325			.56	5.626	24.33	31		30.8
R-23 F	8.418	533		8.5	21.65	6.177	.1799			.37	3.737	23.37	30		18.2
T	7.425	539		8.5	22.45	5.263	.1570			.34	3.434	23.05	29		
R-24 F	8.294	533		0.7	23.05	6.330	.1743			.26	3.737	13.21	19		
T	6.530	539		0.7	29.45	4.296	.1783			.26	2.626	14.72	19		
R-25 F	18.912	534		11.5	17.65	11.656	.3301		V	.45	4.545	13.708	17	18.2	
T	15.368	539		8.6	21.55	10.893	.3071			.75	4.545	14.50	19		
R-26 F	16.170	534		5.1	25.05	13.386	.3791		0	.74	7.474	19.79	78	61.5	
T	14.924	539		5.3	24.85	11.735	.3323		0 82	.48	4.848	14.59	78		
R-27 T	8.396	534		7.1	23.05	6.395	.1811		0 52	.75	7.575	41.31	60		
T	6.948	539		3.13	29.85	5.653	.1601		.30 61	1.36	10.706	52.27	67		
R-28 T	7.488	533		1.3	28.85	7.152	.2045		.30 61	1.18	8.868	44.987	63		
T	7.106	539		3.1	27.05	6.293	.1787		.38 61	1.18	11.81	62.13	82		
R-29 T	8.101	533		6.1	24.00	6.501	.1658		.38 61	1.23	9.393	36.43	72		
T	7.110	539		2.0	25.15	5.854	.1558		.0 61	.91	9.79	41.8	67		
R-30 T	7.96	533		1.7	28.45	7.034	.1992		.30 61	1.26	9.791	48.08	61		61.5
T	7.543	539		2.8	27.35	6.759	.1913		0 62	.90	9.090	44.82	63		
R-31 T	8.174	533		6.3	23.85	6.150	.1624		.30 61	1.00	10.20	15.04	7.0		
T	8.257	539	30.15	6.3	23.85	6.448	.1835	10.1	.30 62						
R-32 T	BLANK								.0 62						
R-33 I	19.360	534	30.00	9.1	20.9	13.371	.3786	56	ND	.30	16.8	44.37	56	57	??
I		534		9.1	20.9			58	ND						
R-34 I	14.455	534		1.6	28.4	13.491	.3806	61.5		.55	33.6	88.15	412		57
I		530	30.00	13.4	16.6	23.598	.6655	102 105	ND	.30	14.95	171.98	218	57	276

50 ppb SOL - 160 UGF/M
25 ppb - 27 UGF/M

APPENDIX B-2

PRELIMINARY FIELD PHASE

(a) Lab Results

Sample	conc. (ug/ml)	Sample	conc. (ug/ml)
A2	0.70	I8A	0.56
A3	0.83	I8B	0.37
A4.	1.08	I9A	1.67/1.65
A5	0.73	I9B	0.38
A6	0.85	I10A	0.71
A7	0.78/0.35	I10B	0.78
A8	not enough	I11	0.65/0.65
A9	1.04	I12A	0.47
A11	0.87/0.64	I12B	0.38
A12	not enough	I13A	0.65
A16	0.84 small am-ount of resins	I13B	0.28/0.26
A17	not enough	I14A	0.37
I1A	0.61	I14B	0.27
I1B	2.02/2.11	I15A	0.54
I2A	0.34	I15B	0.60/0.62
I2B	0.32	I16A	0.85
I3A	0.95	I16B	1.54/1.57
I3B	0.49	I17A	0.57
I4A	1.09	I17B	0.99
I4B	0.89/0.89	I18A	0.94
I5A	0.84	I18B	0.71
I5B	0.75	I19A	0.80
I6A	1.02	I19B	0.45
I6B	1.08	I20	0.65
I7A	0.64	I20B	0.46
I7B	0.36/0.42	I21A	0.63

sample	conc.(ug/ml)	sample	conc.(ug/ml)
L2l6	0.7E	Q13	1.66
L22	0.7?/0.77	Q14	1.56/1.59
M1A	0.54	Q15	1.12
M1B	0.5?	Q18	1.74
M2A	0.6?	Q20	1.42
M2B	0.5?	Q21	1.20/1.13
M3A	1.03/1.05	Q22	1.48
M3B	1.03	Q23	1.26
M4A	0.69	Q2L	0.77
M4B	1.17	Q27	0.64
M5A	0.57	S14	0.59
M5B	0.47	S1B	0.44
M6A	0.91/0.15	S2A	0.56
M6?	0.71	S2B	0.43/0.82/0.82
M7?	0.75	S3A	0.62
M7B	1.10	S3B	0.68
M8A	0.6?	S4A	0.63
M8B	0.57	S4B	0.78
M1T	0.?1/0.?4	S5A	0.46
?4?	0.9?	S5B	0.33
M2?A	1.05	S6A	0.49
M1CP	~1.44 (?) masked by chloride	S6B	0.88
M1?	?.6?	S7A	0.56
Q?	0.51	S7B	0.30/0.30
Q?	0.82	S8A	0.44
??	0.99	S?B	0.32

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sample	conc.(ug/ml)	sample	conc.(ug/ml)
S9A	0.76	T30	0.64
S9B	0.42	T31	0.48
S10A	0.71	T32	0.70
S10B	0.52/0.52	T33	0.46
T1	0.53	T34	0.56
T2	0.63	T35	0.59
T3	0.44	T36	0.65/0.65
T4	0.48	T39	0.41
T5	0.43	T40	0.76/0.76
T6	0.72/0.71	T41	0.43
T7	0.46	T51	4.01
T8	0.41	T52	5.45/5.62
T9	0.26/0.27	T53	0.90/0.96
T10	0.43/0.45	T54	47.5/48.0
T10C	0.35	T56	8.55
T11	0.60	T57	0.87
T12	0.41	T58	33.2/35.3/35.3
T13	0.52	T59	21.3
T14	0.41/0.41	T60	5.03
T15	0.58	T61	1.57
T16	0.76/0.75	T62	0.87
T17	0.66	V1	0.95
T18	0.43/0.43	V2	5.05
T19	0.46	V3	47.5/48.0
T20	0.38	V4	2.11
T21	0.53	V5	5.49

Sample	conc. (ug/ml)	Sample	conc. (ug/ml)
V 6	3.06		
V 7	4.96		
V 8	1.33		
V 9	1.23/1.17		
V 10	1.47		
V 11	0.77		
V 12	0.81		
(1	0.66		
' '	0.50		
''	0.97		
' '	0.73/0.85		
' '	1 ''		
('''	0.79		
' ''	0.91		
' '	0.66		
' ''	1.00		
' '	0.69		
' ''	0.97		
' '''	0.98		
' '''	0.20/0.21		
'' '	0.73		
' ''''	0.43		

HF Sampling

sample	conc. (ug/ml)	sample	conc. (ug/ml)
I1A	0.61	M7A	0.75
I1B	2.02/2.11	M7E	1.10
I2A.	0.34	M8A	0.66
I2B	0.32	M8B	0.57
I3A	0.95	M9A	0.81/0.84
I3B	0.49	M9B	0.56
I4A	1.09	M10A	1.05
I4B	0.89/0.89	M10B	~1.49 (?) masked by chloride
I5A	0.89	M11	0.60
I5B	0.75		
I6A	1.62		
I6B	1.08		
I8A	0.56/0.56		
I8B	0.37		
M1A	0.54		
M1B	0.50		
M2A	0.66		
M2B	0.50		
M3A	1.03/1.05		
M3B	1.03		
M4A	0.14		
M4B	1.17		
M5A	0.57		
M5B	0.47		
M6A	0.91/0.75		
M6B	0.71		

.34 99112
.15

.31/1

APPENDIX B-2

PRELIMINARY FIELD PHASE

(b) Calculations

Table 2 Prelim. Filter Runs at CF

DATE	RUN #	VM (ft³)	Pb	Vac	TM	Y	VM570	ug/ml	ug/ml Blk	ug/m Blk	vol		VM570 (m³)	ug/m³	ppHf	ppHf
6/12	A₂	6.936	29.65	5.3	551.5	.979	5.291	1.12	.50	.62	10.1	6.262	.150	41.75	55.66	54.73
	A₃	5.477		10.0	542	.979	3.934	.99		.49		4.999	.098	31.02	61.0	26.19
	B₁	11.834		10.0	550	.944	7.043	.955		.46		4.646		22.97	30.6	30.1
	B₂	11.195		10.3	526	.943	3.535	.97		.27		2.707	.100	27.27	36.86	35.75
	B₃	3.839		9.8	348	.944	2.351	.69		.19		7.972	.067	20.40	37.99	37.2
	C₁	7.343		5.0	552	1.014	5.868	1.42		.92		9.292	.164	55.96	74.63	73.38
	C₂	.909		5.0				.83		.33		3.333				77.00
	C₃	8.538		11.2	552	1.014	5.047	1.35		.85		8.585	.142	60.45	80.61	79.25
	C₄	7.048		5.0	552	1.014	4.540	1.51		.87		8.181	.128	63.91	85.21	83.77
	D₁	3.223		2.0	552	.965	2.739	1.07		.57		5.757	.077	74.76	99.67	78.0
	D₂	5.064		2.3			3.493	1.07		.57		5.757	.097	58.15	77.48	76.23
	D₃	4.333		3.4			3.230	1.06		.56		5.256	.097	72.17	96.19	81.98
6/12	D₄	1.672	29.65	3.0	552	.965	1.370	1.14	.5	.64	10.1	6.464	.039	165.74	220.99	217.27

CITRATE FILTERS

RUN	ug/ml	ug/ml Blk
B2	.37	.36
B2	.38	.36
C4	.36	.36
D4	.35	.36

+   .75   x .9832

Site	Date	Smple	acf Vm	oR Tosm	Pb	Vac	Pb-Vac	VmSTD	Y	(mi) Vm	ug/ml O₃	ug/ml Biomk	ug/ml S	Vd	T	9 in	ppb	68°	77
1BT	6/13	T2	5.105	542	30.05	4.5	25.55	4.245	.944	.123	.63	.26	.37	10.0	3.700	32.74	43.66	42.9	
F	6/13	X18	6.701	543		3.7	26.35	5.738	.944	.153	1.78	1.26	.52	10.1	5.352	34.33	45.77	45.0	
.	6/13	I.1	34.719	545		14.8	15.25	17.144	.980	.476				10.8 113					
2BT	6/13	T4	6.823	545		5.25	24.80	5.479	.944	.146	.76	.26	.22	10.0	2.23	15.06	20.09	19.15	
F	6/13	X20	5.098	544		5.8	24.25	4.010	.944	.107	1.76	1.36	.16	10.1	1.616	15.02	2.14	19.80	
I	6/13	I3	34.293	543		13.8	16.25	18.110	.980	.563				109 104					
B3T	6/13	T6	7.443	543		5.2	24.85	6.011	.944	.161	.71	.26	.45	10.0	4.00	27.95	37.27	36.6	
F	6/13	X14	5.356	543		5.9	24.15	4.204	.944	.112	1.575	1.26	.32	10.1	3.232	28.15	38.47	37.8	
I	6/13	I5	35.462	541		15.5	14.55	16.830	.980	.46.7				99 112					
B4	6/13	T8	5.590	539		5.3	24.75	4.538	.944	.121	.41	.26	.15	10.0	1.500	13.40	16.53	16.53	
A6	6/13	X26	5.593	541		5.8	24.25	4.424	.944	.118	.77	.50	.17	10.1	1.710	14.41	19.52	19.0	
I7	6/13	I7	30.432	539	30.05	13.4	16.65	16.589	.980	.460	.61	.6		112 112					
B5	6/14	T11	7.368	537	30.10	5.6	24.5	5.932	.944	.158	.60	.38	.22	10.0	2.30	13.72	17.57	18.20	
	6/14	X15	8.258	537		4.2	25.9	7.029	.944	.187	1.08	.50	.58	10.1	5.855	31.33	41.77	19.00	
	6/14	I9	31.878	535		14.65	15.55	16.351	.980	.459	1.40	.65		111 133					
C1	6/14	T13	8.451	540		4.4	25.7	7.017	.944	.190	.52	.26	.26	10.0	2.00	13.08	18.29	17.93	
	6/14	X6	8.277	540		4.5	25.6	6.951	.944	.186	.97	.50	.47	10.1	4.747	25.52	34.07	33.45	
	6/14	I13	31.626	537		5.8	17.3	17.980	.980	.481	.65			108 96					
C2	6/14	T15	6.983	542		5.2	24.9	5.66	.944	.151	.58	.26	.32	10.0	3.2	21.19	28.26	27.7	
	6/14	X26	8.163	542		4.0	26.1	6.937	.944	.182	.97	.50	.47	10.1	4.747	25.52	34.07	33.4	
	6/14	I15	31.607	537		12.5	17.6	18.292	.980	.508	.64	.54		90 93					
C3	6/14	T17	7.871	544		5.5	24.6	6.381	.944	.168	.66	.26	.40	10.0	3.0	28.86	31.74	31.27	
	6/14	X22	7.989	544		3.2	26.9	6.093	.999	.186	1.00	.50	.50	10.1	5.050	27.15	36.20	35.59	
	6/14	I19	30.313	544		10.3	19.8	19.970	.980	.548	.80 .45			96 96					
C4	6/14	T19	8.687	546		5.8	24.3	4.347	.944	.170	.66	.38	.24	10.0	2.00	16.47	21.90	21.40	
	6/14	X30	6.917	545		5.8	23.3	5.540	.944	.147	.66	.50	.16	10.1	1.414	10.99	14.66	19.4	
	6/14	I17	33.558	545	30.10	12.4	17.7	19.233	.980	.584				96 108					

		Vm	Tm	ΔH	Po	Vms₁₀	Y	Vms₁₀ (m³)		μg/ml Samp	μg/ml Blank	μg/ml Sample	Vol.	Tot μg	μg/m³	ppb
6/13	A 1 I-2	17.380	555	1.0	30.05	16.647	1.10	.570					176			
	2 I-4	17.604	554	1.0	30.05	16.891	1.10	.526					163			
	3 I-6	17.471	562	1.0	30.05	16.526	1.10	.515					154			
													138			
6/13	4 I-8	17.754	561	1.0	30.05	16.823	1.10	.524					134			
6/14	A 5 I-10	16.953	548.4	1.0	30.10	16.461	1.10	.513					141			
	D 1 I-12	18.024	548.3	1.0	30.10	17.509	1.10	.545					156			
													198			
	2 I-14	21.155	553	1.0	30.10	20.370	1.10	.635					108.5			
													135.5			
	3 I-16	21.585	551	1.0	30.10	20.859	1.10	.650					132.5			
													139			
	4 I-18	23.380	553.5	2.0	30.10	22.549	1.10	.702					126			
													156			
6/14	D 5 I-20	20.497	555	1.5	30.10	19.689	1.10	.613					137			
													104			
6/18	A 1 S-1	22.299	565	1.5	30.26	21.152		.659					141			
													74			
	2 S-3	22.255	584	1.5		20.424		.636					96			
													118			
	3 S-5	22.277	588	2.0		20.329		.633					108			
													113			
	4 S-7	23.761	571.5	1.9		22.309		.695					119			
													119			
6/18	A 5 S-9	25.043	588	2.0	30.26	22.854	1.10	.712					109			
													112			
6/19	C 1 M1	16.588	567.4	1.0	30.21	15.624		.487					108			
													115			
	2 M3	23.802	588.75	2.0		21.668		.675					120			
													122			
	3 M5	21.207	594	1.5		19.138		.596					108			
													150			
	4 M7	21.335	574	1.5		19.888		.620					87			
													97			
6/19	C 5 M9	17.629	575	1.5	30.21	16.405	1.10	.511					124			
													113			

AUTO ANALYSER

								ppb HF								
	S1 A	.659 .740	96	.049	11.09	28.98	27.35	28.76								
	B		113		2.96											
	S3 A	.636 .685	108	.049	15.98	14.80	22.65	23.85								
	B		113		1.48											
	I 20 A	.413 .636	141	.049	28.16	39.19	40.88	42.89								
	B		74		3.07	3.4										
	I 22	BLANK		.049												

| | Vms₁₀ (m³) | vol | Blank | Total Blank | μg/m³ | ppb | | | | | | | | | | |

(sample)

S/N	DATE	SAMPLE	Vm	°R Tdrum	Pb	Vac	Pb-Vac	Vm STD (ft³)	Y	Vmstc (m³)	ug/ml S	ug/ml blank	real ug/ml	vol				ppb HF
D1	6/19	T52	7.370	564	32.1	5.4	24.81	5.721	.944	.153				10.0				
	6/19	FV2	6.024	566	32.1	6.2	24.01	4.520	.944	.120				10.1				
	6/19	IM2	26.015	565	32.1	9.2	21.01	17.077	.980	.473				102				
D2	6/19	T54	6.668	585	32.1	6.3	25.8	5.373	.944	.144				10.0				
	6/19	FV4	7.651	567	32.1	5.9	24.31	5.789	.944	.155				10.1				
	6/19	IM4	27.876	566	32.1	9.5	22.6	19.642	.980	.545				116				
D3	6/19	T61	6.304	566	32.1	6.2	24.01	4.731	.944	.126				10.0				
	6/19	IM6	27.507	568	32.1	10.7	21.4	18.288	.980	.508				120				
D4	6/19	T56	9.620	560	32.1	4.9	27.2	8.246	.944	.220				10.0				
	6/19	FV8	5.944	561	32.1	6.9	25.2	4.712	.944	.126				10.1				
	6/19	m8	31.428	561	32.1	12.0	20.1	19.871	.980	.551				118				
D5	6/19	T58	8.486	561	32.1	6.0	26.1	6.887	.944	.186				10.0				
	6/19	FV10	9.772	563	3.1	8.7	23.4	7.167	.944	.192				10.1				
	6/19	IM10	24.704	583	3.1	10.7	21.4	16.571	.980	.460				111				
B1	6/18	T32	8.372	554	30.26	5.8	24.46	6.523	.944	.174	.70	.26	.44	10.0	4.4	25.29	33.72	33.15
	9/8	V4	6.699	556	30.26	6.3	23.96	5.094	.944	.136	1.08	.50	.58	10.1	5.858	43.07	57.43	57.4 B1
	6/18	S4	29.753	554	30.26	11.3	18.96	17.969	.980	.498	.64			117				
B2	6/18	T34	7.774	558	30.26	6.0	24.26	5.965	.944	.159	.56	.26	.30	10.0	3.0	18.57	25.16	24.74
	6/18	A6	12.453	560	30.26	6.6	23.66	9.282	.944	.248	.85	.38	.47	10.1	4.747	19.14	25.52	25.5 B2
	6/18	S2	28.065	558	30.26	10.8	19.46	17.292	.980	.479				114				
B3	6/18	T30	10.277	562	30.26	6.0	24.26	9.829	.944	.209	.64	.26	.35	10.0	3.5	18.18	24.24	23.1
	6/18	A9	6.843	562	30.26	6.4	23.86	5.127	.944	.137	1.04	.70	.34	10.1	3.434	25.0	33.33	33.17
B3	6/18	S6	32.875	562	30.26	12.5	17.86	18.333	.980	.509	.49			151				
B4	6/18	T36	8.377	565	30.26	5.9	24.36	6.394	.944	.171	.65	.26	.39	10.0	3.9	23.03	30.71	30.2
F	6/18	A12	6.582	565	30.26	6.6	23.66	4.864	.944	.130		.34	.34	10.1	3.939	30.03	40.9	39.7
	6/18	S8	29.248	565	30.26	10.7	19.56	17.868	.980	.495				108				
	6/18	T40	8.291	568	30.26	5.6	24.66	6.358	.944	.180	.76	.26	.56	10.0	5	29.11	39.22	38.56

AGRICO

AGRICO

Sample	Vm	OR Toem	Pb	Vac	Pb-Vac	VmSTD	Y	m³/VmSTD	ug/ml	ug/m³	ug/h	vc-t				
F 6/17/79 A1	6.722	568	32.6	6.4	23.86	4.983	.944	.133 ✓	.87	.5	.37	10.1	3.757		28.10	37.96 36.8
I 6/18/79 S10	29.500	568	32.6	12.4	17.86	16.364	.980	.454 ✓				102 106				

AUTO ANALYSER

	VmSTD (m³)	Tot ug	ug/m³	ppb		
S2 A B	.479	19.60	40.92	54.56	53.6A	
S4 A B	.988	19.85	29.82	39.76	39.09	
S10 A B	.454	43.01	99.94	126.3	129.2	
734 A B	.159	3.71	23.33	31.11	30.16	25.16
732	.174	4.711	27.04	36.09	35.5	33.77

GCA/TECHNOLOGY DIVISION ●●▲

BURLINGTON ROAD, BEDFORD, MASSACHUSETTS 01730 / PHONE: 617-275-9000

SHEET_____ OF_____

BY_____

DATE 7/24/70

CH'K. BY_____

DATE CH'K._____

B'K. CH'K. BY_____

JOB NO. 1-451-239

PROJECT 1h2

SUBJECT Imp.ys 1'5/1h   TC

run #		vol Imp me	ug/ml	ug/Total	vmskl m³	ug/m³	PPB ÷ .877
I	1 A	108	0	0			
	B	113	2.00	226			
	T			116	0.476	474.7	~~580~~ .611.
III 3	A	104	0.30	31.2			
	B	104	0	0			
	T			31.2	0.503	52.03	~~75.08~~ 57
2 4	A	154	0.44	67.76			
	B	158	0.24	37.92			
	T			105.68	0.526	200.9	~~245.67~~ 78
5	A	99	0.24	23.16			
	B	112	0.10	11.6			
	T			34.96	0.467	74.86	~~915~~ 96
6	A	134	0.97	129.98			
	B	141	0.43	60.63			
	T			190.61	0.515	370.11	~~455.4~~ 476
9	A	111	1.01	112.11			
	B	132	0	0			
	T			112.11	0.454	246.94	~~304.8~~ 343
10	A	126	0.06	7.56			
	B	108	0.13	14.04			
	T			21.6	0.513	42.11	~~51.47~~ 54
14	A	131	0	0			
	B	129	0	0	0.635	0	0 0
	T						
16	A	116	0.10	15.6			
	A	78	0.80	62.4			
	T			78.0	0.650	120	~~146.7~~ 154
19	A	96	0.91	87.36			
	B	96	0	0			
	T			87.36	.540	161.7	~~1917~~ 201
20	A	141	0	0			
	B	74	0	0			
	T				.613	0	0 0
21	A	111	0	0			
	B	110	.03	33			
	T			124	0.510	6.47	~~7.9~~ 8

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BURLINGTON ROAD, BEDFORD, MASSACHUSETTS 01730 / PHONE: 617-275-9000

SHEET_____ OF_____
BY_____
JOB NO._____
PROJECT_____
SUBJECT_____
CH'K. BY_____
DATE_____
DATE CH'K._____
B'K. CH'K. BY_____

IC

6/18 A+S	1 A	96	0	6					
	B	112	0	0	0.659	0	0	0	
	T								
14 6/18-62 S	2 A	114	0	0					
	B	119	0.8	a̶i̶r̶		150.4	183.4 194	
	T			41.2	0.633				
6/18 A·2S	3 A	108	0	6					
	B	113	0	0	.636	0	0	0	
	T								
6/18 01 S	4 A	117	0	0					
	B	116	0.03	3.48					
	T			3.118	.497	6.99	8.54	9	
S	5 A	114	0	0					
	B	119	0	0	.633	0	0	0	
	T								
S	9 A	112	0.11	12.32					
	B	108	0	0					
	T			12.32	.712	17.30	24.7	72	
S	ω A	102	0.10	10.2					
	B	106	0	0					
	T			10.2	.454	22.46	22.46	29	
M	1 A	115	0	8					
	B	120	0						
	T				.487	0	0	0	
6/14 01	M	2 A	102	0.06	6.12				
	B	105	0	0					
	T			6.12	.473	12.94	15.82 17	
M	3 A	102	0.44	44.88					
	B	108	0.43	46.44					
	T			91.32	.675	135.29	165.4 174	
M 10	A	106	0.45	47.7					
	B	111	0.89	98.79					
	T			146.49	0.460	318.5	388 409	

GCA/TECHNOLOGY DIVISION ●●▲

BURLINGTON ROAD, BEDFORD, MASSACHUSETTS 01730 / PHONE: 617-275-9000

JOB NO._____

PROJECT_____

SUBJECT_____

SHEET____OF____

BY____

DATE____

CH'K. BY____

DATE CH'K.____

B'K. CH'K. BY____

A P

I 19A	.215	96	20.64				
B	.007	96	.67				
T			21.31	.540	39.46	48	5 V
20 A	.135	141	19.04				
B	.028	74	2.07				
T			21.11	.613	34.4	42	54
S 2A	.125	114	19.45				
B	.0	119	0				
T			19.45	.633	31.6	39	50
53 A	.095	108	10.26				
B	.008	113	.91				
T			11.17	.636	17.6	21	27.
54/ A	.115	117	13.46				
B	.02	116	1.39				
T			14.85	.498	29.82	37	48

APPENDIX B-3

FORMAL FIELD PHASE

(a) Lab Results

Agrico - Autoanalyser Results

	mg/l				mg/l	
F 1	.58	5.4944	T 6	.83	7.5245
2	.57	5.3934	7	.57	4.8185
3	.49	4.5854	8	.57	4.8985
4	.75	7.2114	9	—	NOT ENOUGH
5	.80	7.7164	10	.63	5.5045
6	.98	9.5344	11	.96	8.8375
7	.35	3.1714	12	.76	6.8175
8	.99	9.6354	13	.64	5.6055
9	.95	9.2314	14	.83	7.5245
10	.99	7.6354	15	.96	8.8375
11	.73	7.0094	16	.69	6.1105
12	.90	8.7264	17	.76	6.8175
13	.97	9.4334	18	.54	4.5955
14	.97	9.4334	19	.89	8.1305
15	.71	6.8074	20	.81	7.3225
16	.96	9.3324	21	.065	BLANK
17	1.12	10.9484	T 14 F	.20	1.0403
18	.82	7.9184	T 19 F	.17	.7373
19	.88	8.5244	T 20 F	.29	1.8993
20	.84	8.1204	T 21 F	.097	BLANK
21	.036	BLANK			
F 10 C	.21				
F 11 C	.090				
F 20 C	.078				
F 21 C	.036	BLANK			
F 80	.15				
T 1	.58	4.9995			
T 2	1.06	9.8475			
3	.61	5.3025			
4	.95	8.7365			
5	1.04	9.6455			

Small Bottles Agrico Samples
.2 — 2 PPM F

ID	PPM F		ID	PPM F	
F 24 C	.040		T23	.85	4.949
F 25 C	.037		T 25	.69	3.333
F 42 C	.040	BLANK	26	1.16	8.08
T 25 C	.11		27	.72	3.636
T 31 C	.049		28	.63	2.727
T 36 C	.16		29	.79	4.343
T 41 C	.071		30	.69	3.333
T 42 C	.15	BLANK ↑	31	.87	5.151
F 22	1.07	10.4131	32	1.30	9.494
F 23	.99	9.6051	33	.90	5.454
F 24	1.24	12.1301	T 34	.81	4.545
25	.68	6.4741	35	.81	4.545
26	.90	8.6961	36	.79	4.343
27	.60	5.661	37	.68	3.232
28	.68	6.4741	38	2.19	18.483
29	.64	6.0701	39	2.28	19.392
30	.93	8.89911	40	.49	1.313
31	.84	8.0901	41	.93	5.757
32	.84	8.0901	42	.36	BLANK
33	.96	9.3021			
F 34	1.10	10.7161			
35	.88	7.42754			
36	.97	9.4031	F 64 BUGS		
37	.56	5.2621	T 43 Hit Fixer		
38	1.15	11.2211			
39	.75	7.1811			
40	.81	7.7871			
41	.98	9.5041			
42	.039	BLANK			
T 22	.80	4.444			

Agrico AutoAnalyzer Results

F⁻   July 31, 1979

ID	PPM	ID	PPM	ID	PPM
F 50	.59	F 97 *	.045	F 70	.51
F 43 C	.026	F 69 Blank	.055	F 59	.59
F 60	.58	F 80 Blank	.12	F 74	.63
F 44	.49	F 81	.76	F 63	.85
F 58	.55	T 62 C	.11	F 62 C	.035
F 56	.95	T 45	.083	T 66 C	.085
F 44 C	.049	T 52 C	.021 X	F 96	.74
F 95	.99	T 68 C	.092	F 65	.55
F 53	.75	F 72	.59	T 50 C	.094
F 45	.72	F 48 C	.040	F 94	.75
F 52	.81	F 68	.66	F 56 C	.030
F 54	.86	T 58 C	.038	F 101	.67
F 67	.74	F 61	.67	F 49	.71
F 55	1.15	F 43	.44	F 85	.63
F 47	.72	T 51 C	.068	T 75 C	.12
F 89	.70	F 48	.63	T 61	.63
F 66	.61	F 57	.37	T 61 C	.22
T 48 C	.062	T 55 C	.088	F 65	.077
F 69 C Blank	.019	F 57 C	.086	T 60 C	.16
T 59	.069	F 87	.45	T 65	.73
F 70 C	.049	F 51 C X	.055	T 49 C	.19
F 83	.61	F 50 C	.047	F 65 C	.10
F 71	.57	F 97	.70	T 46 C	.14
F 80 C	.041	F 51	.77	T 48 C	.098
F 56 C	.081	F 62	.23	T 47 C	.10
F 75	.60	T 54 C X	.077	T 62	.55
F 90	.56	F 63 C	.057	T 52	.90
F 88	.84	F 55 C	.039	T 54	.91 8.332
F 71 C	.040	F 73	.75	T 55	.90
F 49 C	.055	F 46	.66	T 64	.74

C = Controls

Agrico Auto Analyzer results
July 31, 1979

I.D.	PPM	F^-
r 4.5	.84	
r 47	.75	
r 46	.70	
r 48	.65	
T 75	.084	
T 51	.96	8.989
T 66	.94	
T 58	.60	
T 68	.60	
T 56	.69	
T 50	.81	.81 ÷ 12 = 6.969
T 60	.79	
T 44	.80	
T 57	.69	
T 49	.12	
T 67	.66	
T 43	.54	

HF Samples - IC Results

8-9-79

sample	conc. (ug/ml)	sample	conc. (ug/ml)
✓F1	1.97/2.01	✓F27	1.97
✓F2	1.80	✓F28	1.88
✓F3	1.73	✓F29	1.88
✓F4	2.33	✓F30	2.32/2.25
✓F5	1.49	✓F31	1.82
F6	*	✓F32	1.88
✗F7	0.86	✓F33	1.97
F8	*	✓F34	2.32
✓F9	1.58	✓F35	2.07
✓F10	1.61/1.67	✓F36	2.32/2.28
✓F11	1.63	✓F37	2.23
F12	*	✓F38	2.25
F13	*	·F39	1.93
✓F14	1.61	✓F40	2.16
✓F15	1.72	✓F41	1.88
F16	1.98	✓F42 ✗	1.39
✓F17	1.97	T1	0.97/1.24/1.05/1.03
✓F18	1.83/1.86	T2	1.73
·F19	1.86	T3	0.88/0.93
·F20	1.61	T4	1.37
F21	1.44 ←	T5	1.43
✓F22	1.52	T6	1.26
✓F23	2.08	T7	1.15
✓F24	2.08/2.17	T8	1.37
F25	2.72	T9	0.63/0.69
·F26	2.53	T10	1.19

* not enough sample

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T11	1.42

HF samples   IC Results

sample	conc. (μg/ml)
T12 ✓	1.04/1.04
T13 ✓	1.01
T14 ✓	1.04/1.03
T15 ✓	1.23/1.26
T16 ✓	1.02
T17 ✓	1.08
T18 ✓	0.77/0.82
T19 ✓	1.26
T20 ✓	1.24
T21	0.58 ← Blk.
T22 ✓	1.12
T23 ✓	1.15
T25 ✓	1.03/1.08
T26 ✓	1.65
T27 ✓	0.98
T28 ✓	1.21
T29 ✓	1.05
T30 ✓	1.85/1.87
T31 ✓	1.24
T32 ✓	2.15/2.08
T33 ✓	1.39
T34 ✓	1.28
T35 ✓	1.28
T36 ✓	1.26
T37 ✓	0.97/0.92
T38 ✓	2.53

sample	conc. (μg/ml)
T39 ✓	2.47
T40 ✓	0.76
T41 ✓	1.17
T42	0.73 ← Blk.
F10C	0.28/0.22
F11C	0.70
F20C	0.83
F21C	1.01
F24C	0.63
F25C	0.37
F42C	1.13/1.13
T25C	2.86
T31C	1.91
T36C	0.25/0.25
T41C	1.08
T42 (not enough for diln.)	~5.5 (higher than highest std. of 5ppm)
T14F	0.32
T19F	1.20
T20F	0.43
T21F	0.33/0.28
I80	0.89

APPENDIX B-3

FORMAL FIELD PHASE

(b) Calculations

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(+) BASED ON **AUTO** ANALYZER   FILTERS ONLY

(*) BASED ON **ION** Chromatoscopy

NM = NO MEASUREMENT

Date	Plant	Run #	Site	Sample #	Vm m³	F (tot) conc.	ug F/m³	µg HF /m³	ppb HF *.818	total ug F	µg/m³ F	(*.818) ppb HF
7/24	CFI	1	A	F3	.225	4.585	20.38	21.46	26.23	2.93	13.71	16.76
			B	F1	.196	5.494	28.03	29.52	36.09	5.56	29.84	36.48
			C	F2	.187	5.393	28.53	30.04	36.72	3.64	20.26	27.77
			D	F4	.231	7.211	31.22	32.87	40.18	8.99	42.78	50.10
								Avg ppb = 34.81			Avg ppb = 32.93	
7/24	CFI	3	A	F7	.264	3.171	12.01	12.65	15.46	NM	NM	NM
			B	F5	.215	7.716	35.89	37.79	46.23	2.51	2.47	3.02
			C	F10	.240	9.635	40.15	42.28	51.69	2.02	8.86	10.83
			D	F8	.236	9.635	40.82	42.98	52.54	NOT	ENOUGH	sample taken
								AVG. ppb = 41.47			AVG. ppb = 6.73	
7/24	CFI	5	A	F11	.280	7.009	25.03	26.36	32.22	1.92	7.22	8.83
			B	F9	.246	9.231	37.52	39.51	32.32	1.41	6.05	4.95
			C	F6	.239	9.534	39.89	42.00	34.36	NOT enough sample taken		
			D	F12	.239	8.726	36.51	38.46	31.46	NM	NM	NM
								AVG. ppb = 32.57			AVG. ppb = 6.87	
7/24	CFI	7	A	F15	.250	6.807	27.23	28.67	35.05	2.83	11.91	14.56
			B	F17	.247	10.949	44.33	46.68	57.07	5.35	22.82	27.90
			C	F14	.242	9.453	38.98	41.05	50.18	1.72	7.47	9.13
			D	F16	.242	9.332	38.56	40.60	49.63	5.45	23.73	29.01
								Avg. ppb 47.98			Avg ppb 20.15	
7/24	CFI	9	A	F19	.248	8.524	34.37	36.19	44.24	4.24	18.01	22.02
			B	F13	.251	9.433	37.58	39.57	48.37	NOT ENOUGH SAMPLE taken		
			C	F18	.239	7.918	33.13	34.89	42.65	4.09	18.02	22.03
			D	F20	.231	8.120	35.15	37.01	45.24	1.72	7.83	9.57
								Avg ppb 45.13			Avg ppb 17.87	

(+) BASED ON AUTO ANALYZER
(*) BASED ON ION CHROMATOGRAPHY
NM = NO MEASUREMENT

Filters only

Date	Plant	Run#	Site	Sample#	V_m std m³	F (tot.) conc.	ug F/m² x 1.053	ug/m³ HF ÷ .818	ppb HF (+)	total ug F (*)	ug/m³ HF (*)	ppb HF (÷.818)(*)
7/25	CFI	11	A	F27	.244	5.661	23.20	24.43	29.87	5.86	25.28	30.90
			B	F37	.248	5.262	21.22	22.34	27.31	8.48	36.01	44.12
			C	F25	.232	6.474	27.11	29.37	35.93	13.43	60.97	74.54
			D	F32	.237	8.090	34.14	35.95	43.75	4.95	21.99	26.88
								Avg ppb = 34.27			Avg ppb = 44.39	
7/25	CFI	13	A	F28	.244	6.474	26.53	27.94	34.16	4.95	21.36	26.11
			B	F38	.255	11.221	44.68	47.26	57.76	8.69	36.59	44.73
			C	F26	.261	8.696	33.32	35.08	42.89	11.51	46.45	56.78
			D	F33	.242	9.302	37.32	39.30	48.04	5.86	25.49	31.16
								Avg ppb = 45.71			Avg ppb = 37.70	
7/25	CFI	15	A	F29	.245	6.070	24.78	26.89	31.89	4.95	21.29	26.00
			B	F39	.269	7.181	26.70	28.12	34.38	5.45	21.55	26.10
			C	F22	.263	10.413	39.59	41.69	50.97	1.31	5.26	6.43
			D	F34	.183	10.716	(*)58.56	61.66	75.38	9.39	54.05	66.08
								Avg ppb = 48.16			Avg ppb = 31.15	
7/25	CFI	17	A	F30	.243	9.900	40.74	42.90	52.44	9.04	39.17	47.89
			B	F40	.269	7.787	28.95	30.48	37.26	7.78	30.44	37.21
			C	F23	.261	9.605	36.80	38.75	47.37	6.97	28.12	34.38
			D	F35	.228	7.428	32.58	34.31	41.93	6.87	31.73	38.79
								Avg ppb = 44.75			Avg ppb = 39.57	
7/25	CFI	19	A	F31	.243	8.090	33.29	35.05	42.85	4.34	18.82	23.01
			B	F41	.228	9.504	41.68	43.89	53.66	4.95	22.86	27.95
			C	F24	.259	12.130	46.83	49.31	60.28	7.42	30.18	36.89
			D	F36	.228	9.4031	41.24	43.43	53.09	9.19	42.45	51.89
								Avg ppb = 52.47			Avg ppb = 34.9?	

(*) Take value after sampling

⊕ BASED ON AUTO ANALYZER
NM= NO MEASUREMENT.
⊕

<u>Filters Only</u>

Date	Plant	Run#/Site	Sample#	V_m STD m³	F⁻(tot.) conc.	ug F/m³	ug HF ×1.053	ppb HF ÷.818
7/26	AGRICO	21 A	F43	.257	3.889	15.13	15.93	19.47
		B	F57	.213	3.182	14.94	15.73	19.23
		C	F64	.269	No Sample			
		D	F50	.227	5.404	23.806	25.07	30.65
							AVG. PPB=	23.12
7/26	AGRICO	23 A	F44	.257	4.394	17.10	18.01	22.02
		B	F58	.239	5.000	20.92	22.03	26.93
		C	F65	.238	5.000	21.01	22.12	27.04
		D	F51	.229	7.222	32.24	33.95	41.50
							AVG. PPb=	29.37
7/?	AGRICO	24 A	F45	.257	6.717	26.14	27.53	33.66
		B	F59	.238	5.404	22.71	23.91	29.23
		C	F66	.225	5.606	24.92	26.24	32.08
		D	F42	.227	7.626	33.59	35.38	43.25
							AVG. ppB=	34.56
7/28	Agrico	26 A	F46	.257	6.111	23.78	25.04	30.61
		B	F60	.237	5.303	22.38	23.56	28.80
		C	F67	.266	6.919	26.61	28.02	34.25
		D	F53	.215	7.020	32.65	34.38	42.03
							AVG. PPb=	33.92
7/28	Agrico	27 A	F47	.247	6.717	27.19	28.63	35.00
		B	F61	.237	6.212	26.21	27.60	33.74
		C	F68	.225	6.111	27.76	28.60	34.96
		D	F54	.227	8.131	35.82	37.72	46.11
								39.45

Filters only

DATE	PL	#/%		V_m m³	F (H₂O) cfm	µg/	$\times$ 1.053	÷.818 H=
7/24	Agrico	21 A	F48	.255	5.151	26.30	3.31	26.00
		B	FG2	.242	6.161	25.46	26.7	32.78
		C	F01	.251	6.464	28.476	21.18	36.66
		D	F60	.23	5.47	45.78	46.41	59.19
							AVG PPE=	38.66
7/24	Agrico	30 A	F-7	.25+	5.959	23.	24.73	30.20
		B	F63	.251	7.373	8.24	29.75	36.37
		C	F	.224	5.555	24.80	26.11	31.72
		D	F	.314	8.383	39.17	41.25	50.43
							AVG. PPE =	37.23
7/26	Agrico	32 A	F72	.2	4.747	17.65	18.56	22.71
		B	F01		NO SAMPLE (moisture?)				
		C	F13	.181	3.838	21.0	23.33	27.50
		D	F14	.215	6.343	29.51	31. 6	38.09
							AVG PPE=	29.37
7/26	Agrico	33 A	F73	.253	6.243	24.95	26.28	32.13
		B	F	.051	5.352	25.31	26.72	32.66
		C	F01	.031	5.345	25.13	26.47	32.36
		D	F75	.216	8.787	40.68	4.24	52.37
							AVG. PPE=	37.38
7/26	B	A	F	.051	5.151	17.81	23.74	55.60
		B	F89	.051	5.153	23.24	4.58	30.04
		C	F65	.222	5.151	2.21	24.54	36.0
		D	F16	.27	6.356	30.6	31.85	38.74
							AVG. PPE =	31.15

④ BASED ON Auto Analyzer

Filters Only

Date	Plant	Run#/site		Sample#	Vm std/m³	F⁻ (tot) conc.	ug F/m³	ug HF/m³ × 1.053	④ ppb HF ÷ .818		
7/16	Agrico	36	A	F 75	.255	4.848	19.01	20.02	24.47		
			B	F 90	.259	4.444	17.16	18.07	22.09		
			C	F 83	.223	4.949	22.19	23.38	28.57		
			D	F 97	.224	5.858	26.15	27.54	33.67		
								AVG. ppb	27.20		

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⊕ Based on Auto Analyzer

✳ Based on Ion Chromatograph.

Tubes only

Date	Plant	Run #	Site	Sample #	V in Std. m³	F⁻ (Total) conc.	µg F⁻/m³	µg HF⁻/m³ ⊕ x 1.053 ÷ .818	ppb HF	✳ µg/m³ F	✳ ppb HF
7/24	CFI	2	A	T7	.239	4.17	20.0	21.59	26.39	5.70	25.36 5.00
			B	T10	.507	5.505	20.62	21.71	36.54	6.16	24.30 29.71
			C	T1	.243	5.333	23.32	30.67	26.49	4.49	19.46 55.79
			D	T7	.24	8.31	43.26	42.31	51.82	7.18	58.72 47.55
								Avg. ppb = 32.81		Avg. HF = 26.16	
7/24	CFI	4	A	T3	.251	5.33	21.13	22.25	27.30	3.28	13.77 5.83
			B	T2	.270	9.548	33.16	35.76	43.72	11.62	42.17 51.55
			C	T5	.241	1.646	40.02	42.14	51.52	8.59	37.51 45.76
			D	⊕ T8	.237	4.17	20.69	21.17	26.1	7.98	5.6 4.0
								Avg. ppb = 37.26		Avg. HF = 37.31	
7/24	CFI	6	A	T11	.256			6.35	44.44	2.36	51.10 42.0
			B	T17	.241	.818	20.1	1.77	4.45	7.35	32.0 36.77
			C	T9	.262	not enough tube				.81	5.0 4.18
			D	T12	.24	6.04	30.1	5.1	6.3	7.6 29.5	34.82
								Avg. ppb = 31.09		Avg. HF = 24.66	
7/24	CFI	8	A	T15	.24	8.232	36.2	37.83	46.25	.36 28.76	35.16
			B	T18	.248	4.516	18.53	19.51	23.85	2.17 9.22	11.27
			C	T14	.242	7.53	31.0	32.	40.14	4.60 20.5	24.45
			D	T16	.259	6.11	25.52	34.8	39.68	4.44 17.56	21.71
								Avg. ppb = 34.96		Avg. ppb = 23.70	
7/24	CFI	10	A	T7	.247	8.131	32.92	34.66	42.37	6.87 27.29	35.81
			B	T6	.24	7.525	30.84	32.47	39.69	6.87 29.64	36.23
			C	T13	.241	5.606	23.26	24.49	29.94	4.34 18.96	23.18
			D	T20	.236	7.323	31.03	32.67	37.94	6.67 29.74	36.36
								Avg. ppb = 37.99		Avg. ppb = 32.70	

✳ TUBE BROKE AFTER SAMPLING

⊕ BASED ON AUTO ANALYZER
✱ BASED ON ION CHROMATOGRAPHY

Tubes or ↓

Date	Plot	Km#	Site	Sample#	Vm std. m³	F-(tot) conc.	µg F m³	µg HF m³ ✕ 1.053	⊕ HF HF ÷(.818)	✱ F⁻ µg/m³	✱ µg/m³ HF	✱ HF F⁻
7/25	CFI	12	A	T27	.245	3.636	14.84	15.63	19.11	2.53	10.87	13.29
			B	T37	.277	3.232	11.67	12.29	15.02	3.17	8.25	10.09
			C	T22	.262	4.444	16.96	17.86	21.83	3.94	15.64	19.36
			D	T32	.240	9.494	39.56	41.66	50.93	13.99	61.37	75.02
								avg. ppb=	26.72		avg. ppb=	29.44
7/25	CFI	14	A	T28	.247	2.727	11.04	11.63	14.22	4.85	20.68	25.28
			B	T36	.279	18.480	73.57	86.55	98.30	17.57	74.72	91.57
			C	T23	.260	4.949	19.03	20.04	24.50	4.24	17.18	21.00
			D	T33	.241	5.454	22.63	23.13	29.13	6.67	29.14	35.62
								avg. ppb=	41.51		avg. G ppb=	43.37
7/25	CFI	16	A	T29	.249	4.343	17.44	18.36	22.44	3.23	13.68	16.72
			B	T31	.235	19.393	82.52	86.89	106.22	17.57	78.75	96.27
			C	T24	.241		SAMPLE				VOID	
			D	T34	.240	4.545	16.91	17.79	21.78	5.56	24.37	29.77
									51.01			47.51
7/25	CFI	18	A	T30	.247	3.333	13.49	14.20	17.36	11.41	48.66	59.49
			B	T40	.243	1.313	5.403	5.69	6.96	.303	1.31	1.60
			C	T26	.260	8.808	33.88	35.68	43.62	9.29	37.63	46.00
			D	T35	.242	4.545	18.78	19.78	24.18	5.56	24.19	29.57
								avg. ppb=	23.03		avg. ppb=	34.18
7/25	CFI	20	A	T31	.243	5.151	21.20	22.32	27.29	5.15	22.32	27.29
			B	T41	.243	5.757	23.69	24.95	30.50	4.44	19.26	23.55
			C	T25	.260	3.333	12.82	13.50	16.50	3.28	13.29	16.25
			D	T36	.237	4.343	18.32	19.29	23.58	5.35	23.78	29.07
								avg. ppb=	27.47		avg. ppb=	24.04

(+) Crl·· ⊙ HT. H·H··FE   T··c··· q

Date	Plant	Run#	Site	Sample#	Vm std.	F (tot) conc.	µg F/m³	µs/m³ x 1.555	⊕ ppb HF ÷(818)
7/25	Agrico	25	A	T43	.262	6.242	16.7	17.15	20.11
			B	T57	.242	5.73	62.85	··.··	29.41
			C	T64	.221	6.052	26.21	23.77	28.69
			D	T50	.624	6.761	31.11	32.16	40.55
								Avg. ppb =	29.75
7/26	Agrico	25	A	T44	.251	6.868	26.52	27.76	34.13
			B	T58	.249	4.648	26.00	21.27	26.00
			C	T65	.250	6.751	26.71	28.61	35.70
			D	T51	.236	8.484	35.64	37.55	45.88
								Avg. ppb =	35.43
7/26	Agrico	28	A	T45	.254	7.272	28.63	30.15	36.86
			B		NO	SAMPLE	TAKEN		
			C		NO	SAMPLE	TAKEN		
			D	T52	.225	7.872	35.01	36.87	45.07
								Avg. ppb =	40.17
7/30	Agrico	31	A	T46	.256	6.222	24.30	25.59	31.28
			B	T63	.245	5.212	21.27	22.40	27.38
			C	T66	.233	8.282	35.54	37.43	45.76
			D	T54	.247	8.332	33.73	35.53	43.42
								Avg. ppb =	36.96
7/26	Agrico	34	A	T47	.256	6.727	26.27	27.67	33.83
			B	T61	.237	5.516	23.27	24.50	29.95
			C	T67	.224	5.818	25.97	27.35	33.40
			D	T55	.218	7.878	36.13	38.05	46.52
								Avg. ppb =	35.93

⊕ BASED on Auto AnalyzER

<u>Tubes Only</u>

Date	Plant	Run #	Site	Sample #	$Vm \frac{std.}{m^3}$	$F^- (\#x)$ conc.	$\frac{\mu g F}{m^3} \times 1.053$	$\frac{\mu g HF}{m^3}$ ⊕ $(\div .118)$ ppb HF			
7/20	Agrico	37	A	T48	.283	5.727	22.20	21.27	26.00		
			B	T62	.238	4.707	19.77	20.82	25.45		
			C	T68	.222	5.212	23.47	24.72	30.22		
			D	T56	.223	6.120	27.45	28.90	35.33		

Avg. ppb = 29.25

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APPENDIX C

ROSE RESULTS

ROSE #	START		AREA SUBTRACT BY COMPUTER 5/80	ABSORBANCE SUBTRACT BY HAND — r — K from Data Ave 3/81	AREA SUBTRACT BY COMPUTER 3/81	
CFI 3	7:57					
4	8:59					
5	9:10					
6	9:31					
7	10:07					
(3-7)	xx					
CFI 9	10:37		43	42		*Obtained by averaging the
10	11:19		40	39		spectra in each group,
11	11:52		41	40		then calculating concentration
13	12:27		39	43		
14	12:43		30	30		
15	13:04		43	43		
16	13:26	*	34	32		
(9-16)	xx	(Data Ave)	39	38		
CFI 17	8:10		X	(22)		
18	8:30		28	27		
19	9:42		27	28		
20	10:10		27	32		
21	10:27		39	39		
22	10:49		27	28		
23	11:15		30	29		
24	11:33		39	38		
25	11:54		36	38		
26	12:14		41	43		
(17-26)	xx	(Data Ave)	33	34		
AGR 30	10:38		21	21		
31	11:06		25	23		
32	11:30		37	32		
33	11:49		33	35		
34	12:09		35	36		
35	12:30		40	41		
36	12:51		55	34		
38	13:11		41	38		
(32-38)	xx	(Data Ave)	42	37		
AGR 40	15:36		X	(35)		
41	15:48		40	39		
42	16:07		43	41		
43	16:32		38	37		
44	17:04		62	46	44	
45	17:32		59	46	48	
46	17:46		37	37	42	
47	18:09		46	41	47	
48	18:30		46	38	40	
(40-48)	xx	Data Ave	41	40		

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APPENDIX D

SAMPLING EQUIPMENT CALIBRATIONS

I.   Dry Gas Meters for Laboratory Phase

II. Dry Gas Meters and RAC Control Box for Preliminary
     Field Phase

III. RAC Control Boxes for Final Field Phase

APPENDIX D-1

DRY GAS METERS FOR LABORATORY PHASE

Leak Test @ 15 psi   3/3?/79

Ambient { BAR. 30.28
         { Temp. 62

CFM/60 sec.

K d 9/c.

D.G.M Calibration 59338

Time	Δ H MAN	D.G. Initial	D.G. Final	D.G. Net	W.T. Initial	W.T. Final	W.T. Net	D.G.T.°F In	D.G.T.°F Out	W.T.M. T. °F	W T
0											
2	.5	530·5?0			12	17		59	61	63	
4		531·24						59	61		
6	14:18	532·??	$Y = .?5/$		$\Delta HQ = 2.250$			59	61		
8		532 9··						59	61		
10	14.??	53?·??						60	62		
12		534·??						60	62		
		53?·7·						60	62	6?.429	
				53?·? ?.?0?							
	?.44	53? ?·??			?8	23		60	62	63	
		53?·??	$Y = .978$					60	62		
	?.7??	53?·??			$\Delta HQ = 2.083$			60	62		
		53?·						62	62	61.0	
				5? ?57 5?.?							
	.5?										

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LEAK Test @ 15 psi   3/31/79   K   Bar. 30.26 "Hs
_____ CFM/60 sec.   Ambient { Temp. 66 °F

D.G.M Calibration 642440 wide orifice

Time	Δ H MAN	D.G. Initial	D.G. Final	D.G. Net	W.T. Initial	W.T. Final	W.T. Net	D.G.T.°F IN	D.G.T.°F OUT	W.T.M. T. °F	W.T.M Ps
0	.5	909.845			26	37		67	66	63	
2											
4		910.25						68	66		
6		910.66						67	66		
8	25.09	911.07	Y .982			ΔH 6.585		67	66		
10		911.47						67	66		
12	25.15	911.88						67	66		
		912.29						67	66		
		912.70						67	66		
		913.10						67	66		
		913.51						67	66		
		914.32						67	66	66.5	
			914.967	5.122							
0	1	916.005			32	37			67	63	
2		916.60							67		
4	17.35	917.18							67		
6		917.77							67		
8		918.40	Y=.968			ΔH=6			67		
10	17.583								67		
12		919.55									
14		920.14									
16		920.74									
18			921.202	5.197						67.5	
20											

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APPENDIX D-2

DRY GAS METERS AND RAC CONTROL BOX
FOR PRELIMINARY FIELD PHASE

LEAK TEST @ 15 V   # 5/33?12   BAR 30.19

CFM / 60 sec.

D.G.M. CALIBRATION   62

K. Joyce   # 642437

TIME	Δ H MAN	D.G. INITIAL	D.G. FINAL	D.G. NET	W.T. INITIAL	W.T. FINAL	W.T.		RPM T°F	BAR
0	.5	134.075			77				65	
2		134.73								
4		134.00	$Y = 1.014$ ΔH@ =							
6	15:30	136.02	2.599							
8		136.7								
10		137.32					80 70			
12	15.5	137.96					80 70			
14			139.094	5.019			70 70		75000	30.19
0	.5	140.095			13	18	70 71		65	
2		140.74					80 71			
4		141.38					80 71			
6	15:36	142.02	$Y = 1.017$ ΔH@ = 2.630				80 71			
8		142.66					80 71			
10	15.60	143.00					80 71			
12		143.95					80 71			
14		144.59					80 71			
16			145.102	5.007			80 71		75.50	30.19
0	1	146.150			19	24	80 71		65	
2		147.09					80 71			
4	10:63	148.01	$Y = 1.011$ ΔH@ = 2.560				80 71			
6		148.94					80 71			
8	10.888	149.86					80 71			
10		150.78					80 71			
			151.183	5.033					75.5	30.19
0	1	152.189			25	30	71 80		65	
2		153.10					71 80			
4	10:59	154.20	$Y = 1.012$ ΔH@ = 2.608				71 80			
6		154.93					71 80			
8	10.983	155.85					71 80			
10		156.77					71 80			
			157.217	5.028					75.5	

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CFM / 60 SEC

K. Jay:

5/30/79

D.G.M CALIBRATION
385

V	Δ m MAN	D.G INITIAL	D.G FINAL	D.G NET	W.T INITIAL	W.T FINAL	W.T NET	DGM T°F IN	OUT	W.T.M T°F	W.T.M PS
0	.5	860.925				41		68	62	65	
2		8,11						68	62		
4	14.11	861.53						68	62		
6		862.56	Y=.995		ΔH@=2.207			68	62		.5
8	14.183	863.80						68	62		
10		865.73						68	62		
12		867.67						68	62		
14			865.490 5.042					68	62	62.5	
0	.5	866.470			42	47		68	67	65	
2		867.12						68	67		
4	14.09	867.90						68	67		
6		868.97	Y=.996		ΔH@=2.176			68	67		
8		869.32						68	67		30.20
10	14.150	870.03						68	67		
12		870.74						68	67		
14			871.506 5.03					68	62	67	
0	1	875.615			51	56		68	67	65	
2		876.65						68	62		
4	10.00	877.64	Y=.993		ΔH@=2.194			68	67		
6		878.65						68	67		30.20
8	10.00	879.66						68	67		
		880.662 5.04						68	67	67.5	
0	1	881.675			57	62		69	67	65	
2		882.72						60	67		
4	10.03		Y=.993		ΔH@=2.314			69	67		
6								69	67		30.2
8	10.00							69	67		
		886.85 5.050						69	67	68.00	

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① CFM / 60 sec.

D.G.M. CALIBRATION
667384

4/6	ΔH MAN	D.G. INITIAL	D.G FINAL	D.G NET	W.T. INITIAL	W.T. FINAL	W.T. NET	D.G.T. IN OUT	W.T.M. T°F	BR
0	.5	546.636			66	71		61 63	65	
2		547.33						61 63		
4		548.02						61 64		
6	15.09	548.72	y = .947		ΔH@=2.5??			61 64		
8		549.40						61 64		30.20
10	15.150	550.00						61 65		
12		550.71						61 65		
14		551.48						61 70	62.375	
			551.882	5.296						
0	.5	552.935			72	77		61 64	65	
2		553.65						61 64		
4	14.35	554.37	y = .945		ΔH@=?.?55			61 64		
6		555.09						61 64		
8		555.81						61 64		30.?0
10	14.583	556.54						62 64		
12		557.26						61 64	62.5	
14			558.197	5.262						
0	1	559.250			78	83		61 65	65	
2		560.27						61 65		
4	10.17	561.30	y = .940		ΔH@=2.340			62 65		30.20
6		562.32						61 65		
8		563.35						61 65	63.0	
10	10.283		564.535	5.285						
0	1	565.595			84	89		62 66	65	
2		566.63						62 66		
4	12.02	567.66	y = .943		ΔH@=3.287			62 66		30.??
6		568.70						62 66		
8	12.20	569.74						62 66	64.00	
10			570.872	5.277				62 66		

APPENDIX D-3

RAC CONTROL BOXES FOR FINAL FIELD
SAMPLING PHASE

Date _____6/1/1969_____   Box No. _____S-1725_____

Barometric pressure, P_b _____30.30_____ in. Hg   Dry gas meter No. _____

1 Orifice manometer setting, ΔH, in. H_2O	2 Gas volume wet test meter V_w, ft^3	3 Gas volume dry gas meter V_d, ft^3	4 Temperature				6 Time θ, min	γ	ΔH_θ	Deviation
			Wet test Meter t_w, °F	Dry gas meter						
				Inlet t_{di}, °F	Outlet t_{do}, °F	Average t_d, °F				
0.5	5	5.202	69	94.4	85.2	89.8	9.47	1.001	1.687	.001
1.0	5	5.187	69	95.28	86.42	90.857	12.300	1.00	1.583	.002
2.0	10	10.241	69	89.10	78.6	83.9	12.6	.997	1.709	.003
4.0	10	10.370	69	104.67	83.5	94.061	9.317	1.28	1.835	.002
6.0	10	10.350	69	104.60	88.20	98.9	7.60	1.000	1.836	.004
8.0	10	10.398	69	112.70	91.250	102.5	6.00	1.003	1.499	.001
						Average		1.002	1.443	

Calculations

ΔH	$\dfrac{\Delta H}{13.6}$	γ $\dfrac{\dot{V}_w\, P_b\, (t_d + 460)}{V_d\left(P_b + \dfrac{\Delta H}{13.6}\right)(t_w + 460)}$	ΔH_θ $\dfrac{0.0317\,\Delta H}{P_b\,(t_d + 460)}\left[\dfrac{(t_w + 460)\,\theta}{V_w}\right]^2$
0.5	0.0368		
1.0	0.0737		
2.0	0.147		
4.0	0.294		
6.0	0.431		
8.0	0.588		

γ = Ratio of accuracy of wet test meter to dry test meter.   Tolerance = ± 0.01

ΔH_θ = Orifice pressure differential that gives 0.75 cfm of air at 70° F and 29.92 inches of mercury, in. H_2O.   Tolerance = ± 0.15

Leak Test @ 15 psi

0.00 CFM/60 sec

Ambient { BAR. 30.30 "H
Temp. 74 °F

D.G.M Calibration S-1725

Time	ΔH MAN	D.G. Initial	D.G. Final	D.G. Net	W.T. Initial	W.T. Final	W.T. Net	D.G.T.°F in	out	W.T.M. T.°F	W.T. Px
0	1.0	885.20			70			83	99	69°	
2		886.57						84	99		
4		887.70						84	99		
6		888.845						84	99		
8	8.050 min	889.01						84	99		
10		890.585	890.585	5.65	75	5		85.8	99	91.4	70.0
12											
0	1.0	877.755			76			85	91	69°	.3
2		822.1						85	93		
4		824.6						85	95		
6		825.8			81	5		86	96		
8	9 min	826.7						85	97		
10		826.547		5.787				86.2	94.4		
8.917 min											
0	.5	897.994			72			86	84	69°	.3
2		898.6						85	95		
4		899.6						86	96		
6		900.5						86	96		
8		901.3			87	5		86	97		
10		902.5						87	97		
12		903.1						87	97		
14	(MIN)	903.194	903.110	5.200				86.429	95.286		
								Avg T 90.857			
0	2.0	904.515			95			78	81		
2		905.84						78	82		
4		907.47						78	85		
6		909.70						78	90		
8		910.85						79	92		
10		912.85						79	85		
12	2.6 min	913.97						80	87		
		914.156	914.156	10.341	107			78.6	89.743	83.9 Avg T	
0	2.0	915.85						96	82		
2								102	82		
4								103	83		
6	7.30 min							103	84		
8		925.70						104	75		
		925.765	925.751	10.390	19			103.167	83.500	94.084 Avg	

Y=1.009
ΔH@=1.695

Y=1.001
ΔH@=1.557

Y=1.001
ΔH@=1.573

Y=.997
ΔH@=1.709

Y=
ΔH@=

Leak test @ 15 psi

0.00 CFM / 60 sec.

Ambient { BAR. _____ / Temp. __74__

D.G.M Calibration S-1725

Time	Δ H MAN	D.G. Initial	D.G. Final	D.G. Net	W.T. Initial	W.T. Final	W.T. Net	D.G.T. °F In	out	W.T.M. T °F	W
0	6.0	926.810			20			102	87	69	
2		929.50						107	87		
4		932.20		Y = 1.00€				110	88		
6	7.10	934.915		ΔH@ = 1.936				112	89		
8		937.160	927.160	10.350				112	88		
10						30		108.0	87.88		
12										98.9 Avg	
0	8.0	939.283			22			110	90		
2		942.70						113	91		
4	6.0	946.16						112	92		
6		949.643	939.643	10.398				114	92		
8						32		113.250	91.250		
			Y = 1.003							102.50 Av	
			ΔH@ = 1.499								

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Date _6-1-79_   Box No. ___

Barometric pressure, P_b ___ in. Hg   Dry gas meter No.

Orifice manometer setting, ΔH, in. H₂O	Gas volume wet test meter V_w, ft³	Gas volume dry gas meter V_d, ft³	Temperature wet test meter t_w, °F	Temperature dry gas meter inlet, °F	outlet, °F	Average, °F	θ, min	Y	$\Delta H_@$	
0.5		5.251	65				92.214	3.567	1.000	1.929	.00
1.0		5.185	65				87.0	9.833	1.002	2.076	.002
2.0		10.638	65				123.4	14.150	1.00	2.057	.001
4.0		10.731	65				108.8	10.217	1.000	2.124	.009
6.0		12.364	62				94.3	8.35	1.010	2.167	.01
8.0		10.456	65				140.25	7.35	1.002	2.295	.0
							Average		1.004	2.086	

Calculations

$$\frac{\Delta H}{13.6} \qquad \frac{V_w P_b (t_d + 460)}{V_d (P_b + \frac{\Delta H}{13.6})(t_w + 460)} \qquad \frac{0.0317 \Delta H}{P_b (t_d + 460)}\left[\frac{(t_w + 460)\theta}{V_w}\right]^2$$

ΔH	$\dfrac{\Delta H}{13.6}$		
0.5	0.0368		
1.0	0.0737		
2.0	0.147		
4.0	0.294		
6.0	0.431		
8.0	0.588		

Y = Ratio of accuracy of wet test meter to dry test meter   61

$\Delta H_@$ = Orifice pressure differential that gives 0.75 cfm of air at 68°F ...   29.92
     tolerance ± 15

$Y = 1.$

$\Delta H_@$

K.J. 3/3/79   R.A.C.   ~~D.G.M~~ Calibration ~~2749~~ 1726

Ambient Temp. 65

Time	ΔH MAN	D.G. Initial	D.G. Final	D.G. Net	W.T. Initial	W.T. Final	W.T. Net	D.G.T.°F In	Out	W.I.M. T.°F	
0	.5	148.782			54	59		102	82	65	
2		146.56						102	83		
4	13.34	147.32	Y=1.000		ΔH@=1.929			103	84		
6		148.10						103	85		30.
8	13.557	148.86						104	86		
10		149.64						105	87		
12		150.42						105	87	92.24	
			151.031	5.251							
0	.1	137.545			48	53		92	76	65	
2		140.60	Y=1.002		ΔH@=2.046			94	77		
4	9.50	141.65						96	78		30.
6		142.70						98	79		
8	9.823	143.75						100	80	97.00	
10			144.730	5.185							
0	2	154.465			62	72		111	90	65	
2		155.76						113	91		
4	14.09	157.47						114	91		
6		168.97	Y=1.003		ΔH@=2.057			115	92		30.
8	14.150	160.47						115	93		
10		161.98						116	93		
12		163.48						116	94	103.143	
14			165.103	10.638							
0	4	168.300			45	55		120	96	65	
2		170.40						120	96		
4	10.13	172.50	Y=1.000		ΔH@=2.124			121	97		30.
6		174.40						121	97		
8	10.217	176.50						122	98	108.8	
			179.031	10.731							
0	6	228.725			35	42		105	78	62	
2		230.19						107	80		30.
4	8.81	232.60	Y=1.010		ΔH@2.157			108	81		
6		235.16						109	82		
8	8.35	237.65						110	83	94.3	
10			238.919	10.364							
0	8	245.375			57	69		112	86	62	
2		248.20	Y=1.007		ΔH@=2.205			113	87		
4	7.21	251.04						113	88		30.
6		253.90						114	89	100.25	
8	7.35		255.456	10.456							

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Date ___6/6/77___   Box No. __2282__

.Barometric pressure, P_b = 30.07 in. Hg   Dry gas meter No. _____

Orifice manometer setting, ΔH, in. H_2O	Gas volume wet test meter V_w, ft^3	Gas volume dry gas meter V_d, ft^3	Temperature Wet test Meter t_w, °F	Dry gas meter Inlet t_{di}, °F	Outlet t_{do}, °F	Average t_d, °F	Time θ, min	Y	ΔHθ	Y	ΔHθ
0.5	5	5.255	67.0	92.0	106.857	95.429	12.983	0.998	1.791	0.002	0.184
1.0	5	5.239	69.0	90.8	110.2	96.50	9.50	1.002	1.919	0.002	0.061
2.0	10	10.523	69.0	93.143	111.714	98.429	13.592	0.998	1.952	0.002	0.023
4.0	10	10.49?	69.0	94.6	114.4	100.50	9.80	1.00	2.022	0.000	0.047
6.0	10	10.47?	69.0	96.25	117.15	103.00	8.125	0.999	2.076	0.001	0.101
8.0	10	10.416	69.0	97.75	120.?	104.875	7.083	1.005	2.096	0.005	0.121
							Average	1.000	1.975		

Calculations

ΔH	$\dfrac{\Delta H}{13.6}$	Y $\dfrac{\dot{V}_w\, P_b\,(t_d + 460)}{V_d\left(P_b + \frac{\Delta H}{13.6}\right)(t_w + 460)}$	ΔHθ $\dfrac{0.0317\,\Delta H}{P_b\,(t_d + 460)}\left[\dfrac{(t_w + 460)\,\theta}{V_w}\right]^2$
0.5	0.0368		
1.0	0.0737		
2.0	0.147		
4.0	0.294		
6.0	0.431		
8.0	0.588		

Y = Ratio of accuracy of wet test meter to dry test meter. Tolerance = ± 0.01

ΔHθ = Orifice pressure differential that gives 0.75 cfm of air at 70° F and 29.92 inches of mercury, in. H_2O. Tolerance - ± 0.15

LEAK TEST @ 15 PSI

200 CFM / 60 sec.

Ambient { DATE: _____ Hg.
{ Temp. _____ 66 _____ °F

D.G.M Calibration 2282

Time	Δ H MAN	D.G. Initial	D.G. Final	D.G. Net	W.T. Initial	W.T. Final	W.T. Net	D.G.T. °F IN	OUT	W.T.M. T. °F	W.T.M. PS
0	1.0	807.001			25			98	77	69	.5
2		810.08						101	78		
4		811.4	γ=1.025	ΔH₂ 1.914				103	79		
6		812.2			30		5	104	80		
8	9.45	813.3						105	81		
10			814.065	5.064			Avg.	102.0	79.0	90.5	
12											
0	1.0	815.290			31			94	83	69	
2		816.3	γ=1.018					97	83		
4		817.4	ΔH₂ 1.931					100	83		
6	9m.39s.	818.4						103	84		
8	9.50	819.37			36		5	105	84		
10			820.298	5.108				99.8	83.4	91.6	
0	1.0	821.390			37			98	85	69	
2		822.4						102	85		
4		823.50	γ=1.013	ΔH₂ 1.893				104	85		
6		824.61						106	86		
8	1.26	825.71						106	86		
10			826.543	5.153		42	5	103.2	85.4	94.3	
12	1.43										
0		827.603			43			99	87		
2		828.70						104	87		
4		829.79	γ=1.012	ΔH₂ 1.901				106	87		
6		830.89						108	88		
8	9m.289s	831.70				48	5	109	88		
10	9.467		832.734	5.181				105.2	87.4	96.3	
0	1.0	835.890			51			78	86	69	
2	9m.27s	836.970	γ=?	ΔH₂ .977				78	89		
4		838.1						79	92		
6		839.1				56	5	79	94		
8	9.482	840.2						79	96		
10			841.028	5.152				78.6	91.4	85.0	
0	1.0	856.685			72			89	110		
2		858.79						89	110		
4		857.89						89	110		
6		860.00						90	110		
8		862.10				77	5	90	111		
10			862.950					89.4			
0	1.0	863.980			78			90	109		
2		865.07						90	110		
4	9m.30s	866.18	γ=1.009	ΔH₂ = 1.900				91	110		
6		867.28						91	111		
8	9.50	868.39				83	5	92	111		
10			869.319	5.239				90.8	110.2	100.5	

Leak Test @ 15 PSI

_____ CFM/60 sec.

D.G.M Calibration _____

Time	Δ H MAN	D.G. Initial	D.G. Final	D.G. Net	W.T. Initial	W.T. Final	W.T. Net	D.G.T. °F IN	D.G.T. °F out	W.T.M. T. °F	W.T.M. Ps
0	.5				9			12			
2								7			
4								92	107		
6		.10						92	107		
8								92	107		
10								92	107		
12		5.13			1		5	92	107		
	2.0	876.5			90			92	109		
		8.23						93	110		
		1.66						93	112		
		1.21						93	112		
	13 mi	.77						93	113		
	35.55 sec	88 .3						94	113		
		5.2						94	113		
		.103			100		10	93 113	111.714		
	4.0	172			101			94	111		
		29						94	113		
	4 mi	12.75						95	115		
		14.5						95	116		
		16.73						95	117		
			870.668			111	10				
		899.			112			95	115		
	8 mi	102.31						96	118		
	7.5 sec	904.84						97	119		
		907.47						97	119		
		910.223			122						
0	7 mi	911.370			123			97	119		
2	5 sec	914.24						95	119		
4		917.20						98	121		
6		920.17						98	121		
		924.786			133		10	98	119		

(114707)

✱ Dilomite used was 4° higher than other Dich. in - calculations adjusted.

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Barometric pressure, P_b = 29.74 in. Hg   Dry gas meter No. _____

Orifice manometer setting, ΔH, in. H_2O	Gas volume wet test meter V_w, ft³	Gas volume dry gas meter V_d, ft³	Temperature					Time θ, min	γ	ΔH@	DEV. γ	DEV. ΔH@
			Wet test Meter t_w, °F	Dry gas meter								
				Inlet t_{di}, °F	Outlet t_{do}, °F	Average t_d, °F						
0.5	5	5.232	67	98.1	78	88.1	13.17	.923	1.874	.004	.009
1.0	5	5.228	67	101.5	78.8	90.2	9.22	.996	1.830	.001	.035
2.0	10	10.595	68	120	87	103.5	13.25	1.002	1.854	.005	.011
4.0	10	10.540	68	118.5	86.17	102.3	9.63	1.001	1.963	.004	.098
6.0	10	10.510	68	115	85.8	100.4	7.43	.995	1.759	.002	.106
8.0	10	10.448	68	115.8	83.2	99.5	6.70	.995	1.910	.002	.045
							Average	.997	1.865		

Calculations

ΔH	$\dfrac{ΔH}{13.6}$	γ $\dfrac{\bar{V}_w\, P_b\, (t_d + 460)}{V_d\left(P_b + \frac{ΔH}{13.6}\right)(t_w + 460)}$	ΔH@ $\dfrac{0.0317\, ΔH}{P_b\, (t_d + 460)}\left[\dfrac{(t_w + 460)\, θ}{V_w}\right]^2$
0.5	0.0368		
1.0	0.0737		
2.0	0.147		
4.0	0.294		
6.0	0.431		
8.0	0.588		

γ = Ratio of accuracy of wet test meter to dry test meter. Tolerance = ± 0.01

ΔH@ = Orifice pressure differential that gives 0.75 cfm of air at 70° F and 29.92 inches of mercury, in. H_2O. Tolerance - ± 0.15

Leak Test @ 15 PSI   5-23-79   BAR. 29.74 "Hg.

CFM /60 sec.   Ambient { Temp. 65 °F

D.G.M Calibration 2550

Time	ΔH MAN	D.G. Initial	D.G. Final	D.G. Net	W.T. Initial	W.T. Final	W.T. Net	D.G.T.°F IN	out	W.T.M. T.°F	W.T.M. Ps
0	.5	793.630			70	75		90	78	67	
2											
4	13.10	779.22		Y=.993		ΔH@=1.874		95	78		
6		800.42						97	78		
8	(13.17)	830.81						98	78		
10		801.60						99	78		
12		802.39						101	78		
		802.862		5.232			98.125	107	78	78.0	88.063
0	1	803.900			76	81		95	78	67	
2		805.03						99	79		
4	9.13	806.16		Y=.996		ΔH@=1.830		101	79		
6		807.30						103	79		
8	(9.22)	808.44						105	79		
10			809.128	5.228			101.5	106	79	78.833	90.167
0	2	868.137			37	47		120	87	68	
2		869.74						120	87		
4	13.15	871.34		Y=1.002		ΔH@=1.854		120	87		
6		872.94						120	87		
8	(13.25)	874.53						120	87		
10		876.13						120	87		
12		877.74						120	87		
14			878.732	10.595			120	120	87	87	103.5
0	4	879.780			48	58		115	86	68	
2		881.96		Y=1.001				117	86		
4	7.55	884.13				ΔH@=1.963		118	86		
6		886.33						119	86		
8	(9.63)	888.52						120	86		
10			890.320	10.54			118.5	122	87	86.17	102.34
	6	892.500			60	70		105	85	68	
		895.31		Y=.995				114	86		
		898.14				ΔH@= ▓▓▓		117	86		
	7.56	900.77				1.959		119	86		
	7.93		903.005	10.51			115.00	120	86	85.8	100.4
0	8	923.800			90	00		111	83		
2		926.90						112	82		
4	6.42	930.00		Y=.995		ΔH@=1.910		118	83		
6		933.13						119	84		
8	(6.79)	934.248		10.448			115.8	119	84	83.2	99.5

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REPORT DOCUMENTATION PAGE	1. REPORT NO. EPA-340/1-80-019	2.	3. Recipient's Accession No.

4. Title and Subtitle	5. Report Date
Correlation of Remote and Wet Chemical Sampling Techniques for Hydrogen Fluoride from Gypsum Ponds	June 1981
	6.

7. Author(s) H. F. Schiff, D. Bause, J. Fitzgerald, M. McCabe, D. Montanaro, and V. Shortell	8. Performing Organization Rept. No. GCA-TR-80-76-G

9. Performing Organization Name and Address	10. Project/Task/Work Unit No.
GCA Corporation GCA/Technology Division Bedford, MA 01730	Task Order 59
	11. Contract(C) or Grant(G) No. (C) 68-01-4143 (G)

12. Sponsoring Organization Name and Address	13. Type of Report & Period Covered
Division of Stationary Source Enforcement, Headquarters Office of Enforcement U.S. EPA Washington, D.C.	Final March 1979 to June 1981
	14.

15. Supplementary Notes

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16. Abstract (Limit: 200 words)

For several years, the Environmental Protection Agency (EPA) has used the Remote Optical Sensing of Emissions (ROSE) system to characterize the gaseous pollutants emitted by a variety of point and extended area sources. The purpose of this program was to extend the data base of this versatile and promising pollutant sensor by comparing the data generated by the ROSE system with data generated by standard techniques for the sampling and analysis of hydrogen fluoride. The program was divided into five phases including a literature review, pretest survey, sampling and analytical trials in the laboratory, preliminary field phase, and the final, collaborative field phase. The field sampling efforts were conducted along gypsum ponds at two phosphate fertilizer facilities. For the formal sampling phase, both the double filter cassette and sodium bicarbonate-coated tube were used for the point sampling. The point sampling effort was conducted simultaneously with the operation of the ROSE system. A sampling period of 15 minutes was compatible with the sensitivity requirements of the analytical methods. The fluoride collected by the wet chemical methods was analyzed colorimetrically using a semiautomated method with lanthanum-alizarin complexone for the colorimetric reagent. Two data reduction methods, a peak area and peak height procedure, were used to compute the HF concentrations from the spectra obtained by the ROSE system. In 32 independent tests of comparable ambient HF concentrations, the overall average HF concentration was 37.6 ppb (ROSE system, peak area method), 36.1 ppb (ROSE system, peak height method) and 36.4 ppb (wet chemical techniques). The standard deviation between the ROSE system data and the manual sampling results was 11.9 ppb and 9.7 ppb for the peak area and peak height computation procedures, respectively.

17. Document Analysis   a. Descriptors

Keywords:
    Hydrogen fluoride   Remote sampling
    Sampling methods   Correlation
    Air pollution

b. Identifiers/Open-Ended Terms

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Unlimited	Unclassified	165
	20. Security Class (This Page)	22. Price
	Unclassified	