United States
Environmental Protection
Agency

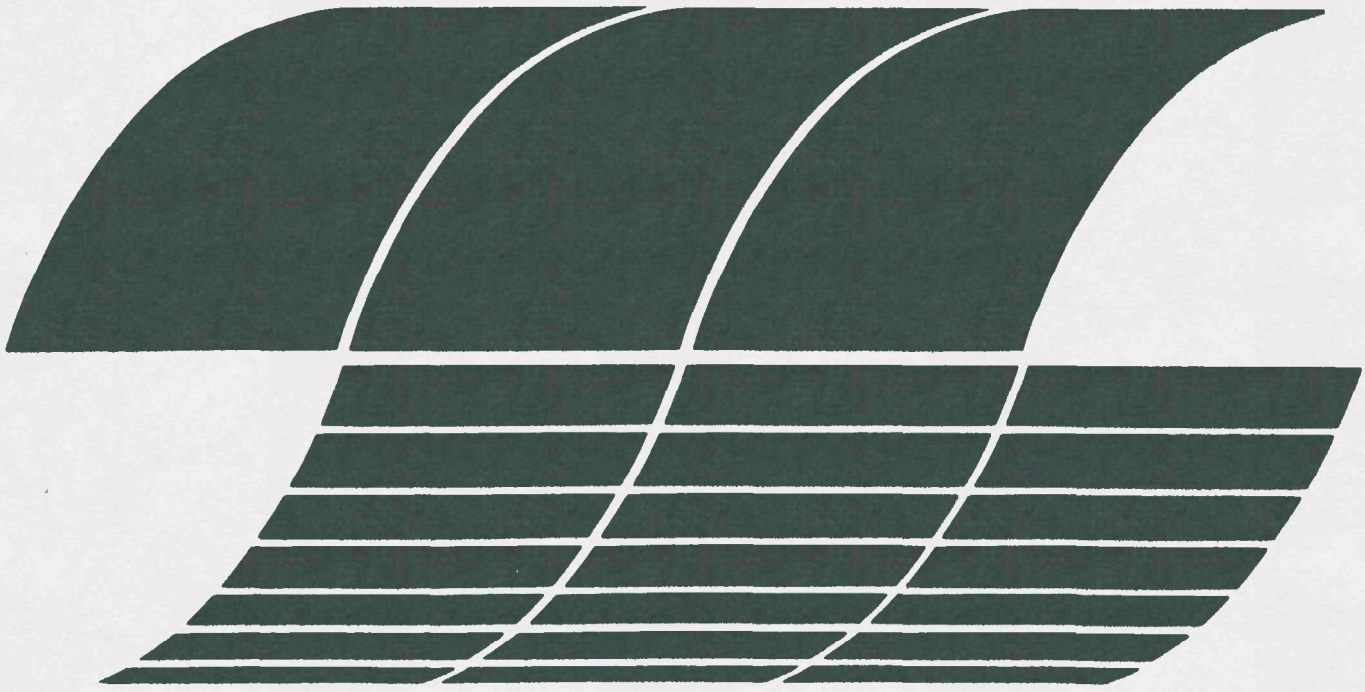
Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/7-79-151
July 1979

EPA

Chemical Analysis of Wet Scrubbers Utilizing Ion Chromatography

Interagency Energy/Environment R&D Program Report



RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the INTERAGENCY ENERGY-ENVIRONMENT RESEARCH AND DEVELOPMENT series. Reports in this series result from the effort funded under the 17-agency Federal Energy/Environment Research and Development Program. These studies relate to EPA's mission to protect the public health and welfare from adverse effects of pollutants associated with energy systems. The goal of the Program is to assure the rapid development of domestic energy supplies in an environmentally-compatible manner by providing the necessary environmental data and control technology. Investigations include analyses of the transport of energy-related pollutants and their health and ecological effects; assessments of, and development of, control technologies for energy systems; and integrated assessments of a wide range of energy-related environmental issues.

EPA REVIEW NOTICE

This report has been reviewed by the participating Federal Agencies, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Government, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/7-79-151

July 1979

Chemical Analysis of Wet Scrubbers Utilizing Ion Chromatography

by

Tobias R. Acciani and Ray F. Maddalone

TRW Defense and Space Systems Group
One Space Park
Redondo Beach, California 90278

Contract No. 68-02-2165
Task No. 214
Program Element No. INE624

EPA Project Officer: Frank E. Briden

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

FIGURES

FIGURES (Continued)

TABLES

1.0 INTRODUCTION

This manual has been prepared for the Process Measurement Branch of the Industrial Environmental Research Laboratory of the Environmental Protection Agency, Research Triangle Park, North Carolina, as Task 48, Contract No. 68-02-2165. Task 48 is devoted to chemical analysis of wet scrubbers utilizing ion chromatography and is under the direction of EPA Project Officer, Frank Briden.

The intended use of this manual is to provide the user with enough background to develop a sampling and analysis program for a wet scrubber utilizing ion chromatography as the main analytical technique. The first part of the manual describes a sampling program for two different types of wet scrubbers. The second part evaluates the use of ion chromatography to analyze wet scrubber samples.

The two wet scrubbers described in the sampling program are the venturi/spray tower (limestone) scrubber which is part of the EPA/TVA Shawnee Test Facility, Paducah, Kentucky and the Arthur D. Little dual alkali pilot scrubber. These two wet scrubbers were selected for inclusion here because the Shawnee scrubber is representative of the current technology and the dual alkali scrubber is representative of future technology. The sampling section is broken down into three subdivisions: scrubber type, sample collection and sample preservation.

The analysis section of this manual describes the theory and practice of ion chromatography as applied to wet scrubber samples. The analysis section consists of three subdivisions: analytical procedures, qualitative analysis, and quantitative analysis. The analytical procedures subdivisions consists of the anion and cation and analysis scheme for wet scrubber samples, the theory of ion chromatography, and current problem areas involving the use of ion chromatography for wet scrubber related samples. The qualitative analysis subdivision describes the use of retention time to identify the various ions found in wet scrubber samples. The quantitative analysis subdivision discusses the method of peak height and calibration curves for correlation of the ion chromatographic detector response

to sample concentration. Also, included in this subdivision is the verification of the precision and accuracy of the analytical scheme presented in the analytical procedures section.

2. SAMPLE COLLECTION PLAN

In order to develop a successful sample collection plan for a lime/limestone or a dual alkali wet scrubber, the basic concepts of flue gas scrubbing must be understood. This section discusses the sampling criteria necessary for collecting a representative sample from a wet scrubber. The sample collection plan is broken down into three subdivisions: the scrubber type, sample collection, and sample preservation. The subsection on the scrubber type will discuss lime/limestone and dual alkali wet scrubbers. The subsections on sample collection and preservation will discuss the techniques employed which are independent of the type of scrubber.

2.1 TYPE OF SCRUBBER

This section of the manual is written so that the reader will have a clear understanding of the concepts of scrubbing flue gas by the lime/limestone or dual alkali systems. Each scrubber type is discussed individually with regard to: chemistry, scrubber design, sampling points, and species of interest for control of the scrubber.

2.1.1 Lime/Limestone Wet Scrubber

2.1.1.1 Chemistry of Lime/Limestone Scrubbing --

The Shawnee venturi/spray tower wet scrubber is a representative example of most lime/limestone wet scrubbers. The term "lime/limestone" scrubber means that the flue gas could be scrubbed with either lime or limestone. The overall reaction of lime with SO_2 is:

$$CaO + SO_2 \rightarrow CaSO_3 \qquad (1)$$

The absorbent slurry liquor pH for lime is maintained between 7 and 9 at the scrubber inlet and runs 4.5 and 5.5 at the outlet. The stoichiometric ratio (moles of lime added per moles of SO_2 absorbed) ranges from 1.0 to 1.2.

The overall reaction of limestone with SO_2 is:

$$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2 \qquad (2)$$

In limestone based scrubbers the stoichiometric ratio (moles of limestone added per moles of SO_2 absorbed) is 1.1 to 1.6. The absorbent slurry liquor pH for limestone is maintained at a much lower pH value than lime, between 5 and 6. The reaction products for both lime and limestone scrubbers are actually a mixture of calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$) and calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$, an oxidation product). The pH value of the limestone slurry at the outlet of the scrubber runs the same as lime, between 4.5 and 5.5.

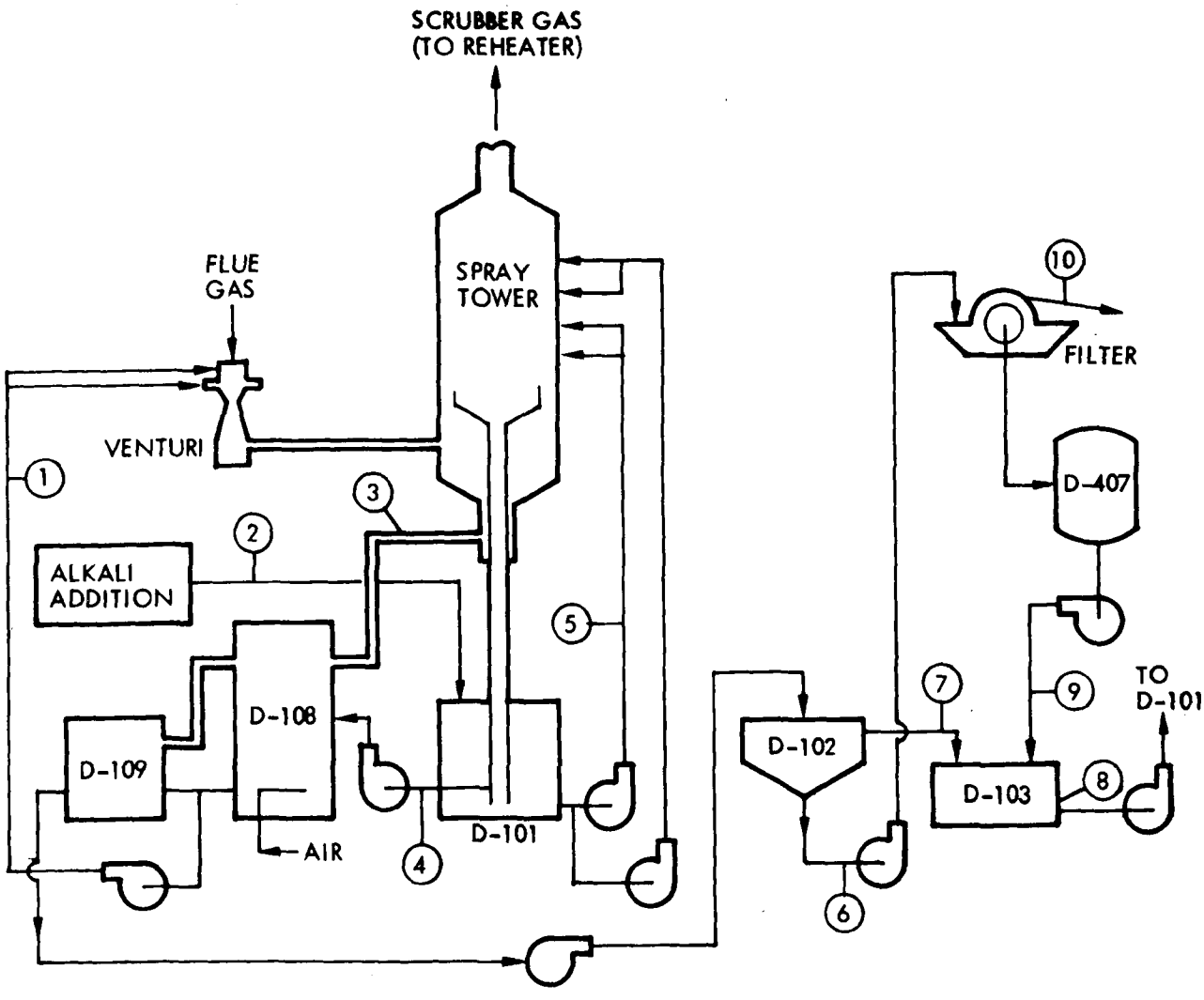
2.1.1.2 Scrubber Design --

Figure 1 shows the schematic flow diagram of a venturi/spray tower lime/limestone wet scrubber. Flue gas entering the scrubber passes through the venturi (particulate removal) and upward through the spray tower counter-current to the scrubbing liquor that is recirculated from the effluent hold tank (D-101). The pH of the effluent liquor is adjusted with a slaked lime slurry in the effluent hold tank. A bleed stream from the effluent hold tank is routed through the oxidation tank and supersaturation tank to a clarifier. The oxidation tank is the vessel where any $SO_3^=$ ions in the scrubber effluent are oxidized to $SO_4^=$ ions. Sulfate ions and their compounds have better handling properties (less disposal volume) than sulfite ions and their compounds. The clarifier overflow is returned to the effluent hold tank via the fill tray receiving tank (D-407) and process water hold tank (D-103). The filter catch is discharged to a disposal pond.

2.1.1.3 Sampling Points and Species of Interest --

The main objective for sampling a lime/limestone wet scrubber is to monitor the chemical species in the scrubber liquid. By sampling at key points and for certain species, the scrubber can be controlled so that it is operated efficiently and effectively. This section describes the sampling and analysis requirements for each process stream.

Each number on Figure 1 refers to process streams where samples are taken. Each process stream has been classified into one of three groups; solution, slurry, and solubles in cake. Figure 2 shows an overall view of the types of analyses for each process stream line for the Shawnee lime/limestone scrubber. The important species are calcium,



D-101 SPRAY TOWER EFFLUENT HOLD TANK
D-102 CLARIFIER
D-103 PROCESS WATER HOLD TANK
D-108 OXIDATION TANK
D-109 SUPERSATURATION TANK
D-407 FILL TRAY RECEIVING TANK

Figure 1. Schematic Flow Diagram of the Venturi/Spray Tower Scrubber at the EPA/TVA Shawnee Limestone Test Facility

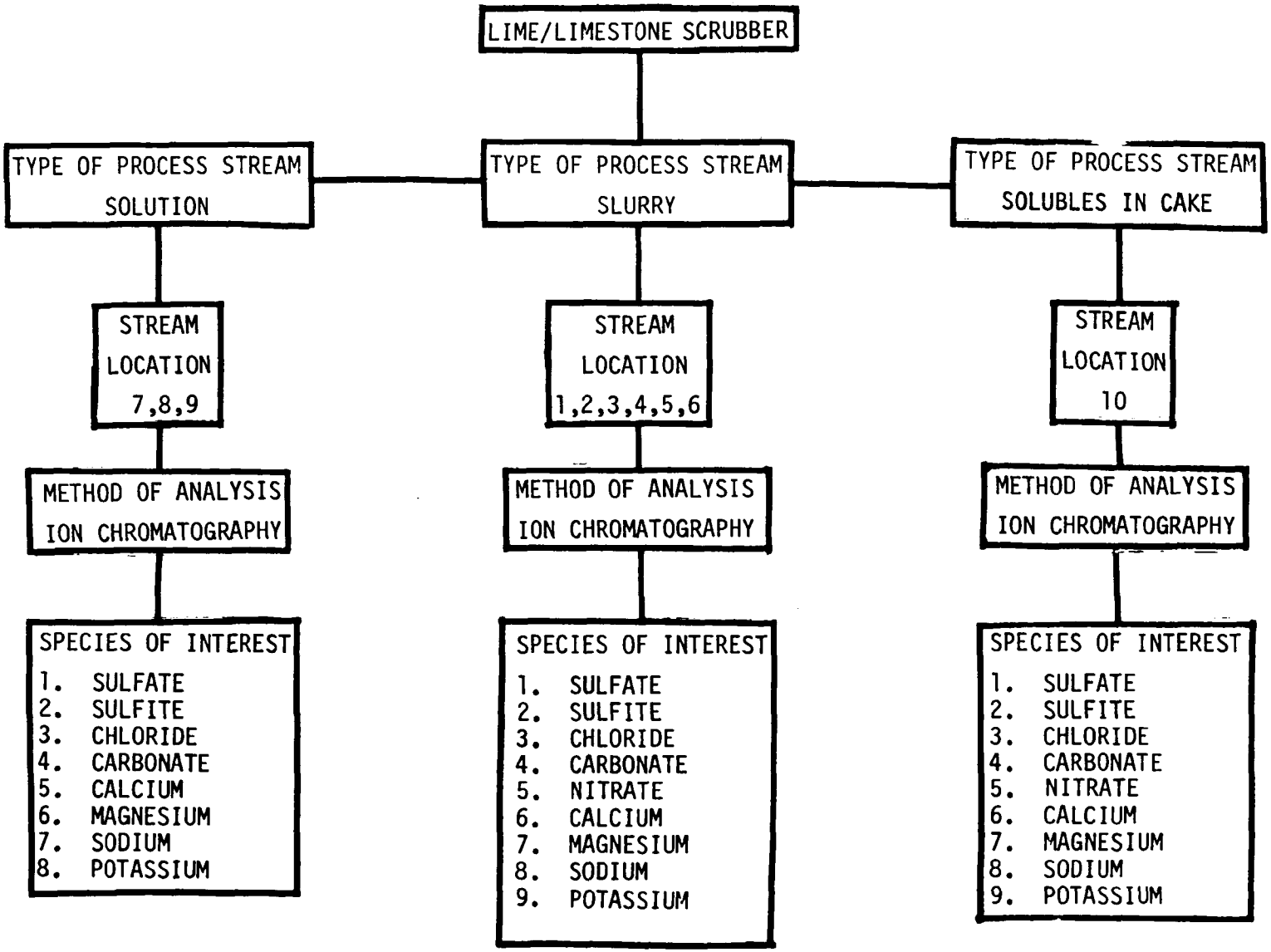


Figure 2. Breakdown of Species of Interest and Process Stream Location for the Venturi/Spray Tower Scrubber

sulfate, sulfite, magnesium, and chloride. The concentration of these species is determined in all the process streams throughout the scrubber unit. The calcium and sulfate concentration is determined for lime/limestone utilization data. In addition, the sulfite concentration is determined before and after the scrubber so that the scrubbing efficiency can be determined. Magnesium is an additive for increased scrubber efficiency so its concentration must be monitored and controlled for maximum efficiency. Chloride reacts with magnesium and will deplete the magnesium additive so the chloride concentration must be monitored and kept extremely low. Also, chloride will react with the stainless steel equipment and pipes. Chloride is the only species which is not added to the system for scrubbing, but enters as a component of the flue gas and river water.

2.1.2 Dual Alkali Scrubber

2.1.2.1 Chemistry of Dual Alkali Scrubbing --

A number of processes are similar and can be considered technically dual alkali. In these processes, a soluble sodium based alkali (NaOH, $NaHCO_3$, Na_2SO_3, Na_2CO_3) absorbs SO_2 from the flue gas in the scrubber, then a calcium based alkali ($Ca(OH)_2$, CaO, $CaCO_3$) reacts with the SO_2 rich scrubber effluent liquid to precipitate the insoluble $CaSO_3 \cdot 1/2\ H_2O$, $CaSO_4 \cdot 2H_2O$, and regenerate the sodium based soluble alkali for recycle to the scrubber system. This manual only considers the sodium sulfite/lime or limestone based dual alkali process.

The overall scrubber reaction of sodium sulfite with SO_2 is:

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3 \qquad (3)$$

The overall regeneration reactions are:

$$Ca(OH)_2 + 2NaHSO_3 \rightarrow Na_2SO_3 + CaSO_3 \cdot 1/2\ H_2O + 3/2\ H_2O \qquad (4)$$

$$CaCO_3 + 2NaHSO_3 + 1/2\ H_2O \rightarrow Na_2SO_3 + CaSO_3 \cdot 1/2\ H_2O + CO_2$$

2.1.2.2 Scrubber Design --

Interest in dual alkali scrubbing has grown because there are two main difficulties with lime/limestone scrubbers: scaling ($CaSO_4$ plating on interior walls which causes plugging of scrubber), and disposal of $CaSO_3 \cdot 1/2\ H_2O$ and $CaSO_4 \cdot 2H_2O$ which generally necessitates the use of holding ponds.

Scaling is greatly reduced in dual alkali systems because sodium sulfite is the active scrubbing species not lime or limestone. Instead of calcium ions and sulfate ions forming $CaSO_4 \cdot 2H_2O$, sodium sulfite in the dual alkali system reacts with SO_2 forming sodium bisulfite which is soluble. Since the lime or limestone employed for the regeneration reaction is maintained in a separate system component, the operation of the scrubber section of the dual alkali system should be free from plugging of lines caused by scaling. This is extremely important for continuous operation because scaling can be controlled and limited to a smaller part of the scrubber system. In the dual alkali system, scaling problems will occur in lime or limestone feed areas, but will not directly affect the scrubber unit. Figure 3 shows a schematic flow diagram of a dual alkali pilot plant. The calcium slurry is monitored at sampling points 4, 5, and 6 of Figure 3 and any soluble calcium (sample point 10) is minimized by the addition of Na_2CO_3 or Na_2SO_4.

The waste products from dual alkali scrubbers have better handling properties than lime/limestone scrubbers. Dual alkali scrubbers produce a high gypsum sludge ($CaSO_4 \cdot 2H_2O$) which can be filtered to cakes of over 65% solids whereas lime/limestone can only be filtered to 40-50% solids. The Shawnee lime/limestone scrubber is an exception to the above statement. Shawnee employs an oxidation system which converts the calcium sulfite in the effluent to calcium sulfate producing a sludge which can be filtered to 80% solids.

The basic scrubber unit for the dual alkali process (Figure 3) is very similar to the lime/limestone unit (Figure 1); both have a venturi, spray tower and a recycle tank. The major difference between the two systems beside the scrubbing species is the concentration and solids content of the absorber feed stream. Lime/limestone scrubber employs an absorber

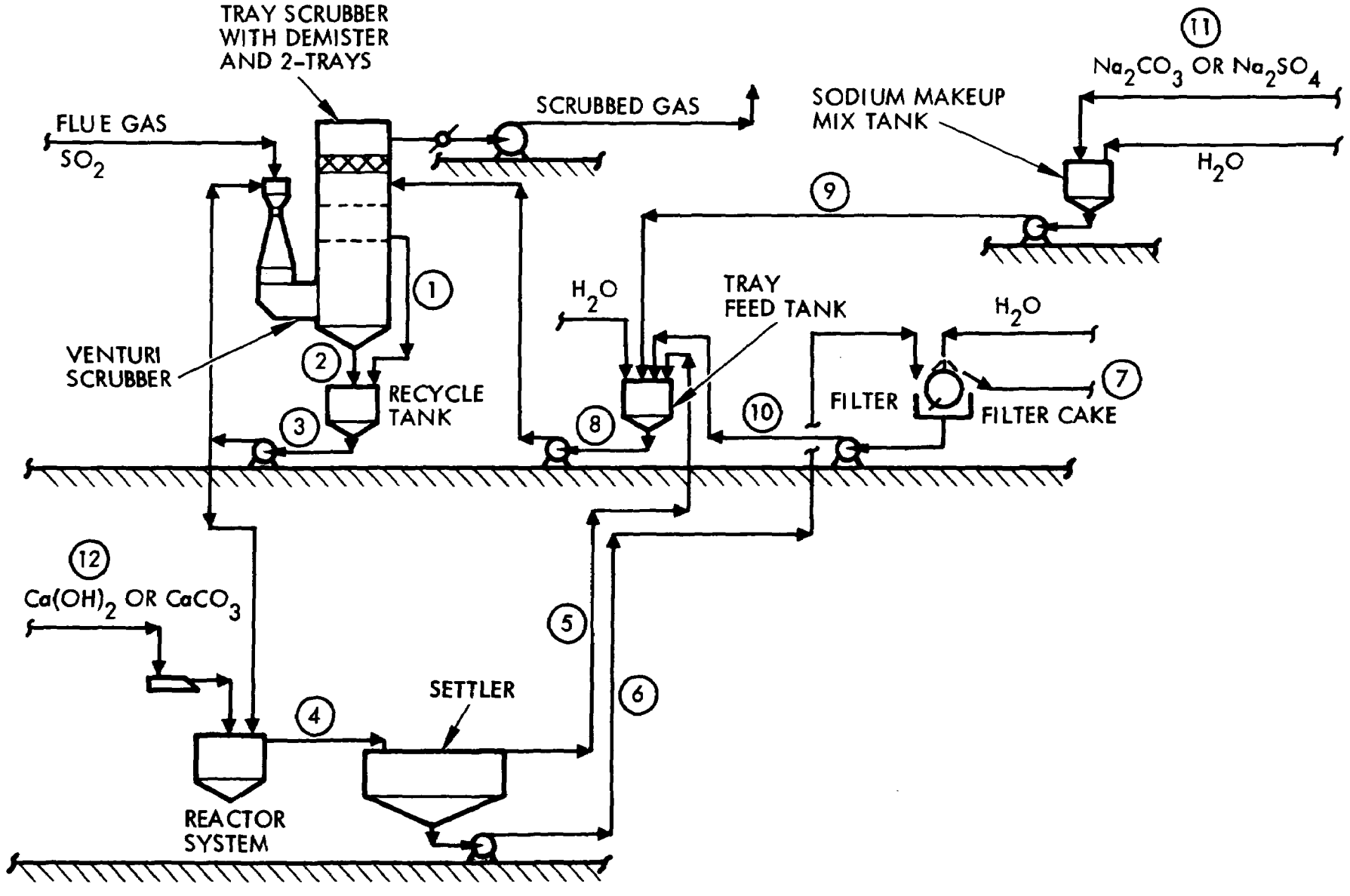


Figure 3. Schematic Flow Diagram of a Dual Alkali Pilot Plant

feed stream which is a slurry with solids (CaO or $CaCO_3$) content of 8% where dual alkali scrubbers employ an absorber feed stream which is a 1 to 2 molar sulfite solution with little or no solids present.

The flue gas enters the venturi and moves upward through the tray scrubber; the recycle liquor (mostly sodium bisulfites) drops into the recycle tank and is transferred to the reactor system. At the reactor system, lime or limestone is added to the liquor to convert the HSO_3^- to $SO_3^=$. This solution contains calcium which must be removed before entering the scrubber. The process of adding Na_2CO_3, which reduces the dissolved calcium ion concentration in the regeneration liquor, is known as softening. The purpose of softening the scrubbing liquor before recycling to the scrubber is to assure that soluble calcium is minimized which reduces the gypsum scaling potential in the scrubber.

2.1.2.3 Sampling Points and Species of Interest --

Control of process stream concentrations is extremely important for dual alkali scrubbing. Each number in Figure 3 refers to process streams where samples are taken. Each process stream has been classified into one of four groups: solution, slurry, solid, and solubles in cake. Figure 4 shows an overall view of the types of analyses to be performed on the samples from a dual alkali wet scrubber. The major species of interest are: calcium, total oxidizable sulfur (TOS), carbonate, magnesium, chloride, and sulfate.

The calcium concentration must be known throughout the scrubber system because of the potential scaling problems. The most important sampling point for calcium is the feed line into the tray scrubber (point 8, Figure 3). Any buildup of a gypsum scaling will prohibit the flue gas from contacting the sodium sulfite solution which would cause poor scrubbing efficiency. A second important area for calcium monitoring is the regeneration of the soluble alkali (points 12, 4, 5, 6; Figure 3). The concentration of calcium must be known for lime or limestone utilization data.

Total oxidizable sulfur (TOS) value refers to sulfur in the +4 oxidation state.

$$TOS\ (mole/liter) = [SO_3^=] + [HSO_3^-])$$

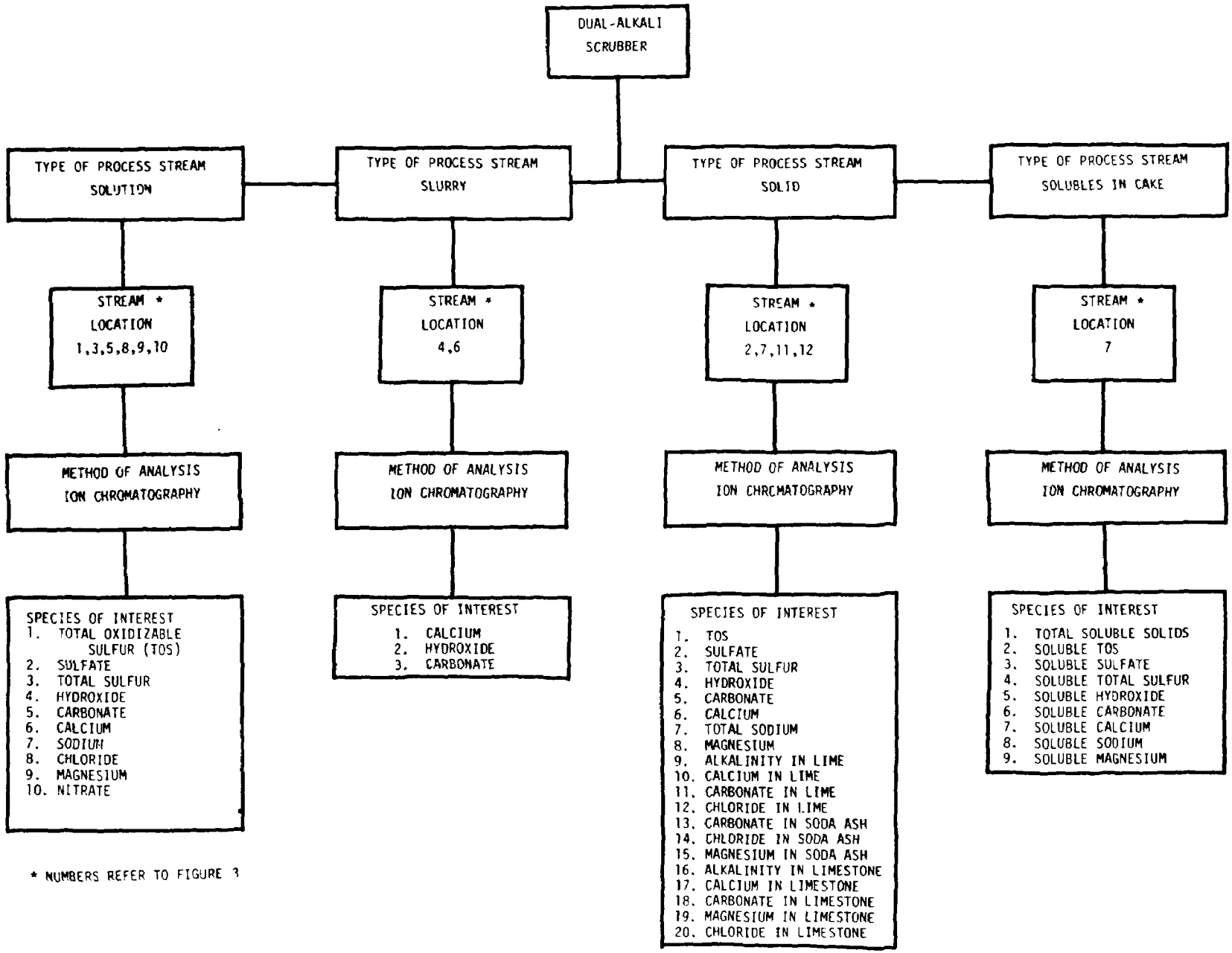


Figure 4. Breakdown of the Species of Interest and Process Location for a Dual Alkali Scrubber.

The TOS value is important because of the oxidation reactions:

$$SO_3^{=} + 1/2\ O_2 \rightarrow SO_4^{=} \tag{5}$$

$$HSO_3^{-} + 1/2\ O_2 \rightarrow SO_4^{=} + H^{+}$$

These reactions have the effect of deactivating the sodium solutions. TOS species are sampled in the process stream lines which feed into and out of the venturi and tray scrubbers, (points 8, 1, 2, 3; Figure 3). The filter cake is also analyzed for TOS because any loss of these species will drastically cut the efficiency of the scrubber.

The carbonate concentration like calcium must be known throughout the scrubber. The carbonate ions serve two functions, removal of calcium (softening):

$$Ca^{++} + Na_2CO_3 \rightarrow 2Na^{+} + CaCO_3 \tag{6}$$

and removal of SO_2 from the flue gas:

$$Na_2CO_3 + 2\ SO_2 + H_2O \rightarrow 2NaHSO_3 + CO_2 \tag{7}$$

The sampling points for carbonate ions are the feed lines to the sodium makeup tank and tray feed tank (points 11, 9; Figure 3). The feed line into the tray scrubber (point 8, Figure 3) contains the carbonate ions for scrubbing the flue gas.

Magnesium, unlike carbonate, calcium, or TOS, is not a basic chemical to the scrubber, rather it is an additive used to increase scrubbing efficiency. The magnesium concentration is determined in all samples from the scrubber for utilization data.

The sulfate concentration is another important quantity which must be known through the scrubber unit. Sulfates are the reaction products of the oxidation of TOS species. Increases in the sulfate concentration indicate that the effective scrubbing potential of the dual alkali scrubber is being reduced through the loss of sulfite. The efficiency of the dual alkali

Scrubber is measured by maintaining high concentration of TOS while minimizing the sulfate level. The outlet process stream lines from the tray scrubber (points 1, 2, 3) are the important points where sulfates would be found and should be monitored.

2.2 SAMPLE COLLECTION (LIME/LIMESTONE AND DUAL ALKALI)

There are three possible types of process streams found in lime/limestone and dual alkali wet scrubbers: solid, slurries and solutions. Figures 2 and 4 show a breakdown of each stream for both scrubbers according to their type and the species of interest. For lime/limestone wet scrubbers, most process streams are slurries with the solids content for each stream depending on the location. Feed lines into the lime/limestone spray tower and recycle stream lines will be below 10% solids while other lines will be above 10%. For dual alkali wet scrubbers, all three types of process streams will be found. Feed lines into the dual alkali tray scrubber are solutions; feed lines into the mixing tanks are solids and all other process streams are slurries with varying solids content. The following section describes how to sample the general types of process streams regardless of the type of scrubbers.

2.2.1 Sample Acquisition

Sample acquisition is extremely important because the sample must be representative of the source. The factors which determine representativeness of the sample are stream homogenity and flow rates. In general, most process streams for wet scrubbers have areas where high enough flow rates exist for good homogenity. Grab samples can be taken from these places. For the scrubbers shown in Figures 1 and 2 built-in sampling ports already exist, so grab samples will be easy to obtain. The areas where stratification of slurries may occur are in the clarifier and hold tanks for these scrubbers. This problem can be solved by taking grab samples from the feed line into the clarifier and hold tank or at their exit lines.

2.2.2 On Site Solution and Slurry Sample Treatment

Most samples taken from either scrubber system can be taken using grab techniques. If the sample contains solids, they are removed back in the laboratory using N_2 pressure filtration system to separate the liquids

and solids. Filtration accomplished using a Gelman Acropore 1.2 μm filter in the apparatus shown in Figure 5. This approach is preferred over gravity or Buchner filtration, since O_2 contact is minimized preventing $SO_3^=$ oxidation.

Due to the chemical nature of several streams, the distribution of inorganic species in the liquid phase will be disturbed unless the liquid and solid phases are immediately separated. At most wet scrubber sites, demister wash return, recycle slurry, and absorber sludge bleed-off streams will require on-line filtration.

The on-line filtration apparatus is shown in Figure 6. This system uses a large (142 mm) filter holder with a Gelman Acropore 1.2 μm filter to separate the solids from the slurry. The valving is arranged, so that all the lines can be purged prior to sampling. While a pump is shown, most streams are under sufficient pressure (especially downstream of a pump) to force the slurry through the filter. The samples are filtered directly into plastic containers which have been first rinsed with high purity HNO_3 and then rinsed thoroughly with deionized water. When the solutions are placed into the plastic container, exposure to air should be minimized to prevent oxidation. The solution should be filled to the top of the container to also minimize oxidation. Analysis for sulfite should be conducted on site and immediately after the sample is taken. Because carbonate is one of the species of interest, bubbling and shaking of the solution should also be minimized.

2.2.3 Solution and Slurry Sample Size Requirement

An important factor which is always considered in sampling process streams is the size of sample required. Normally, there are two factors that determine how much sample must be collected. First, the amount of sample collected must be sufficient for the testing and analysis procedures to furnish accurate and precise results and provide enough sample to reduce the stastical sampling error. A 1 L grab sample will be sufficient to provide approximately five hundred mL of filtered sample. Because of the restricted filtration capability of the on-line filter, as little as 100 mL of filtrate is sufficient.

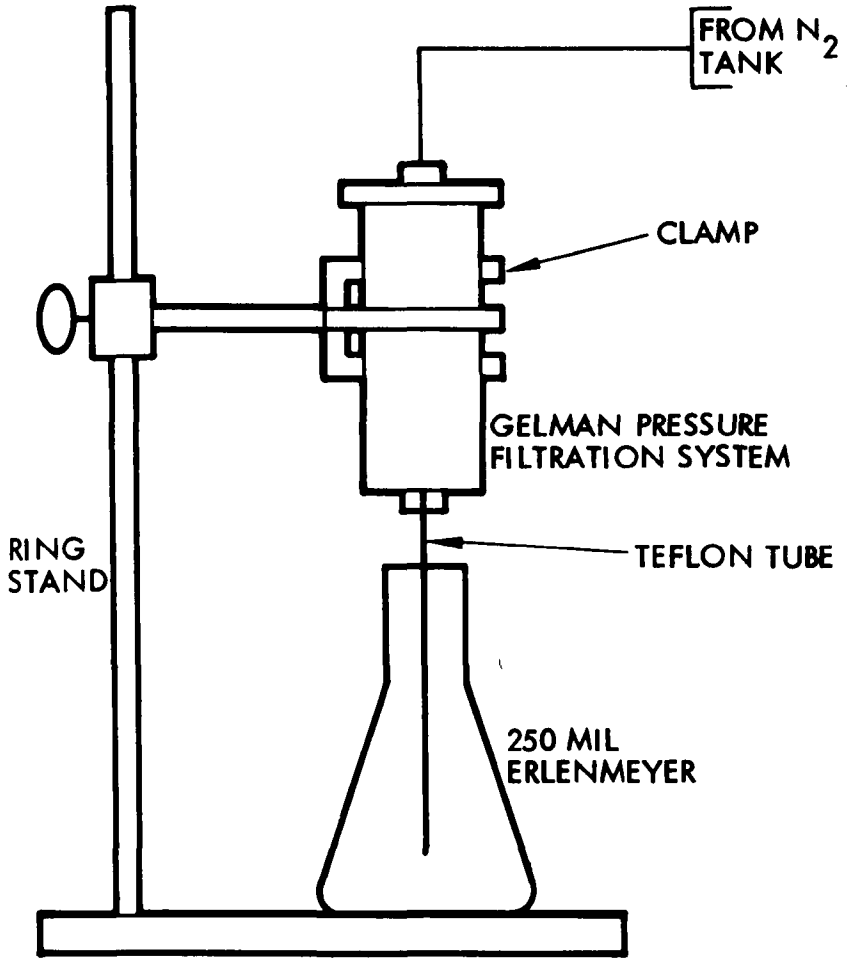


Figure 5. Pressure Filtration Apparatus

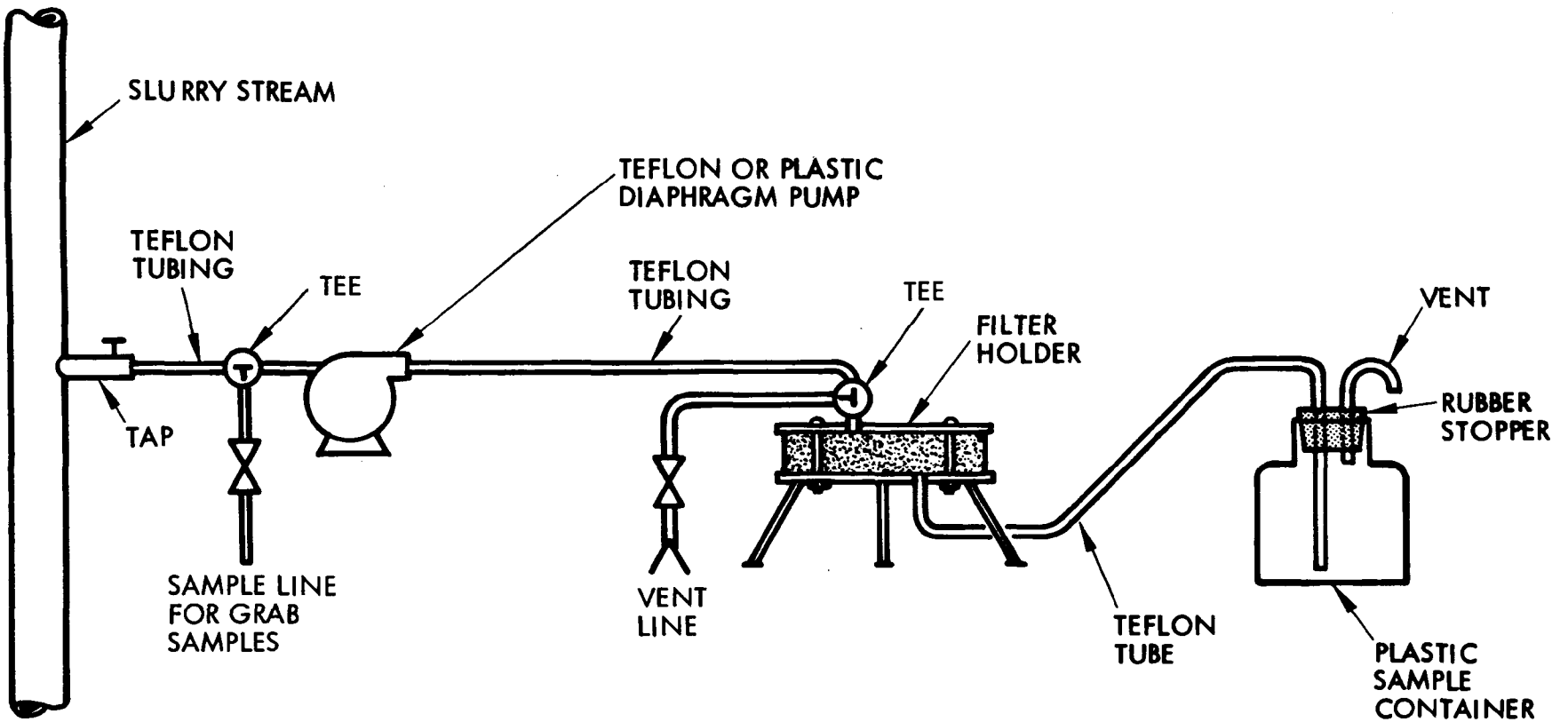


Figure 6. On-Line Liquid Slurry Filtration System

For ion chromatographic analysis, 100 µL of the sample is analyzed, but one millimeter of sample is used to fill the sampling loop and connecting lines. Since the species of interest for the wet scrubber analyses are in concentrations greater than 100 ppm, the 100 µL analyzed sample is sufficient to meet the sensitivity requirements based on the instrument detection limits.

2.2.4 Solid Samples

Solid samples will be obtained by filtration of the solids from the slurry streams or taken from the filter cake produced by either the lime/limestone or double alkali FGD systems. Prior to analysis, it is recommended that these samples be rinsed with a 50% acetone soluton to remove most of the free water and to expedite the drying process. The rinse is performed by placing the solids in a precleaned Buchner funnel, pouring the acetone/water solution over the solids, and filtering. Approximately 20-30 grams of material can then be dried to constant weight in an explosion proof oven set at 60°C.

2.3 SAMPLE PRESERVATION

Chemical preservation should not be used when analyzing process streams where the species of interest are in equilibrium. Reagents like strong mineral acids, when added to a sample for preservation, will cause a shift in equilibrium forcing a species into or out of solution. Sample preservation should only be employed when there is a long time period between sample acquisition and analysis. The time period between sample acquisition and analysis depends on the species of interest. If sulfite is the species of interest, then time is important because sulfite will gradually oxidize to sulfate once exposed to air. The analyst will have to run experiments to determine the allowable time period between sample acquisition and analysis.

These experiments would consist of taking ten similar samples, then allowing each sample to stand for a specific time period before analysis. All samples will be analyzed for concentration by ion chromatography for a specific ion or species vs the time the sample was allows to stand. The plot would look something similar to Figures 7 or 8 and would give the analyst an indicator when sample preservation would be necessary.

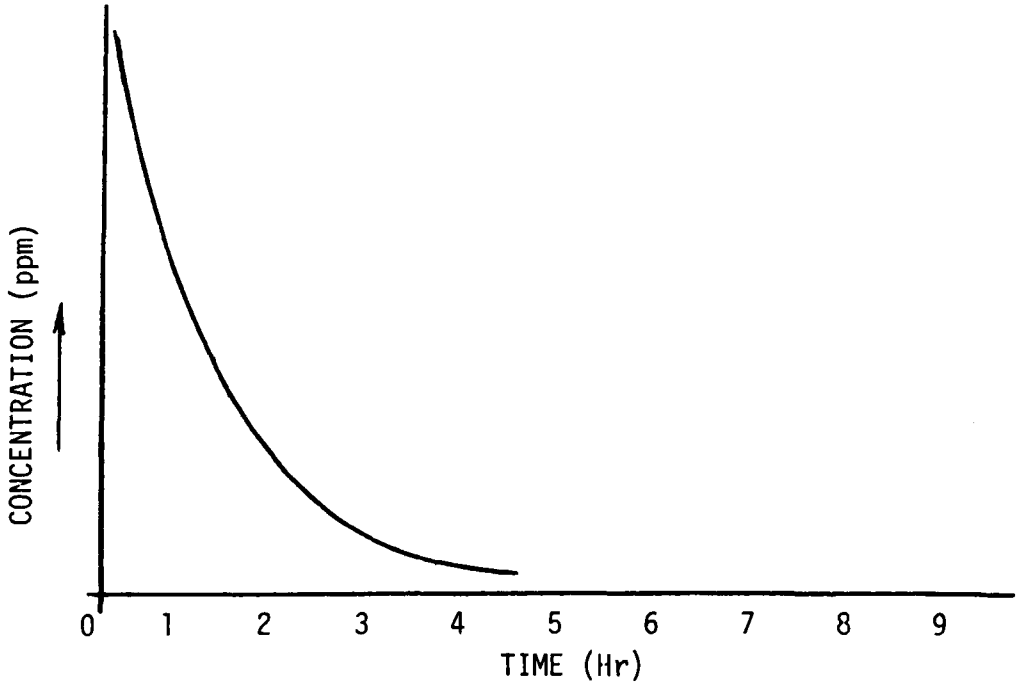


Figure 7. Plot of Species Concentration vs Time (Immediate Sample Preservation Required)

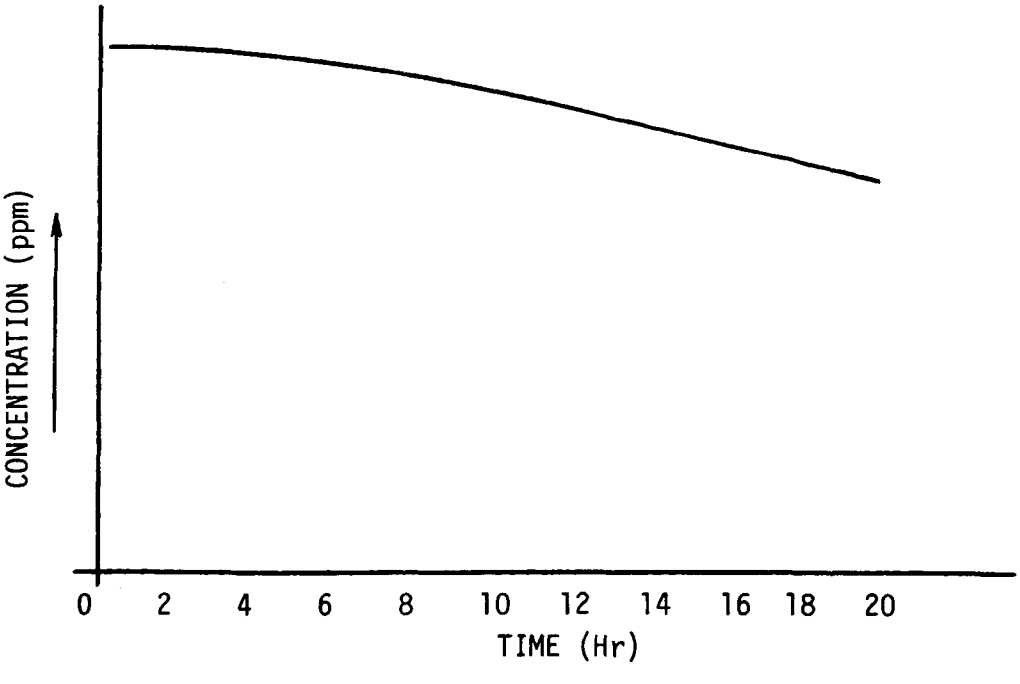


Figure 8. Plot of Species Concentration vs Time (No Immediate Sample Preservation Required)

Figure 7 indicates the analysis would have to occur immediately after sample acquisition where Figure 8 indicates the analyst would have a few hours before preservation is necessary. The following section describes the procedure which should be employed for sample preservation.

2.3.1 Procedures for Sample Preservation

Plots of species concentration vs the time period between sample acquisition and analysis will indicate whether a sample should be preserved. Samples from process streams whether dual alkali or lime/limestone will be separated into either solids or solutions after filtration. Solution samples and filtrate from slurry samples will be further divided into five groups depending on the species to be analyzed and preserved, according to the procedures in Table 1. Solid samples, filter cake samples, and solids from slurry samples after the 50% acetone rinse will not require the addition of any preservation agent, but are placed into sealed plastic containers. Exposure to air should be minimized in all sampling activities.

TABLE 1. RECOMMENDATIONS FOR SOLUTION PRESERVATION

Measurement	Container	Preservative	Holding Time
Total oxidizable sulfur Sulfate Hydroxide Acidity Carbonate Chloride	Plastic	Cool, 4°C	24 hrs
Calcium Sodium Magnesium	Plastic	HNO_3 to pH 2	6 mos
pH	Plastic	Cool, 4°C Detection on site	6 hrs
Total Sulfur	Plastic	Cool, 4°C Zn Acetate	24 hrs
Nitrate	Plastic	Cool, 4°C H_2SO_4 to pH 2	24 hrs

3. ANALYTICAL PROCEDURES

This section describes the theory and practice of ion chromatography. It presents the anion and cation analysis scheme for wet scrubber samples. Also, included in this section will be definitions and discussions of problem areas involving the use of ion chromatography for wet scrubber related samples.

3.1 INTRODUCTION

Ion-exchange chromatography is a process whereby ions of the same charge in solution compete for positions with other ions of the same charge, which are bound to the surface of a solid.

$$A^- + Y^- \boxed{\begin{array}{c}\text{Resin}\\ \text{Functional Group}\\ \text{and Backbone}\end{array}} \rightleftarrows Y^- + A^- \boxed{\begin{array}{c}\text{Resin}\\ \text{Functional Group}\\ \text{and Backbone}\end{array}} \qquad (8)$$

where

A^- is the sample ion

Y^- is the mobile phase

(anion exchange reaction)

As indicated in Equation (8), sample ion A^- is exchanging with the mobile phase ion Y^- which is bound to a functional group or the active site of a resin. The functional group is always opposite in charge to the exchanging ions. The rate at which the ions exchange positions is determined by the ion's affinity for the functional group. The physical characteristics of size and charge determines the ions affinity or interaction with the functional group of the resin. Ions which have a charge that can be polarized toward the functional group will have a stronger interaction with the resin thus a slower rate of exchange. The attraction between an ion and the resin can be thought of as an ion-pair. In practice, the rate of exchange (ion-pair interaction) determines the elution order on the chromatogram. The slower the rate of exchange, the stronger the ion-pair interaction resulting in a longer elution time.

A second factor which also can control an ion-exchange reaction is the mobile phase. The mobile phase is usually an acid or base. Consider a weak acid HX, the dissociation of the acid is:

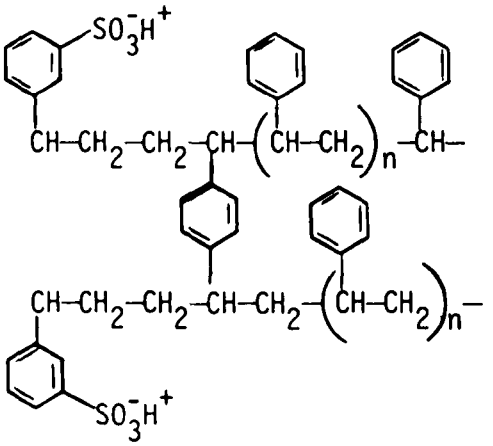
$$HA + H_2O \rightleftarrows H_3O^+ + A^- \qquad (9)$$

The degree of the dissociation can be controlled by the pH of the systems. An increase of H^+ ions causes the equilibrium in Equation 9 to shift to the left. The resulting shift causes less A^- ions to be available for interaction with the anion exchange resin or less A^- ions competing with sample ions for the resin which may result in longer elution times.[1]

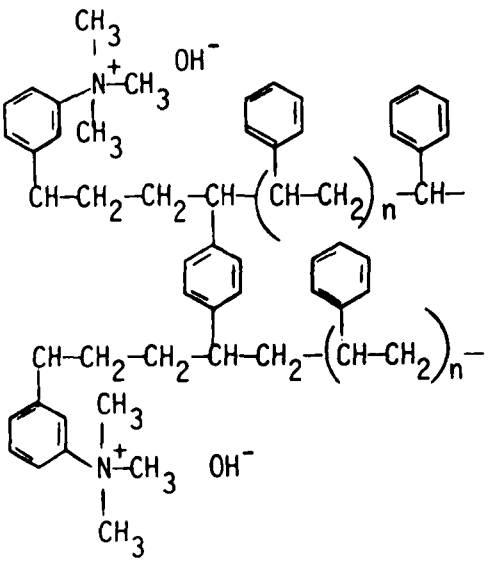
When ions elute from the resin, they are in a background of the mobile phase ions. For many years, research was spent in attempting to develop a universal detector which would be compatible with the mobile phase ions. In 1975, Bauman, Small and Stevens[2] presented a paper which established the principles of modern ion chromatography. These workers minimized the chemical effects of the mobile phase so that a conductivity meter could be used as the detector system. Bauman, Small and Stevens placed a second ion-exchange column behind the first which suppressed or neutralized the mobile phase but did not interfere or alter the sample ions. The second ion-exchange column is always opposite in chemical nature (acid or base) to the mobile phase. If the mobile phase ions are protons, the second ion-exchange column is a hydroxide ion exchanger for neutralization. Modern ion chromatography employs an anion or cation ion-exchange column followed by a second acid or base ion-exchange column to produce a deionized water background with the anion or cation present as an acid or base respectively.

3.1.1 Column Packing

The solid material or resin where the ion-exchange occurs is referred to as the column packing. The column packing is usually spherical particles of divinylbenzene cross-linked polystyrene which forms the backbone of the resin. The chemical functional groups fixed to the backbone gives the resin its chemical exchange characteristics. Figure 9 shows the two



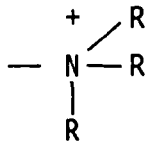
CATION RESIN



ANION RESIN

Figure 9. Structure of Varian Aerograph Anion and Cation Exchange Resins

different Varian Aerograph ion-exchange resins with $-SO_3^-$ for cation analysis or



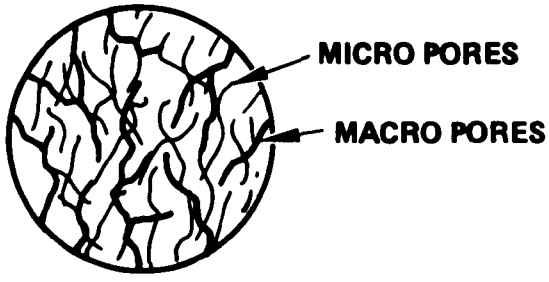
for anion analysis.

There are only two types of column packings employed for ion chromatography, high capacity or macroreticular and low capacity or pellicular. Capacity refers to the amount of active sites or functional groups available for ion-exchange. High capacity packings are porous because they contain both micropores and rigid pores. Low capacity packings are only slightly porous because they have a solid inert core with a thin coherent film of ion-exchange material on the surface. Figure 10 illustrates the difference between high and low capacity ion-exchange packings.[1]

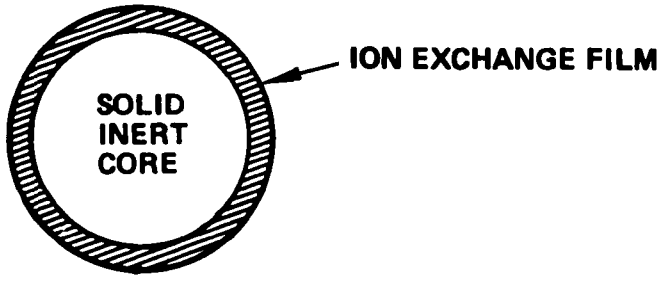
The first ion-exchange column is called a separator and is usually a low capacity column. The second column, called a suppressor, neutralizes the mobile phase and is usually a high capacity column. Also, the mobile phase is usually referred to as the eluent in ion chromatography.

3.1.2 Practical Ion Chromatography

The following example illustrates the use of practical ion chromatography.[2] A sample containing Li^+, Na^+, and K^+ enters an ion chromatography which has been set up for a cation separation. The first column is a cation-exchanger (low capacity-sulfonated). The eluent is dilute nitric acid which has been constantly pumped through the column before the sample enters, therefore, the function group is occupied by H^+ ions before the sample is injected into the column. When the sample enters the first column, Li^+, Na^+, and K^+, now try to displace H^+ from the active site or function group of resin. Lithium ion being the smallest ion of the three will have the least affinity to the resin because its charge is hardest to polarize. Potassium ion being the largest will be most attracted because its charge will polarize and form a strong ion-pair. The order of elution from the first column will be Li^+, Na^+ and K^+ in a H^+, NO_3^- background. The NO_3^- ions from the eluent and all other anions



MACRORETICULAR ION EXCHANGER RESIN
(HIGH CAPACITY)



PELLICULAR ION EXCHANGER RESIN
(LOW CAPACITY)

Figure 10. Cross Sections of a Macroreticular and Pellicular Resins

will not be retained by the first column. A key point to realize is that some of the protons used in the original eluent are now bound to the resin. Each time a Li^+, Na^+, or K^+ ion becomes bound to the resin, it replaced a proton on the resin. Later, the Li^+, Na^+, and K^+ ions would be displaced by a proton from the eluent before exiting the column. The rate of exchange between the coupling eluent ions and the cations of interest is determined by their concentrations and their individual affinities for the function group as previously described. Because of the constant exchanging between the eluent and the sample ions, no regeneration of the first column is necessary in ion chromatography. The eluent constantly provides the necessary protons for regeneration. As the separated ions elute the first column, they directly enter the second column.

The second column, or suppressor, contains a basic hydroxide exchange resin which neutralizes the acid eluent. Two reactions take place simultaneously in the suppressor column:

$$Li^+, Na^+, \text{ or } K^+ + NO_3^- + \text{Resin } OH^- \rightarrow \quad (10)$$

$$Li^+, Na^+ \text{ or } K^+ + OH^- + \text{Resin } NO_3^-$$

$$H^+ + NO_3^- + \text{Resin } OH^- \rightarrow H_2O + \text{Resin } NO_3^- \quad (11)$$

The first reaction (10) is an ion-exchange reaction between NO_3^- and OH^- which essentially liberates OH^- from the resin and converts the alkali metal chloride to their hydroxide. The second reaction (11) is a stripping reaction where H^+ will pull a OH^- ion from the resin. The sample ions are not affected by the second column and remain in the same elution order. As the sample ions elute the second column, they are now in a deionized water background and pass into the conductivity cell for detection.

Because the suppressor column is depleted of OH^- ions, it must be regenerated. The suppressor column is regenerated by flushing with NaOH:

$$NaOH + \text{Resin } NO_3^- \rightarrow \text{Resin } OH^- + Na^+ + NO_3^- \quad (12)$$

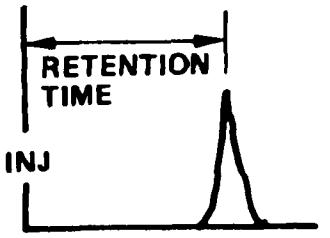
The Dionex instrument has a semi-automatic procedure for regeneration and this is usually done at the end of each day.

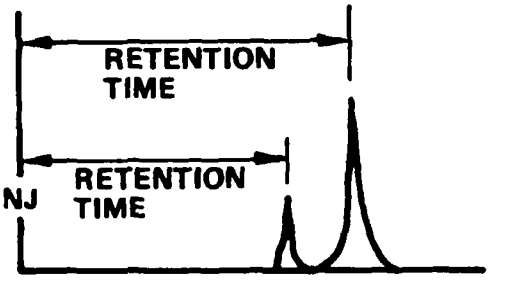
3.2 ION CHROMATOGRAPHY - DEFINITIONS

This section will define specific key concepts involving ion chromatography. These concepts are retention time, overloading or column capacity, resolution, temperature, columns, and filtration. Other chromatographic concepts like temperature programming, solvent efficiency, programmed eluent gradient solution, etc. will not be discussed because they are currently not employed in ion chromatography. Ion chromatography is a relatively new technique and most research has been involved in the application areas using standard columns. As ion chromatography develops, research will find new packing material for more types of separation, or develop techniques like programmed gradient elution. The concepts defined in this section will help the analyst avoid problem areas which could occur during an I.C. analysis.

3.2.1 Retention Time

Retention time refers to the time between the injection point and the peak maximum.





Retention times are used for qualitative analysis. The most important factor for all types of chromatographic systems is that the retention time must be reproducible. For ion chromatography, the retention time of a species may vary by ±20 sec. Any large deviation in retention time usually indicates a change in column conditions. Standard mixtures are analyzed to monitor column performance and correct for changes in column conditions.

3.2.2 Resolution

Resolution refers to the separation of two consecutive peaks. Usually increasing column length or reducing the acidity or basicity of the eluent will improve resolution of two consecutive peaks. Ion chromatography offers distinct advantages over other chromatographic techniques through the use of wet chemical techniques and deviatives[3]. Figure 11 shows an ion chromatogram where $SO_3^=$ and NO_3^- peaks are not completely resolved. The use of wet chemical techniques can completely resolve the $SO_3^=/NO_3^-$ problem without any changes to the columns or eluent. The addition of perixode to a second sample will oxidize $SO_3^=$ peak. The second sample is run on the ion chromatography and the difference between the first ion chromatogram and the second will determine the $SO_3^=$ concentration. Figure 11 shows the second ion chromatogram with the addition of peroxide. The initial peak at 2.5 min mark of the ion chromatogram indicates the peroxide and peroxide by-products. Figure 12 shows a chromatogram of a 100 ppm $SO_3^=$ standard (9 min RT). The large peak at 13.8 min is $SO_4^=$. Figure 12 shows the same $SO_3^=$ standard with the addition of H_2O_2, which converts all the $SO_3^=$ to $SO_4^=$. Figure 12 shows the chromatogram of a 100 ppm standard of NO_3^- (9 min RT). Notice that the NO_3^- response is much stronger than the $SO_3^=$ response for the same concentration. The detector response is a function of concentration and ion conductance.

3.2.3 Column Capacity - Overloading

The term column capacity refers to the amount of active sites available for ion-exchange. Separator columns are low capacity resins which can be easily overloaded because the active sites are scattered on the surface. The term overloaded means that all the active sites on the resin are being occupied and there is an excess of ions still competing for the active sites. Overloading a column's capacity is indicated by a reduction in the retention time of the operation and changes in peak shape. Both reduction in retention time and a change in peak shape occur simultaneously. The peak shape for most species on an ion chromatogram are usually sharp spikes or gaussian. When overloading occurs, the shape of the peak moves from gaussian to skewed with increased tailing.

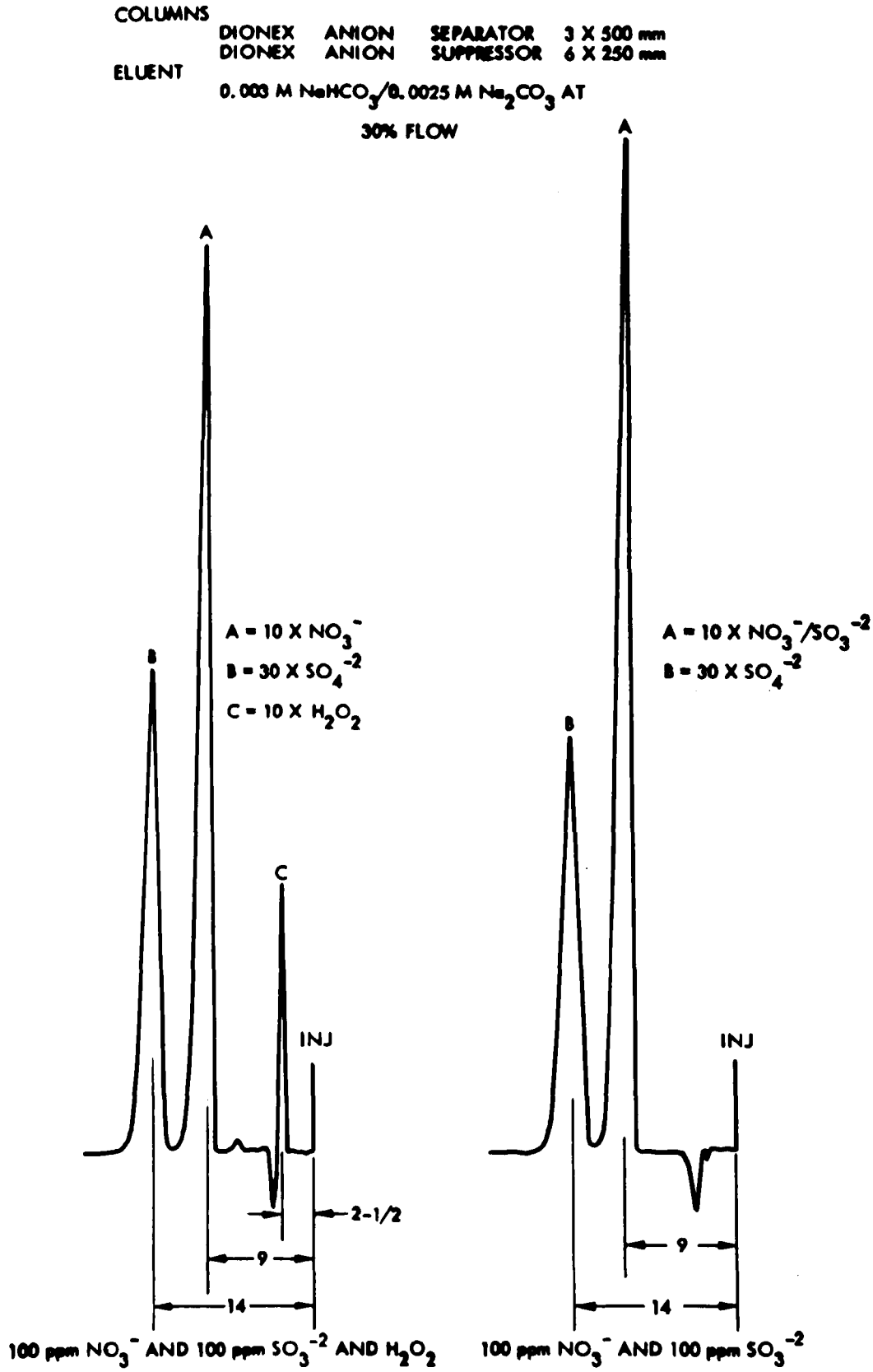


Figure 11. Use of Peroxide to Resolve the Peak Overlap of Nitrate/Sulfite

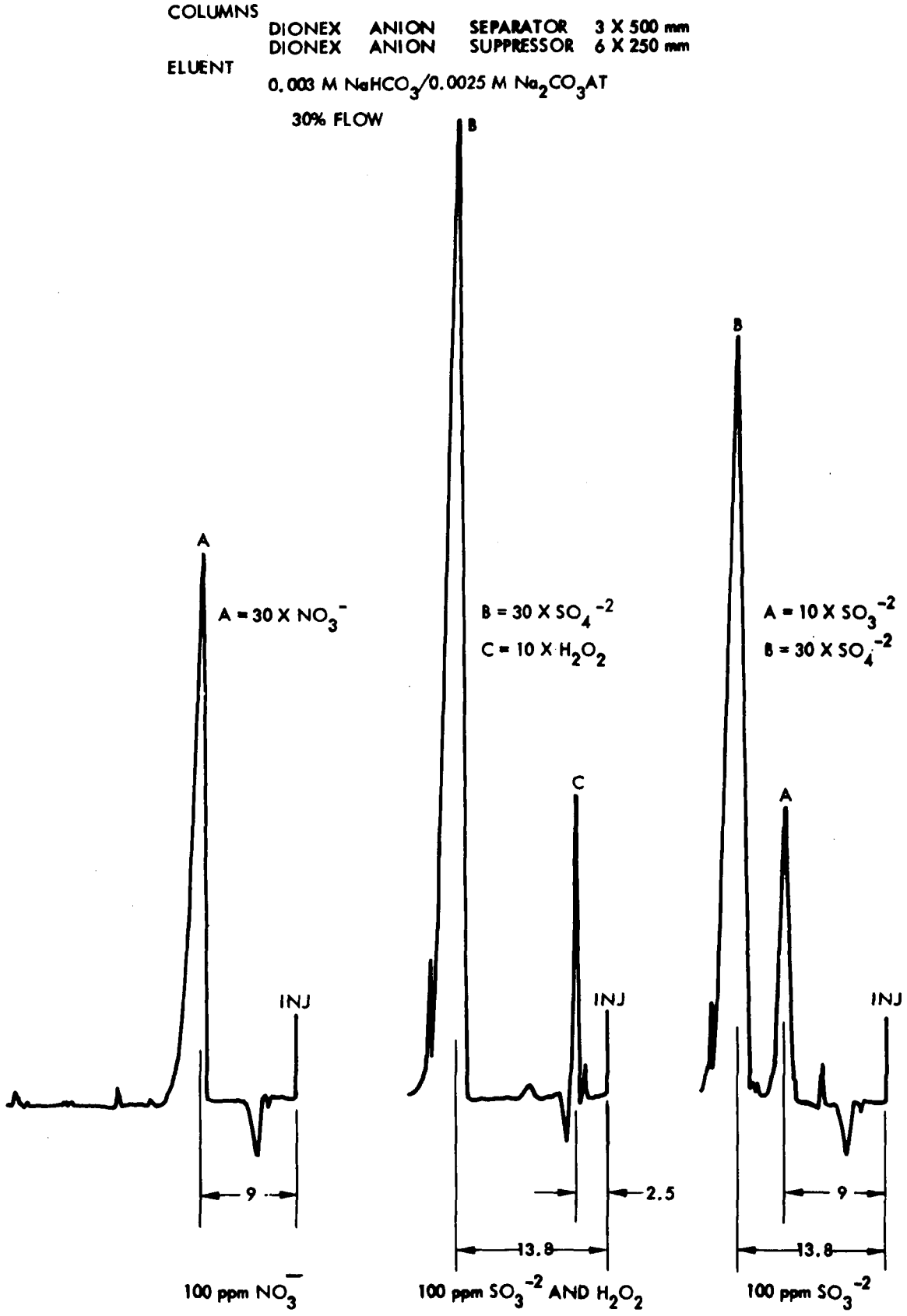
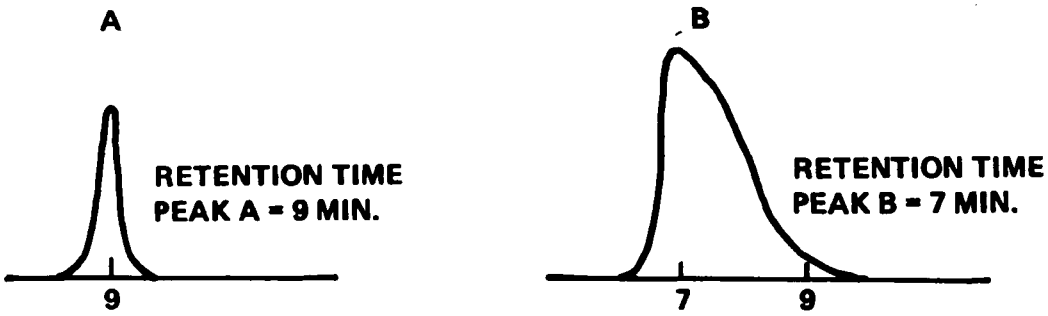


Figure 12. Ion Chromatograms of Sulfite, Sulfite and Peroxide, and Nitrate



The change in peak shape and the decrease in retention time is caused by similar ion agglomeration at the overloaded active site. Ions at the overloaded site are not absorbed but just associated with the others. These ions tend to be more loosely held and migrate faster than those ions directly associated with the functional group causing the skewed peak shape. The tail of the overloaded or skewed peak will always coincide with the tail of the gaussian peak. Comparing the tailing of overload peaks to standard peaks sometimes can be used to distinguish or identify certain unresolved ions.

3.2.4 Temperature

In general, temperature does not affect an ion chromatography analysis of scrubber samples. Temperature changes of 3-5°C/24 hr period can be tolerated without significant degradation of retention time or calibration curves. Temperature changes above 1°C/hour are not acceptable.

3.2.5 Pre-columns

Pre-columns are short (5 to 20 mm) columns packed as the separator, and are placed before the separator column. Since separator columns are expensive, pre-columns are employed to extend the separator column life. By holding up or filtering out trace impurities in the sample, the pre-columns prevent contaminants from contacting the separator column.

3.2.6 Sample Filtration

Samples should be filtered before injection into the ion chromatograph. In the sample collection section, it was recommended to filter the wet scrubber sample with a Gelman Acropore 1.2 μm filter before injection. If samples contain particulate matter and are not filtered before injection

into the I.C., they will eventually restrict the flow of the element and problems with pressure drop will develop.

3.3 SOLID SAMPLE PREPARATION

All liquid samples can be run directly after dilution as long as the results are on scale. Sample preparation is required for all solid samples prior to I.C. analysis. The solids from both the lime/limestone and dual alkali systems will have to be treated in a similar fashion so that cations and species like $SO_3^=$, $SO_4^=$, Cl^- and $CO_3^=$ can be analyzed. Table 2 summarizes the extraction procedures that may be used to solubilize components of the filter cake. A distinction between water soluble and acid soluble species is made for the dual alkali systems, since $NaSO_3$ or $NaSO_4$ might be contained in the cake. The two acid extraction procedures are designed to stabilize the scrubber related solids ($CaSO_4$, $CaSO_3$, $CaCO_3$, CaO) and leave the fly ash. The difference in sulfate values between the oxidizing acid extraction and the acid purging procedures is the sulfite concentration. In systems where the spent slurry streams are oxidized prior to filtration, a direct measure of the sulfite is preferred. In this case the N_2 purge stream is collected in a 1% H_2O_2 trap and analyzed for $SO_4^=$, which can be related back the original concentration of sulfite in the solids.

3.4 CATION ANALYSIS

The cations of interest for both dual alkali and lime/limestone wet scrubbers are: Na^+, K^+, Mg^{++} and Ca^{++}. The analytical procedure for cation analysis utilizes the Dionex Ion Chromatograph. Since the cations of interest for the wet scrubber analysis are in concentrations greater than 100 ppm, the Minimum Detectable Limit (MDL) for all cations in this procedure is one ppm. The Dionex ion chromatograph using this analytical procedure will have much lower MDLs for all cations. However, the objective of this manual is to apply ion chromatography to wet scrubber samples, not to evaluate the capabilities of the instrument. The cation analysis procedure contained in this manual is based on the procedures called for in the Dionex instruction manual, as modified by TRW for these types of samples.

Table 2. Extraction Approaches for Solid Samples

System	Extraction System	Procedure	Species Extracted
Dual Alkali	1. O_2 free H_2O	Extract 1 g of solids with 10 mL O_2 free air, filter and dilute to 50 mL.	- Cl^- - Water soluble $SO_4^=$, $SO_3^=$, $CO_3^=$ - Cations
Lime/ Limestone - Dual Alkali	2. 0.1 m HCl/3% H_2O_2	Extract 1 g of solids with 10 mL of 3% H_2O_2 followed by 10 mL of 0.1 N HCl. Dilute to 100 mL.	- Total sulfur (as $SO_4^=$) - Cations
Lime/ Limestone - Dual Alkali	3. 0.1 m HCl with N_2 purging	Place 1 g of solids into a small impinger. Add 10 mL of O_2 free 0.1 M HCl to impinger and begin sparging with O_2 free N_2. Continue until no more solids dissolve. Dilute to 100 mL. (NOTE: For non-water soluble $CO_3^=$ a dilute NaOH trap should be added to collect the CO_2 for analysis).	- $SO_4^=$ - $SO_3^=$ (Total Sulfur - $SO_4^=$) - TOS ($SO_3^=$) - $CO_3^=$ (if NaOH trap used)

3.4.1 Sodium and Potassium Analysis

Sodium and potassium are run on the Dionex cation separator (6 x 250 mm) and suppressor (9 x 250 mm) columns. The pump is set for 40% flow rate with 0.005 N HNO_3 as eluent. The retention time for 10 ppm Na^+ is seven minutes and twelve minutes for 10 ppm K^+.

Trace metals sometimes tend to build up in the Dionex cation separator column and this is reflected in changes in retention time and peak height. By flushing the cation separator column with ultra pure 1 N nitric acid for 15 to 30 minutes, the trace metal buildup will usually be removed. In general, it is a good practice to always flush the ion chromatograph with deionized water for 30 minutes, after a set of analyses or column changes. This includes flushing the detector system and not just the columns.

3.4.2 Magnesium and Calcium Analysis

Magnesium and calcium are separated with a Dionex cation separator (6 x 250 mm) and suppressor (9 x 250 mm) columns. The pump is set for 40% flow rate with 0.001 M p-phenylenediamine dihydrochloride as eluent. The retention time for 10 ppm Mg^{+2} is eight minutes and 12 minutes for 10 ppm Ca^{+2}.

The same type of columns are used in the Mg^{+2}/Ca^{+2} separation as in the Na^+/K^+ separation but the two groups of separations must be run on a different set of columns. Since the p-phenylenediamine dihydrochloride eluent tends to deteriorate the columns and the Na^+/K^+ separation is poor on columns that are exposed to this eluent. Because of the cost of the columns, it is more practical to run the two groups of separations on two sets of columns rather than the one set. Nitric acid does not work as an eluent for the Mg^{+2}/Ca^{+2} separation.

The deterioration of the cation separator is very easy to identify because the column turns from white to dark gray to black. The nitric acid eluent does not deteriorate or change the color of the cation separator column and, therefore, it is very easy to distinguish between two sets of columns. Whenever p-phenylenediamine dihydrochloride is employed as an eluent, it should be made up fresh every day. This is a modification of the Dionex procedure which states that p-phenylenediamine dichydrochloride should be made up fresh every week. TRW found that this eluent lost its

ability to force the Mg^{+2}, Ca^{+2} separation, and the deterioration of the column was more rapid when the eluent was not fresh. After using p-phenylenediamine dihydrochloride, the ion chromatographic should be flushed with deionized water overnight, including the conductivity cell. This can be done by filling the water reservoir (4 liters) and employing a flow rate of 20%. Sometimes, flushing the columns with 1 N nitric acid for one hour will remove some of the dark gray or black in the separator column followed by the overnight deionized water rinse. It is extremely important to rinse the conductivity cell after each Mg^{+2}/Ca^{+2} run because p-phenylenediamine dihydrochloride tends to cause a buildup of particles in the cell.

3.5 ANION ANALYSIS

The anions of interest for both dual alkali and lime/limestone wet scrubbers are: sulfite, sulfate, carbonate, chloride and nitrite. The anion analysis procedure was not developed by TRW but was taken directly from the Dionex instruction manual. The MDL for sulfite, sulfate and nitrite is one ppm. Chloride could vary between 0.1 and 10 ppm depending on conditions, and carbonate's MDL is 5 ppm. In the chloride analysis, the MDL improves if eluent is added to the sample before analysis. The addition of eluent to the sample suppresses the water dip on the ion chromatogram which occurs immediately before the chloride peak. The carbonate usually has a high MDL because of the carbonate found in the blanks.

The analytical scheme is based on the retention time for sulfate which is the last species of interest to elute from the columns. The conditions stated below will cause sulfate to elute in 15 to 17 minutes, but the sulfite and nitrate peak will only be partially resolved. Conditions can be changed so that sulfite and nitrate will be completely resolved, but the retention time of sulfate will increase to about 45 minutes. The main problem with increased retention time is that peak heights or areas become very difficult to determine and thus introduces errors into the analysis. With shorter retention times, the peaks are gaussian and, therefore, much easier to quantitate. Since wet scrubbers samples normally have very little nitrate, this scheme uses the shorter analysis time procedure.

3.5.1 Chloride, TOS and Sulfate Analysis

The first anion sample run determines the amounts of chloride, total oxidizable sulfur (TOS) and sulfate. TOS species are sulfite and bisulfite. Both sulfite and bisulfite elute as a single peak because bisulfite cannot exist in the eluent which has a pH of 10. The columns employed are the Dionex anion separator (3 x 500 mm) and suppressor (6 x 250 mm). The pump is set for 30% flow rate with 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3 as eluent. The retention time for 10 ppm Cl^- is 4.5 min, ten min for TOS and 16 min for SO_4^{-2}. If sulfite/nitrate separation becomes a problem, then the eluent strength should be changed to 0.003 M $NaHCO_3$/0.0012 M Na_2CO_3.

3.5.2 Sulfur and Nitrate Analysis

If one is interested in total sulfur or determining nitrate but not increasing analysis time, a second anion sample should be run. The ion chromatographic columns and conditions are the same except that the anion sample is pretreated with H_2O_2. The peroxide oxidizes the sulfur in solution to $SO_4^=$, so that the total sulfur can be determined, and it removes any $SO_3^=$ /NO_3^- peak overlap.

3.5.3 Carbonate Analysis

Carbonate is run on a BioRad AG50W suppressor column (200-400 mesh, 6 x 500 mm). The pump is set for a 30% flow rate with deionized water as the eluent. The BioRad resin separates out $CO_3^=$ from all other anions by ion exclusion. The retention time for 10 ppm $CO_3^=$ is 6 minutes where all other anions will elute in 2 minutes. The carbonate determination employs only a single column, the suppressor is not used. Bicarbonate is converted to carbonate by the eluent and total carbonate is analyzed in a fashion analogous to $SO_3^=/HSO_3^-$.

3.5.4 Hydroxide Analysis

Hydroxide cannot be determined by ion chromatography. The alternate method for determination of hydroxide is titration. Because the wet scrubber samples also contains $CO_3^=$ ions, the titration will require two indicators (phenolphthalein and methyl orange). The sample is titrated with standard acid, first to the phenolphthalein endpoint (pH 9-10), and then further to the methyl orange endpoint (pH 4-5). The following example[4] illustrates the dual endpoint titration technique.

Example: A 25.00 mL aliquot of a solution containing NaOH and/or Na_2CO_3 and/or $NaHCO_3$ requires 24.23 mL of 0.100 N HCl to the phenolphthalein endpoint and an additional 22.37 mL from the phenolphthalein to the methyl orange endpoint. Assuming that endpoint errors are negligible, calculate the composition of the sample.

Since A_m(24.23 + 22.37, or 46.60 mL) is less than twice A_p(24.23 mL), the sample must contain NaOH as well as Na_2CO_3.

To the phenolphthalein endpoint:

$$OH^- + H_3O^+ \rightarrow 2H_2O$$

$$CO_3^= + H_3O^+ \rightarrow HCO_3^- + H_2O$$

$$\left(\begin{array}{c}\text{mmoles NaOH +} \\ \text{mmoles } Na_2CO_3\end{array}\right) = \left(\begin{array}{c}\text{mmoles HCl used to} \\ \text{phenolphthalein endpoint}\end{array}\right) \qquad (13)$$

$$= 0.1000 \times 24.23 = 2.423$$

To the methyl orange endpoint:

$$OH^- + H_3O^+ \rightarrow 2H_2O$$

$$CO_3^- + 2H_3O^+ \rightarrow H_2CO_3 + 2H_2O$$

$$\left(\begin{array}{c}\text{mmoles NaOH +} \\ 2 \times \text{mmoles } Na_2CO_3\end{array}\right) = \left(\begin{array}{c}\text{mmoles HCl used to} \\ \text{methyl orange endpoint}\end{array}\right) \qquad (14)$$

$$= 0.1000 \times 46.60 = 4.660$$

From the difference between Eqs. (13) and (14), the number of mmoles of Na_2CO_3 in the 25 mL aliquot is 4.660 - 2.423, or 2.237. The Na_2CO_3 concentration is therefore 2.237/25.00, or 0.0895 M.

By difference, the number of mmoles NaOH in the 25 mL aliquot is 2.423 - 2.237, or 0.186. The NaOH concentration is therefore 0.186/25.00 or 0.00744 M.

4. QUALITATIVE ANALYSIS

This section is devoted to the identification of the various species found in the process streams of wet scrubbers. In general, species of interest for wet scrubbers are found in concentrations of greater than 100 ppm. Compound and species identification by ion chromatography (I.C.) is based upon the retention time of standard solutions. Since most resins employed for I.C. are low capacity, the retention time can vary with sample concentration. As stated in the previous section, the retention time of various species analyzed by I.C. can vary approximately ±20 sec. where any larger time deviations usually indicate changed column conditions. In this manual, all retention times refer to 10 ppm standards of the stated species.

4.1 RETENTION TIME TABLES

The retention times for the various wet scrubber species are listed in Table 3. The retention time was determined for a 10 ppm standard solution of each species. The standard solution consisted of dissolving the appropriate amount of soluble salt in deionized water. Because I.C. is a separation technique, it should not suffer from matrix interferences like atomic absorption. I.C. interferences usually center around the incomplete resolution of two species. Table 3 is a reference table which will give an analyst some approximate indication where and in what order species will separate. An analyst should develop his own retention time table.

TABLE 3. RETENTION TIME OF VARIOUS IONS FOUND IN WET SCRUBBERS

Species	Conc.	Retention Time	Dionex Separator Column	Dionex Suppressor Column	Flow Rate	Eluent	Temp.
Cl^-	10 ppm	4.5 min	Anion 3 x 500	Anion 6 x 250	30%	0.003M $NaHCO_3$/ 0.0025M Na_2CO_3	24°C
$SO_3^=$	10 ppm	10	Anion 3 x 500	Anion 6 x 250	30%	0.003M $NaHCO_3$/ 0.0025M Na_2CO_3	24°C
NO_3^-	10 ppm	8	Anion 3 x 500	Anion 6 x 250	30%	0.003M $NaHCO_3$/ 0.0025M Na_2CO_3	24°C
$SO_4^=$	10 ppm	16	Anion 3 x 500	Anion 6 x 250	30%	0.003M $NaHCO_3$/ 0.0025M Na_2CO_3	24°C
$CO_3^=$	10 ppm	6	BioRad 6 x 500	None	30%	Water	24°C
Ca^{+2}	10 ppm	12	Cation 6 x 250	Cation 9 x 250	40%	for both cations 0.001 M p-phenylene-diamine dihydrochloride	24°C
Mg^{+2}	10 ppm	8	Cation 6 x 250	Cation 9 x 250	40%		24°C
Na^+	10 ppm	7	Cation 6 x 250	Cation 9 x 250	40%	.005N HNO_3	24 C
K^+	10 ppm	12	Cation 6 x 250	Cation 9 x 250	40%	.005N HNO_3	24 C

5. QUANTITATIVE ANALYSIS

This section is devoted to the quantification of the species of interest found in the process streams of wet scrubbers. This section will describe the ways for relating the ion chromatographic response to sample concentration and the statistical treatment of data.

5.1 DETERMINATION OF SAMPLE CONCENTRATION

The ion chromatographic response is quantified using peak height and calibration curves. Peak height is measured as the distance from the baseline to peak maxima as shown in Figure 13. The peak height is plotted vs sample concentration for a given conductivity scale and the resulting curve is known as an ion chromatographic calibration curve. The calibration curve is linear within a conductivity scale, but may plateau at higher ion concentration levels. A calibration curve is constructed by first preparing standard solutions of known ion concentration. The standard solutions are run on the ion chromatograph and their peak height is determined. Finally, the plot of sample concentration vs peak height is constructed. For routine analysis, calibration curves are very easy to use and concentrations can be read directly from the curve. Other techniques such as single point external standard (or internal standard) can also be employed.

When constructing the calibration curve, many data points should be taken between the limits of the conductivity scale. This will give the working range for the linearity of the calibration curve. Figure 14 shows that the linear range for Cl^- ions is from less than 1 ppm to 10 ppm and covers a peak height range from 1 to 25 cm, the full range on the strip chart recorder. The calculation of the slope of the curve is determined by a "least squares" fit of the data points.

Chromatograms can also be quantitated by measuring the peak area. A series of experiments have shown that peak height is better than peak area for quantification. Figure 15 shows the results between quantification by peak area and peak height. Peak areas were calculated by full width at half maximum (FWHM), baseline triangulation, and planemetry. The results indicate that peak height is a more consistent way for quantification of the ion chromatographic response.

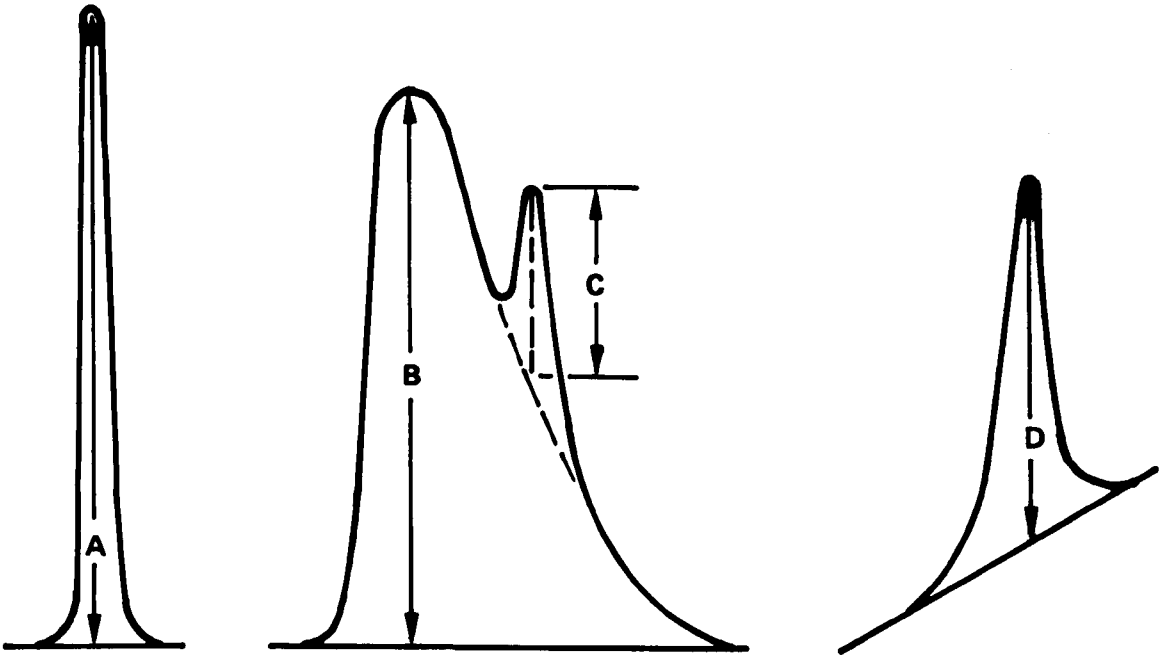


Figure 13. Example of Peak Height Measurements

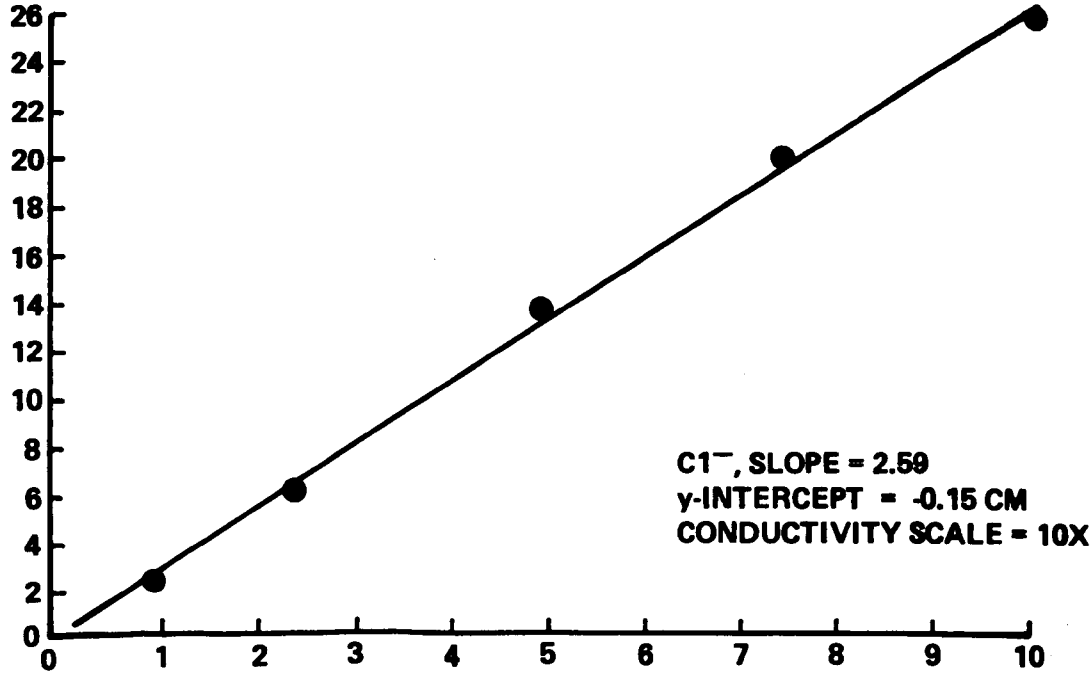
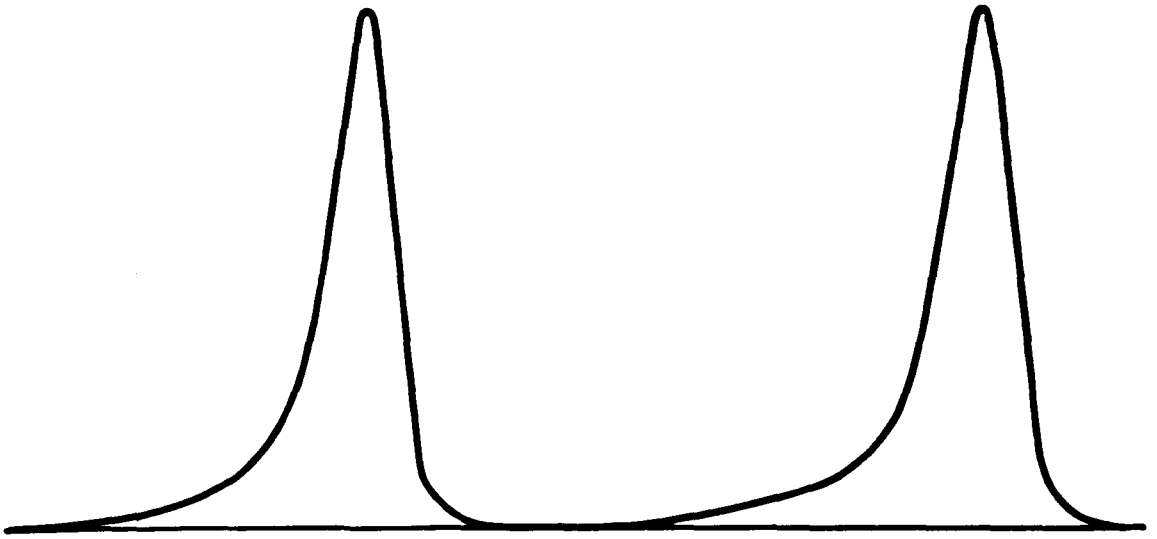


Figure 14. Calibration Curve for Chloride Ion Analysis



Na^+, 5 PPM, 10X

Na^+, 5 PPM, 10X

			RELATIVE ERROR
PEAK HEIGHT	= 6.97 CM	PEAK HEIGHT	= 7.00 CM 0.4%
FWHM	= 6.60 MM^2	FWHM	= 7.35 MM^2 10.2%
TRIANGULATION	= 7.13 MM^2	TRIANGULATION	= 7.32 MM^2 2.6%
PLANEMETRY	= 1.37	PLANEMETRY	= 1.42 3.5%

Figure 15. Example of Quantification by Peak Height and Peak Area

Determination of peak area by electronic integration is difficult. The peak shape from a chromatographic technique usually depends on the detector and type of column packing, and under most conditions all peaks will have the same shape. Ion chromatography does not follow the general characteristics stated above. The peak shape for each species is different for the same chromatographic conditions. Figure 16 is an ion chromatogram of a solution which contains F^-, Cl^-, NO_2, PO_3^{-3}, Br^-, NO_3^-, and SO_4^{-2}. Each ion has its own basic shape, F^- and Cl^- are sharp spikes whereas SO_4^{-2} is a broad gaussian. Electronic integration works by calculation of the change in slope of the peaks. Since each peak on the ion chromatogram has its own shape, the electronic integrator is normally set for one peak shape and cannot adjust to a different peak shape. If an analyst sets up the electronic integrator for Cl^-, then SO_4^{-2} cannot be determined. Also, species in high concentrations have a great deal of peak tailing, and an electronic integrator has difficulty determining where the peaks ends. Before an analyst uses a standard gas chromatograph integrator, he should check its operation for the above flaws. There are electronic integrators available (like the Spectra Physics SP4000) which have the capability to record peak height, and peak shape and these would be more adaptable to I.C. analysis.

A second reason why ion chromatography should not be quantified by electronic integration is the conductivity meter response. The meter response is only linear within a single scale or attenuation but nonlinear from one scale to another or changes in attenuation. The change in linearity between scales is significant enough to force the analyst to develop separate calibration curves for each scale, as in Figure 17. The Dionex instrument has nine scales but the analyst can employ dilution techniques to reduce the number of calibration curves. Usually, establishing calibration curves for the 1,3,10,30 μMHO scales gives an analyst a good workable concentration range.

The quantification of ion chromatography by peak height also has some problems. During the evaluation of the ion chromatograph, it was observed that the peak height for the same sample could change from day to day. Table 4 illustrates the changes in peak heights of various ions over a period of two months. The data in Table 4 shows that at the early part of

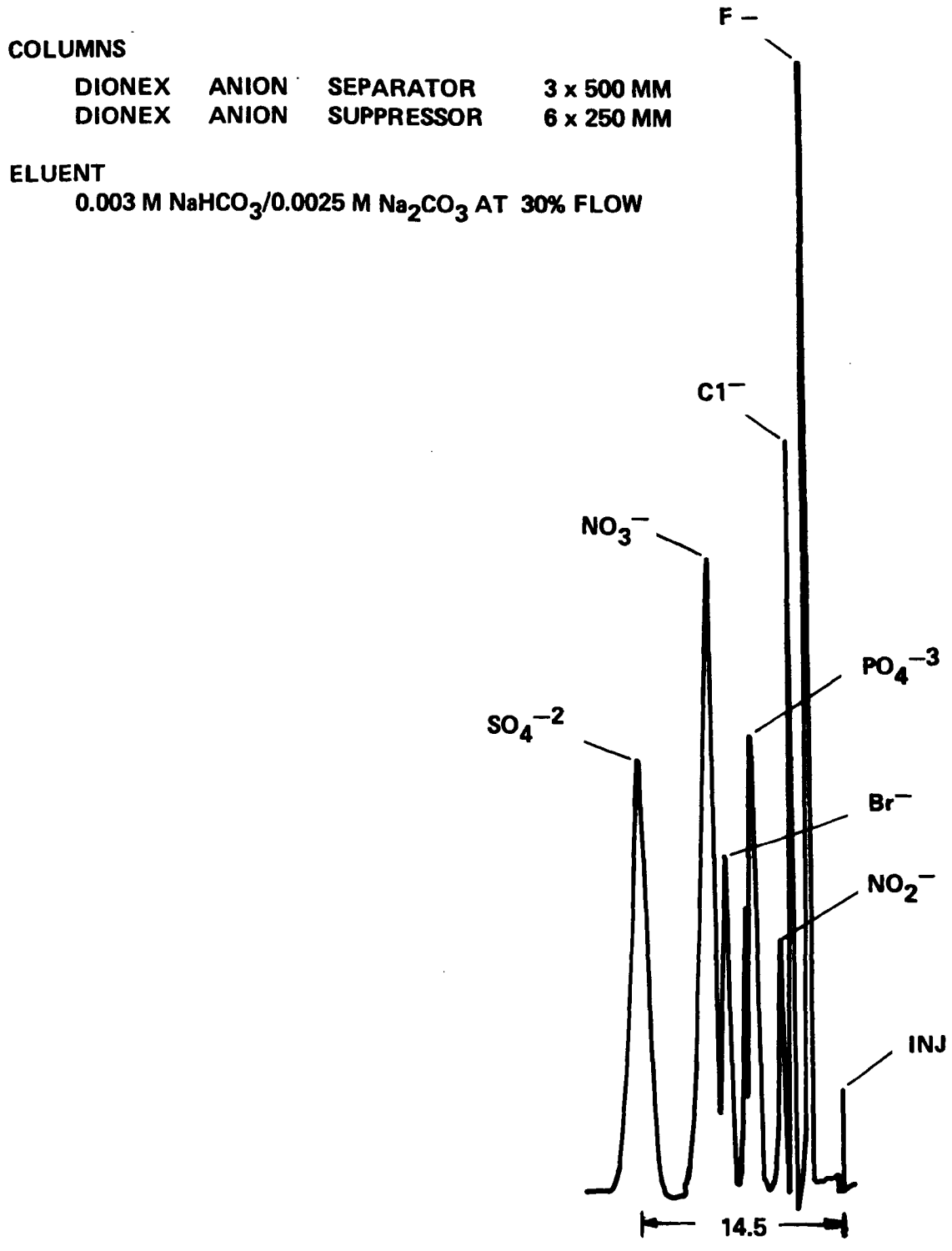


Figure 16. Ion Chromatogram of the Dionex Anion Standard Solution

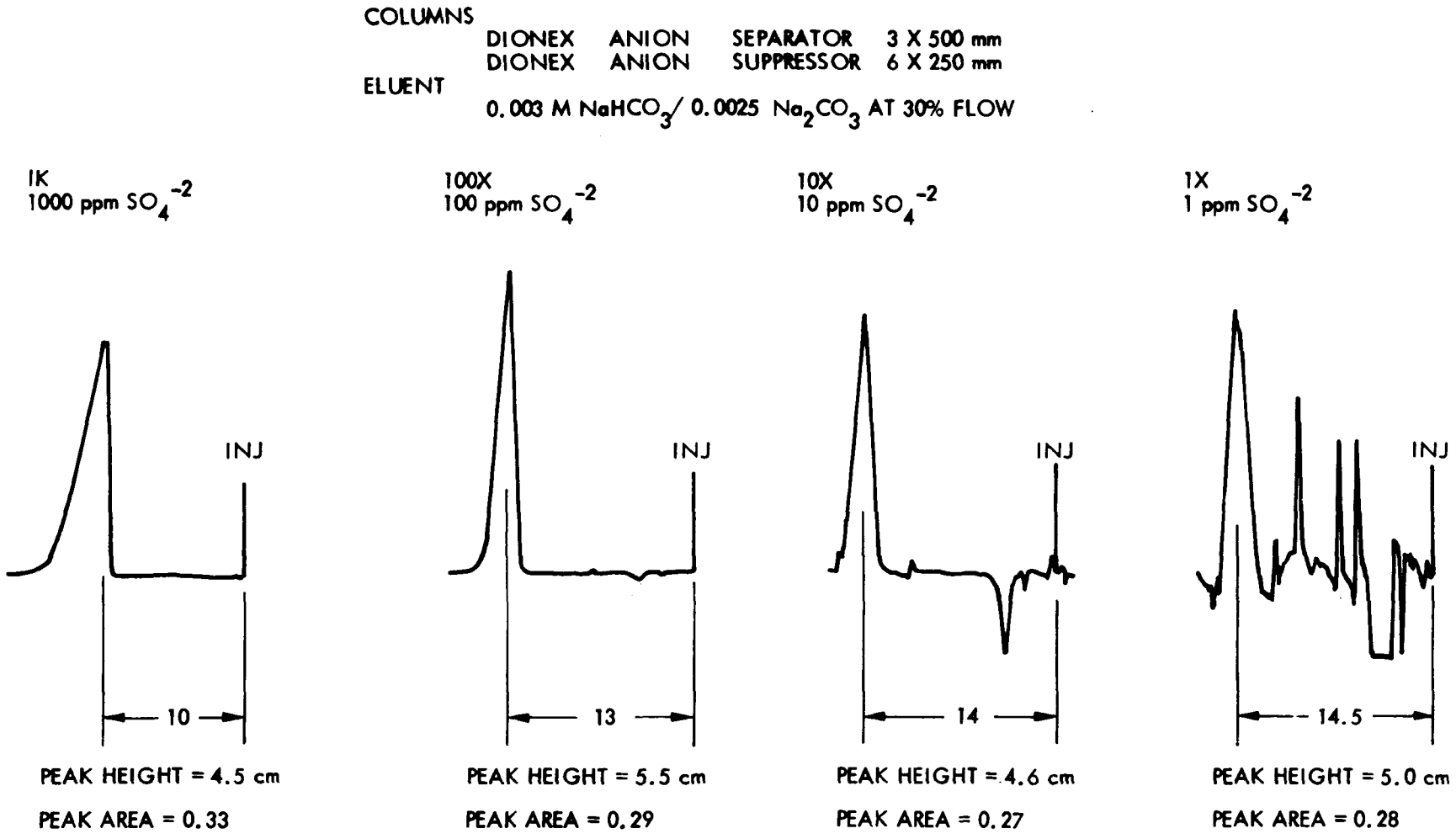


Figure 17. An Illustration of the Nonlinear Ion Chromatographic Detector Response

Table 4. PRECISION OF PEAK HEIGHT MEASUREMENTS

		Determinations							
Ions	Scale	1	2	3	4	5	6	Average	Standard Deviation
F^-	30X	20.7	20.0	20.1	20.8	23.3	23.5	21.4	1.6
Cl^-	10X	14.2	13.7	13.9	14.35	10.5	10.1	12.8	1.9
NO_2^-	10X	4.8	4.7	4.2	5	1.7	1.7	3.6	1.6
Br^-	10X	6	6	5.7	5.8	3.5	1.2	4.7	2
NO_3^-	10X	11.7	11.2	11.5	11.4	8.4	2.8	9.5	3.5
SO_4^{-2}	30X	8.2	8.3	8.0	8.4	8.1	8.3	8.2	0.15

the evaluation, determinations 1 through 4, the peak heights were consistent. As the column aged, the peak height became less consistent for certain species. This is shown with Br^- and NO_3^- while SO_4^{-2} vlaues indicate no loss. A column will also lose its ability to separate ions because of buildup of trace metals and impurities on the column packing.

Upon further examination of the above problem, it was observed that the slope of the calibration curve did not change, only the y-intercept. This observation is shown in Figure 18. The results of Figure 18 means that once a calibration curve is established, the analyst could continue to use it even though the column may be aging. The analyst must check the slope of the calibration curve by running two standards at the beginning and end of the analysis. When there is a change in the peak height of the standard, an analyst can make the connection by using the equation for a straight line:

$$y = mx + b$$

where y is the peak height, m is the slope of the curve, x is the concentration of the species, and b is the y-intercept. The analyst finds the y-intercept from the standard run on the day. The slope has already been known for the calibration curve and the peak height is directly measured from the ion chromatogram. By placing the corrected y-intercept into the equation for a straight line, the concentration of the ion is determined.

5.2 VERIFICATION OF PRECISION AND ACCURACY OF ANALYTICAL SCHEME

It should be emphasized that changes in the column or flow conditions, will cause changes in the qualitative and quantitative results obtained by this technique. The analyst should monitor and compensate for changes using the appropriate standards. The accuracy and precision of the analytical scheme was tested using real samples from the lime/limestone wet scrubber at the EPA/TVA Shawnee Test Facility in Paducah, Kentucky. Table 5 shows a direct comparison between TVA and TRW sample analyses for the lime/limestone wet scrubber. The relative error for each set of values is listed. Whenever large (> 20%) errors were found, an alternate analysis was employed as a check.

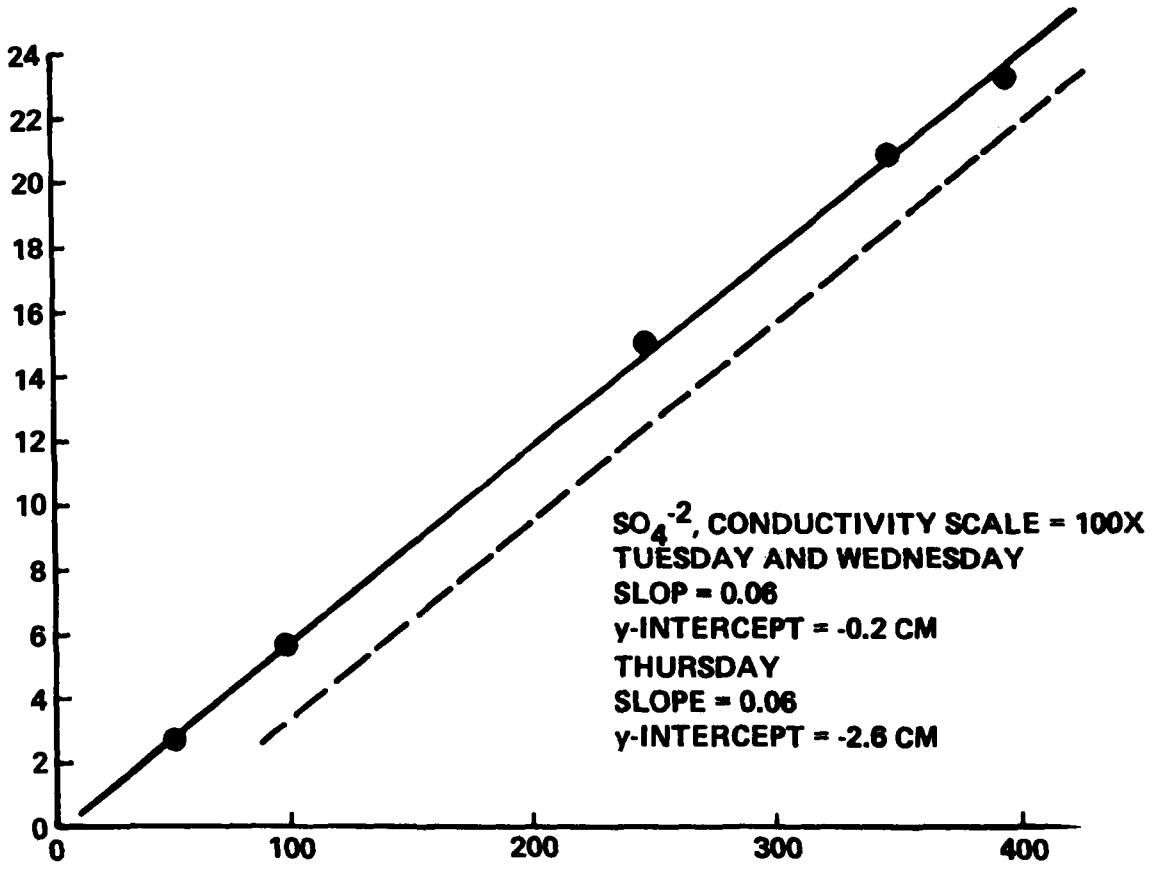


Figure 18. Calibration Curve for Sulfate Ion Analysis

TABLE 5. DIRECT COMPARISON BETWEEN TVA AND TRW SAMPLE ANALYSIS FOR THE VENTURI SPRAY TOWER SCRUBBER

Species	Method of Analysis	Concentration (ppm), Relative Error, and TVA Sample Identification			
		#5253	#5254	#5255	#5256
Calcium	Atomic Absorption (TVA) Ion Chromatography (TRW)	604 551 9%	624 618 1%	618 614 1%	667 541 19%
Magnesium	Atomic Absorption (TVA) Ion Chromatography (TRW) Atomic Absorption (TRW)	8219 10506 26% 11025 5%	5269 5030 5%	4629 5536 16%	8179 10014 22% 10490 5%
Sodium	Atomic Absorption (TVA) Ion Chromatography (TRW) Atomic Absorption (TRW)	186 172 8%	192 197 2% 195 1%	55 99 46% 102 3%	47 92 48%
Sulfate	Ion Exchange (TVA) Ion Chromatography (TRW)	32994 34000 3%	17584 16209 8%	17700 16660 6%	31442 34404 9%
Chloride	Potentiometric (TVA) Ion Chromatography (TRW)	2676 2726 2%	1418 1454 3%	1418 1485 5%	2614 2675 2%

The magnesium values reported by TRW differed greatly from the TVA values and a second determination was carried out by atomic absorption at TRW. The results of the atomic absorption analyses by TRW were in agreement with the ion chromatography values. The magnesium results indicated that there must be a shift in the solution equilibrium because of the time difference between sampling at Paducah and analysis at TRW. A check of the pH of the sample solutions showed that all the solutions decreased in acidity to almost neutral or slightly basic. Figure 19 shows an ion chromatogram of the magnesium/calcium analysis.

The chloride ion values were very consistent for both analytical techniques employed. Chloride is completely ionized in solution and should be less susceptible to changes in pH. The relative differences between the reported values ranged from 1.8% to 4.5%.

Sodium ions are also completely ionized in solution and their values should not vary with changes in pH. Only two of the four TVA determinations for sodium showed good agreement with the TRW results. The two values which disagree are approximately one-half less than the TRW values. Again, atomic absorption was used as a check and the TRW values agreed with the ion chromatography analyses. Figure 20 shows an ion chromatogram of the sodium analysis.

Process streams which contain both sulfate and sulfite ions when sampled will constantly increase in sulfate due to oxidation. The TRW values for sulfate show both high and low values compared to the TVA results, but both sets still showed good agreement. The variations between the TVA and TRW analyses seem to be due to sampling and time and not instrumental problems. Figure 21 shows an ion chromatogram of the chloride/sulfate analysis.

Real samples could not be acquired from a dual alkali wet scrubber because none were in operation. The results of the Shawnee tests would indicate that ion chromatography is capable of analyzing samples from a dual alkali process. Remembering that one-half of the dual alkali process involves lime and/or limestone, these process streams are very similar to the Shawnee scrubber streams and should be amiable to I.C. analysis.

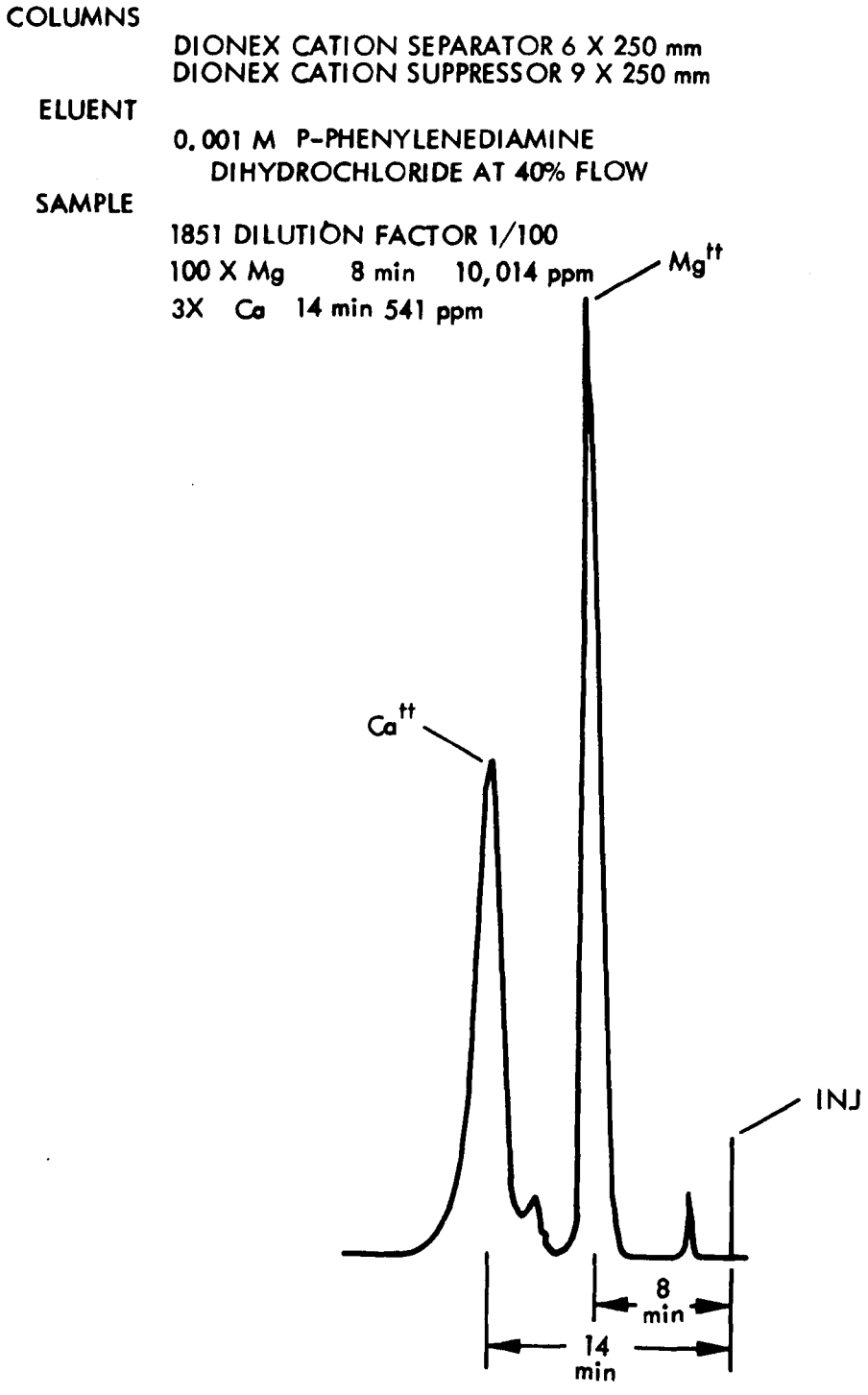


Figure 19. Ion Chromatogram of the Magnesium/Calcium Analysis

COLUMNS

DIONEX CATION SEPARATOR 6 X 250 mm
DIONEX CATION SUPPRESSOR 9 X 250 mm

ELUENT

0.005 N HNO_3 AT 30% FLOW

SAMPLE

1851 DILUTION FACTOR 1/100
Na 10X 193 ppm 5.5 min

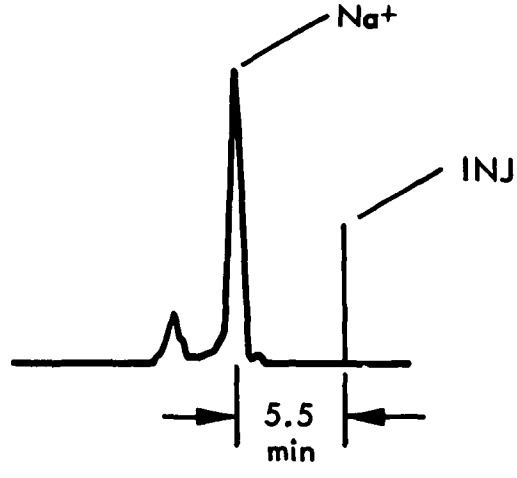


Figure 20. Ion Chromatogram of the Sodium Analysis

COLUMNS

DIONEX ANION SEPARATOR 3 X 500 mm
DIONEX ANION SUPPRESSOR 6 X 250 mm

ELUENT

0.003 M $NaHCO_3$/0.0025 M Na_2CO_3 AT 30% FLOW

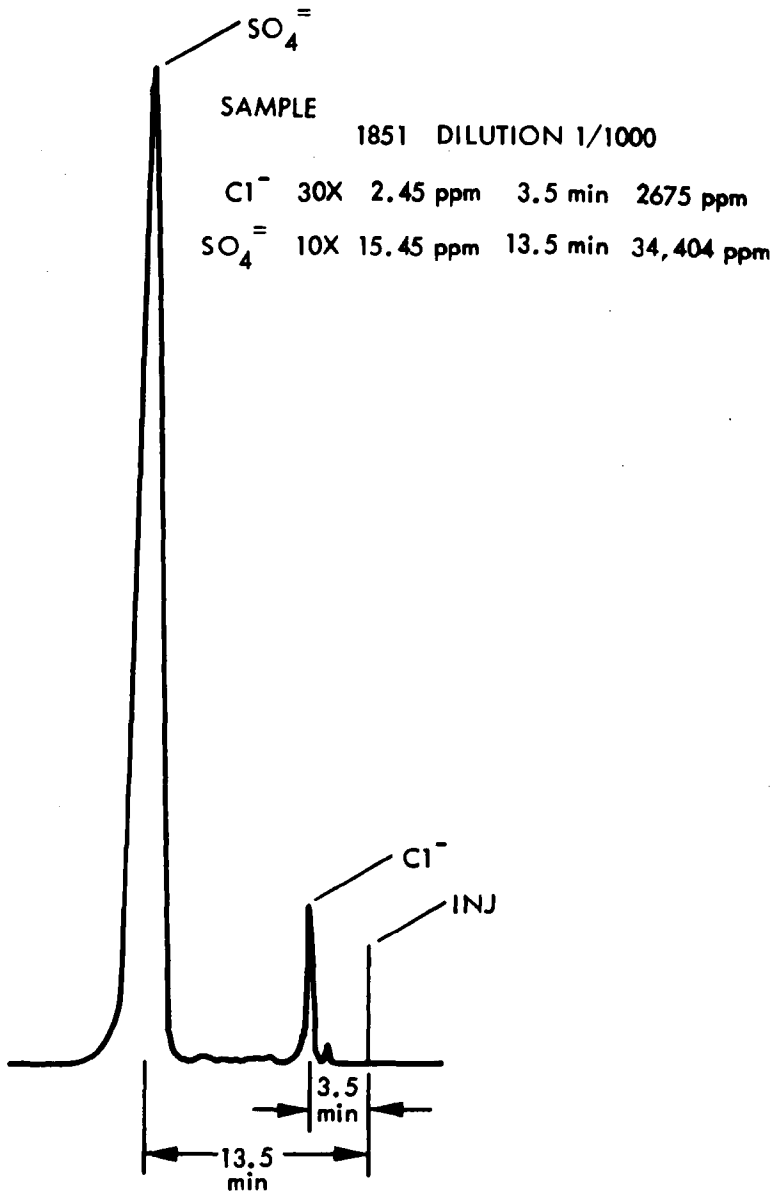


Figure 21. Ion Chromatogram of the Chloride/Sulfate Analysis

6. REFERENCES

1. Snyder, L. R. and Kirsland, J. J., Introduction to Modern Liquid Chromatography, Wiley-Interscience, New York, 1974, P. 283.

2. Small, H., T. S. Stevens and W. C. Bauman, "Novel Ion Exchange Chromatographic Method Using Conductimetric Detection," Anal. Chem. 47:1801 (1975).

3. Mulik, J. D., Todd, G., Estes, E., Puckett, R., Sawicki, E., and Williams, D. "Ion Chromatographic Determination of Atmospheric Sulfur Dioxide," Ion Chromatographic Analysis of Environmental Pollutants, Sawicki, E., Mulik, J. B., and Wittgenstein E., Eds. Ann Arbor Science, Ann Arbor, Mich., 1978, p. 23-40.

4. Blaedel, W. J. and V. W. Meloche, Elementary Quantitative Analysis, Harper and Row, New York, 1963, p. 796-7.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/7-79-151		

4. TITLE AND SUBTITLE	5. REPORT DATE
Chemical Analysis of Wet Scrubbers Utilizing Ion Chromatography	July 1979
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Tobias R. Acciani and Ray F. Maddalone	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
TRW Defense and Space Systems Group One Space Park Redondo Beach, California 90278	INE624
	11. CONTRACT/GRANT NO.
	68-02-2165, Task 214
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711	Task Final; 9/77 - 9/78
	14. SPONSORING AGENCY CODE
	EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Frank E. Briden, MD-62, 919/541-2557.

16. ABSTRACT The report describes the key elements required to develop a sampling and analysis program for a wet scrubber utilizing ion chromatography as the main analytical technique. The first part of the report describes a sampling program for two different types of wet scrubbers: the venturi/spray-tower (limestone) scrubber which is part of the EPA/TVA Shawnee Test Facility, Paducah, Kentucky; and the Arthur D. Little dual alkali pilot scrubber. The sampling section of the report describes the scrubber type, sample collection, and sample preservation. The analysis section of the report, describing the theory and practice of ion chromatography as applied to wet scrubber samples, describes analytical procedures, qualitative analysis, and quantitative analysis. The analytical procedures portion covers the anion and cation analysis scheme for wet scrubber samples, the theory of ion chromatography, and current problems involving the use of ion chromatography for wet scrubber related samples.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Alkalies	Stationary Sources	07D
Chromatography	Ion Chromatography	07B,07C
Ionization	Dual Alkali System	07A,13I
Scrubbers		14B
Analyzing		
Calcium Carbonates		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	61
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)