

DEVELOPMENT OF MEMBRANE BASED DEVICES AND
ION CHROMATOGRAPHY SYSTEMS AND THEIR
APPLICATIONS IN ATMOSPHERIC
MEASUREMENTS

by

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ABSTRACT

Ion chromatography (IC) is presently the preeminent technique for ionic analysis in atmospheric measurements. High temporal resolution measurement of atmospheric gases and constituents of particulate matter (PM) is important to understand the chemistry and sources of atmospheric pollution. The application of hollow and filament-filled single asymmetric membrane fibers, consisting of a thin silicone layer on a tubular microporous support for removing CO₂ in suppressed ion chromatography effluents is described. With appropriate choice of the removal device and operating conditions, CO₂ can be essentially quantitatively (99+%) removed. This device further reduces the background conductivity from carbonate-based eluents after suppression. In hydroxide eluent chromatography, the device largely removes the response from CO₂ present in the samples; this greatly aids atmospheric trace gas analysis by IC.

A low-pressure (400 psi), fully automated, semi-continuous Gas Particle Ion Chromatography (GPIC) system has been developed. Soluble gas collection is accomplished with a parallel plate wet denuder (PPWD). A hydrophobic filter based continuous particle collector (PC) collects and continuously extracts the soluble component in atmospheric particulate matter. Two conductivity detectors are used for anion signals and ammonium, respectively. This instrument measures three most important constituents, ammonium, sulfate and nitrate in fine particulate matter (PM_{2.5}) as well as soluble acidic and basic gases like HNO₃, SO₂ and NH₃.

A second Gas Particle Ion Chromatograph (GPIC) was developed. This compact instrument also measures soluble ionogenic gases and ionic constituents in PM_{2.5}. A

closed liquid flow path membrane denuder collects soluble gases and a continuously wetted hydrophilic filter-based particle collector collects the particles. A single, multi-port, syringe pump handles all the liquid aspiration and dispensation. Preceded by the sampling devices, the sample processing part interfaced with an ion chromatograph permits automated collection and measurements of collected samples. A single conductivity detector is used to measure not only anions but also ammonium. The flow configuration results in an ammonium peak before anion peaks in the chromatogram. The system measures ammonia, organic acids (such as acetic, formic and oxalic acids), HCl, HONO, SO₂, HNO₃, and the corresponding ions in the aerosol phase.

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LIST OF ABBREVIATIONS

APC	anion preconcentrator column
cm	centimeter
CPC	cation preconcentrator column
CRD	CO ₂ removal device
°C	degree Celsius
d.c./DC	direct current
DVB	divinylbenzene
EG	electrodialytic KOH generator
ft	feet
GCS	gas collection system
HPLC	high performance liquid chromatography
hr	hour
in.	inch
i.d.	inner diameter
IC	ion chromatography
L	liter
LOD	limit of detection
MFC	mass flow controller
MS	mass spectrometry
m	meter
µeq	microequivalent
µg/m ³	microgram per meter cube

μL	microliter
μm	micrometer
μM	micromolar
μS	microSiemen
mA	milliampere
mL	milliliter
mm	millimeter
mM	millimolar
min	minute
MPPD	membrane-based parallel plate denuder
ng	nanogram
nL	nanoliter
nm	nanometer
o.d.	outer diameter
PPWD	parallel plate wet denuder
PC	particle collector
PCS	particle collection system
ppb	part per billion
ppm	part per million
ppt	part per trillion
$w_{1/2}$	peak half-width
PFA	perfluoroalkoxy Teflon
PEEK	polyether ether ketone

PS	polystyrene
PVC	polyvinyl chloride
PVDF	polyvinylidene fluoride
RE	relative humidity
RSD	relative standard deviation
s	second
S/N	signal-to-noise ratio
SLPM	standard liters per minute
PTFE	Teflon
TTL	transistor transistor logic
UV	ultraviolet
V	volt
W	watt
w	width

CHAPTER I

INTRODUCTION

1. Chromatography

Chromatography is a powerful separation method that finds application to all branches of science. In 1897 Day, an American geochemist, separated crude oil on a powdered limestone column and observed that thinner and lighter fractions came out first.¹ Chromatography was invented and so named by the Russian botanist Mikhail Tswett at the beginning of the twentieth century. He separated plant pigments in a glass column packed with finely divided calcium carbonate. This marked the first systematic study and is recognized as the beginning of chromatography.² The separated species appeared as colored bands on the column. Chromatography (Greek chromatus = color and graphein = to write) has come a long way since it was first invented by Tswett.

Chromatography encompasses a diverse and important group of methods that permits the separation of closely related compounds in complex mixtures; many of these separations are impossible by any other means.² The separated components are detected downstream with an appropriate detector. Any chromatographic process involves two mutually immiscible phases called the stationary and the mobile phase.³ The stationary phase could be solid or liquid attached to an inert support material. The mobile phase, also referred to as the eluent or the carrier, is the solvent that flows through the stationary phase. The mobile phase, which could be liquid or gas, mobilizes the sample through the stationary phase in a process known as migration. Separation occurs because different compounds have different migration rates due to their different affinity for the stationary

vs the mobile phase. During the migration process, each compound is equilibration between the mobile and the stationary phase. Those components that are strongly retained by the stationary phase have slower migration rates and vice-versa.

The chromatographic system can be classified as columnar and planar based on the physical means of contact between stationary and mobile phases. In column chromatography, the stationary phase is held in a narrow tube through which the mobile phase is made to flow.⁴ The practice of chromatography has experienced many changes and undergone many improvements.⁵ The advent of paper chromatography in the 1940's and thin-layer chromatography (TLC) in the 1950's greatly simplified the practice of analytical liquid chromatography. Today column chromatography routinely produces faster separation and better resolution than TLC. Column chromatography can be divided into gas chromatography (GC), Liquid Chromatography (LC), and supercritical fluid chromatography (SFC) to reflect the physical state of the mobile phase.²

Modern Liquid Chromatography typically operates at high pressure up to several thousand psi.⁶ It is referred to as high-pressure liquid chromatography or high performance liquid chromatography (HPLC). Often it is just called liquid chromatography or LC. LC embraces several distinct types of interaction between the liquid mobile phase and the various stationary phases. When the separation involves predominantly a simple partition between two immiscible liquid phases, one stationary and one mobile, the process is called liquid-liquid chromatography (LLC). In liquid-solid chromatography (LSC), also called adsorption chromatography, the retentive ability of the stationary phase is mainly due to physical surface forces.

2. Ion Chromatography

Columns of ion-exchange resins have been used for many years to separate various cations and anions.⁷ In ion exchange chromatography, ionic or charged species are separated by selective exchange with counterions of the stationary phase. The practice of ion exchange chromatography dramatically changed in 1975 with the landmark publication by Small, Stevens and Bauman.⁸ In general, conductivity was not useful as a detection method in ion exchange chromatography because it could not differentiate between an eluent ion and an analyte ion. Small et al. developed a novel system where the eluent ion was carefully chosen such that it could be removed/converted into a largely nonconducting species by a device called “suppressor” after separation and the analyte ion could be selectively and sensitively detected. Such an “Ion chromatography” (IC) system made it possible to automatically detect and record the chromatogram of samples containing down to trace levels of analyte ions.⁹ Modern suppressed IC is utilized in every field of sciences and especially in the environmental sciences.¹⁰ Ion chromatography is the principal analytical tool used in this dissertation.¹¹ The general system components are described in this section with more focus on anion chromatography. Modern IC system requirements are in many regards similar to those of an HPLC system. However, there are some components that are unique to IC. The general components include a high pressure eluent pump, a separator column (usually preceded by a guard column), a suppressor and finally a detector as shown in Figure 1.1.

2.1 Pump

A high-pressure (up to 5000 psi) piston pump is used to pump the eluent or, in today's state-of-the-art IC systems, deionized (DI) water through the chromatography system. IC pumps may have single head or dual heads. Each head has its own piston and minimally two check valves to ensure that liquid flow is unidirectional. A compression seal around a reciprocating piston prevents eluent leakage out of pump head. The pistons are connected to an eccentric cam whose movement controls that of the pistons. In IC, usually all liquid transfer lines and components in the wetted system are made of polyetherether ketone (PEEK). Stainless steel is also used with non-corrosive eluents. Isocratic separations connote that the eluent concentration does not change during a chromatographic run. In gradient elution, the eluent strength increases during the chromatographic run. This can be accomplished by a gradient pump, that utilizes a proportioning valve and increases the concentration of one eluent component in a programmed manner during chromatographic run.⁹ Alternately, the eluent can be electrochemically generated and its concentration can be increased by increasing the electrochemical drive current during the run.

2.2 Eluent system

The most commonly used eluents are KOH, NaOH, Na₂CO₃ and NaHCO₃ for anion IC and HCl, HNO₃, H₂SO₄ and methanesulfonic acid for cation IC. Modern state-of-the-art IC systems require just water to operate. Eluents are electrolytically generated^{12,13} online during the analysis. The process offers substantial benefits to the

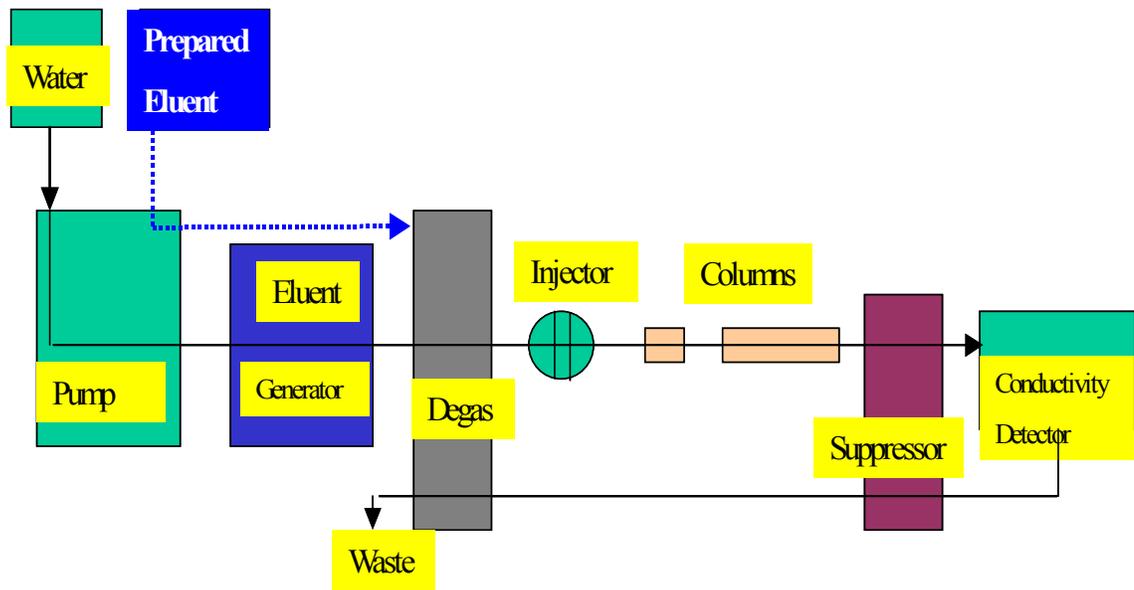


Figure 1.1. General schematic of Ion Chromatography system.

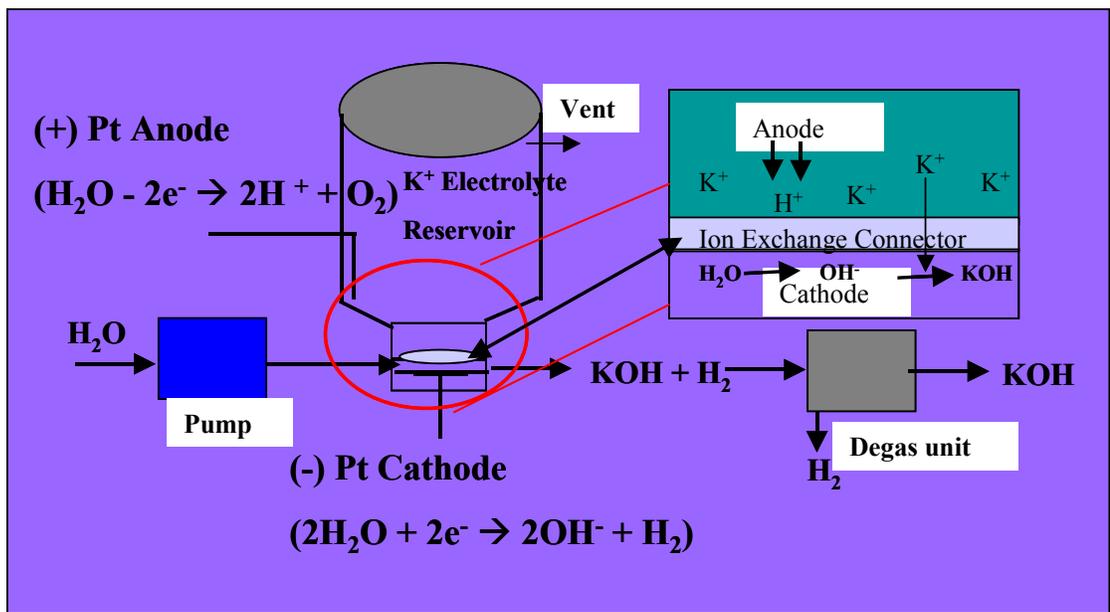


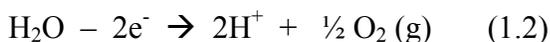
Figure 1.2. Schematic of eluent generation.

practice of IC. In addition to the operational simplicity of such a system, it is effective in eliminating carbonate formation in manually prepared hydroxide eluents. Carbonate is a stronger anion eluent than hydroxide and its presence in variable concentrations as impurities in the KOH or NaOH eluents can lead to poor separation, reproducibility and detection limits. In suppressed conductometric detection it increases background levels and generates baseline shifts in gradient separations.

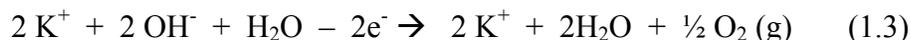
The eluent generator unit is placed after the pump and contains a cartridge of potassium hydroxide (KOH) or methanesulfonic acid (MSA) for anion or cation eluent generation, respectively. The cathode and anode are separated by ion exchange membranes. For anion chromatography hydroxide is generated (Figure 1.2.) at the cathode according to the following reaction.



A counterion to hydroxide is needed to conserve electroneutrality. Also, an oxidizing reaction occurs simultaneously at the anode.



However, the feed solution for anode also contains KOH.



This K^+ is transferred across the cation exchange membrane to the cathode to form KOH.

The concentration of the eluent produced is changed by simply changing the supplied DC current. Recent state-of-the art IC systems also use an continuously regenerated anion trap column (CR-ATC) just after eluent generator for removing any other anionic impurities present in OH^- anion eluent.¹⁴ A degas unit is used for degassing the eluent.

2.3. Columns of Ion Exchange Resin

Ion exchangers are the most widely used stationary phase in IC. It is the stationary phase that determines the separation mechanism and in turn dictates the choice and composition of the mobile phase. An ion exchanger comprises three important elements: an insoluble matrix, fixed ionic sites and functional groups. Ion exchange resin beads can be made of silica but more commonly of polymers such as polystyrene or polyacrylate. The polystyrene (PS) based exchange resin are made by copolymerizing styrene with a small amount divinylbenzene (DVB) for crosslinking. The amount of DVB added affects the rigidity of the beads. Microporous beads (gel type) are made with up to 25% weight of DVB while in macroporous resins the % weight of DVB can reach 55%. Most common anion exchangers are made of two substrate types: microporous substrates, which are mainly used as a support for latex coated microbeads; or macroporous substrates.¹⁵

Ion exchangers are created by chemically introducing suitable functional groups into the polymer matrix. Anion exchangers are usually functionalized with quaternary ammonium group. The polymeric benzene ring is first chloromethylated followed by a reaction with tertiary amine. Latex agglomerated ion exchangers have also been successfully used for various applications of IC. These ion exchangers are made by electrostatically attaching latex microbeads with an approximate diameter of 0.1 μm to the surface of a relatively large core substrate (5–30 μm). The core PS-DVB substrate is sulfonated and then coated the outside surface with a layer of latex particles functionalized with quaternary ammonium groups. These resin are chemically and physically stable, provide moderate backpressure and high chromatographic efficiency.¹⁶

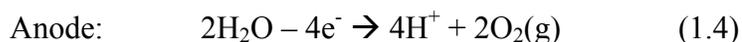
Dionex Corp. has made a variety of latex agglomerated resin to develop IC columns for different applications.¹⁷

Most current cation exchangers are either strong or weak acid exchangers. Strong acid exchangers are functionalized with sulfonic acid groups.¹⁸ Weak acid exchangers are functionalized with carboxylic acid or a mixture of carboxylic and phosphonic acid groups.¹⁹

2.4. Suppression

Suppression provides simple, yet elegant way to reduce the background conductance of the eluent in addition to enhancing the conductance of the analyte ion. As a result both sensitivity and detection limits are improved. After separation the column effluent passes through a suppressor where Na^+ or K^+ from the eluent is exchanged with H^+ , thus neutralizing the eluent hydroxide and changing the analyte from the Na^+ or K^+ salt form to the more conducting acid form. In its original form that reported by Small, a second ion-exchange column was placed between the separator column and conductivity cell.⁸ Early suppressors were simply columns of cation exchange resins that required frequent offline regeneration and caused considerable peak dispersion and broadening. Since then, the technique has passed through several refinements. In 1981 fiber suppressors were introduced²⁰ followed by flat membrane suppressors in 1985.²¹ Basically an ion exchange membrane was used with a constant flow of a regenerant solution. Though the devices did not require offline regeneration, they consumed a relatively large volume of the regenerant solution. In 1989 Strong and Dasgupta²² introduced the electro-dialytic suppressor. Based on the same principle, in 1992 Dionex

Corp introduced the Self Regenerating Suppressor (SRS).²³ Basically the anion SRS is composed of a cathode and an anode separated by two cation exchange membranes, thus, forming three compartments for liquid flow. The column effluent containing the eluent and elute flows in the middle channel between the membranes. At the anode side, water flows between the anode and the membrane generating hydrogen ion and oxygen (Figure 1.3.).



The hydrogen ions permeate through the membrane into the middle channel and replace the eluent cation (example: Na^+ or K^+) thus, neutralizing OH^- and changing the analyte from the salt to the acid form which is then measured by conductivity in a neutral medium, H_2O . The eluent cation (K^+) attracted to negatively charged cathode and permeates through the other cation exchange membrane into the cathode. Water flowing between the cathode and the membrane generates hydrogen gas and hydroxide ion that paired off with the eluent cation (K^+) to maintain electric neutrality (Figure 1.3.).



Waste gases, hydrogen from cathode and oxygen from anode, are vented with a liquid waste of KOH. In case of Na_2CO_3 and NaHCO_3 eluents, H_2CO_3 is produced after suppression that has more conductivity response than H_2O . Ullah et al. recently introduced a very low volume asymmetric membrane based carbon dioxide removal device that can removed dissolved carbon dioxide or H_2CO_3 from suppressed carbonate

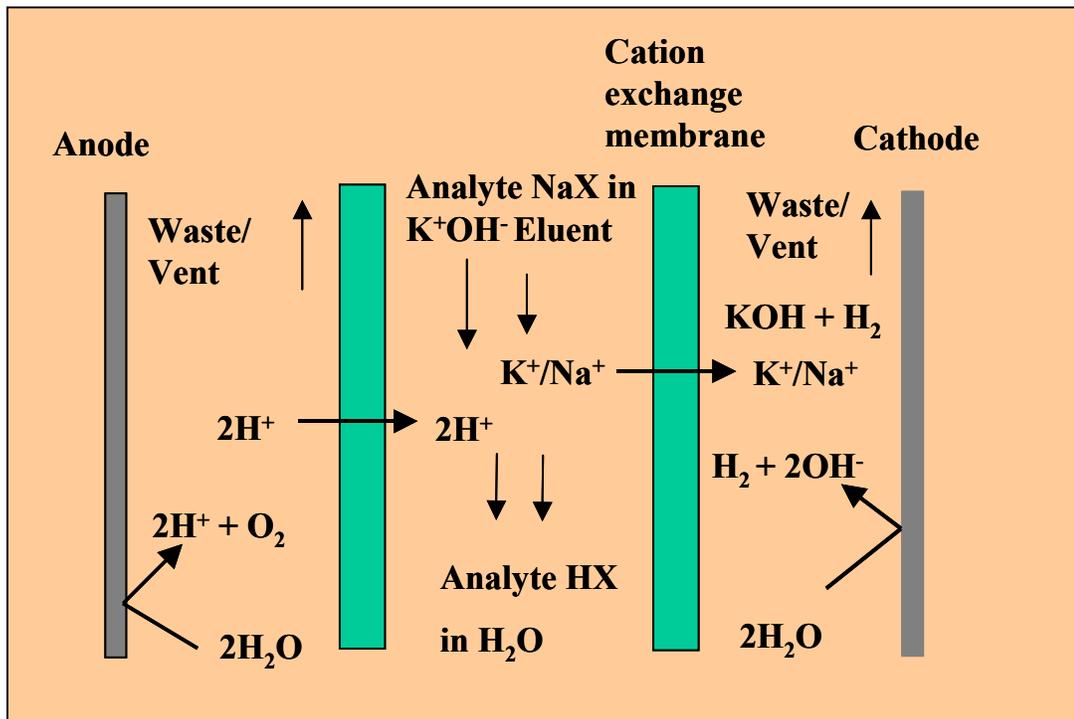


Figure 1.3. Anion Self Regenerating Suppressor (ASRS)

eluent thus further reducing the background conductivity contribution from H_2CO_3 .²⁴

Dionex Corporation is commercialized this device recently as carbonate removal device (CRD).²⁵

2.5. Detection

Detection of the separated species is as important as the separation in IC. It is the development of appropriate detection technique that has led to the rapid evolution of IC.⁸ Several detection techniques are currently used with IC, most commonly suppressed conductivity, UV-Vis absorption, pulsed amperometry and mass spectrometry.⁹ Suppressed conductivity is by far the most widely used detection techniques associated with IC. Conductometric detection offers several characteristics that are particularly attractive for IC analysis. Conductivity is a universal characteristic of all ions, and the technique is simple and non destructive.

For a strong acid passing through a conductivity detector the signal G_s ($\mu\text{S}/\text{cm}$) at any point in the eluite band is directly proportional to sample anion concentration C (in Molar)^{9,26} according to the equation 1.5.

$$G_s = 1000C(\lambda_{\text{H}^+} + \lambda_{\text{X}^-}) \quad (1.5)$$

λ_{X^-} and λ_{H^+} and are the equivalent conductance of X^- and H^+ (due to the equivalent concentration of H^+ as a result of suppression), respectively.

3. Measurement of atmospheric gases and particulate matter by IC

A variety of methods have been used to collect gases and aerosols (also called particulate matters, PM) for subsequent quantification by techniques such as IC or

colorimetric or other analyses.²⁷ These include filter methods, denuders, scrubbers, impactors and other particle collectors. Sampling must be carried out for sufficient periods of time to collect measurable amounts of the species of interest. Water soluble gases and aerosol fractions become ion in water or suitable absorber solution. Small amount of oxidant also used in water to convert SO₂ to sulfate ion.^{24,28} Once in solution, IC analyzes the collected sample ions corresponding to the target gases and PM fractions. Both off line or inline IC are used for atmospheric analysis. Recent researches focused on instrument that automates the collection of air samples for analysis with sensitive ion chromatography equipment.²⁸

4. Research Presented in this Dissertation

The primary goal of the research was to fabricate a single instrument instead of two different instruments for the measurement of gas and particulate species in the atmosphere in a cost benefit way with high temporal resolution. Such measurement is substantially powerful that can provide chemical and physical differentiation and correlate tropospheric conditions with gas particle chemical and physical interaction^{29,30,31}. PM constitute a wide range of different kinds of particles, that vary widely in chemical composition, size and toxicity.³² Ion chromatography provides a convenient analytical tool for measuring ionic constituents of PM along with their soluble precursor gases.^{33,34} However, ambient CO₂ causes some problems for quantifying nitrate or sulfate peaks in the vicinity of CO₂ induced carbonate peak. Chapter I discusses the introductory information about the ion chromatography. Chapter II describes the development of a carbon dioxide removal device for reducing carbonic acid

background as well as removing CO₂ from environmental samples. Then the Chapters III and IV describe two fully automated systems for the collection and measurement of soluble PM constituents and precursor gases with state-of-the art features. The results of field measurement of ambient air in Bondville, IL are shown using these two automated gas particle ion chromatography (GPIC) systems. Finally, Chapter V emphasizes the significance of this work and presents conclusions and future directions. The content of Chapter II has been published. The content of Chapter III is accepted for publication while Chapter IV is currently under review in a journal.

Asymmetric Membrane-Fiber based Carbon Dioxide Removal Devices for Ion Chromatography

The application of hollow and filament-filled single asymmetric membrane fibers, consisting of a thin silicone layer on a tubular microporous support for removing CO₂ in suppressed ion chromatography effluents is described. With appropriate choice of the removal device and operating conditions, the CO₂ can be essentially quantitatively (99+%) removed. For carbonate-based eluents, the use of such devices greatly reduces or eliminates the water dip, permitting better quantitation of poorly retained anions that elute close to the dip, allows practical gradient chromatography and improves noise levels and attainable detection limits. In hydroxide eluent chromatography, the device largely removes the response from CO₂ present in the samples; this greatly aids atmospheric trace gas analysis by IC. Device dimensions are such that the dispersion introduced by the device is small.

Automated Low Pressure Carbonate Eluent Ion Chromatography System with Postsuppressor carbon Dioxide Removal for the Analysis of Atmospheric Gases and Particles

We present a low-pressure, fully automated, semi-continuous Gas Particle Ion Chromatography (GPIC) system for the measurement of soluble ionic constituents in $PM_{2.5}$ e.g. ammonium, nitrate and sulfate and soluble acidic gases like HNO_3 and SO_2 and basic gas ammonia. This instrument utilizes two independent sampling channels for gases and particles. In one channel, a wet denuder collects soluble gases. In the second channel, a cyclone removes large particles and an identical wet denuder removes the soluble gases. A hydrophobic filter based continuous particle collector (PC) collects and continuously extracts the soluble component in atmospheric particulate matter. The water and dissolved constituents are aspirated by a peristaltic pump on to serial cation and anion preconcentrator columns housed in a 10 port valves particle sample loading. Similarly, gas denuder sample is loaded to a serial cation and anion preconcentrator columns housed in another 10 port valve. Ammonium captured by the cation preconcentrator is eluted with NaOH and is passed across an asymmetric membrane device. Ammonia diffuses from alkaline donor stream into deionized water flowing countercurrent; the conductivity of the latter provides a measure of ammonium. The anions on the anion preconcentrator column are eluted and measured by fully automated ion chromatography system (Dionex DX-320). This system provides every 30 min data for both particles (nitrate, sulfate and ammonium) and gases (HNO_3 , SO_2 and NH_3), each collected for 15 min and staggered 15 min apart. The ion chromatography uses 2.4 mM Na_2CO_3 and 2.3 mM $NaHCO_3$ eluent and short separation column (100 mm). Particle and

gases are collected and analyzed alternately in 15 min time interval. The LOD (S/N = 3) for nitrate, sulfate and ammonium were 2.6, 5.3 and 2.1 ng/m³ for a 75-L total sample volume.

A Versatile Gas Particle Ion Chromatograph

A new compact Gas Particle Ion Chromatography (GPIC) instrument has been developed for the measurement of soluble ionogenic gases and ionic constituents in PM_{2.5}. This instrument has two independent sampling channels for gases and particles. A closed liquid flow path membrane denuder collects soluble gases. In the second channel, a cyclone removes larger particles and an identical membrane denuder removes the soluble gases. Then a continuously wetted hydrophilic filter-based particle collector collects the particles. A single multiport syringe pump handles both channels, following principles of Sequential Injection Analysis and Zone Fluidics. A single conductivity detector is used to measure not only gaseous acid derived anions but also ammonia and ammonium. Relative to previous systems, no peristaltic pump is used and the system operates with lower gas and liquid flow rates. Robustness is greatly improved and the system is compact at the cost of time resolution. Using electrodialytically generated gradient hydroxide eluents and 3 mm bore high efficiency columns, providing every 40 min data for both gases and particles, each collected for 40 min but staggered 20 min apart. The liquid samples from the gas denuder and particle collector are drawn by the syringe pump and preconcentrated on a sequential cation and anion concentrator housed in a 10-port valve, staggered 20 min in time. The Ion Chromatograph (Dionex ICS-2000) and associated software controls all valves and the syringe pump. The preconcentrated

samples (cations and anions) are injected to ammonia transfer device and anion separation column using respective eluents. The flow configuration and valve timing results in the ammonia peak appearing in front of the anion peaks, thus constituting a single chromatogram that separates and detects ammonia, organic acid like acetic and formic acids, HCl, HONO, SO₂, C₂H₂O₄, HNO₃ and ammonium, acetate, formate, chloride, nitrite, sulfate, oxalate and nitrate in particle phase in a single chromatogram. Detection limits of low to subnanogram per cubic meter concentrations of most common gases and particulate constituents are readily attained.

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CHAPTER II

ASYMMETRIC MEMBRANE FIBER-BASED CARBON DIOXIDE REMOVAL DEVICES FOR ION CHROMATOGRAPHY*

1. Introduction

Ion chromatography (IC), originally invented by Small *et al.*¹ is presently the preeminent technique for anion analysis. During the development of IC at Dow Chemical, sodium hydroxide was originally tried as an eluent. However, the eluent concentration required with columns then available and was too high to suppress. Intrusion of atmospheric CO₂ into the NaOH stored over a long weekend led to the serendipitous discovery that carbonate made a much more convenient eluent. More recently, the development of hydroxide selective columns² and electrodynamic generation of high purity hydroxide eluents³ have made hydroxide eluent based chromatography practical and attractive. As with any technology, new problems emerge as new horizons unfold. Carbon dioxide is omnipresent: its intrusion into the water used for the electrodynamic generation of hydroxide eluents is not a new event but is now considered an important problem to be overcome. Indeed, an electrodynamic regenerated trap to remove the carbonate⁴ has recently been introduced.

Nevertheless, there are occasions where one may want to trade the ultimate in performance provided by an electrodynamic generated, electrodynamic cleaned hydroxide eluents for inexpensive to make carbonate eluents. Such an eluent is easily made from pure chemicals, is not greatly affected by intrusions of small amounts of

* Ullah, S.M.R.; Adams, R.L.; Srinivasan, K.; Dasgupta, P.K. Anal. Chem. 2004, 76, 7084-7093

atmospheric CO₂, is not perturbed by dissolved CO₂ in the samples and can thus be particularly convenient for trace analysis of other species in carbonates,⁵ and permits a broad range of anions to be separated under isocratic conditions. The price paid is steep, however: (i) poorer detection limits, (ii) considerable nonlinearity of response (due to the pliant baseline resulting from the weak acid character of carbonic acid^{6,7}), (iii) large water dips and the difficulty of accurate quantitation of ions that elute near this dip, and (iv) incompatibility with gradient elution.

Some of these problems may be ameliorated by removing the CO₂ after suppression and prior to detection. The fact that with carbonate-based eluents, membrane-based suppressors lead actually to a lower background conductance compared to packed bed suppressors, ostensibly due to loss of some of the generated CO₂ through the membrane^{8,9}, was recognized early on. In carrying out gradient elution with carbonate eluents, Sunden *et al.*¹⁰ encountered the large baseline shift problem even earlier and recognized the potential benefit of CO₂ removal. Their first attempt utilized microporous PTFE tubes (1 mm id, 2 μm pores) with CO₂-free air flowing on the outside.¹¹ A hollow tube performed poorly. Their best design, a pair of twisted 400 μm dia. wires inserted inside a 2-m long tube, gave 90% CO₂ removal. These membranes leak easily, however. Siemer and Johnson¹² used a 3.6-m long thin-wall long narrow bore (310 μm i.d. and 600 μm o.d.) silicone rubber tube immersed in 0.1 N KOH to achieve 73% CO₂ removal. They achieved essentially quantitative removal by increasing the KOH bath temperature to ~78 °C. Although the dispersion induced by such a tube was not a concern then, the dispersion induced by such a length of an easily inflatable elastomeric tube is not likely to be considered negligible today. Subsequently, Shintani

and Dasgupta¹³ used the same total length of 250 μm dia. filament-filled silicone-coated porous polypropylene membrane fibers (400 μm i.d., resulting in a hydraulic diameter of 310 μm) as a multiple fiber bundle (12 fibers, each 30 cm long) and reported $\sim 85\%$ CO_2 removal at room temperature. The coating procedure they used resulted in a relatively thick silicone coating (~ 90 μm) leading to inefficient CO_2 transfer. Multiple parallel fibers always lead to greater than optimal dispersion because an identical residence time in each fiber can never be assured.

Much work has appeared in the interim period regarding CO_2 transfer across membrane interfaces. The salient lessons here are that: (a) due to liquid film transfer resistance in systems containing a liquid, removal rates are always less than those in corresponding purely gaseous systems, (b) the liquid film resistance is lowered by the use of a base on the sink side which rapidly converts CO_2 to HCO_3^- , (c) over long periods, aqueous liquids penetrate into the pores of a hydrophobic microporous membrane, forming a stagnant layer and increasing the mass transfer resistance, (d) with hydrophilic asymmetric membranes, e.g., polyethersulfone, the liquid fills up the micropores causing high mass transfer resistance, and (e) in gas-liquid and likely liquid-liquid systems, the transport efficiency of a composite membrane, such as one containing a 1 μm polyurethane layer between two 12.5 μm layers of microporous polyethylene is ~ 100 times poorer than a comparable purely microporous membrane.¹⁴⁻¹⁶

There has also been a lot of interest in CO_2 removal in the specific context of IC in recent years, as evident from recent publications.¹⁷⁻²⁰ The authors are justifiably enthusiastic about water dip reduction, improvements in linearity, and the practicality of performing gradient elution (indeed, the same figure showing the difference in gradient

performance with and without CO₂ removal illustrates in the same issue of a journal in multiple articles!). These authors used a Teflon[®] AF tube of unspecified dimensions for the removal of CO₂¹⁷ and achieved significant reduction of background conductance (from ~21 to 8 μS/cm¹⁷ or 15-20 to 1-2 μS/cm¹⁸). Others have devised a scheme of electro dialytic generation of carbonate-based eluents that can go from pure bicarbonate to bicarbonate-carbonate to carbonate-hydroxide by using a bicarbonate solution, rather than water, as feed to a conventional hydroxide generator.²¹

It is well known that compared to other types of Teflon[®], Teflon[®] AF is very permeable to gases. We have previously exploited this to make gas sensors.^{22,23} Further, Teflon[®] AF is most permeable to CO₂ (it is in fact soluble in liquid CO₂); indeed this property causes problems in some applications.²⁴ Teflon[®] AF may thus seem to be the best choice for CO₂ removal. On the other hand, Teflon[®] AF is the most expensive commercially available polymer (at a cost of several times more than gold), and even research use of this material requires licensing agreement with the manufacturer. Perhaps most importantly, the gas transport properties of some other polymers are better. Presently we use other types of tubular membranes (with superior results) for the same gas sensing applications for which we previously used Teflon[®] AF.²⁵ With specific reference to CO₂, the permeability of silicone rubber^{26,27} is 4550 barrers (1 barrer = 10⁻¹⁰ cc-cm/(cm².s.cm Hg)) compared to 2800²⁸-3900²⁹ barrers for Teflon[®] AF. (It is of interest that a polyalkyne type silicon based polymer, poly(trimethylsilyl-1-propyne), exhibits a permeability of 33,100 barrers³⁰). Perhaps more importantly, while asymmetric membranes (membranes with an exterior skin of a different polymer or same polymer with different morphology) containing a very thin (few or sub- micron) layer of

silicone rubber on a microporous host are readily made in-house and are also commercially available. No membranes with a thin active Teflon AF layer are commercially available. Because of the well known difficulty of adhesion of fluorocarbons to most other surfaces, this may not be simple to fabricate.

Our specific interest lies in the practical measurement of atmospheric gases and particles by IC. For the best possible sensitivity, we,³¹⁻³⁷ as well as others,³⁸ have commonly used hydroxide eluents. However, atmospheric CO₂ is present at a concentration 10⁴- 10⁶ times higher than other ionogenic trace gases and the CO₂-induced H₂CO₃ peak can cause serious problems. In particular, the broad tailing CO₃²⁻ peak obscures the NO₃⁻ that elutes in this region.³⁵ Chromatographic conditions must be carefully tailored to avoid this as much as possible. Removal of CO₂/H₂CO₃ prior to detection will be of significant help.

In this work we show the efficient removal of CO₂/H₂CO₃ with a single asymmetric membrane fiber, superior to that obtained with Teflon AF, with good chromatographic performance.

2. Theoretical Considerations

H₂CO₃ is a weak acid with a K₁ of 7.47 x 10⁻⁷ at 25°C. For solutions of H₂CO₃ of relevance to us, the second dissociation step plays no role. The ionic composition of an H₂CO₃ solution is readily solved by solving the relevant charge and mass balance equations. The conductance of the solution can then be calculated from the known ionic equivalent conductance values. The relationship between the conductance and concentration of H₂CO₃ is highly nonlinear (Figure 2.1.a); removal of some of the H₂CO₃

results in better ionization of the remaining concentration, so that reduction in the $[\text{H}_2\text{CO}_3]$ is not proportionally reflected in the conductance. When CO_2 is removed from a 9 mM H_2CO_3 solution (9 mM Na_2CO_3 is a popular IC eluent) the residual conductance follows a log-log relationship with the residual H_2CO_3 concentration (Figure 2.1.b); the conductance changes approximately linearly with the square root of the concentration.

3. Experimental Section

3.1. Reagents and IC System

All reagents used in this work were of analytical grade. Nanopure water was used for reagent preparation and for IC. All experiments were carried out with IC equipment from Dionex Corporation (specific equipment important to given results are discussed with the results). Unless otherwise stated, all interconnecting tubing were 0.25 mm i.d. PEEK. Instrument control and data acquisition was carried out with PeaknetTM software. Except as stated, the eluent flow rate was 0.4 and 1.0 mL/min for 2 and 4 mm columns, respectively, with 100 mM NaOH solution pumped peristaltically or pneumatically at ~ 0.5 mL/min. In some experiments, the suppressor waste (in the case of a hydroxide eluent IC) was used as the sink solution. Elevated temperature operations were either carried out within an oven (LC-30, maintained at 30°C) or a miniature in-line heater (*vide-infra*) to heat the stripping solution.

3.2. Construction of CO_2 Removal Device (CRD)

Microporous tubular polypropylene membranes (400 μm i.d., 25 μm wall, nominal pore size 0.02 μm , surface porosity 40%, Celgard X-20, Celanese Corp.,

Charlotte, NC) were coated with silicone rubber by immersing the membrane tube in a solution of silicone rubber adhesive (Macklanburg-Duncan or General Electric, translucent type for household use) in hexane. Unless otherwise stated, the concentration was 1.5-2% (w/v). A length of the membrane tube was pulled through the solution in one direction and then pulled back in the opposite direction. The membrane was then suspended vertically and allowed to dry in a dust free enclosure for ≥ 4 h. The desired length of the coated membrane tube was cut and a 200 μm diameter nylon monofilament (4 lb strength, STREN, duPont) was inserted in the hollow fiber, with ends of the filament protruding out of the fiber. One end of the fiber was passed through a 10-32 male-male union U (Dionex, the union opening was drilled to enlarge the bore) and inserted into a Teflon tube segment F (FEP Teflon Tubing, 0.02 inch i.d. 0.062 inch. o.d., Upchurch). The tube end was sealed with a compression ferrule C and 10-32 male nut N to the union. The fiber end with union-connector assembly was affixed to a small-bore steel tube ($1/16$ in. o.d.) with PTFE tape. The filament-filled membrane tube was coiled around the steel tube and the free end was again affixed with PTFE tape. The whole assembly was immersed in boiling water for 30 min to thermoset the filament. The tapes and the helical tube assembly were then removed from the support and as shown in Figure 2.2.a, the assembly was then enclosed in a hard nylon jacket tube NT (0.188 inch o.d., 0.137 inch i.d., 4.5 to 5 inch length), provided at each end with 10-32 threads so it could be directly connected to U. NT was further provided with inlet/outlet apertures, to which PEEK tubes (0.03 inch i.d., 0.062 inch o.d., Upchurch) were connected and epoxied in place. These provided for flow of the external fluid. The free terminal end of the membrane tube was now sealed in the same manner as the first end. In some cases

the inlet/outlet aperture for the external fluid was provided directly in the fitting U by drilling it appropriately. Unless specifically indicated, the results given are for the silicone-coated Celgard tubing.

A 200 μm i.d. microporous polypropylene membrane, containing a 3-4 micron thick layer of plasma-polymerized disiloxane was obtained from Neomecs (Eden Prairie, MN). The complete device was made the same way as the previous description, except without further silicone coating or inserted filaments. Terminal Teflon tubes used for connection was 0.3 mm in i.d.

Unless otherwise noted, a CRD based on a 80 cm long Celgard membrane tube singly coated with a 1.5% silicone rubber solution was used and was placed between the suppressor and the detector.

3.3. In-line Heater

An in-line heater that directly heats the influent stripping solution was constructed similar to a heater design recently described.³⁹ A 40-ga. nichrome wire was inserted through a PEEK tube ($0.03 \times \frac{1}{16} \times 5$ inch long) and the ends were sealed by segments of hypodermic stainless steel tubing with epoxy adhesive put in at the ends to avoid leakage (Figure 2.2.b). Excess nichrome wire was trimmed off. A variable voltage DC power supply was used to apply voltage to the two steel tube termini that also functioned as liquid inlet/outlet. Up to a maximum of 10 V was applied, leading to ~ 4 W of dissipated power. If the heated external solution (0.5 mL/min) is in thermal equilibrium with the internal solution (1.0 mL/min) and the system were adiabatic, the overall temperature rise will be ~ 40 °C. In practice, there was large heat losses at the low flow rates involved.

The exit temperature of the liquid from the heater was $\sim 72^{\circ}\text{C}$ but decreased to 54°C by merely the 10 cm passage to the CRD inlet. The measured CRD lumen outlet temperature was only 10°C above the lumen inlet temperature. The majority of subsequent experiments were conducted by incorporating the CRD within an oven.

4. Results and Discussion

4.1. Effect of the Silicone Coating Thickness

Figure 2.3 shows the fraction of CO_2 that remains as a function of the amount of silicone rubber in the coating solution both at room temperature and with the in-line heater (4 W). As a first approximation, we assume that the thickness of the coating is directly related to the concentration of the silicone rubber in the solution. For the relatively short membrane tube length used in this experiment, the fractional removal efficiencies (f) are low. Under these conditions, the transport to the membrane is not the limiting factor and transport through the membrane, related to the reciprocal thickness of the transport layer, may become the dominant factor. Accordingly, $(1-f)$, the residual fraction of CO_2 , is approximately linearly related to the reciprocal thickness. At elevated temperatures, however, removal is much more efficient and $\log(1-f)$, rather than $1-f$ shows a better linear relationship with $1/t$, suggesting that mass transport to the membrane becomes the limiting factor.

Not surprisingly, the least amount of silicone used in the coating solution (1.5%) led to the best removal efficiencies (91% and 99% in the cold and heated modes respectively). We also found that the membranes coated in this manner are not always free of pinhole leaks. The extent and frequency of occurrence of such leaks increases

with decreasing silicone content of the coating solution and with the prescribed coating regimen, 1.5% silicone content of the coating solution was a practical lower limit. This was therefore used henceforth. At a flow rate of 1 mL/min, the backpressure induced by the CRD itself plus the detector cell and the postdetector exit tubing was 38 psi (~70% of this was contributed by the detector cell and associated tubing). The maximum liquid leakage observed through membrane pinholes under this conditions was 1 ± 0.1 $\mu\text{L}/\text{min}$, with no fluid flow exterior to the membrane (this required 10-12 h collection with the outer jacket closed and may even contain contributions from permeation of water vapor and recondensation in the jacket). As long as there is a significant positive pressure differential between the interior of the membrane and outside, external liquid leakage into the lumen does not occur and the observed degree of leakage, amounting to 0.1% of the original flow, presents no practical issues. With a flow of 1 mL/min, the Neomecs 200 μm i.d. membrane was used in a maximum length of 50 cm; the head pressure on such a CRD (plus detector etc) was 60 psi. There was no observable liquid leakage with this membrane.

4.2. Microscopy

Scanning electron micrographs of the membranes show the exposed pores in the uncoated membrane (Figure 2.4.a) while the silicone coating covers most of the membrane surface in the coated membrane (Figure 2.4.b). Microscopic measurements of the wall thickness indicated that the coated membrane wall is ~ 1.4 μm thicker than the virgin membrane. The internal surface roughness is evident even in the relatively low magnification cross sectional image of the coated tube (Figure 2.4.c) and the image also

suggests that the coating is present on both sides. This is consistent with the fact that the hexane solution of silicone rubber is seen to readily wet the membrane. With a density of 1.15 and a measured 3% volatile content of silicone rubber adhesive, a 40-50 μm thickness of the liquid film (per passage of the membrane through the coating solution for each of two passages) is sufficient to produce the observed film thickness for a coating solution containing 1.5-2% silicone rubber.

The manufacturer of the commercial disiloxane coated membrane does not specify the thickness of the disiloxane layer. With a stated effective permeability of $8.36 \times 10^{-4} \text{ cc}/(\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg})$,⁴⁰ the known permeability of 4550 barrers for silicone rubber²⁶ (this is for poly(dimethylsiloxane) and may not be exactly true for disiloxane), one estimates a barrier layer thickness of 5.4 μm . The cross sectional image of the membrane tube (Figure 2.4.d), suggests a coating thickness of 3-4 μm , consistent with this estimate.

4.3. Effect of Membrane Fiber Length and Temperature

Figure 2.5.a shows the effect of the tube length on the CO_2 removal efficiency. Removal as a function of length follows a linear relationship between the logarithm of the fraction remaining and the length of the tube as predicted by the Gormley-Kennedy equation.⁴¹ The 80 cm long tube removed $\sim 97\%$ of the CO_2 at room temperature and essentially quantitatively ($\geq 99.9\%$, it is very difficult to measure the exact removal efficiency at these high efficiencies) with the in-line heater. The difference in the two temperatures (22 $^\circ\text{C}$ vs 32 $^\circ\text{C}$) cause approximately a doubling of the slope of the $\ln(1-f)$ vs. length plot. If the Stokes-Einstein relationship adequately defines the liquid phase diffusion coefficient and we consider that the temperature change results in a factor of

1.25 change in the viscosity, the temperature change will result in a 1.3x change in the diffusion coefficient (which appears in the exponent in the Gormley-Kennedy expression) thus assisting mass transfer *to* the membrane. There are other aspects of CO₂ removal that are assisted by an increase in temperature. It is CO₂ and not H₂CO₃ that permeates (dissolves in and then diffuses out through the membrane. H₂CO₃ must dehydrate to CO₂; this process is not instantaneous. Based on literature data,⁴² and assuming Arrhenius behavior, the rate constant of the dehydration process will increase from 19.4 s⁻¹ at 22 °C to 47.2 s⁻¹ at 32 °C. With a typical residence time of ≥ 4.5 s in the CRD, the dehydration rate is likely not a major factor. The pressure differential between the two sides of the membrane drives the removal process. Since exterior pCO₂ is ~zero, the motive force is directly related to the interior pCO₂. Based on available thermodynamic data, the Henry's law solubility of CO₂ decreases by a factor of 1.3 between 22 °C and 32 °C. Finally, an increase in temperature also aids the diffusive transfer of CO₂ across the membrane. Based on the (room temperature vs. elevated temperature) difference that we observe (Table 2.2) between otherwise identical lengths of 400 μm i.d. Celgard and Neomecs devices where the polymer coating differs, this is likely an important factor.

4.4. CO₂ Removal Efficiency Exhibited by Different CRDs

Since elevated temperature operation was clearly advantageous, further experiments were conducted with the CRD located in the chromatographic oven maintained at 30 °C. Table 1 shows the results for different CRD devices at room temperature and at 30 °C. It is interesting to note that the uncoated membrane performs slightly worse than the coated membrane, especially at elevated temperatures. As

previously noted, a mass transfer limiting step with a conventional microporous membrane is the formation of a stagnant liquid film within the micropores. With both sides of the membrane coated, this possibility is obviated. In either case, it is not possible to operate over a continued period with uncoated membranes because of serious leakage. Although a 50 cm long 200 μm i.d. Neomecs membrane does not provide quantitative removal for CO_2 at 1 mL/min, since Gormley-Kennedy behavior is obeyed (see below), such a device is expected to remove 99.5 and 99.97% of the CO_2 at flow rates of 0.5 and 0.25 mL/min at 30 °C, respectively. The comparison between a 50 cm 400 μm Neomecs device and a coated Celgard device, made in an identical filament filled manner, shows that the room temperature performance of both devices to be the same but at elevated temperature, the coated Celgard device performs perceptibly better.

4.5. Options for Removing CO_2 and the Effect of Lumen Flow Rate

Table 2.2 shows the results of using different options external to the membrane for removing CO_2 . Gas flow is superior to a liquid sink, presumably because diffusion limitations are less. Using soda-lime treated air flow, one of the best options, as well as 100 mM NaOH (used as the benchmark sink for all tests), the removal efficiencies as a function of the lumen flow rate are shown in Figure 2.5.b. Again, Gormley-Kennedy behavior is observed.

4.6. Filament-Filled Helix Geometry

Especially for the larger bore membrane tube, the filament-filled helix (FFH) geometry provided for better mass transport to the membrane and lowered dispersion.

This is in keeping with previous reports in the literature.^{8, 43} We compared the performance of a 50-cm-long 400 μm silicone-coated Celgard CRD in three different configurations: (a) straight hollow; (b) straight, 200 μm filament filled; and (c) FFH construction as described. It was not possible to maintain a helical configuration in the absence of the inserted filament. In all cases, 1 mL/min water flowed through the lumen and 200 mL/min CO_2 -free (soda-lime treated) air flowed on the outside. The test system used a suppressor before the CRD but no chromatographic columns. The removal of CO_2 was tested with a 25 μL injected sample of 9 mM Na_2CO_3 (lower removal efficiencies will likely be attained with continuous flow of a carbonate eluent). Band dispersion was tested with 25 μL of injected NaCl with and without the test device and calculated according to ref. 44. Device a removed $79.2 \pm 0.2\%$ of the CO_2 and produced an dispersion of $48.2 \pm 8.6 \mu\text{L}$. Due to the decrease in residence time without the benefit of secondary centrifugal transport, merely inserting the filament actually marginally reduced CO_2 removal to $77.1 \pm 0.2\%$ while band dispersion also decreased marginally to $44.0 \pm 9.2 \mu\text{L}$ for (b). The FFH geometry (c) dramatically improved CO_2 removal to $97.9 \pm 0.1\%$ and also reduced the dispersion to $29.5 \pm 2.4 \mu\text{L}$. It should be noted, however, that the advantages of this geometry will decrease as the lumen diameter decreases because better mass transfer is attained even in a straight geometry and there can be significant problems from the added pressure drop from an inserted filament.

4.7. Performance : Isocratic Elution-Removal of CO_2 from the Sample

This aspect concerns our primary interest in CO_2 removal – to facilitate field atmospheric measurements. Figure 2.6.a shows the important role a CRD can play in

devising a simple relatively low pressure (450 psi) separation scheme that attempts to measure the two most important ions of interest in atmospheric measurement, nitrate and sulfate. The nitrate and sulfate content are equivalent to 0.25 ppb HNO₃ and 0.43 ppb SO₂ that will be collected in a 15 min 5 L/min sample as in present practice.³⁶ The Chromatography is conducted with a very low concentration of hydroxide that allows nitrate to elute long before carbonate (the amount of which in this sample is much less than that would be encountered in the real atmospheric sample, see Figure 2.6.b). The difference in having and not having a CRD here is whether or not sulfate can be quantitated at all. Figure 6b shows two actual field chromatograms, one without a CRD and the other with a CRD obtained under comparable conditions; in the latter case, it was possible to use a slightly higher eluent concentration and a lower eluent flow rate because of the drastic reduction in the carbonate peak. The difficulty of quantitating low levels of HNO₃ without the CRD (even after optimizing the elution time difference between carbonate and nitrate under the available total elution time constraints), and the very significant improvement in the presence of the CRD is evident. It is also worthwhile to note that the quality of the water (especially with regard to its CO₂ content) can rarely be controlled in field work. As a result, even with an electrodialytically generated hydroxide eluent, the water dip is visible and is significantly reduced with the CRD.

The CRD can also be used to remove CO₂ from the sample before chromatography. Figure 2.7 shows a comparison chromatogram in which a carbonated soft drink was (a) injected directly into a chromatographic system and (b) loaded into the sample loop via the CRD before injection. This chromatogram exemplifies the differences that are observed on prior CO₂ removal. While the very large difference in

the (asterisked) CO₂ peak is the most obvious feature, in the presence of the large amount of carbonate, analyte *x* coelutes with chloride and is not seen without the CRD. All peaks elute slightly earlier without the CRD because of the high carbonate concentration associated with the sample. This is illustrated with the timeline drawn at the retention time of peak *d* for the CRD-introduced sample. Because of the large carbonate response, it is impossible to see analyte *y* in the directly injected sample. While the peak for analyte *c* is clearly discernible and quantifiable with the CRD, at best a hint of it is seen without it. The tail of the carbonate peak extends far beyond what appears at the first sight. while the response from analyte *z* is clearly visible with the CRD, at the same magnification it is not discernible without the CRD. The only drawback of using the CRD is that analyte *b* is significantly lost; this, however, identifies it as a volatile component.

The CRD permits the use of a carbonate eluent in a relatively low pressure system in field atmospheric measurements without any major sacrifice in sensitivity. The low system pressure contributes to lower maintenance. Figure 2.8 shows a chromatogram from atmospheric samples from an instrument situated at a rural location in Bondville, IL, similar in design to that described in ref. 37 but with a carbonate eluent and a CRD. This instrument alternately measures gaseous and particulate constituents and has been operated with a single CRD for 11 months at the time of this writing.

4.8. Carbonate Eluents: Improvement of Detection Limits and Linearity

The CRD can significantly improve limits of detection (LODs) with carbonate eluents (Table 2.3). LODs were calculated on the basis of three times the standard

deviation of a standard with a concentration near the LOD. Improvements are observed across the board for the test ions. Fast eluting ions such as fluoride that elute very close to the water dip cannot be detected at all from low level standards in the absence of a CRD. These LODs are expected to improve further with the use of an oven. It is of interest to compare these LODs with what can be attained by a hydroxide eluent system. However, it is not possible to cover this entire suite of analytes with an isocratic hydroxide eluent in a reasonable period, so we have used (a) a standard mixture without phosphate with isocratic elution under otherwise identical sample size and column dimensions and (b) a gradient hydroxide elution scheme with all seven ions using a 4 mm column (due to the availability of columns and equipment) and a smaller injection volume that is typical of today's state of the art practice. The LODs attained with the carbonate system with the CRD are respectable. It will be noted that isocratic carbonate-bicarbonate run (conditions a,b, Table 2.3) requires 12 min whereas the gradient hydroxide run to separate the same ions require 16 min plus another 4.5 min to re-equilibrate to initial conditions.

Overlaid isocratic carbonate eluent chromatograms, carried out under the conditions described in Table 2.3, with and without a CRD, are shown in the right part of Figure 2.9. The left inset shows the vast improvement in the water dip that is observed in the presence of a CRD. As the chromatograms indicate, the additional dispersion induced by the CRD is minor. Band dispersion, defined as $(W_{1/2}^2 - W'_{1/2}{}^2)^{1/2}$ where W and $W'_{1/2}$ are the half band volumes of an analyte peak with and without the CRD, are indicated for each peak in μL with uncertainties ($n=3$). For the majority of the analytes shown in Figure 2.9, the peak area actually increased with the use of the CRD, the peak

area for phosphate increasing by 12%. The enhanced sensitivity is directly traceable from the removal of CO₂ and the associated pliant baseline.

The linearity of response is best examined with a Cassidy plot,⁴⁴ as shown in Figure 2.10. The sensitivity with the CRD is higher and it reaches a constant value faster than without it. Theory predicts that at even higher concentrations, the sensitivity of the two will eventually be the same.

4.9. Bicarbonate-Carbonate Gradient Chromatography

Ammonium carbonate gradients have been commonly used in liquid chromatography-mass spectrometry due to the volatile nature of the buffer material.^{45,46} As already noted, the basic attractions of carbonate gradients has been previously discussed in the literature;^{10,17, 18-21} it becomes particularly valuable with an efficiently functioning CRD. Figure 2.11.a shows such a chromatogram generated by running a gradient between 2.5 mM NaHCO₃ and 2.5 mM Na₂CO₃. At first sight, it may seem that this should not result in a change in the H₂CO₃ concentration reaching the detector but in fact the column sites are initially filled with bicarbonate and as divalent carbonate replaces the bicarbonate, one carbonate taking the place of two bicarbonate ions, the excess bicarbonate must come out of the column. The great difference with and without a CRD is readily apparent. Figure 2.11.b shows an electrodialytically generated gradient chromatogram according to Novic *et al.*²¹ demonstrating rapid separation of all seven common test ions.

4.10. Loss of Other Volatile/Semivolatile Analytes

The loss of other volatile weak acid analytes through the CRD may be undesirable. However, the most obvious analytes susceptible to such loss, e.g., sulfide and cyanide are not sensitively detected in any case by suppressed conductometry. It is difficult to estimate exact loss of carboxylic acids such as formic and acetic acids in a comparison between heated and unheated systems because available thermodynamic data indicate that the dissociation constant of these carboxylic acids decreases with increasing temperature. In “area loss” experiments with and without the CRD under the presently recommended conditions of an oven enclosure at 30 °C, no loss was discernible for these analytes.

If the CRD is designed with an external jacket that is concentric to the gas removal membrane, then the external fluid can also be operated in a low dispersion configuration. With such a geometry, gases that do transfer efficiently through the membrane, e.g., H₂S, HCN etc., can be detected in a second stream, selectively and sensitively with electrochemical detectors. We have used a similar arrangement to measure ammonia from an alkaline stream using a conductivity detector.³⁷

5. Conclusions

In this work, we have demonstrated that efficient CRD devices are easily constructed from inexpensively available membranes, are readily used with existing suppressor and detector systems and are of great benefit to atmospheric analysis and a variety of other applications.

Table 2.1. Carbon dioxide removal by different CO₂ removal devices

Tubing	Membrane dimension		Nylon filament dia. mm	Silicone coating	%CO ₂ removal, 22°C	%CO ₂ removal, 30°C
	Length, cm	I.D., mm				
Celgard	50	0.4	0.2	No	91.4±0.1	95.3±0.8
Celgard	50	0.4	0.2	Yes	91.5±0.3	96.6±0.6
Celgard	80	0.4	0.2	Yes	95.4±0.1	98.6±0.3
Celgard	80	0.4	0.2	Yes	95.9±0.1	97.8±0.1
Celgard	100	0.4	0.2	Yes	97.7±0.2	99.4±0.2
Neomecs	50	0.2	N/A	N/A	81.8±0.5	90.5±0.8
Neomecs	50	0.4	0.2	N/A	91.5±0.1	92.9±0.2

Lumen flow 1 mL/min; Sink solution: 100 mM NaOH at 0.5 mL/min.

Table 2.2. Performance of different CO₂ removal options external to the membrane^a

Fluid Flow mode at outside channel of CRD	Flow rate, mL/min	%CO ₂ removal
Pressurized Nitrogen	200	99.2±0.1
Nitrogen with inline soda-lime cartridge	200	99.3±0.1
Pump suction	200	99.2±0.1
Pump suction with soda-lime cartridge at the inlet	200	99.3±0.1
Pressurized air	200	99.3±0.1
Pressurized air with inline soda-lime cartridge	100-500 ^b	99.4±0.1
Vacuum (pump suction with inlet restriction)	200	99.1±0.1
Vacuum (pump suction with inlet restriction plus soda-lime cartridge)	200	99.3±0.1
Water	1	42.3±2.0
50 mM NaOH	1	96.9±0.1
100 mM NaOH	1	97.8±0.1
Suppressor waste	1	95.8±0.6

^a80 cm CRD; Lumen Flow 1 mL/min; Eluent 9.0 mM Na₂CO₃; Oven at 30°C.

^bthere is no difference in removal efficiency in this flow rate range

Table 2.3. Detection limits of common ions, ppb

	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	
Test Conc'n ppb	10	10	20	50	50	100	50	
Carbonate, no CRD ^a		3.8	3.4	8.3	5.8	25.0	14.4	n=13
Carbonate, CRD #31 ^b	0.7	2.2	2.4	3.2	3.4	15.0	3.5	n=12
Gradient hydroxide ^c	0.7	2.6	1.3	2.7	3.8	10.3	7.8	n=10
Isocratic hydroxide ^d	0.7	1.4	1.0	0.7	0.6	nd ^e	0.8	n=12
Test Conc'n ppb	5	5	10	25	25	50	25	
Carbonate, CRD #31 ^b	1.0	2.3	1.3	3.5	1.9	5.8	2.4	n=14
Isocratic hydroxide ^d	1.2	3.3	1.2	1.1	0.9	nd ^e	1.2	n=12

^a2 mm AG12/AS12, 0.3 mM NaHCO₃, 2.7 mM Na₂CO₃, 0.4 mL/min, 2 mm ASRS-Ultra, 50 mA recycle mode, room temperature operation (no oven), background 13.6 -14.4 μS/cm, 100 μL injection

^bAs in a, except CRD 31 (80 cm silicone coated Celgard) at room temperature (no oven), background 0.90-0.96 μS/cm.

^c4 mm AS17/AG17; CR-ATC; 1.5 mL/min; 50 μL injection; 1 to 35 mM electrogenerated KOH gradient, in oven at 30 °C

^d2 mm AS18, 20 mm electrogenerated KOH, all other conditions identical to a, no oven.

^enot determined, does not elute in 10 min

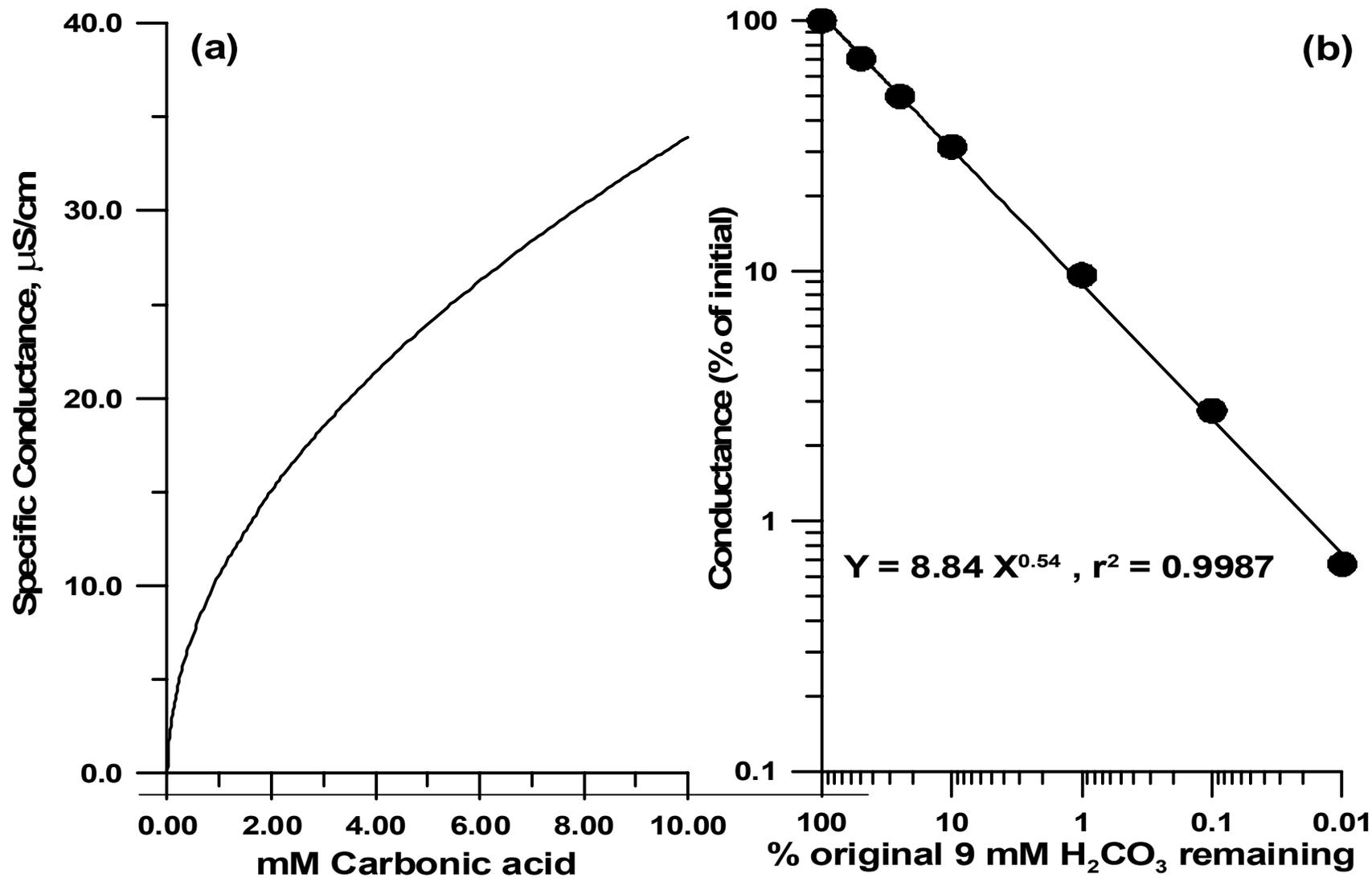


Figure 2.1. (a) Computed specific conductance of carbonic acid as a function of concentration at 25 °C, (b) Fraction of original conductance that remains for a 9 mM H_2CO_3 solution as CO_2 is removed from it.

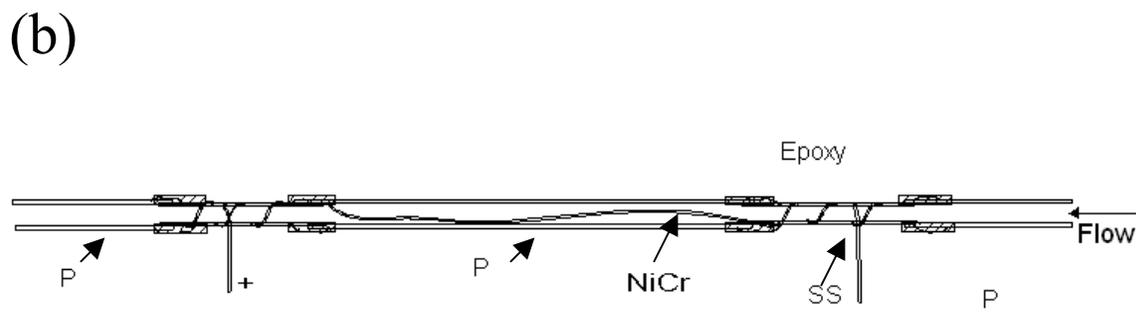
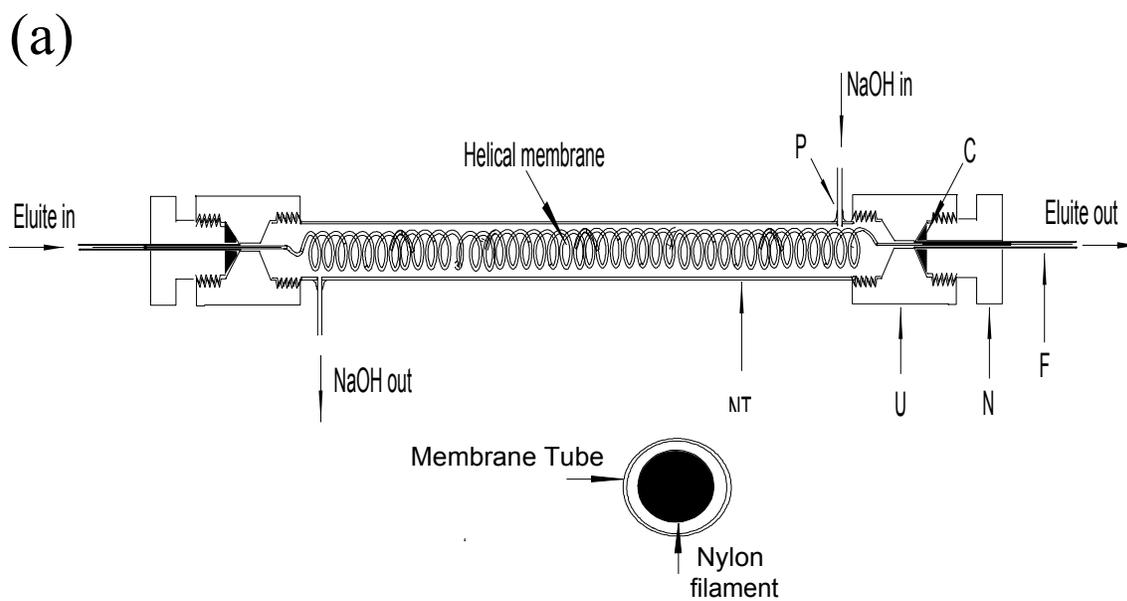


Figure 2.2. (a) Schematic for CRD, inset shows cross-section of membrane and nylon filament; NT, nylon jacket tube; U, union; N, male nut; F, FEP tube; C, ferrule; P, PEEK tube. (b) Inline heater; P, PEEK tube; SS, stainless steel tube; NiCr, nichrome wire; +-, power connections.

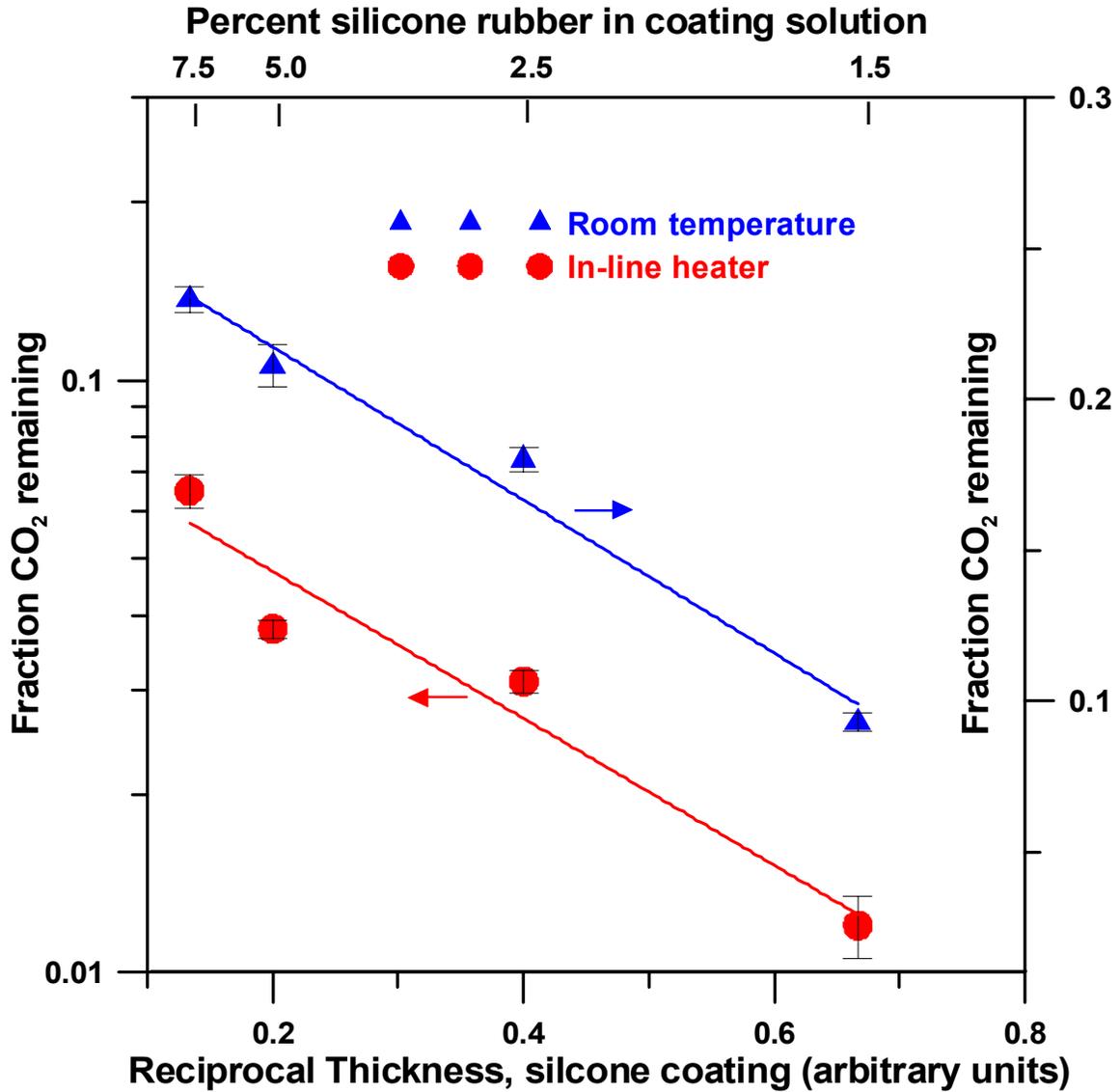


Figure 2.3. Residual CO₂ as a function of the silicone rubber content of the coating solution with the device operated at room temperature (right, linear ordinate) and with an in-line heater (left logarithmic ordinate). The coating thickness was measured to 1.4 μm for the 1.5% silicone rubber coating solution and is assumed to be proportional to the coating solution concentration.

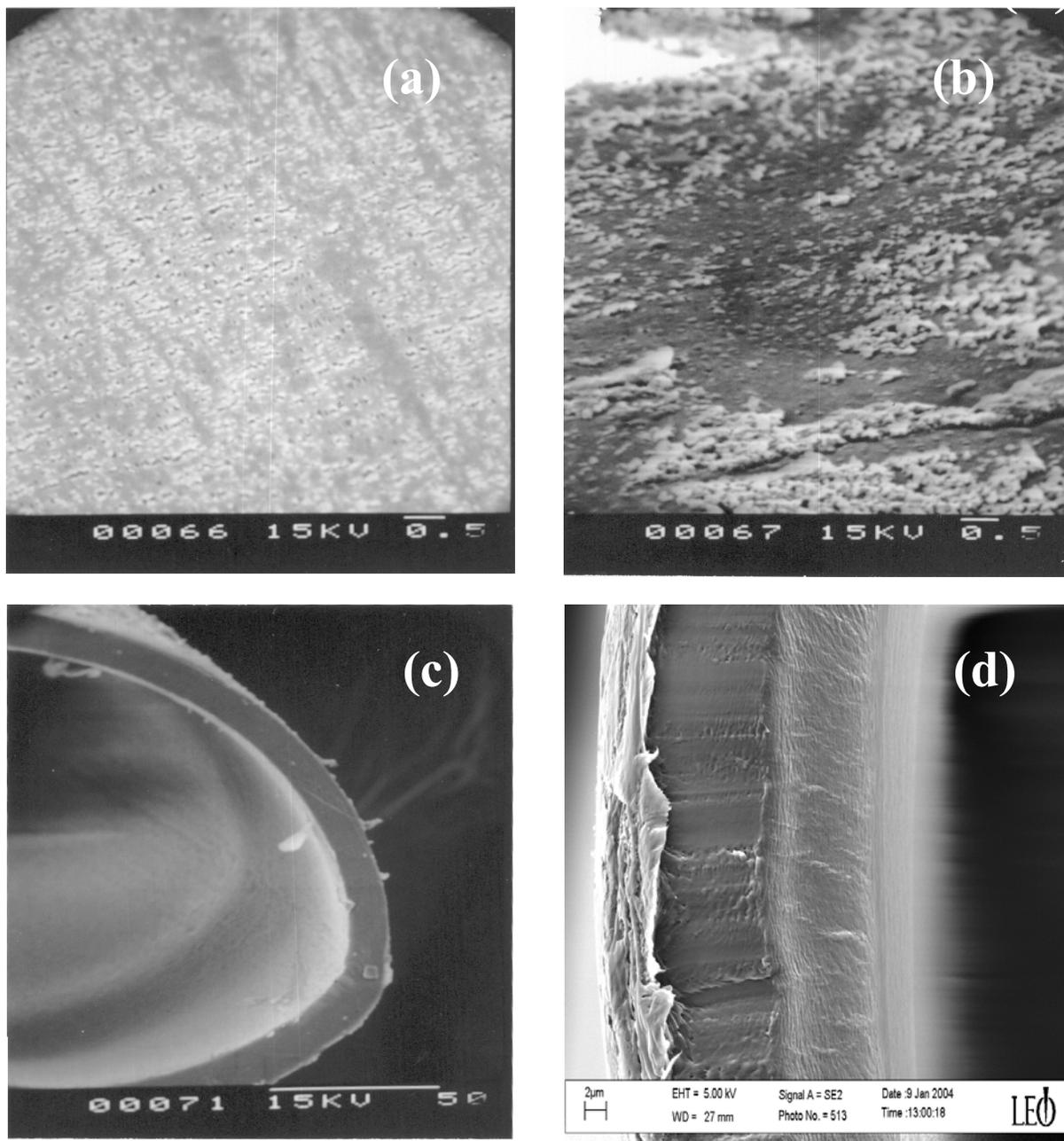


Figure 2.4. Scanning electron micrograms: (a) uncoated membrane-outer surface, scale bar 0.5 μm ; (b) coated membrane-outer surface, scale bar 0.5 μm ; (c) coated membrane-cross section, scale bar 50 μm ; (d) commercial Neomecs membrane, scale bar 2 μm .

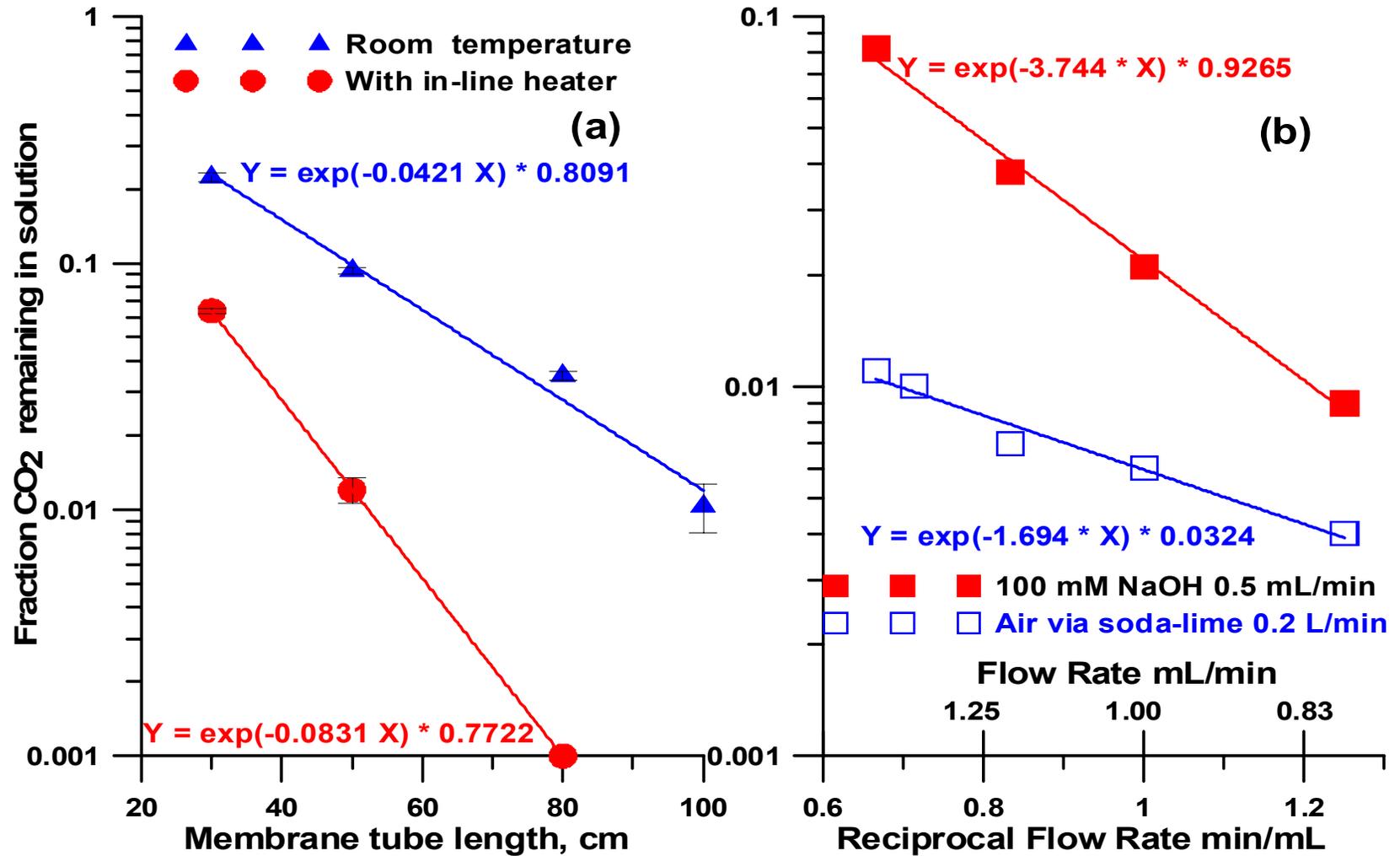


Figure 2.5. Gormley-Kennedy plot of the residual CO₂ as a function of (a) the tube length at room temperature and at 32 °C. and (b) as a function of the lumen flow rate (80 cm CRD) with air or 100 mM NaOH flowing in the jacket.

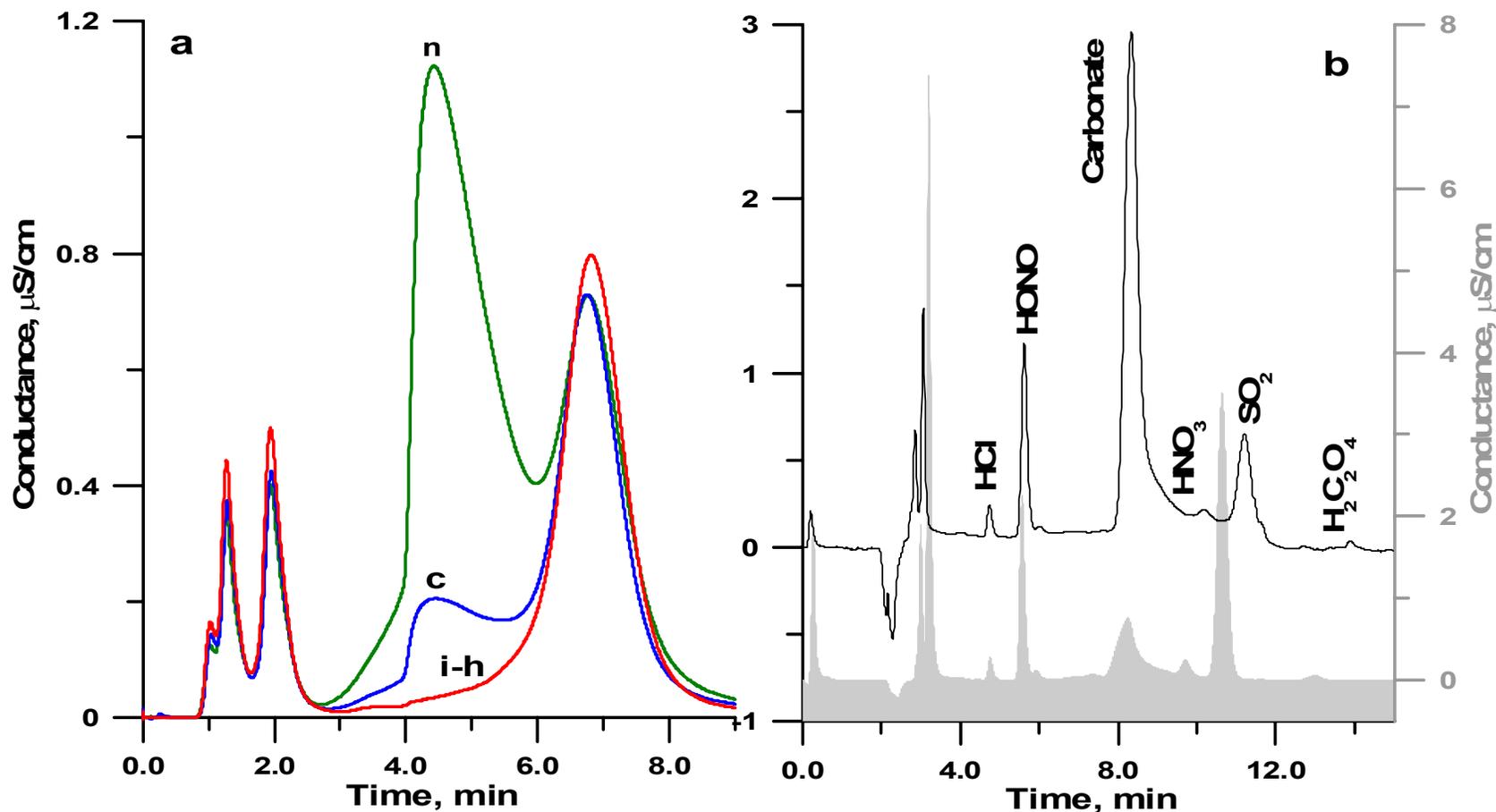


Figure 2.6. Removal of CO₂ present in samples in hydroxide eluent chromatography (a) 4 mm TAC LP-1 + AG-11 HC columns, 2 mM electrogenerated KOH at 1 mL/min, $\Delta P = 450$ psi (includes 150 psi drop prior to columns), 35 μL sample containing 150 $\mu\text{g}/\text{L}$ Cl⁻, 770 $\mu\text{g}/\text{L}$ NO₃⁻, 74 mg/L CO₃²⁻ and 3.1 mg/L SO₄²⁻ injected; n, no CRD, c, CRD at room temperature; i-h, in-line heater with CRD. (b) 4 mm AG11 + AS 11 columns, electrogenerated KOH eluent, 30 °C in LC-30 oven, atmospheric gas sample at Sydney, FL, collected at 5 L/min and preconcentrated for 15 min. Line trace (left ordinate): May 1, 2002, 12:20-12:35 AM, 15.5 mM KOH @ 1.5 mL/min, no CRD, 16 ppt HCl, 160 ppt HONO, 40 ppt HNO₃, 90 ppt SO₂, 8 ppt H₂C₂O₄; solid shade (right ordinate): October 4, 2003, 3:44 -3:59 am 17.5 mM KOH @ 1.4 mL/min, CRD at 30 °C, 40 ppt HCl, 410 ppt HONO, 85 ppt HNO₃, 510 ppt SO₂, 13 ppt H₂C₂O₄.

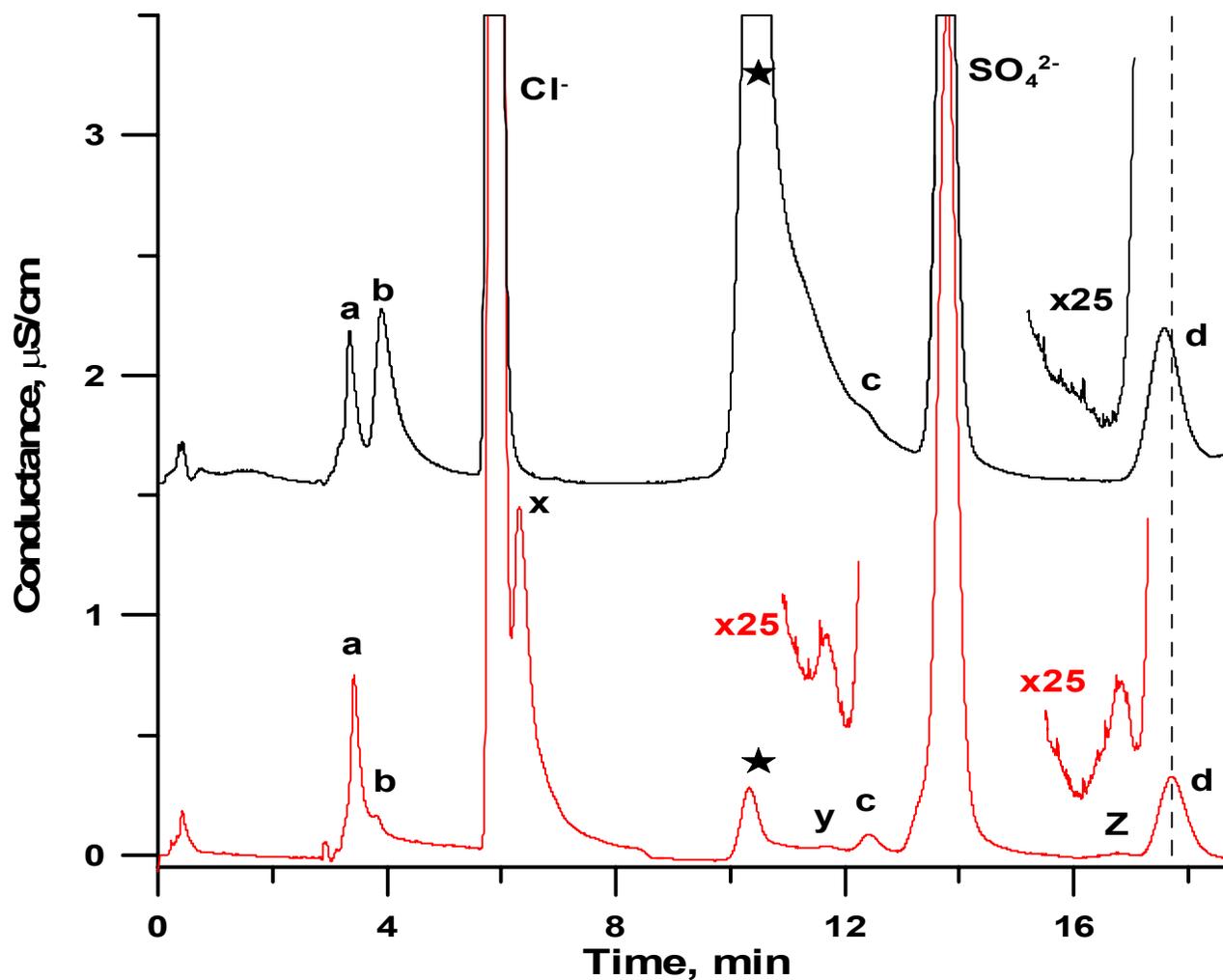


Figure 2.7. Chromatograms of an undiluted lemon-lime soda. 4 mm AG11/AS11 columns, 17 mM electrogenerated KOH at 1 mL/min; 2 μ L injected; top: no CRD, bottom: sample introduced through a CRD at 0.5 mL/min with a 0.25 x 1000 mm long tube after the valve for backpressure. Baseline offset applied to top chromatogram to facilitate evaluation. Some strongly retained peaks, e.g., citrate, elutes after 20 min and is not shown. See text for details.

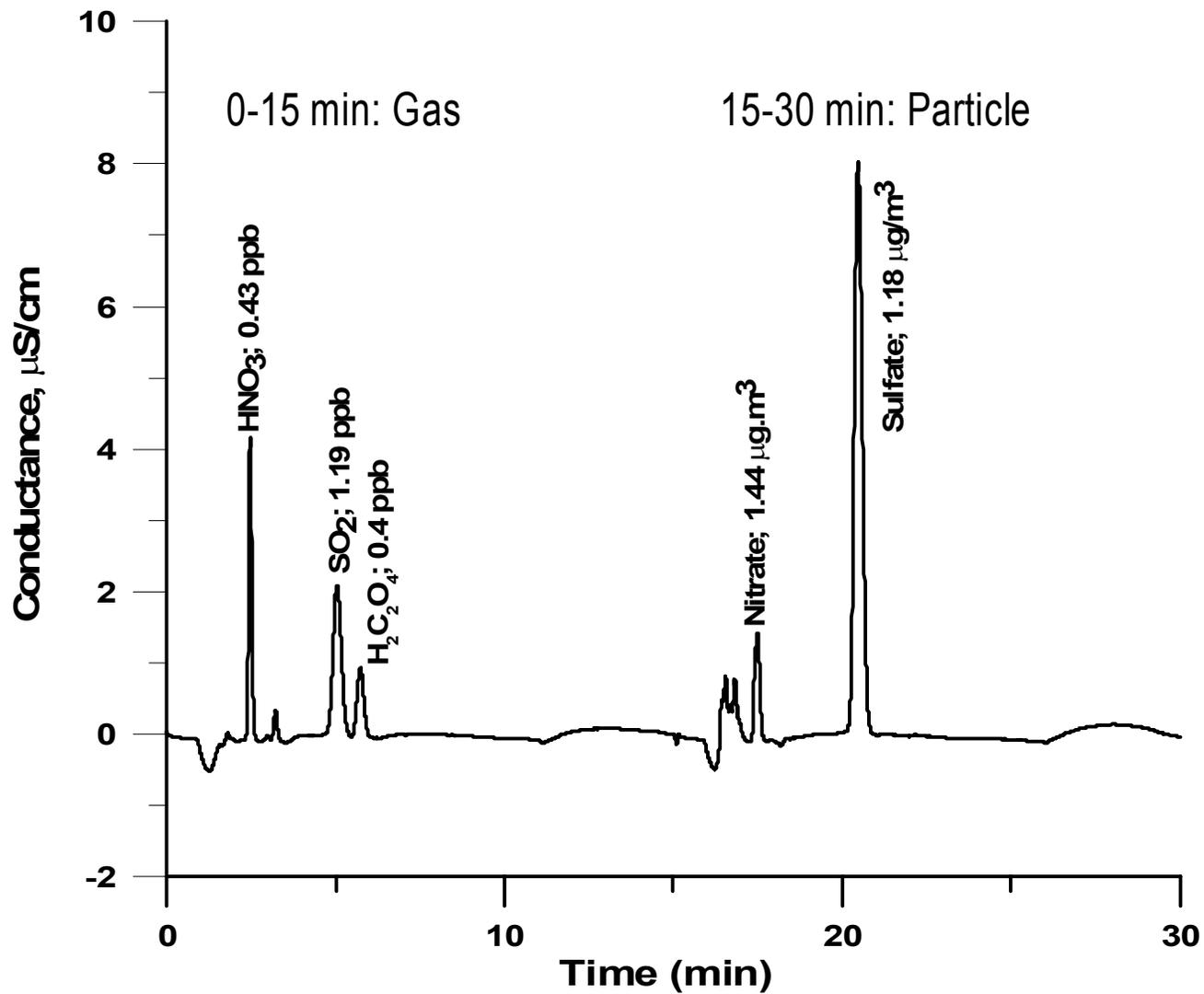


Figure 2.8. Automated sequential chromatograms of collected gas and aerosol samples (see e.g., ref. 37), with 2.4 mM Na_2CO_3 and 2.3 mM NaHCO_3 , eluent, 4x150 mm AG11 column, 1.0 mL/min, CRD, oven at 30 °C.

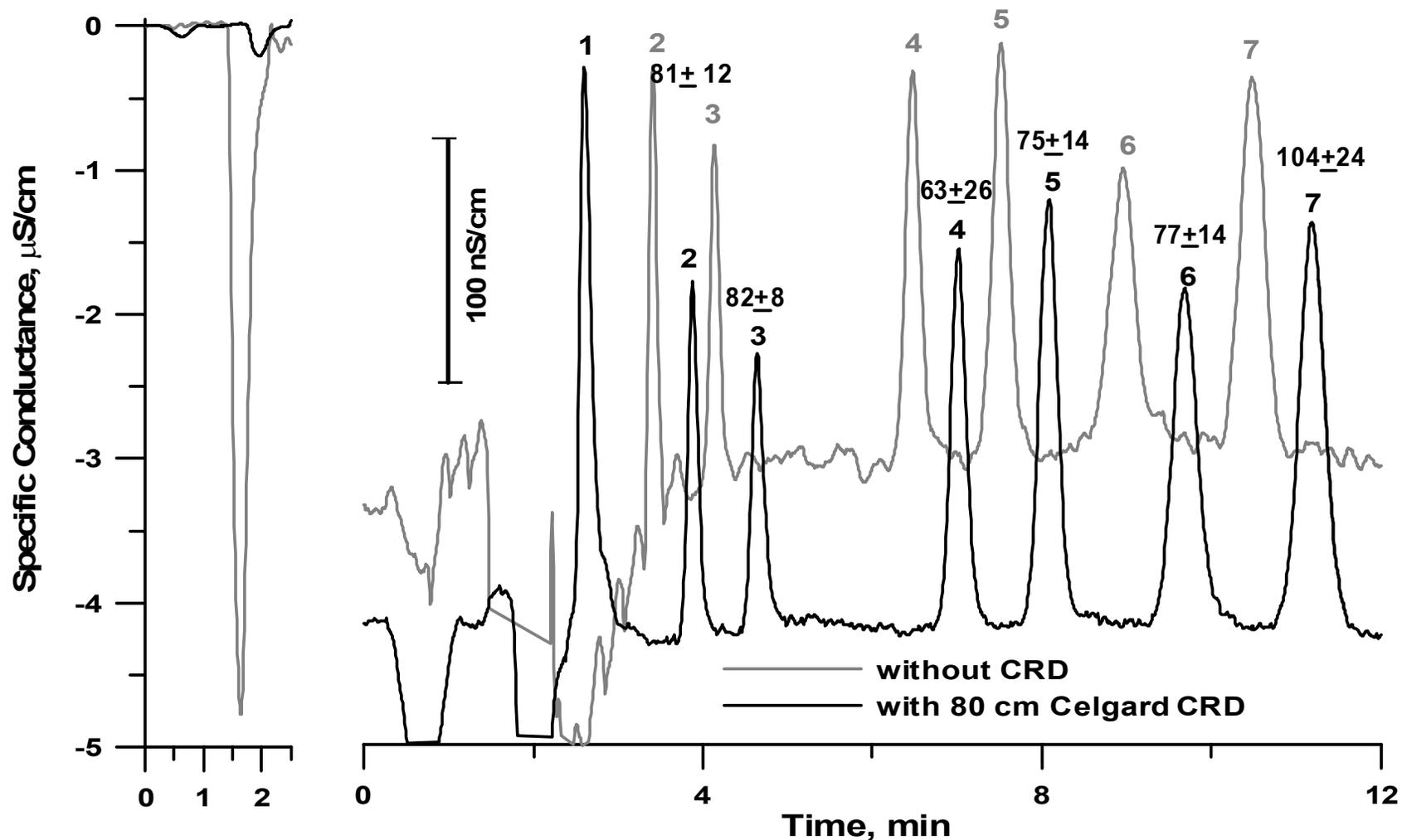


Figure 2.9. Isocratic carbonate-bicarbonate elution with performance near the LOD. 2 mm AG12/AS12, 0.3 mM NaHCO_3 , 2.7 mM Na_2CO_3 , 0.4 mL/min, 2 mm ASRS-Ultra, 50 mA recycle mode, Background 13.6 -14.4 $\mu\text{S/cm}$ without CRD (light trace), 0.90-0.96 $\mu\text{S/cm}$ with CRD at room temperature (dark trace), 100 μL injections of 10 $\mu\text{g/L}$ F^- , 10 $\mu\text{g/L}$ Cl^- , 20 $\mu\text{g/L}$ NO_2^- , 50 $\mu\text{g/L}$ Br^- , 50 $\mu\text{g/L}$ NO_3^- , 100 $\mu\text{g/L}$ PO_4^{3-} , 50 $\mu\text{g/L}$ SO_4^{2-} . The left panel shows the dramatic difference in the water dip. The computed band dispersion (uncertainty in parentheses, $n=3$) is shown on top of each CRD peak in the right panel. Fluoride at this level cannot be detected without the CRD.

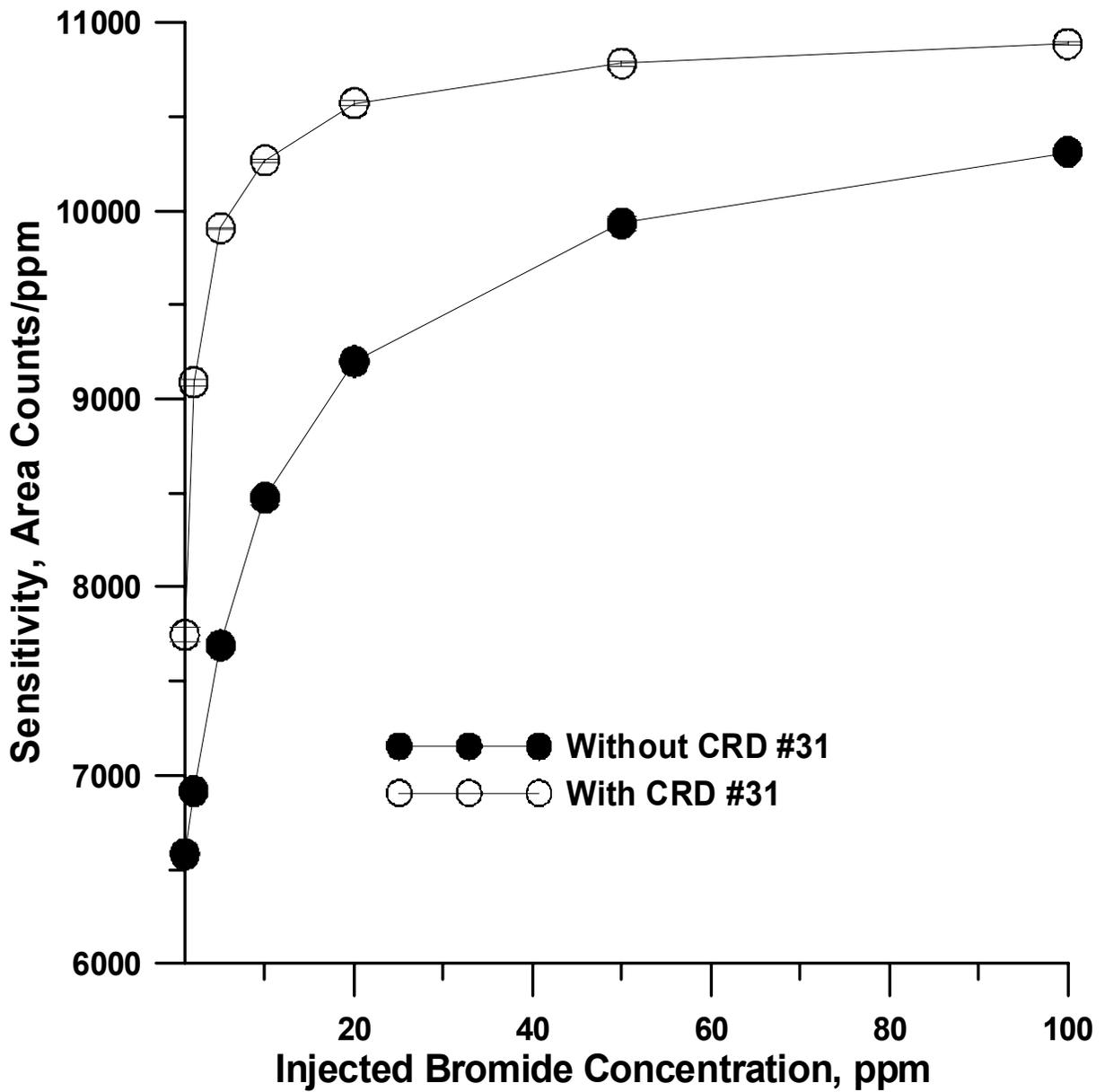


Figure 2.10. Cassidy linearity plot for a carbonate eluent for bromide, an analyte ion of intermediate retention in the most common concentration range of 1-100 ppm. Same conditions as Figure 9, background 0.6 $\mu\text{S}/\text{cm}$ with CRD.

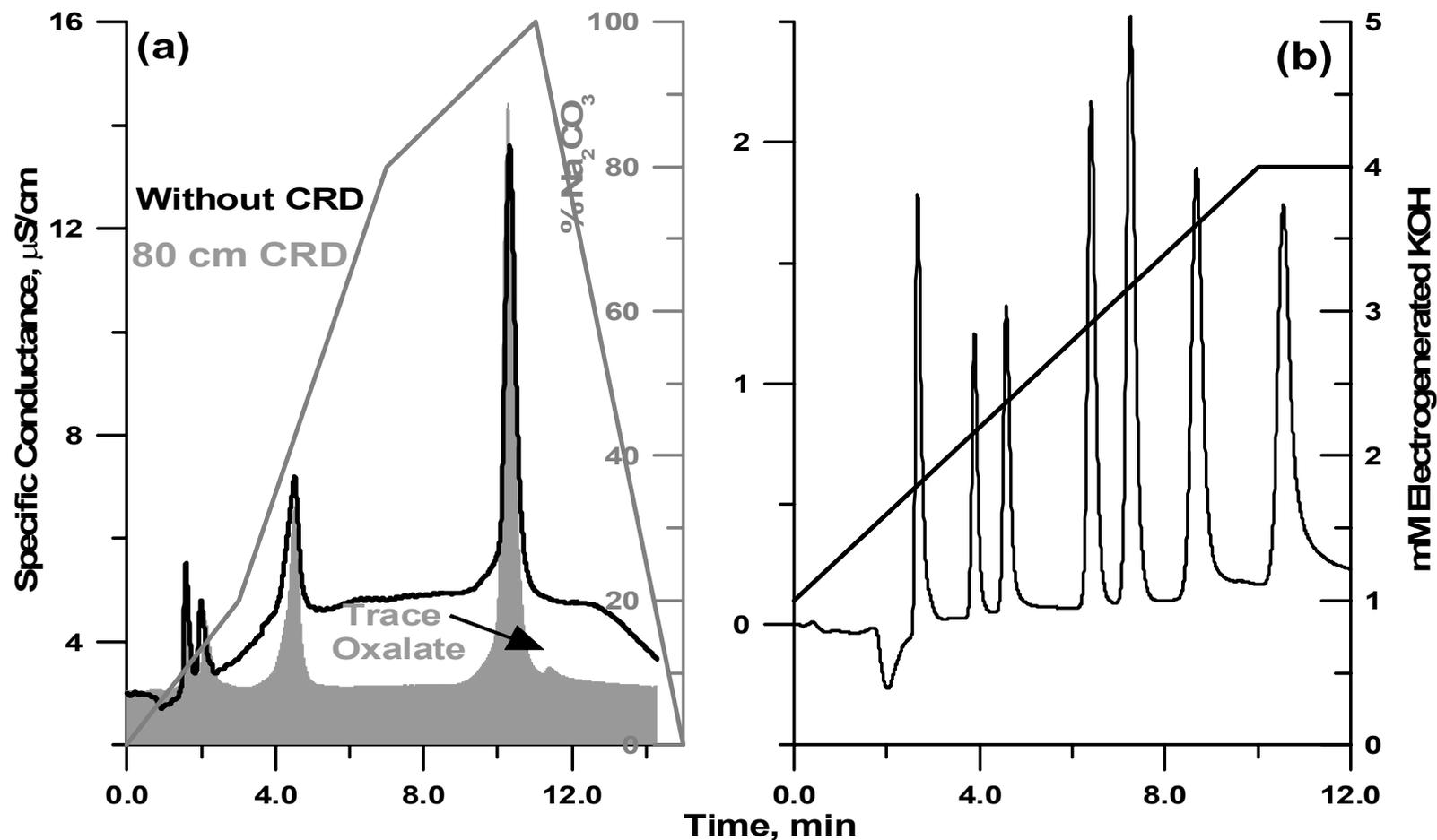


Figure 2.11. Carbonate gradient chromatograms (a) 4 x 100 mm AS11HC, 1 mL/min, gradient program 2.5 mM NaHCO₃ to 2.5 mM Na₂CO₃ as shown. 35 μL Cl⁻ (1.5), NO₂⁻ (2.1), NO₃⁻ (7.7) and SO₄²⁻ (31) injected, without (shaded solid) and with (dark line trace) a CRD at room temperature. (b) electrogenerated carbonate gradient (ref. 21), 2 x 50 mm AG12A + 2 x 250 mm AS12A, 0.4 mL/min, 100 μL F⁻ (1), Cl⁻ (1), NO₂⁻ (2), Br⁻ (5) NO₃⁻ (5) SO₄²⁻ (10) PO₄³⁻ (10) Eluent: 4 mM NaHCO₃ feed into electro-dialytic generator with 1 - 4 mM KOH gradient over 10 min; (concentrations in mg/L).

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CHAPTER III

AUTOMATED LOW PRESSURE CARBONATE ELUENT ION CHROMATOGRAPHY SYSTEM WITH POSTSUPPRESSOR CARBON DIOXIDE REMOVAL FOR THE ANALYSIS OF ATMOSPHERIC GASES AND PARTICLES

1. Introduction

The long-range transport of air pollutants is of interest because of their environmental impact. This includes nitrogen deposition, acid rain, and the deterioration of atmospheric visibility due to haze. In most regions of the US, fine particles constitute the major reason for reduced visibility caused by the scattering and absorption of light by particles and to a lesser extent, gases.¹⁻³ Adverse health effects of fine particulate matter (PM, PM_{2.5} refers to particles ≤ 2.5 μm in aerodynamic diameter) have been the major focus of research for over a decade now.^{4,5} Several epidemiologic studies have indicated strong correlations between ambient PM concentrations and mortality and morbidity.^{6,7} Correlations between fine PM concentrations and the incidence or exacerbation of respiratory diseases are of particular concern.^{8,9} The association between fine particles and adverse health effects may be due both to particles and gases, as excursions in ambient fine PM are often accompanied by excursions in the precursor ionogenic gases.^{10,11}

Major primary PM_{2.5} sources include automobiles, power plants, wood burning, and industrial processes.¹⁻² Secondary formation in the atmosphere from the transformation of SO₂, NO_x (NO and NO₂), and various organic gases can, however, be

even more important.² Ambient HNO₃ and nitrates are the end products of the oxidation of NO_x produced during combustion. The primary source of atmospheric SO₂ and sulfates is the combustion of fossil fuels. Ambient NH₃ is derived primarily from animal waste and the use of fertilizers. In particulate matter, ammonia is primarily present as ammonium salts of sulfate and nitrate, which constitute the major components of PM_{2.5}.¹² Optical, deliquescent and reactive properties determine the ability of the aerosol to scatter light, to form larger particles and to participate in secondary reactions.^{13,14} These properties are determined by the composition of the aerosol.^{13,15,16} It is thus important to have accurate data on ambient concentrations of particles, *and their composition*, as well as data on the major primary precursor gases with sufficient time resolution to understand their diurnal behavior and relationships with one another. Such data, along with meteorological information can be used to investigate the chemistry, transport and thermodynamic aspects of aerosols.¹⁷ A legally important issue, source apportionment of particulate matter, can also be achieved using such information.¹⁸

Atmospheric gas measurement methods have been reviewed by Finlayson-Pitts and Pitts,² Parrish and Fehsenfeld¹⁹ and Sipin et al.²⁰. Diffusion-based collection and analysis of atmospheric gases have been specifically reviewed by Dasgupta^{21,22} and most recently Toda²³. Many automated systems for the measurement of atmospheric gases uses a diffusion-based collector.²⁴⁻³⁰ Many of these systems are IC-based and permit simultaneous analysis of several gases.^{24,26-29}

While continuous instrumentation for the assessment of physical characteristics of atmospheric aerosols are available,³¹ similar measurement of the ionic composition of atmospheric aerosols is more difficult.^{20,32} Current practice is dominated by manual

methods where filters are used for aerosol collection, followed by extraction and analysis, typically by IC. Such methods, however, generally suffer from artifacts induced by on-filter gas-particle and particle-particle reactions, as well as from reequilibration under changing conditions of relative humidity (RH) and temperature. Mass spectrometry (MS) has been used for online real-time analysis of PM composition,^{33,34} single particle mass spectrometry can determine individual particle composition in real-time.^{35,36} However, MS use is limited by cost, complexity and lack of quantitative measurements. Besides MS cannot measure gas and aerosol phase species simultaneously.

For more conventional analysis, particles must be continuously collected and extracted. It is difficult to collect very small particles by impaction. Work here at Texas Tech provided a solution that involved growing particles with steam condensation prior to impaction.^{37,38} The same concept was also used by Khlystov and co-workers.³⁹ and used extensively by the same group⁴⁰ as well as others.^{27,41,42,43} The latest of these, due to Weber et. al.⁴² makes use of the steam-based particle growth system of Okuyama et al.⁴⁴ Samples are analyzed with separate cation and anion IC systems. LODs of 10-50 ng/m³ for each anion and a time resolution of 3.5-4 min have been achieved. The use of steam, however, may result in nitrite and nitrate artifacts from NO_x-steam reactions, as neither NO nor NO₂ are removed by a wet denuder.³² Additionally, steam generation is energy intensive and requires extra steps.

Several approaches that do not use steam have been reported.³² Hering and Stolzenburg introduced individual instruments that selectively measure particulate sulfate and nitrate,^{45,46} respectively; these are commercially available.⁴⁷ An automated IC-based system due to Boring et al.⁴⁸ utilizes a parallel plate wet denuder (PPWD) to first collect

soluble gases. Particles are then collected by one of two glass-fiber filters that alternate between sampling and washing/drying. The filter extract is preconcentrated for IC analysis. The filter-based system has many merits, but practical difficulties (leaching of fibers from fibrous filters create problems with fouling of downstream components) limit application. Al-Horr et al.⁴⁹ described a hydrophobic filter-based PC that uses water instead of steam. It is capable of continuous collection and extraction of soluble PM. The hydrophobic filter functions as a reflux element with the aerosol and coalesced liquid refluxing from the filter.

Atmospheric NH_3 and NH_4^+ are important analytes because NH_3 is the principal base that neutralizes atmospheric acidity and particulate NH_4^+ is the product of that process. It is often the only non- H^+ cation of interest in $\text{PM}_{2.5}$ samples and is by far the dominant non- H^+ cation in samples that have little coastal influence. Chromatography is therefore unnecessary if ammonium can be selectively measured among other cations in the sample. A preeminent approach involves alkalization of collected NH_4^+ to liberate NH_3 that diffuses across a membrane to a water or mildly acidic receptor the conductivity of which is measured. This 25+ year old approach of Carlson^{50,51} has been widely used⁴⁹ and frequently without acknowledgement^{40,52,53} and is also used in the present work.

IC was originally introduced with carbonate eluents. Unlike hydroxide eluents, such eluents can be (a) reproducibly prepared in pure form, (b) used at much lower concentrations than hydroxide, (c) immune to the presence of dissolved CO_2 /carbonate (that is obligatorily present in denuder liquid and particle collector samples and shows up in hydroxide-based eluent chromatogram as a broad tailing peak that can obscure smaller analyte peaks (notably nitrate) that elute in the same region. The disadvantages of

carbonate eluents are that the higher conductance background leads to higher LODs and poorer analyte calibration linearity. These difficulties have been recently removed by an asymmetric membrane fiber-based device that removes 97-99+% of the CO₂ from suppressed IC effluents and produce a background of essentially pure water, thus providing a means to get the best of both worlds.⁵⁴ This low background conductivity also lowers detection limit that is very helpful in atmospheric measurements in remote regions with low pollution. The presently described instrument takes advantage of these developments.

2. Methods

2.1. Reagents

All reagents used in this work were analytical grade. All standards, eluents and reagents were prepared with Nanopure water (Barnstead, 18 MΩ·cm).

2.2. IC and Ammonia Determination Subsystem

Anion chromatography was accomplished on an isocratic IC (Model DX 320, all chromatographic equipment and accessories were from Dionex Corp., Sunnyvale, CA). An AG11-HC guard column (4 x 50 mm) was used with two more identical AG11-HC columns, the latter two functioning as the separator in conjunction with an eluent consisting of 2.4 mM Na₂CO₃ and 2.3 mM NaHCO₃, flowing at 1.0 mL/min for this system. The electrochemical suppressor (ASRS Ultra) was followed by a prototype CO₂ removal device (CRD) and a thermally stabilized DS-3 conductivity cell.

The ammonia transfer device (ATD, *vide infra*) is similar in principle to the CRD⁵⁴ (Ullah et al. 2004) but transfers ammonia across the membrane. It is constructed

slightly differently (with a 0.4 mm i.d., 0.45 mm o.d. 30 cm long silicone-coated filament filled Celgard™ polypropylene tubular membrane as the receptor channel and a 0.86 mm i.d. concentric Teflon jacket (20 SW, Zeus) as the donor channel), so that the receptor volume is small and leads to low dispersion in the measurement of the transferred analyte. The receptor channel output of the ATD was connected to a second DS-3 conductivity cell and connected to an independent conductivity detector.

All columns, valves, CRD, ATD and conductivity cells were maintained inside a 35°C oven (Isotemp, Fisher Scientific). The conductivity detector signals were acquired by a Pentium III class PC in conjunction with a network hub (NetGear EN308). The system was controlled by PeakNet 6.4 software (Dionex). The chromatographic cycles repeat every 30 min (consisting of 15 min chromatograms each for the gas and the particle phase) until deliberately shut off or until a preprogrammed number of cycles have run. System automation and valve control are achieved with PeakNet software using Relay and TTL outputs in the chromatograph.

2.3. Gas and Particle Collection System

Water soluble gases were collected with a PPWD described in detail by Boring et al.⁴⁹ In short, the denuder is composed of textured Plexiglas plates (active area 6.0 x 42 cm each, separated by 0.3 cm). The denuder liquid is pumped to flow down each plate and aspirated from the bottom. Air samples enter the denuder at the bottom. A multichannel peristaltic pump (*vide infra*) pumps liquid to and from the denuder. The denuder effluent is sent for preconcentration and analysis.

The particle collection system (PCS) used here is similar to that described previously by Al-Horr et al.⁴⁹ (2003). The PCS consists of a cyclone (SCC-1-828, SCC 2.5 μm /5 LPM, BGI Inc., Waltham, MA, 50% cut point at 2.5 μm at 5L/min) for large particle removal, followed by a PPWD for removal of soluble gases. The PC collects $\text{PM}_{2.5}$ soluble fractions. The particle collector, PC sits atop the PPWD (identical to that used in the gas collection system) and air enters the PC through a constricted Plexiglas nozzle at the end. Water is pumped through a stainless steel capillary (0.64 mm o.d., 0.33 mm i.d., type 304 stainless steel, HTX-23, Small Parts Inc., Miami Lakes, FL) placed next to the nozzle. High velocity air creates a fine mist, aerosolizing the water that in part attaches to the sampled aerosol. A hydrophobic microporous PTFE membrane filter (Fluoropore FHLP, 0.45 μm pores, 47 mm dia., Millipore) forms the top exit of the PC. The water mist coalesces on the hydrophobic filter surface as large droplets and fall to the bottom of the PC chamber. Water is not aspirated through the highly hydrophobic filter. The air is aspirated from the top of the PC while the liquid sample is aspirated from the cone-shaped PC floor. Two stainless steel rods (0.05 cm dia.), placed radially across the PC liquid outlet aperture, serve as conductivity probes and sense the presence of liquid water. The conductivity probes function as a simple logic sensor; the presence of water across the electrodes causes the electronics (Figure 3.1) to turn on a dedicated, fixed speed single channel peristaltic pump P1 (Figure 3.2, Fisher Scientific). The pump aspirates the liquid for preconcentration and subsequent analysis.

2.4. System Description

The complete system is shown schematically in Figure 3.2. All liquid was pumped by a 12-channel peristaltic pump, PP1-12 (Monostal Carter) at a fixed speed of 30 revolutions per minute. A single channel, fixed speed peristaltic pump, P1, was used for liquid aspiration from the PC (Figure 2). Pharmed[®] pump tubes (Cole-Parmer) with ¼-28 threaded PEEK tubing adapters (PF-S, Global FIA, Gig Harbor, WA) were used throughout the system with male nuts and ferrules. All liquid-transfer lines were 20-ga. standard wall PTFE tubing (0.86 mm, 20 SW, Zeus Industrial Products). Pump channel 1, (PP1, 0.38 mm i.d., 0.06 mL/min, not shown in Figure 1) used 25 mM H₂O₂ as feed. The output of PP1 was joined with a pressurized DI water source as ballast and this was used as the common feed for pump lines 2 and 9 (PP2,9 1.83 mm i.d., 1.4 mL/min/channel). The outputs of PP2 and PP9 were thus used to feed PPWD1 (gas system denuder) and PPWD2 (particle system denuder) with ~0.5 mM H₂O₂ (this nonionic liquid is compatible with the effluent analyzed by IC, see Boring et al. 2002), one on each plate, at a rate of ~0.7 mL/min through a mixed bed resin column MB (6.7 mm i.d, 20 cm long, filled with Dowex MR-3, all MB units are identical). Pump channels 3,4 (PP3,4 1.52 mm i.d.) remove the PPWD1 effluent with a higher flow rate than the input flow rate to ensure that the input liquid is completely removed. The output of PP3 and PP4 are combined and proceeds as the gas sample GS via V5 and V2 to the gas system cation and anion preconcentrator columns (CC1 and AC1) contained in gas system preconcentration valve V3. Liquid flow into the denuder must be sufficiently high to keep the denuder wet at all times and under all conditions of RH and temperature to be encountered, with 5 L/min air flow. It is necessary to keep an upper limit on the liquid flow both to minimize

liquid consumption and to prevent excessive backpressure when preconcentrating the effluent liquid on the columns. The denuder effluent (PP10,11) from the particle sampling channel (PPWD2) is not analyzed and is simply discarded; any liquid that can act as an appropriate sink for acidic and basic gases can therefore be used in PPWD2.

Pump channel 5 (PP5, 0.89 mm i.d., ~0.4 mL/min) pumps 100 mM NaOH into the exterior receiver channel of the CRD. Pump channel 6 (PP6, 1.30 mm i.d., ~0.9 mL/min) pumps house-DI water through column, MB to the PC.

Pump P1, activated by the conductivity sensor, aspirates water containing dissolved aerosol and any undissolved solid from the PC. The particle extract sample PS and excess air are pumped sequentially through a 25 mm 0.2 μm pore size nylon membrane filter MF, via V5 and V2 to particle system cation and anion preconcentrator columns (CC2 and PC2) contained in particle system preconcentration valve V4. CC1 and CC2 are 5 x 35 mm columns filled with a 1:1 mixture of Dowex-50Wx8 H^+ -form 200–400 mesh strong acid resin with a diluent (chloromethylated polystyrene-divinylbenzene, Bio-Beads S-X1, 200–400 mesh, Bio-Rad Inc.). AC1 and AC2 are Dionex anion preconcentrator columns (TAC-ULP1, 5 x 23 mm). V3 and V4 (C2-2340 EP, VICI) are both 10-port electrically actuated high-pressure valves.

Pump channel 7 (PP7, 0.89 mm i.d., ~0.4 mL/min) delivers freshly deionized water via MB to the receiver channel of the ATD (countercurrent to the donor channel flow), to conductivity detector D2 (CD25, Dionex), through a restrictor tubing R (0.125 x 60 mm) to waste. Pump channel 8, (PP8, 1.52 mm i.d. tube, 1 mL/min), pumps 15 mM NaOH via CC1 or CC2 (depending on the position of V3 and V4) to the donor side of the ATD to waste. Pump channel 12 (PP12, 1.52 mm i.d., 1 mL/min) pumps either water or

air, as selected by V1 (all-PTFE solenoid valve, 12-V, 161T031, NResearch, Caldwell, NJ), through the low-pressure 6-port valve V2 (C22Z-3186EH, VICI), to wash columns CC1/AC1 or CC2/AC2 depending on the position of V3 and V4.

2.5. Liquid Phase calibration

The chromatographic system is calibrated by fixed volume identically sized loops L1 and L2 (individually calibrated by dye injection/absorbance measurement to be 31.4 μL in volume each) housed in 10-port, low-pressure, manually operated valve V5 (C22Z-3180, VICI) operated as a dual loop injector. Different concentrations of $(\text{NH}_4)_2\text{SO}_4$ and NaNO_3 were used to calibrate the system in the liquid phase. Air sampling is shut off during such calibration. Loops L1 and L2 were respectively used to load these calibration standards to the gas system (CC1 and AC1) and particle system preconcentrators (CC2 and AC2) housed in V3 and V4, respectively. Standards were then analyzed for 15 min each. The L1 and L2 calibration data are individually used to compute analyte concentrations for the gas and particle systems. Since individual preconcentrators behave differently, these calibrations are not interchangeable between the two systems. Multipoint calibrations in terms of nmol or ng vs. peak height/area were constructed the using the PeakNet software.

2.6. Field Installation

The instrument was deployed for an extended period in Bondville, IL. It was housed in an air-conditioned trailer. Referring to Figure 3.3, the sampling arrangement utilized a 4-inch PVC pipe that vertically traverses the shelter, extending to 1.5 m above

the roof top and terminates in a U, pointing downward to prevent precipitation ingress. A blower fan (BF) beneath the trailer aspirated air through the PVC pipe to aspirate air at 40 L/min. This results in laminar flow but with minimum deposition or adsorptive loss to the wall. If the objective is to measure total particles, it is possible to use a single sampling train, with the denuder serving both as the gas sampling and removal unit. However, two separate sampling trains are necessary if $PM_{2.5}$ is to be measured. Aerosol hydration can change the original particle size distribution if a wet denuder is installed before the PC. On the other hand, if the cyclone is placed before the denuder, significant loss of reactive gases, notably HNO_3 , occurs. A stainless steel tube, SST, (12.7 mm i.d., 15.1 mm o.d., 20 cm long) was fashioned into a rounded L-joint. The SST breaches the PVC tube within the shelter. One end of the steel tube is located at the precise center of the PVC tube, pointing upward in the direction of incoming airflow. The PPWD was fixed to a Plexiglas platform attached to the PVC conduit to maintain vertical alignment. The cyclone (Cy) was interposed between the stainless tube inlet and PPWD2. The inlet of Cy fits snugly inside the long arm of the SST.

The denuder in the gas analysis system, PPWD1, was fixed to the other side of the PVC pipe. A PFA Teflon inlet tube (8.5 mm o.d., 7.5 mm i.d., 1 SW, Zeus Industrial Products) enters the bottom of PPWD1. It breaches the PVC tube downstream of the SST connected to PPWD2. A water trap (WT) and a high flow 0.2 μm cylindrical filter (F) were placed before the mass flow controllers (MFC, model GFC 171, 0-10 SLPM Aalborg, Orangeburg, NY) for each channel to prevent water condensation downstream of the PPWD1/PC entering the MFCs). Aspiration is provided by an air pump (model DOA-P703-FB, Gast Manufacturing Corp, Benton Harbor, MI) for both particle and gas

channels. The air pump was located in an enclosed area within the trailer to reduce noise in the work environment.

2.7. Instrument Operation and Analysis Protocol

The cation preconcentrator is always placed upstream of the anion preconcentrator because the latter contains accessible cation exchange sites and will capture ammonium if the sequence is reversed. Operational actions describing the on/off status of V1 to V4 are highlighted in Table 3.1. Each cycle is 30 min. long, consisting of two 15 min. halves, dedicated to GS collection/particle analysis and PS collection/gas analysis, respectively. Each 15 min period contains three intervals, during two of which the lines leading to the respective concentrators are readied for washing (2 min) and then washed (6 min), prior to fresh sample loading. Washing is important to remove residual NaOH and excess alkalinity so that NH_4^+ can be effectively preconcentrated in the next step. As the analytical cycle begins in either gas or particle sample analysis mode (Step 1 or 4), the 15 mM NaOH eluent (PP 8) elutes NH_4^+ as NH_3 from CC1/2 and the transferred NH_3 is measured by D2 via the ATD. Simultaneously, the chromatographic pump (IS25A) elutes AC1/2 onto GC and SC; after suppression and CO_2 removal, the eluted anions are detected by D1.

Calibration is conducted manually. V5 remains in the off (black) position throughout all analysis cycles and is switched to the red position only for calibration. Air sampling is shut down and the injection loops are washed with deionized water before standards are loaded in the loops and analyzed. Similarly, before the instrument is

switched back to the analysis mode, the loops are washed with deionized water to avoid residual contamination.

Rather than the dedicated arrangement described above for measuring ammonia, a second IC dedicated to cation analysis can be used for the determination of all soluble cations. However, the serial cation/anion preconcentrator arrangement has to be abandoned for a parallel arrangement of the preconcentrators. This is because an acid must now be used in the cation analysis system and the cross-contamination of eluents between cation and anion chromatography systems must be avoided.

2.8. Standard Gas and Aerosol Generation for The Measurement of Collection Efficiency

Sulfur dioxide was used as the test gas for determining denuder collection efficiency, it has a molecular weight (MW, and hence presumably diffusion coefficient D) very similar to that of HNO₃ and substantially lower D and higher MW than the other gas of interest, NH₃. A permeation wafer source (VICI Metronics, Poughkeepsie, NY) was maintained at 30 °C in a permeation device housing (Model 822-1, Mast Development Co., Davenport, IA) and was gravimetrically calibrated to be emitting 9.08±0.26 ng/min. Clean dry air, mass flow controlled @ 0.2 standard L/min (SLPM) purges the thermostated glass permeation chamber. The exit gas was diluted with 10-20 SLPM purified air metered by a second MFC. Both sampling trains simultaneously sampled the test stream at a fixed rate of 5 SLPM, controlled by their respective MFCs. Aerosol generation and characterization and deposition experiments were conducted in the same manner as described by Al-Horr et al.⁴⁹ We used fluorescein-doped (NH₄)₂SO₄ aerosol

(1.16 and 3.58 μm mass median aerodynamic diameter, MMAD), to test collection efficiency and deposition pattern.

3. Results and Discussion

3.1. Gas Collection Efficiency

For a parallel plate denuder of active area $L \times W$ on each plate with the plates separated by the distance s , De Santis⁵⁵ interprets the Gormley-Kennedy equation to predict a gas collection efficiency f at a sampling flow rate Q to be (L , W , D , s , and Q being in compatible units) to be:

$$f = 1 - 0.91 \exp(-2.4 \pi WDL/Qs) \dots \dots (1)$$

For the denuder dimensions given in the experimental section and a diffusion coefficient of $0.13 \text{ cm}^2/\text{s}$,⁵⁶ the predicted value of f is 99.99+% at the sampling rate of 5 L/min. The uncertainty in the present experiments limits the digits to which we can specify collection efficiency, however it can be confidently stated that the collection efficiency for SO_2 under these same test conditions was 99+%. Importantly, no significant increase in the blank sulfate peak was discernible in the particle sample chromatograms while sampling 0.63 ppb SO_2 with the PPWD2 ahead of the PC. Previous experiments with this type of denuder have also shown that collection efficiency at a flow rate of 5 L/min is statistically indistinguishable from unity.²⁹

3.2 Particle Collection Efficiency

Al-Horr et al.⁴⁹ reported a more detailed evaluation of this PC over a broader particle size spectrum. For a MMAD of 1.0 and 2.6 μm , respectively, the total particle

loss was $6.3 \pm 0.2\%$ and $11.6 \pm 0.8\%$, respectively, with the majority of the loss ($4.7 \pm 0.5\%$ and $8.3 \pm 0.7\%$, respectively) occurring in the PC nozzle and $1.2 \pm 0.5\%$ and $2.2 \pm 0.1\%$ of the loss occurring on the wet denuder plates.⁴⁹ The PC nozzle taper was made more gradual (77° from the original 75°) and the nozzle orifice size was increased to 0.5 mm in the present work. The total loss for the 1.0 and 2.6 μm MMAD particles decreased by nearly half to $4.1 \pm 0.9\%$ and $6.7 \pm 0.4\%$ respectively, with the loss on the denuder plates contributing $\leq 1\%$.

3.3. Chromatographic Optimization

A typical IC separation is made on a 250 mm long separation column, more often than not with a 50 mm guard column ahead of the main column. If all one needs is a separation of nitrate and sulfate from other constituents typically present in atmospheric samples, it is possible to use a much shorter column. Such an arrangement holds a number of advantages: (a) it reduces system pressure (thus prolonging pump and seal life), (b) shortens analysis time, and (c) uses less concentrated eluent. However, a shorter column cannot be used with hydroxide eluent because of interference by a large dissolved CO_2 peak present in all atmospheric samples. This interference does not exist with a carbonate-based eluent. The disadvantage of the carbonic acid background generated by a carbonate based eluents is largely (97-99+%) removed by the CRD. The overall arrangement therefore permits the use of easily prepared, inexpensive carbonate based eluents with the advantage of the low background of hydroxide eluents as well as the use of a short column that will allow a lower pressure separation.

The manufacturer generally recommends anion separation columns of the AS 9 variety for use with carbonate-based eluents. We experimented with two 4 x 50 mm long guard columns in series to simulate short 100 mm columns. Based on initial results, three combinations of guard columns (AG9+AG9, AG9+AG11, AG11+AG11) were chosen for further investigation. The AG11+AG11 column combination produced the best separation with an optimized eluent composition of 2.4 mM Na₂CO₃ + 2.3 mM NaHCO₃. Under the operating conditions (a TAC-ULP1 preconcentrator, an AG-11 guard column and further two AG 11 guard columns functioning as the separator), the head pressure at the operating flow rate of 1.0 mL/min was \leq 400 psi and nitrate and sulfate could be quantitated in real samples in \sim 6 min. The suppressed background conductance of this eluent was 16 μ S/cm but decreased to \sim 1 μ S/cm by the use of the CRD as a post-suppressor device. Note that H₂CO₃ is a weak acid and the fractional ionization is higher at lower concentrations; consequently the extent of CO₂ removal by the CRD is substantially greater than a direct comparison of the conductance backgrounds with and without the CRD will indicate (as a first approximation, in this concentration range, the actual H₂CO₃ concentration is proportional to the square of the specific conductance; as such these data indicate 99.6% CO₂ removal, Ullah et al.⁵⁴). Typical instrument output for a 30 min. cycle for (a) anion chromatograms; (b) ammonium/ammonia is shown in Figure 3.4.

3.4. Limits of Detection

LODs (S/N = 3) for nitrate and sulfate were 2.6 and 5.3 ng/m³ for a 75-L total sample volume (15 min at 5 L/min). The separation between nitrate and sulfate is good

enough that it should be possible to operate the instrument at a slightly increased flow rate with a 5 min cycle and measure these ions. Under these conditions, one would expect the LODs to proportionally deteriorate to 8 and 16 ng/m³. Electrodealytically generated hydroxide eluents can indeed lead to lower LODs.⁴⁹ However, the presently attainable LODs are more than adequate for most measurement needs, and isocratic hydroxide eluents cannot perform the necessary separation in this time period. The calibration for NO₃⁻ and SO₄²⁻ was linear at least up to 2.4 and 9.8 μg injected (corresponding to 32 and 131 μg/m³ sampled concentrations) with respective linear r² values of 0.9998 and 0.9999 and intercepts statistically indistinguishable from zero. The measurement of ammonium/ammonia on the other hand relies on the dissociation of the weak base NH₄OH and a quadratic calibration equation produces a good fit (multiple r² = 0.9989). The LOD (S/N =3) for NH₄⁺ was 2.1 ng/m³.

3.5. System Maintenance

Maintenance frequency of any instrument deployed in the field over a significant period is an issue. The hydrophobic filter in the PC begins to lose its hydrophobic character due to sampled surfactants, probably biogenic in nature, resulting eventually in water leakage through the pores. Accumulation of insoluble particles can also slowly block the filter pores, increasing the pressure drop to such a level that the desired flow rate can no longer be maintained; the increased pressure drop can also itself promote water leakage. In rural Bondville, the filter required replacement every 1-2 weeks. Filter replacement require ≤ 5 min. Particle sample data from the next two cycles, however, are discarded because of potential contamination. Both PPWDs and inlet lines are washed

thoroughly with DI water every 4 weeks to remove insoluble particles that are deposited. The denuders must be maintained strictly vertical to prevent developing dry regions within the wetted area and the consequent formation of water channels. To treat persistent dry area problems, the denuder is washed with water, then HPLC grade methanol, then rewashed with water. Peristaltic pump tubes need to be replaced every week. The pump tubes that load gas and particle samples to preconcentrators need inspection between regular replacements. The membrane filter MF positioned after the PC is replaced every 2 weeks. Despite the presence of MF, the inlet frit of columns CC1/CC2 can become clogged with very fine, insoluble PM that passes through F, generating backpressure. Frits should be inspected for soiling every two weeks and replaced as needed. If loss of separation efficiency is evident, the anion and cation preconcentrators are cleaned using the manufacturer's recommended column clean-up procedure. Every month, the 50 mm column most upstream is removed from the system, and a new 50 mm column is placed in the most downstream position. Every three months the preconcentrator columns are replaced. With any change in columns, the system must be recalibrated.

Experience has indicated that the originally used peristaltic pump with plastic rollers was unsuitable for such continuous use; a pump with stainless steel rollers is more suitable.

3.6. Illustrative Field Data

The described system has been deployed in Bondville, IL for an extended period for the semicontinuous measurement of the target analytes. Figures 3.5-3.8 show

selected vignettes of data for the May 16-21, 2003 period that indicate that near-real time, high temporal resolution data can provide insights not available from daily or 12-h measurements. Figure 3.5 shows nitrate and HNO_3 levels. It will be observed that the maximum in nitrate concentration occurs every morning, between 6-11 am. This is generally the period when the temperature (t) is low and the relative humidity (RH) is maximum, promoting condensation of $(\text{NH}_4)\text{NO}_3$ and aided by its deliquescence. Average nitrate levels during of the period shown was $3.4 \mu\text{g}/\text{m}^3$. The average concentration of HNO_3 was approximately half, $1.8 \mu\text{g}/\text{m}^3$, during the same period. It is also seen in Figure 3.5 that the HNO_3 concentration peaks in the afternoon when its photochemical production is maximum. Particulate nitrate remains relatively low in the afternoon to early evening due to a combination of high t and low RH. Particulate sulfate and SO_2 concentrations during the same period is shown in Figure 3.6 and respectively ranged from 0.44-23 and 0.09-27 $\mu\text{g}/\text{m}^3$. While in this case the particulate and gaseous S concentrations are comparable, the situation for gaseous NH_3 vs. particulate ammonium is quite different as shown in Figure 3.7; the latter is vastly higher than the former.

Figure 3.8 shows ratios of nitrate/ammonium, sulfate/ammonium and (nitrate+sulfate)/ammonium in equivalents for May 16 to May 21, 2003. To varying degrees, the early morning hours of each day are dominated by NH_4NO_3 , a composition that ranges between $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 is dominant in the afternoons with almost complete absence of nitrate from the particulate phase. There is thus a daily diurnal transition from a predominantly NH_4NO_3 aerosol to a $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ one. Note that high acidity events are relatively short-lived and will not be detected by integrated measurements.

Figure 3.9 shows back trajectories from NOAA HYSPLIT model over 24 hr starting from May 20, 2003 at 1am.⁵⁷ High episodes of SO₂ and reasonably high PM_{2.5} sulfate were observed during very early hours of May 20, 2003 (Figure 3.6). At these hours, an excursion of SO₂ and sulfate is normally not observed. The back trajectories show that the lower altitude air mass movement for that period happen to precisely pass through several SO₂ emission sources and would account for the observed excursion.

3.7 Artifact incorporation of ammonia in the aerosol?

On a few instances, as on the afternoon/evening of the 18th and 19th, the ammonium content of the aerosol can be seen to vastly exceed the combined nitrate and sulfate content in equivalents. We do not believe that the aerosol is actually alkaline to the extent of the apparently excess ammonium. Rather, unaccounted for anions, possibly organic, likely provide the charge balance.^{58,59} We have considered the possibility that aerosol (NH₄)₂SO₄ or NH₄NO₃ deliquesces and forms a droplet in the denuder and the liquid water contained therein absorbs excess ammonia present in the gas phase. However, detailed numerical considerations suggest that this cannot account for significant ammonia incorporation. Consider air at 298 K and 1 atm, containing 0.1 μmole (13.2 μg) (NH₄)₂SO₄ per m³. We can compute from the AIM (Aerosol Inorganic Model, Clegg et al.,⁶⁰ the amount of the aerosol-associated liquid water in 1 m³ of this air if it is sampled through a PPWD and the effluent exits with a RH between 90-99.9% RH. (The last figure must be a significant overestimate, it is known that²⁹ relative to the saturation water content of the sample air at the inlet air temperature, the water content of the exit air is substantially smaller. First, due to the significant latent heat of evaporation

of water and near-adiabatic cooling, the temperature of the wetted surface is substantially below ambient. For example, with the PPWD operating at an air sampling rate of 15 SLPM and an inlet humidity and temperature of $\leq 30\%$ and $23\text{ }^{\circ}\text{C}$ respectively, within a few cm of the inlet, the temperature of the drops to $11.8\text{ }^{\circ}\text{C}$. At 5 SLPM, with completely dry air being sampled, the data provided by Simon and Dasgupta²⁹ on water evaporation rate suggests a maximum exit RH of 98.3%. Considering the contents of 1 m^3 of this air and running the AIM model produces a liquid water content of 1.8, 3.6, 21.4 and $258\text{ }\mu\text{moles}$ at exit RH values of 90, 95, 99 and 99.9%, respectively, corresponding to dimensionless liquid water contents (L) of 1.3, 2.6, 16 and 190×10^{-9} (L liquid water per L air). According to Dasgupta and Dong⁶¹ (1986), the Henry's law constant (K_H) of NH_3 in water at $25\text{ }^{\circ}\text{C}$ is 56 M/atm , although due to the salting out effect, the solubility of NH_3 in a deliquesced drop of $(\text{NH}_4)_2\text{SO}_4$ must be much lower. Nevertheless, even this value of K_H leads to a dimensionless distribution constant $K_D = K_H RT$ or 1370. In a deliquesced droplet of $(\text{NH}_4)_2\text{SO}_4$ or NH_4NO_3 where $[\text{NH}_4^+]$ is very high, one would not expect any significant further protonation of any ammonia that dissolves, thus total solubility of ammonia should be governed by its Henry's law solubility alone. Assuming that mass transfer is not a limiting factor and complete equilibration is achieved, the effective partition (the mass or mole ratio of dissolved ammonia in the water vs. that in the air) of any ammonia present in the system will thus be directly given by $K_D L$ that will vary from $1.8\text{e-}6$, $3.6\text{e-}6$, $2.2\text{e-}5$, $2.6\text{e-}4$ at RH values of 90, 95, 99 and 99.9%, respectively. In other words, even with an unrealistically high exit RH value of 99.9% and a fairly high aerosol content, and assuming complete

equilibration in deliquescence and dissolution of ammonia, 99.9+% of the ammonia originally present in the gas phase will remain in the gas phase.

4. Conclusions

We have presented here an automated, cost-effective, extensively field tested gas particle ion chromatography (GPIC) system for the measurement of principal ionic species of $PM_{2.5}$ and their precursor gases. This instrument uses a hydrophobic filter-based particle collector without the use of steam. The GPIC system also uses separate sampling trains for both gas and aerosol to avoid the loss of certain gas especially HNO_3 . The developed instrument makes use of IC analyses with carbon dioxide removal after suppression, resulting in a very low background conductivity that also lowers detection limits.

Table 3.1. Timetable for different valves and their operational actions.
(B= Black, G= Grey)

Step	Time, min	Status
1	0-7	V1=B, V2=G, V3=G, V4=G, V5=B -Loading GS on CC1/AC1. -Eluting CC2 and AC2 on V4 for particle sample analysis. -Air flowing through V1; V2 directing GS to V3, PS to W.
2	7-9	V1=G, V2=G, V3=G, V4=G, V5=B -Continuing to load GS on CC1/AC1. -Continuing to elute CC2/AC2. -Water cleaning out line (V1→V2→ V4→W).
3	9-15	V1=G, V2=G, V3=G, V4=B, V5=B -Still loading gas sample on V3. -Washing CC2/AC2 with water.
4	15-22	V1=B, V2=B, V3=B, V4=B, V5=B -Loading PS on CC2/AC2. -Eluting CC1/AC1 for gas sample analysis. -Air flowing through V1; V2 directing PS to V4, GS to W.
5	22-24	V1=G, V2=B, V3=B, V4=B, V5=B -Continuing to load PS on CC2/AC2. -Continuing to elute CC1/AC1. -Water cleaning out line (V1→V2→ V3→W).
6	24-30	V1=G, V2=B, V3=G, V4=B, V5=B -Still loading particle sample on V4. -Washing CC1/AC1 with water.

* V5 position switches only for calibration.

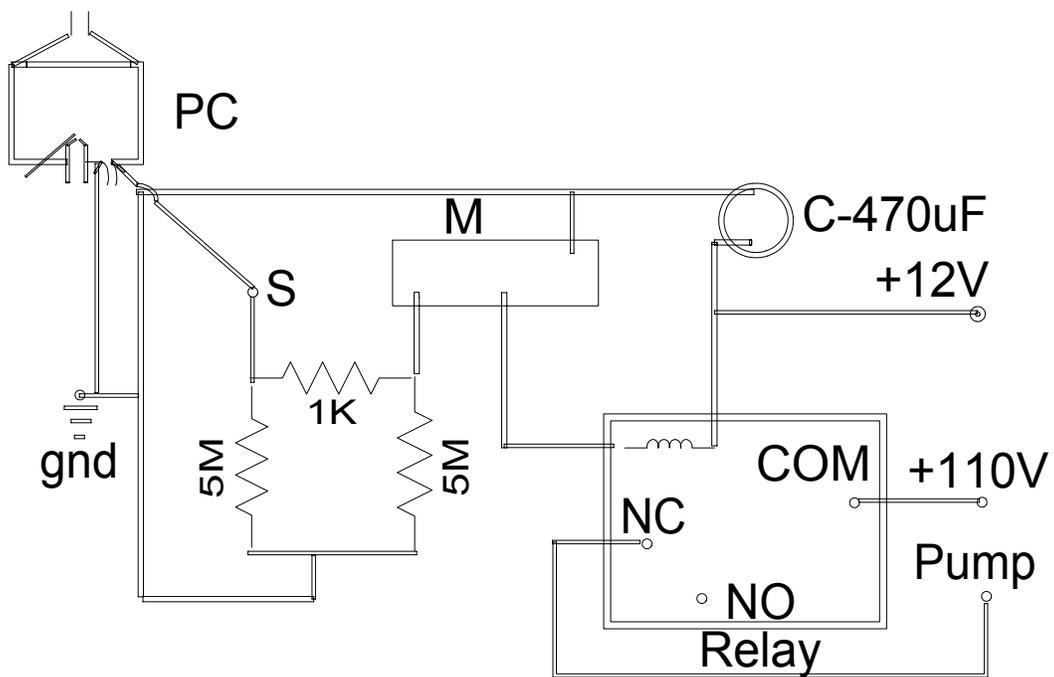


Figure 3.1. Sensor circuit for controlling the P1 peristaltic pump for PC sample. C: capacitor; M: metal oxide semi conductor field effect transistor switch, PC: particle collector; Relay: SPDT relay; S: sensor to electrode connection.

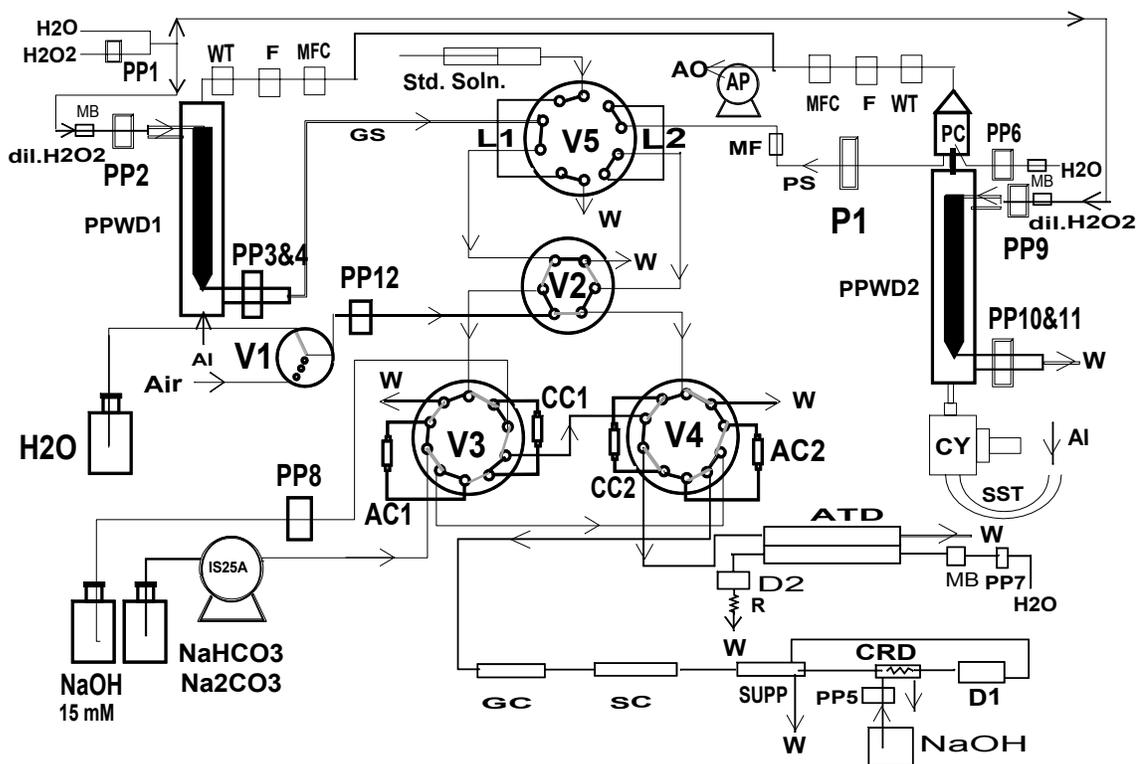


Figure 3.2. Instrument schematic for gas particle ion chromatography system. hydrogen peroxide: 0.5mM hydrogen peroxide solution; PP: peristaltic pump (12 channel); AI: air inlet; WT: water trap; F: filter; MFC: mass flow controller; AP: air pump; AO: air outlet; PPWD1 and PPWD2: parallel plate wet diffusion denuder1 and 2; PC: particle collector; Cy: cyclone; SST: stainless steel tube; GS: gas sample; PS: particle sample; L1: injection loop1; L2: injection loop2; V1: 3way valve; V2: 6port valve; V3: 10 port valve (high pressure); V4: 10 port valve (high pressure); V5: 10 port valve (low pressure); ATD: ammonia transfer device; MB: mixed bed resin; W: waste; D1: conductivity detector1; D2: conductivity detector2; R, restrictor tube; CC: cation concentrator; AC: anion concentrator (TAC-ULP1); GC: anion guard column; SC: anion separation column (short separation column); SUPP: suppressor; CRD: carbon dioxide removal device; Std. Soln.: standard solution.

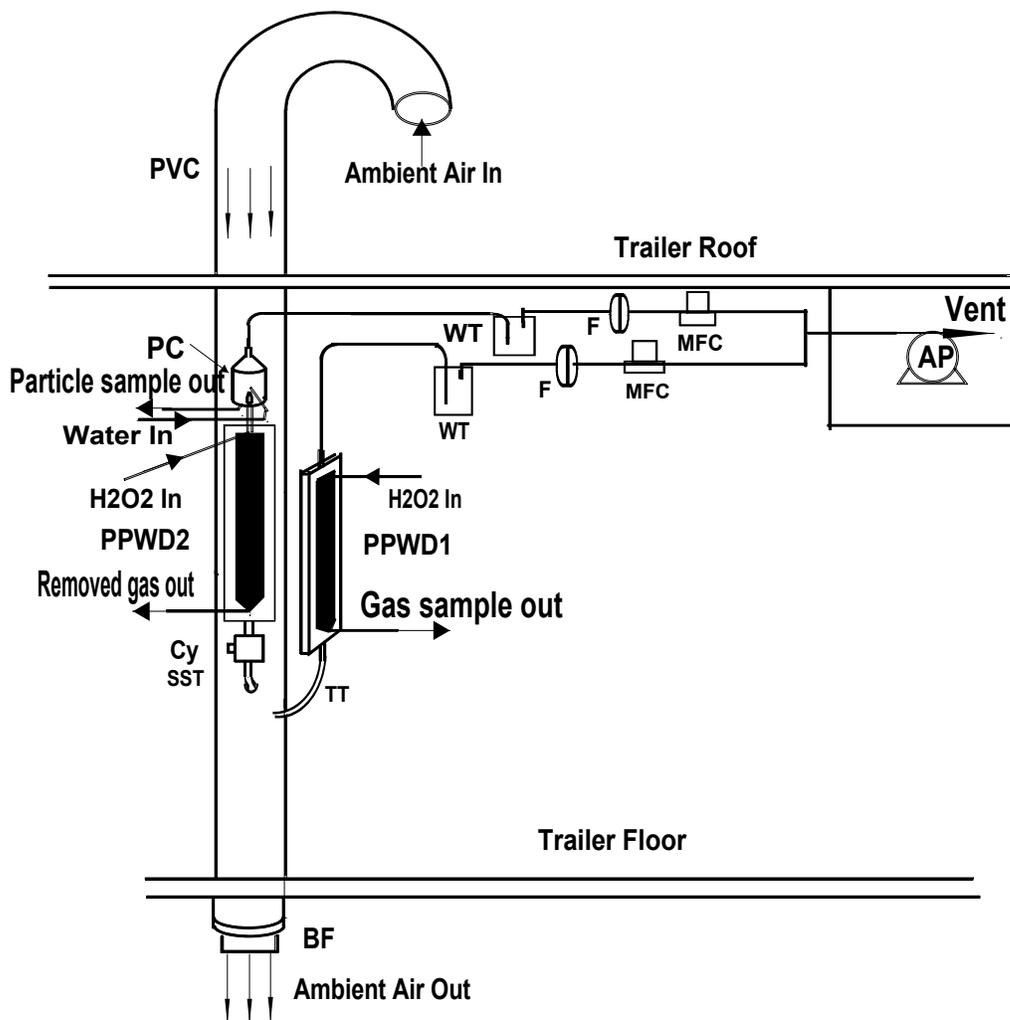


Figure 3.3. Field installation of gas collection system (GCS) and particle collection system (PCS). PVC: 4" PVC pipe; PC: particle collector; H₂O₂ In: 0.5 mM hydrogen peroxide inlet; Cy: Cyclone for 2.5 micron cutpoint; SST: stainless steel tube; BF: blower fan; WT: water trap; F: minicapsule filter; MFC: mass flow controller; AP: air pump.

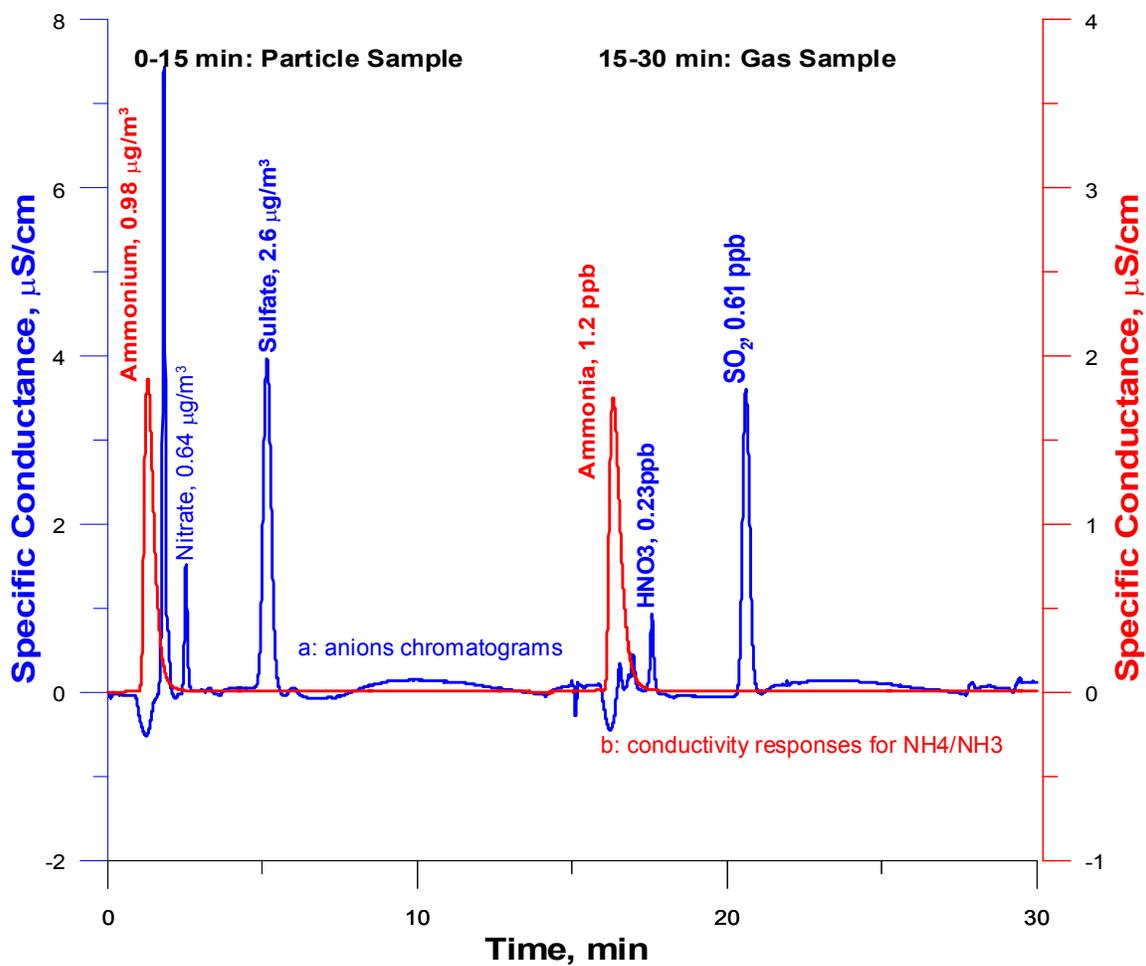


Figure 3.4. Typical instrument output for 30 min cycle including both anion chromatogram conductivity response traces for ammonium/ammonia.

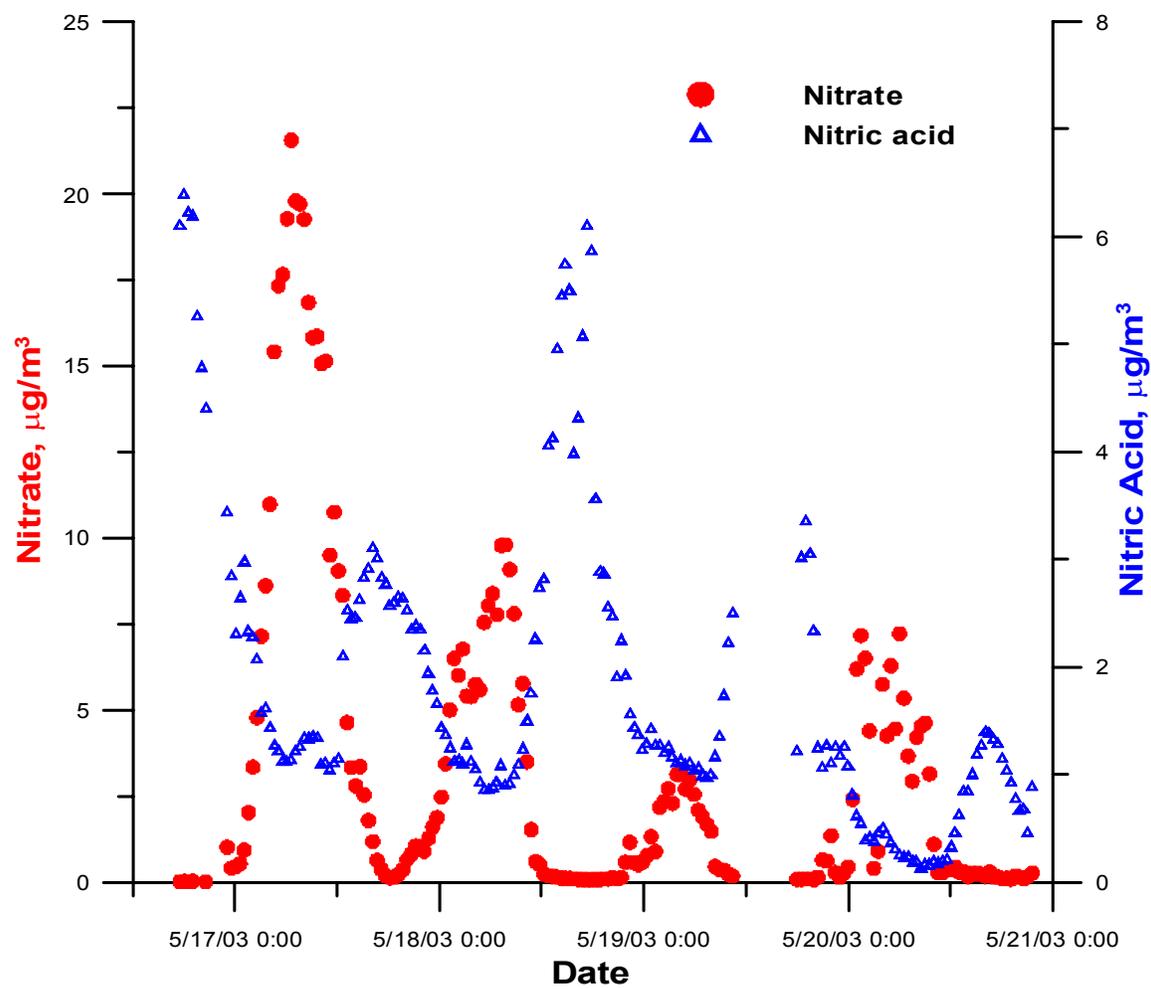


Figure 3.5. Nitrate and nitric acid concentration for May16-21, 2003 in Bondville, IL.

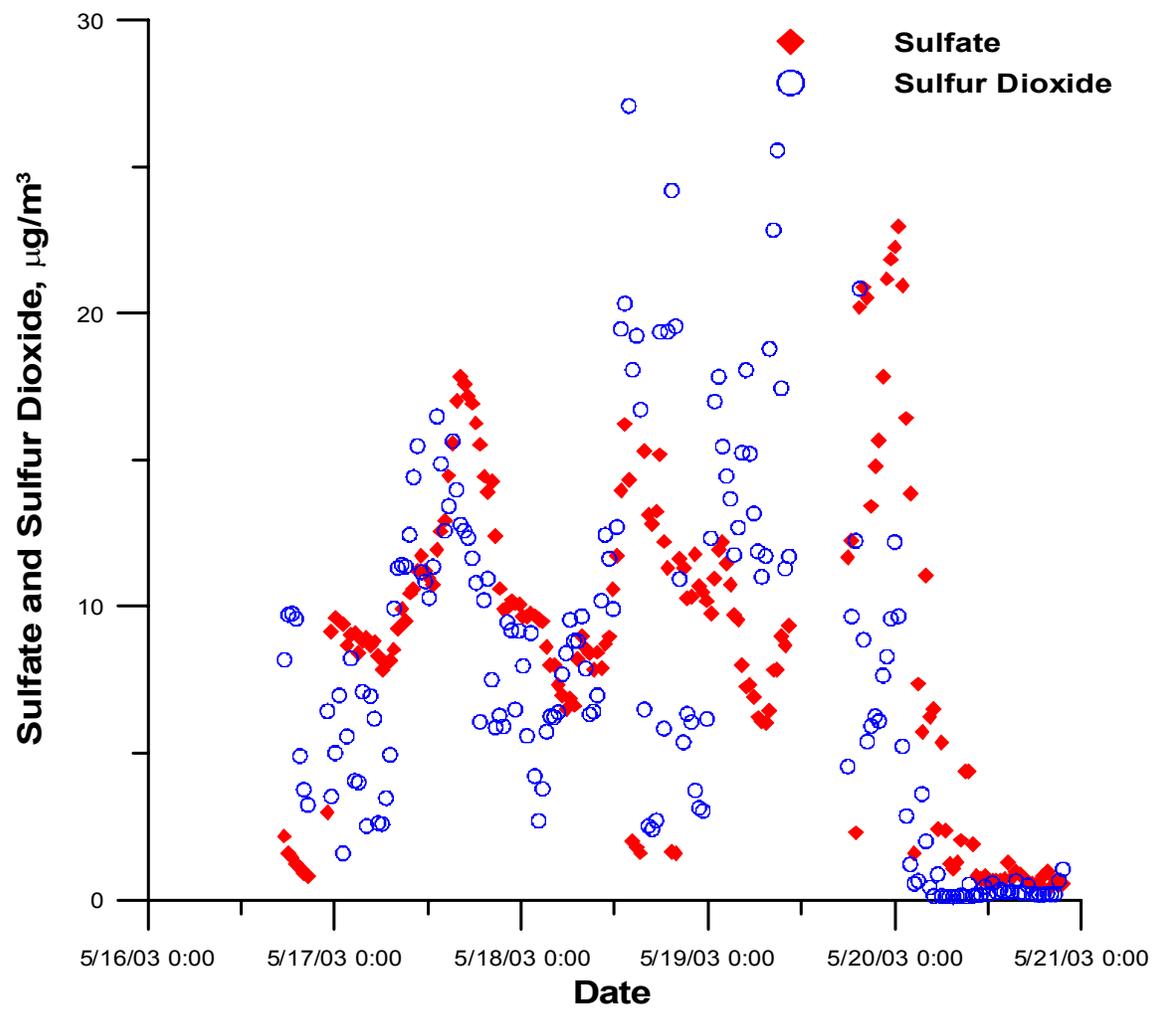


Figure 3.6. Sulfate and sulfur dioxide concentration for May16-21, 2003 in Bondville, IL.

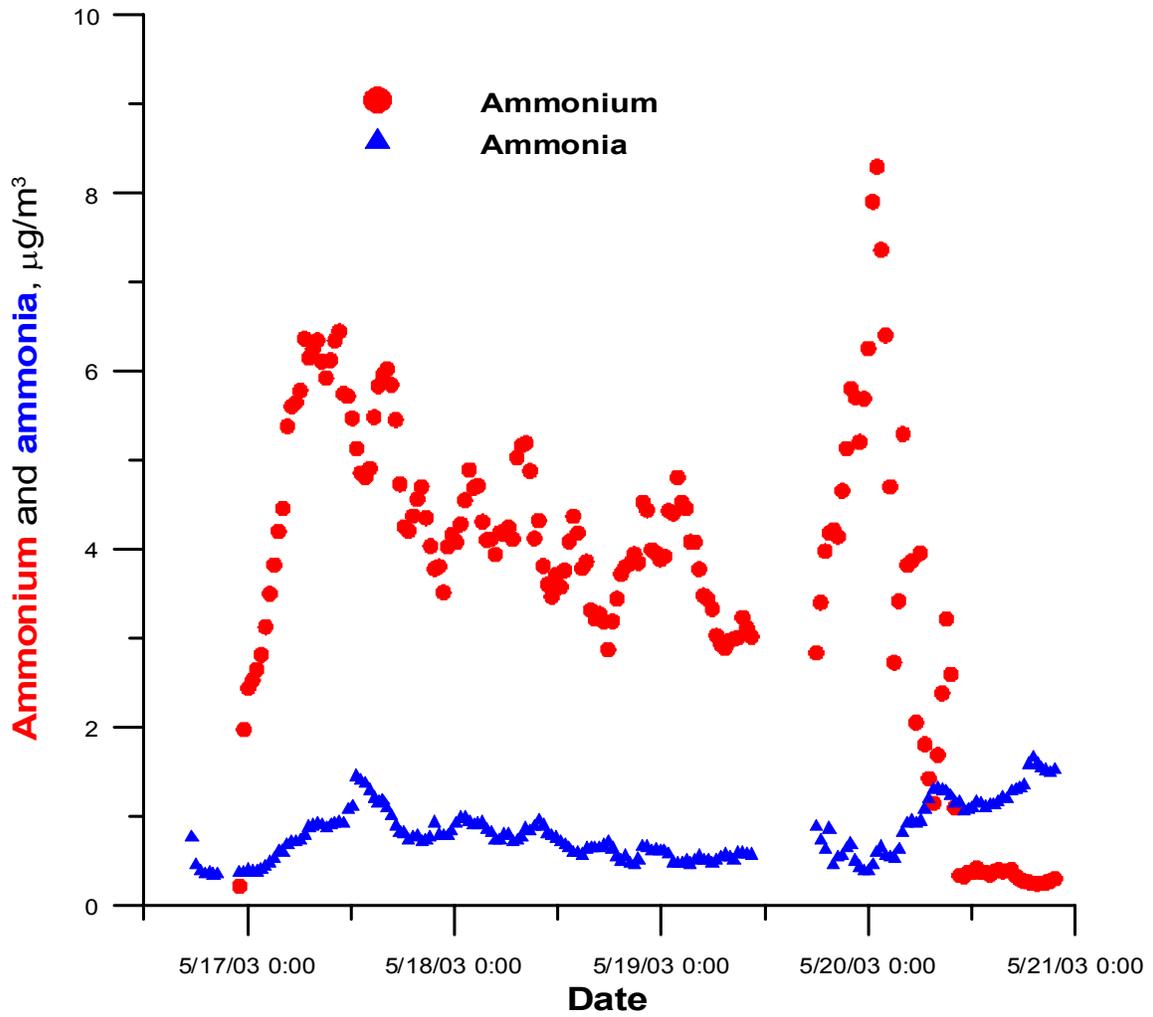


Figure 3.7. Ammonium and ammonia concentration for May16-21, 2003 in Bondville, IL.

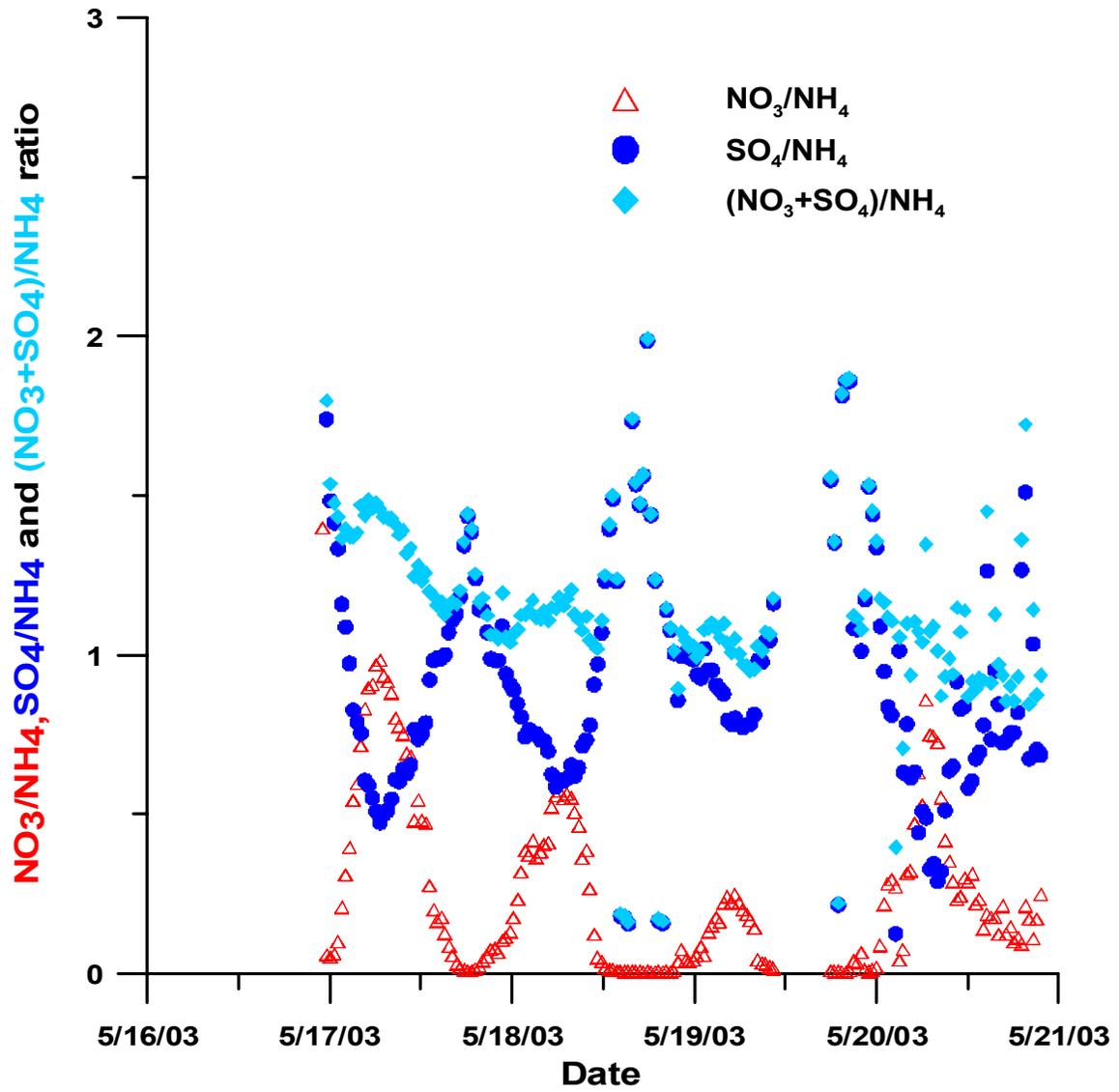


Figure 3.8. Nitrate/ammonium, Sulfate/ammonium and (nitrate + sulfate)/ammonium ratios (in equivalents) for May 16-21, 2003 in Bondville, IL.

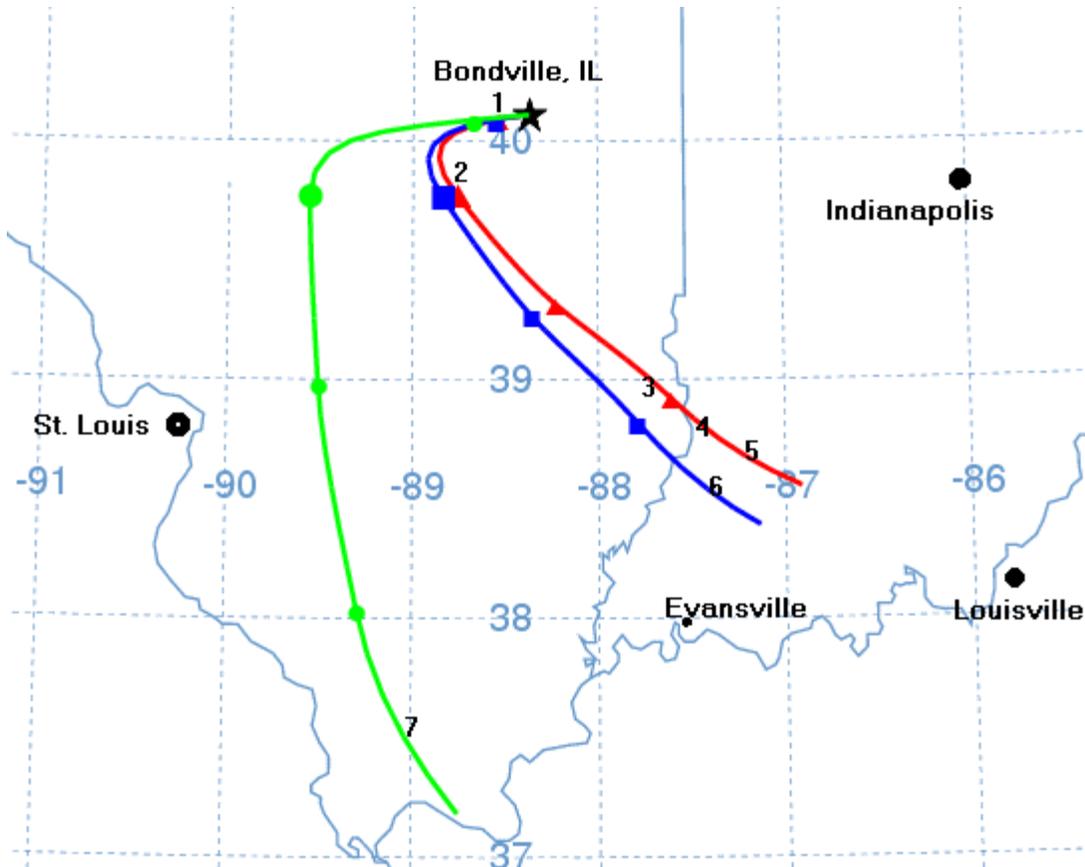


Figure 3.9. NOAA HYSPLIT model with back trajectories estimated over 24 hr starting from May 20, 2003 at 1am. The three trajectories are based on 10, 50 and 500 meters altitude (from right to left lines). The SO₂ emission sources (annual emission data for 1999 are given below) are incorporated from EPA website at (<http://www.epa.gov/air/data/index.html>) for 1999. Key: 1- University of Illinois-Champaign/Urbana (1778 tons), 2-Trigen-Cinergy Solutions (14619 tons), 3-Ameren Cips (10,652 tons), 4- Hoosier Energy Rural Elect. Merom Station (37,357 tons), 5-PSI Energy (11,308 tons), 6-Ipalco-Petersburg (50, 199 tons), 7- Southern Illinois PowerCorp (17, 451 tons).

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CHAPTER IV

A VERSATILE GAS PARTICLE ION CHROMATOGRAPH

1. Introduction

The measurement of aerosols and trace gases are important in many arenas: ascertaining outdoor and indoor air quality, understanding acid or excess nitrogen deposition, photochemical haze and smog formation, to name a few. Many epidemiologic studies have found an association between exposure to ambient particulate matter (PM), especially fine particles, and increased mortality and morbidity.¹⁻⁴ Elevated concentrations of ambient PM has been consistently associated with increased risk of cardiovascular and respiratory illness.⁵⁻⁷ Such findings have led the US Environmental Protection Agency to create a PM_{2.5} (PM of aerodynamic diameter $\leq 2.5 \mu\text{m}$) standard, establish PM health effects centers, and initiate Supersites research.⁸

The main source of ambient small particles is fossil fuel combustion. Secondary particles are formed in the atmosphere by chemical reactions of gases such as sulfur dioxide (SO₂), nitrogen oxides (NO_x), ammonia (NH₃), volatile organic compounds, ozone and other oxidants.⁹ Ammonia neutralizes various acidic gases to form ammonium (NH₄⁺) salts in the particle phase⁹ such that NH₄⁺, NO₃⁻, and SO₄²⁻ are the dominant ionic species in PM_{2.5}.¹⁰ Physical, optical and reactive properties of the aerosol are dependent on its precise composition.¹¹⁻¹⁴ These parameters may be additionally influenced by trace gas concentrations surrounding the particles. Sarnat et al. investigated human exposure to PM_{2.5} and suggested that gaseous co-pollutants play an important role in the observed

adverse health effects.^{15,16} Many atmospheric gases exist in reactive equilibrium with the aerosol phase.^{17,18} Aerosol composition varies temporally and spatially; atmospheric PM is a complex mixture originating from different sources. Along with meteorological information, the chemical compositions of both aerosol and gaseous precursors are essential to understand their diurnal behavior and their relationships with one another.¹⁸ Highly time resolved data can possibly help carry out source apportionment.¹⁹

Measurements techniques used for various gaseous species have been reviewed by Parrish and Fehsenfeld and recently by Sipin *et al.*²⁰²¹ Spectroscopic techniques such as differential optical absorption spectroscopy (DOAS) and tunable diode laser absorption spectroscopy (TDLAS) permit direct measurement of several gases at very low levels; many examples are in the recent literature.²²²³ Direct spectroscopy is not a panacea. Spectral interferences are not unusual; averaging over a long path may not always be desirable. Other techniques that are particularly selective (e.g., the measurement of NO_x by NO-O₃ chemiluminescence) are conversely not generally applicable. The same can be said of thermal decomposition of particulate species such as sulfate or nitrate into specific gases.²⁴⁻²⁷ Ion Chromatography (IC)-based systems offer the unique advantage of being able to perform simultaneous, multi-species analysis. Soluble gases can be collected and removed using diffusion-based collectors without collecting particles. Dasgupta²⁸²⁹ and Toda³⁰ have reviewed methods for diffusion-based collection and analysis of atmospheric gases. Many automated IC-based systems have been developed for rapid determination of gaseous constituents in ambient air that use diffusion based gas collectors such as a wet denuder, or a diffusion scrubber.³¹⁻³⁸

Particle mass spectrometry (MS) offers a wealth of information about particle composition characteristics;³⁹ and recent research focus has largely been on single particle MS.⁴⁰⁻⁴² However, the actual practice of aerosol compositional analysis for major components is rather far removed from this. Usually denuder-filter collection is followed by off-line extraction and subsequent IC analysis. Such methods are subject to both positive and negative artifacts. Automation of the collection/analysis steps and a short sampling period can potentially eliminate many of these artifacts. Automated particle collection and on-line analysis approaches have been reviewed by Dasgupta and Poruthoor⁴³, including their own work on steam-induced particle growth^{44,45} and much significant similar work of others.⁴⁶⁻⁵⁰ A detailed discussion is presented elsewhere.⁵¹ We have, however, been focusing on the development of particle collectors (PCs) that do not use steam and are therefore simpler in principle. Steam-less approaches also have lower artifact $\text{NO}_2^-/\text{NO}_3^-$ formation from NO_2 -steam reactions.^{52,53} A parallel effort has been devoted to miniaturize such systems, harden them for long-term field use and to improve their analytical capabilities while making them affordable. The first step in the latter direction was an orientation-insensitive miniature membrane-based parallel plate denuder (MPPD) operating at 1.5 L/min.⁵⁴ This device has internal holding capacity where liquid can remain stationary, yet the liquid volume is small enough to permit rapid washout/replenishment by a multitasking syringe pump. The second step was a hydrophilic membrane-based PC that ideally complemented the MPPD in size and sampling rate. This PC efficiently collects small particles (98% of 0.3 μm particles) with a 5 μm filter because the effective filter pore size is made to decrease by an order of

magnitude by deliberate continuous wetting during sampling. No filter replacement is needed for month long periods.

Presently, we combine these elements towards a compact IC-based system that uses a single conductivity detector for both gas and particle derived anions as well as ammonia/ammonium by time-sharing the analysis and produces a single chromatogram by parking the ammonia peak in the beginning of the anion chromatogram. The instrument routinely runs gradient chromatograms on high efficiency columns and can provide information not only about chloride, nitrite, sulfate and oxalate but also early eluting ions such as acetate and formate.

2. Experimental Section

2.1. Reagents and IC System

All reagents were analytical grade. All standards, eluents and reagents were prepared with Nanopure water (Barnstead, 18 M Ω ·cm). An ICS 2000 ion chromatograph (Dionex Corp., Sunnyvale, CA, all chromatographic columns and hardware/software were from the same vendor) was used with IonPac AG15-5 μ m guard (3 x 30 mm) and AS15-5 μ m separation (3 x 150 mm) columns along with an electrochemical suppressor (ASRS Ultra II 2-mm). The chromatograph has an isocratic pump, conductivity detector (DS6 heated conductivity cell), electrochemical hydroxide eluent generator (that permits programmed gradient generation), a 6-port injection valve (6 PV) and heat exchanger for columns. The gradient program used herein linearly ramps up the concentration of the NaOH eluent (flowing at 0.60 mL/min) from 5 to 8 mM during 0-3.5 min, 8 to 15 mM during 3.5-5.0 min, 15 to 30 mM during 5.0- 7.9 min, 30 to 45 mM during 7.9-11.4 min

and linearly ramps down from 45 to 5 mM during 11.4-16.5 min and continues at 5 mM up to the end of the chromatogram at 20 min. The same gradient repeats for the next 20 min.

The columns and conductivity cell were maintained at 30°C. The Chromatographic cycles repeat every 40 minutes until deliberately shut off, or until a preprogrammed number of cycles have run. Acquisition of the detector signal, system automation and valve control using relay/TTL outputs in the hardware are all carried out by a personal computer under software control (Chromeleon 6.6).

2.2. Gas Collection System (GCS)

Water soluble gas collection was accomplished with an MPPD, described in detail elsewhere.⁵⁴ The major difference with the previously published description is that cellulose acetate membranes used in the previous work were replaced with hydrophilic Nylon membranes (Magna Nylon, Osmonics Inc., 0.1 μm pore size, $\sim 100\mu\text{m}$ wet thickness). Briefly, the denuders consist of two parallel membranes of active area 13 x 220 mm held 2 mm apart by a spacer. Air enters the MPPD at the top and flows through the space between the membranes, aspirated by a pump at 1.5 liters per minute (LPM) and controlled by a mass flow controller (MFC). Although gas collection efficiency for the MPPD was previously tested, a membrane of different wettability can conceivably change this. Gas-collection efficiency was measured as previously described⁵⁴ with 100 ppbv SO_2 as test gas in the 1.2-2.4 LPM flow rate range.

2.3. Particle Collection System (PCS)

The PCS is designed to sample $\text{PM}_{2.5}$. Two separate channels are necessary because particles grow in size in the moist MPPD and a size cut-off device such as a

cyclone cannot be installed after the MPPD because particle size distribution after the denuder no longer represents ambient distribution. Conversely, when a cyclone is installed before the MPPD, sampling integrity of sticky/reactive gases (e.g. HNO_3 , NH_3) are compromised. If there are no restrictions on size cut off, a single channel system in which the same denuder that removes soluble gases for the PCS will be able to supply the collected gas for analysis. In the present system, however, sampling of $\text{PM}_{2.5}$ was desired and two separate sampling channels had to be maintained. The PCS front end consists of a Triplex cyclone (SCC.062, D_{50} 2.5 μm at 1.5 LPM, BGI Inc., Waltham, MA), a MPPD for gas removal, followed by a hydrophilic filter-based PC. Details will be described elsewhere.⁵¹ A schematic of PC is shown in Figure 4.1. Briefly, inlet air is brought in at 1.5 LPM through a 6 cm long stainless steel inlet tube that couples directly to the exit of the denuder and that terminates into a 75° taper, 0.76 mm orifice nozzle. A peripheral capillary external and adjacent to the nozzle tip (similar to that in ref. 53) delivers water at 0.25 mL/min and results in production of a fine mist. The mist wets a pair of 25 mm filters (14 mm exposed area) a paper filter on top (Whatman No. 1) and a 5 μm pore polycarbonate filter (Millipore Isopore™) on the bottom placed 26 mm below the nozzle. Water and air simultaneously flows through the filter pair and the flowing water effectively reduces the pore size of the filter such that $\text{PM}_{2.5}$ mass is essentially quantitatively collected. The mixed stream goes through an air liquid separator. The air is aspirated through a mass flow controller while the liquid, bearing the soluble component of the aerosol, collects in a reservoir from where it is aspirated at the end of the desired collection period. With typical size distributions of sulfate and nitrate, the collection of $\text{PM}_{2.5}$ mass with this PC is virtually quantitative.⁵¹

2.4. Fluid Handling

The handling of multiple liquids by a single bidirectional pump coupled to a multiposition selector valve was introduced in the analytical context by Ruzicka and Marshall.⁵⁵ We and many others have developed analytical systems based on this concept. In most cases the controlled mixing of different solutions is of importance as the basis of an assay, in others, it is vital that different liquids do not contact each other; an air-buffer before the syringe can be used for this purpose.⁵⁶ In the present case, although a configurationally similar system is used for fluid handling, it is merely used for aspiration and dispensing and any mixing of fluids is undesirable. An air-buffer cannot be used in this case because significant back pressures are involved. However, (repeated) washing between liquids to minimize liquid cross talk is allowable and was implemented here. In all our previous efforts at gas-particle measurement, denuder and PC effluents were continuously exhausted by multi-channel peristaltic pumps.^{52,53} Indeed, continuous liquid flow was mandatory with our previous generation of wetted denuders. While syringe pumps offer a far more robust and lower maintenance frequency pumping alternative, a system based on multiple continuous flow streams is not easily possible with a reasonable number of syringe pumps. The present MPPD and PC can operate in either continuous or intermittent flow mode. In the present instrument, the latter strategy is used with a single syringe pump.

2.5. Sample Processing Unit (SPU)

A custom tower style aluminum computer case (Lian Li PC-6070, 21W x 46H x 52.5D cm) housed the components: (i) A 48000 step V6 syringe pump (SP) with a 8-way

distribution valve (DV) and associated power supply (Kloehn Inc, Las Vegas, NV), (ii) a 10-port high-pressure valve (10PV) with control electronics and power supply (C2-2340 EP, VICI), (iii) two mass flow controllers (MFC) along with power supply control and display modules made in-house (FC 260, Tylan General, Torrance, CA; (iv) one glass wool filled liquid traps (T) ahead of each of the two MFC's to protect them, (v) a 3-way Teflon wetted path solenoid valve (SV) (161T031, NResearch, Caldwell, NJ), (vi) a cooling fan, (vii) a 12 V power supply for the two foregoing items and (viii) a power distribution strip. The syringe pump, the 10-port valve (rear-end with fittings facing front) and both MFC control/display modules are mounted on the SPU front panel. This arrangement facilitates servicing/replacement of syringe, cation/anion preconcentrator columns (CPC/APC, both mounted on the 10 PV). All other connections and electrical and fluid conduits were at the rear of the SPU. Flexible PVC tubing ($\frac{3}{8}$ in. o.d., $\frac{1}{4}$ in. i.d.), were used for gas flow streams, PTFE tubes (20SW, 1.6 mm o.d., 0.8 mm i.d., Zeus Inc., Orangeburg, SC) were used for liquid transport. Low pressure connections that are more frequently (dis)assembled, were made with soft Push-fit connecting tubes (Pharmed[®], 1.30 mm tube, Cole-Parmer). Liquid connections between the 10 PV, SP and IC unit were made with $\frac{1}{4}$ -28 fittings from the front panel.

2.6. System Description

The complete system is shown in Figure 4.2. The capability of the 8-port DV was extended by connecting port A to the common port of 3-way valve SV. Port A and SV allow liquid withdrawal from MPPD1 (this liquid is not analyzed) and disposing any liquid in SP to waste. Port B allows loading of the liquid in SP to the serial

preconcentrators (CPC/APC) in 10PV; this can involve either the sample or water as wash liquid. Port C allows dispensing of 15 mM NaOH, aspirated through port E and used as the CPC eluent, through the CPC and the ammonia transfer device (ATD). Ports B and C are connected to the 10PV by short sections (10 cm) of 0.50-mm i.d. PEEK tubing. Port D, used only for calibration, is connected to a reservoir containing an aqueous standard solution. Port F provides access to deionized (DI) water for washing. Port G allows the periodic withdrawal of the aqueous extract of PM 2.5 from the PC. Port H allows liquid withdrawal from and refilling of MPPD2 for soluble gas analysis.

Both MPPDs were fed from bottles (DL1,2), placed just below the denuder and containing 0.5 mM H₂O₂. Water to the PC is supplied pneumatically via mixed bed resin column MB and through a capillary restrictor CR. Air flows through cyclone Cy, down MPPD1 into PC (normal operation mode). In the zeroing mode, no air is drawn through Cy/MPPD1, rather sufficient zero air is introduced through the T-arm and ZV, excess air flowing out through the normal inlet. The PC outlet is connected via liquid water trap T to MFC and air pump, AP (model DOA-P703-FB, Gast, Benton Harbor, MI). Air flow through MPPD2 is configured similarly, with an arrangement for the introduction of standard calibration gas (or zero air) to MPPD2 via 3-way Teflon solenoid valve, TV while air pump AP continues to aspirate air via a protective filter and 3-way solenoid valve, MV.

Eluent for anion chromatography generated by electrolytic eluent generator, EG pass through a continuously regenerated anion trap column, CR-ATC to remove carbonate impurities. The CPC (5 x 35 mm) is filled with a 1:1 mixture (Dowex-50Wx8 H⁺-form, 200–400 mesh, with chloromethylated polystyrene-divinylbenzene, Bio-Beads

S-X1, 200–400 mesh, Bio-Rad Inc.). The APC (TAC-ULP, 5 x 23 mm, Dionex Corp.) must be placed downstream of the CPC because the APC also contains cation exchange sites and will capture ammonium if placed upstream.

Measurement of ammonium after basification and diffusion of the resulting gaseous ammonia across a membrane to a receptor stream was originally introduced by Carlson⁵⁷⁵⁸ and since then many other groups including us have used this approach.⁵²⁵⁹⁶⁰ Frequently in atmospheric samples, the only non-H⁺ cationic species of interest is ammonium. Ammonium preconcentrated on the CPC is eluted by NaOH in the free base form and the effluent is made to pass through a high permeability tubular membrane device that functions as the ATD. Receptor water on the other side carries the transferred NH₃ to a conductivity detector and the measured specific conductance is used as a measure of the original NH₃/NH₄⁺ content. The ATD is similar in principle to the recently reported CO₂ removal device (CRD)⁶¹ but constructed differently. A 400 μm i.d., 400 μm o.d. 30 cm long CelgardTM polypropylene tubular membrane is coated externally with silicone (~2 μm) and filled with a 200 μm dia. nylon monofilament. This is used as the receptor channel. A 0.86 mm i.d. concentric Teflon jacket tube (20 SW, Zeus) surrounds the membrane tube and the annular space serves as the donor channel. This design keeps the receptor volume and analyte dispersion small.

Ammonium measurement and locating the response at the front of the anion chromatogram is done with the ATD in conjunction with the 4-port valve (4PV, the 6-port valve normally supplied with the chromatograph as the injector can serve this purpose as well). During normal anion chromatographic operation, the 4PV remains in the bold line mode, the suppressed effluent proceeds to the conductivity detector directly

via an optional CRD.⁶¹ Both the 10PV and the 4PV are initially switched at the same time ($t = 0$ min). The suppressor effluent, which at this time is pure water, is routed by the 4PV to the receiver channel of the ATD to the conductivity detector. Ammonia eluted from the CPC comes through the ATD membrane and produces a detector response. By 5 min, the 4PV is switched back and regular anion detection proceeds.

Each 40-min cycle consist of a 20-min half for gas sample analysis followed by a 20-min half for aerosol analysis. Both samples are collected over 40-min periods, staggered 20 min apart. The operational sequence is described in Table 4.1. Washing steps are often critical and cannot be omitted (e.g., residual NaOH in CPC will prevent collection of NH_4^+ , for example.)

For liquid phase calibration, preprogrammed volumes of the aqueous standard, typically containing $12 \mu\text{M NaNO}_3$ and $15 \mu\text{M (NH}_4)_2\text{SO}_4$ is used; calibrations using multiple injected volumes (sub-several mL) can be used to construct a multipoint calibration. Air sampling is shut off during calibration. Loading of the standard is followed by DI water to ensure quantitative transfer. Each mL of the standard corresponds to $9 \mu\text{g/m}^3 \text{NH}_4^+$, $12.4 \mu\text{g/m}^3 \text{NO}_3^-$ and $24 \mu\text{g/m}^3 \text{SO}_4^{2-}$ (for a 60-L air sample). Both chromatographic halves of a 40 min cycle are used for calibration.

2.7. Field Installation

The instrument has been deployed for an extended period in Bondville, IL. Both MPPDs, DL reservoirs and the cyclone/PC were put on the rooftop of the instrument shelter (roofline 10' from ground, 4' above roofline) in a temperature controlled (heated) insulated Plexiglass enclosure as some species such as HNO_3 cannot be effectively

transmitted over significant lengths of tubing. Ambient winter temperatures at this location (Lat/Long: 40.113°/-88.369°) fall substantially below freezing. The SPU and the IC were housed inside the trailer. Shortest possible lengths of PFA Teflon tubes (6.3 mm o.d., 4.8 mm i.d.) were used for air inlets for both MPPD2 and Cy. AP was located inside the shelter, but inside a compartment to reduce noise.

3. Results and Discussion

3.1. New Membrane for Denuder: Gas Collection Efficiency (CE)

Cellulose acetate (CA) membranes previously used⁵⁴ work fine for most applications but always generates an acetate background due to hydrolysis. With gradient IC capabilities in the present instrument it was desirable to eliminate this and actually determine acetate in the samples. Very small pore size (so significant amounts of liquid water do not seep through the membrane) and a high degree of wettability is required. Based on initial explorations on leachability of ionic impurities from the membrane, we chose polyethersulfone (SuporTM) and Nylon (MagnaTM) sheet membranes with 100 nm pore size. The results shown in Figure 4.3 indicate the superior performance of the Nylon membrane compared both to polyethersulfone and CA, likely due to its greater wettability. Up to a sampling flow rate of 1.5 L/min (ambient pressure and temperature in our laboratory is 680 mm Hg and 296 K), the CE with this membrane is experimentally indistinguishable from unity and up to 1.7 L/min the observed CE is indistinguishable from the Gormley-Kennedy efficiency (calculated⁶² for a parallel plate denuder with an active area of 220x13 mm, spacing of 2 mm and diffusion coefficient of SO₂ 0.13 cm²/s). It is only above this flow rate that the CE was sub-theoretical, possibly

due to the development of dry regions. Since these experiments were conducted with dry air, in real ambient air, theoretical behavior may extend to higher flow rates. The behavior of the three membranes is interesting in that at low flow rates CA has the best efficiency, suggesting high wettability but relative to the other membranes this performance falls off rapidly at higher flow rates because lower water transport through the CA membrane must become a limiting factor.

3.2. Optimization of Chromatographic Conditions

Previously used chromatographic conditions lead to the elution of the nitrate peak in close proximity to the CO₂-peak,⁵³ causing problems at very low nitrate levels. While this situation can be remedied with a CRD,⁶¹ With the present choice of higher efficiency columns and electrochemically-generated gradient hydroxide elution, nitrate elutes after sulfate and carbonate closer to and after sulfate, rendering the use of a CRD optional, especially since sulfate/SO₂ levels are most often higher than nitrate/HNO₃ levels. The suppressed eluent before analytes elute is pure water and a low flow rate of this promotes sensitivity when used as the ATD receiver. The gradient program allows sufficient dead time in the beginning for the ammonia response. The use of NaOH, instead of the more commonly used KOH, allows the CPC to remain in the Na-form which facilitates NH₄⁺-uptake because K⁺ has a greater affinity for the resin (LiOH can be used advantageously as well). The separation of the early-eluting fluoride and organic species such as acetate/formate is now possible. While not discussed here, a combination of flow and gradient programming and lengthening the chromatographic time to 30 min from 20 min can be used to obtain even better separation of the early eluters while increasing ammonia

response sensitivity further. Fairly minor modifications of the system can increase capabilities further, a second SP allows the gas and particle sampling times to be synchronous, rather than staggered, and/or allow the use of multiple standards (rather than different volumes of the same standard) for greater flexibility. A second IC can be configured for the analysis of the full suite of cations when such analysis is desirable.

3.3. Instrument Performance and Detection Limits

Typical instrument output for real samples is shown in Figure 4.4. This chromatogram has been obtained without the use of a CRD.⁶¹ The LOD (S/N = 3) for anions is 0.2-0.7 ng/m³ for a 60-L total sample volume (40 minutes at 1.5 L/min) using an electrodialytically-generated, electrodialytically-suppressed hydroxide gradient eluent. This LOD is adequate for measurements of polluted, urban air as well as air in pristine environments. Ammonium is measured as ammonium hydroxide. The latter is a weak base and a quadratic calibration equation must be used for quantitation. The LOD (S/N =3) for ammonium using the current system is 4.3 ng/m³. The concentrations of the major constituents appear in the chromatogram, the separation of sulfate (1) and oxalate (2) (SO₂ and H₂C₂O₄) and the region where acetate (5) and formate (6) elute are shown in magnified detail in insets a and b, respectively. Peak (3) corresponds to the retention time of fluoride, peak (4), (7) and (8) remain unidentified at this time. We venture to suggest that the real power of the present instrumentation for atmospheric research lies in its ability to explore this little known area, rather than the unprecedented mass sensitivity for major components such as sulfate and nitrate.

3.4. System Maintenance

The biggest reservations on long term deployment of wet instruments surround maintenance frequency. This is true for liquid chromatographic (LC) instruments as well, although both process LC and IC are now industrially routine. In the present instrument, low sampling rate allows the use of the PC filters for a long period. They are replaced after a month of continuous operation. Filter replacement takes ≤ 5 min; data from subsequent two cycles are discarded. Both MPPDs and inlet tubes at this time are washed thoroughly with DI water to remove deposited particles. The longevity of the nylon membranes in the MPPDs are presently not known – replacement have not been needed in several months. The CPC inlet frit is inspected every two weeks and replaced if soiled. Our experience indicates that separation column lifetime is at least three months and can be prolonged if just the guard column is replaced every three months. The CPC and APC are cleaned according to vendor recommended procedures when loss of efficiency/calibration response becomes evident.

3.5. Illustrative Field Data

The system has been deployed in Bondville, IL with gaseous NH_3 , CH_3COOH , HCOOH , HCl , HONO , SO_2 , $\text{C}_2\text{H}_2\text{O}_4$, HNO_3 and particulate ammonium, acetate, formate, chloride, nitrite, sulfate, oxalate and nitrate being monitored. As a vignette, a typical weekly data set (Figure 4.5) shows the concentrations of these species and the data range in parentheses for October 10-16, 2004.

The present system has particular capabilities of monitoring light organic acids in both gas and particle phase. Although not commonly monitored and rarely with high time resolution,⁴⁸ organic acids often constitute a major fraction of gas phase atmospheric acidity.⁶³⁻⁶⁵ Figure 4.6 shows the diurnal patterns of gaseous HCOOH and CH₃COOH and their particulate counterparts. With rare exceptions, all the species show a diurnal pattern, peaking in the late afternoon to evening hours, the pattern for CH₃COOH is not pronounced, however. The correlation between the particulate anion and the corresponding acid is much better for the weaker acid CH₃COOH, which will be selectively displaced over HCOOH in a slightly acidic aerosol.

Figure 4.7 shows the behavior of SO₂, HNO₃, sulfate and nitrate. The concentration of HNO₃ peaks during the afternoon hours and nitrate from semi-volatile NH₄NO₃ was typically lower. Sulfate levels are poorly correlated with that of SO₂; the higher levels of SO₂ observed during the first few days coincide with air mass arrival from the direction of major SO₂ sources, as observed from NOAA HYSPLIT back trajectory calculations.

4. Conclusions

A compact, versatile and fully automated gas particle ion chromatography system has been developed for wide variety of ionic species of PM_{2.5} and their precursor gases. The entire instrument can easily be transported into the field for analysis.

Table 4.1. System Operating Sequence

t = 0 min	Initialize syringe pump. Simultaneously switch 4PV and 10PV to inject mode (black lines), begin ammonia elution and analysis, gas extract injected
t = 5 min	Ammonia detection complete, Switch 4PV, anion detection begins, Switch 10PV to load mode (grey), wash CPC and APC with water
t = 8 min	Aspirate PC sample & dispense to CPC and APC, follow with water wash
t = 18 min	Switch 4PV to inject mode, system readied for ammonia analysis
t = 20 min	Switch 10PV, particle extract injected, begin ammonia elution and analysis
t = 25 min	Ammonia detection complete, Switch 4PV, anion detection begins, Switch 10PV to load mode (grey), wash CPC and APC with water, aspirate and refill MPPD1 and dispense to waste, wash syringe, wash CPC & APC
t = 32 min	Aspirate MPPD2, load APC and CPC, follow with water wash
t = 38 min	Switch 4PV to inject mode, system readied for ammonia analysis
t = 40 min	Cycle complete, end and repeat

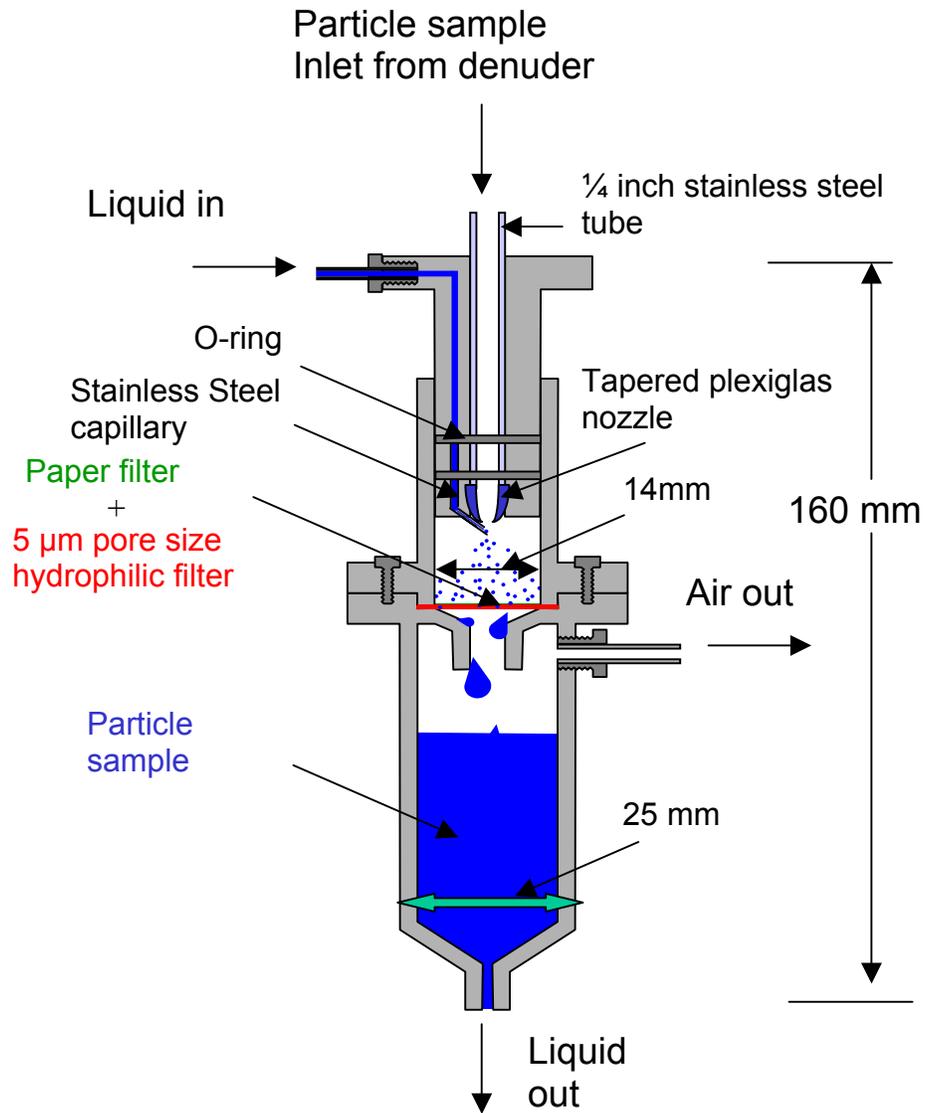


Figure 4.1. Hydrophobic membrane-based particle collector (inverted) shown schematically.

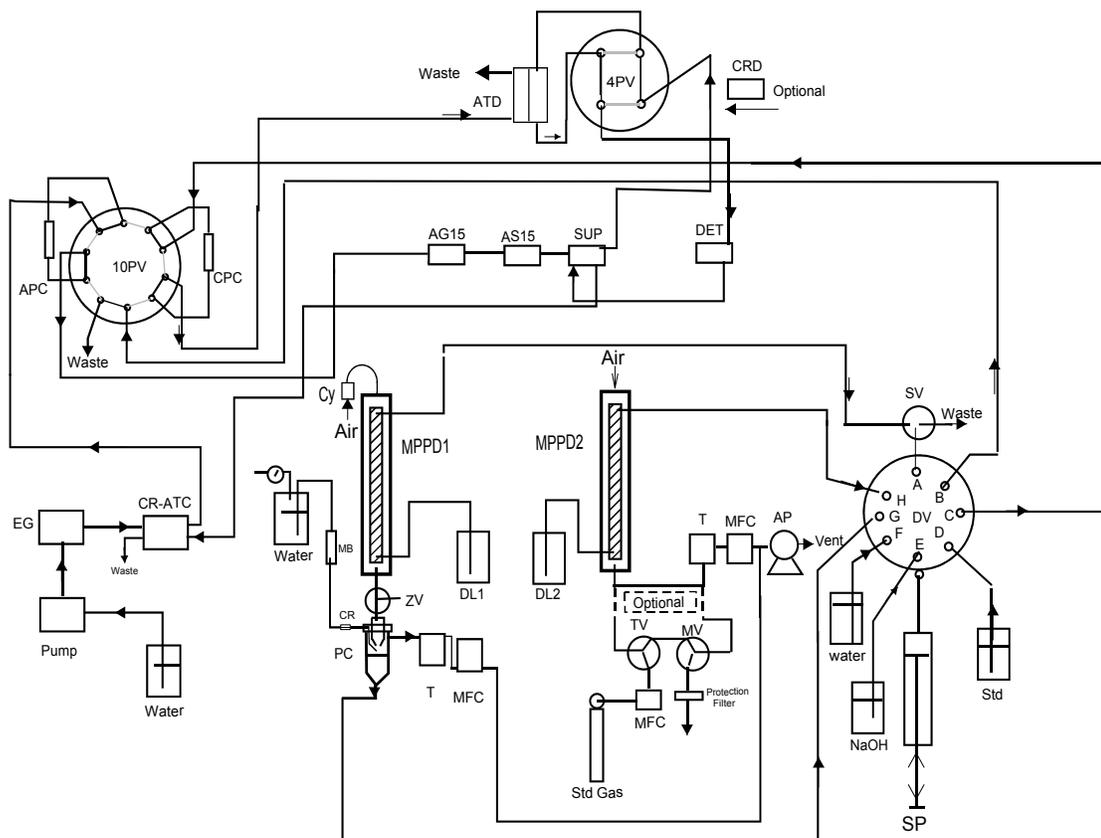


Figure 4.2. Instrument schematic for gas particle ion chromatography system. Key: SP, Syringe pump; Std: Standard solution; SV, 3-way selector valve; 6PV, 6 port valve; ATD, ammonia transfer device; CRD, Carbon dioxide removal device-optional; 10PV, 10 port high pressure valve; CPC, Cation preconcentrator; APC, Anion preconcentrator; AG, Anion guard column; AS, Anion separation column; Supp, Anion suppressor; DET, Conductivity detector; EG, Anion eluent generator; CR-ATC, Continuously regenerated anion trap column; Cy, Cyclone for $PM_{2.5}$ cut point; MPPD1, Membrane based parallel plate denuder for removing gas; PC, Particle collector; MPPD2: Membrane based parallel plate wet denuder for gas sample; DL1 and DL2, denuder liquids ($0.5 \text{ mM H}_2\text{O}_2$ solution); MB, mixed bed resin column, CR; Capillary restrictor; ZV, Zero valve for zeroing particle collection (optional); TV, 3-way solenoid valve (Teflon) for optional standard gas introduction; MV, metal valve-3 way; T, water trap column; MFC, Mass flow controller; AP, Air pump; Waste, Waste line.

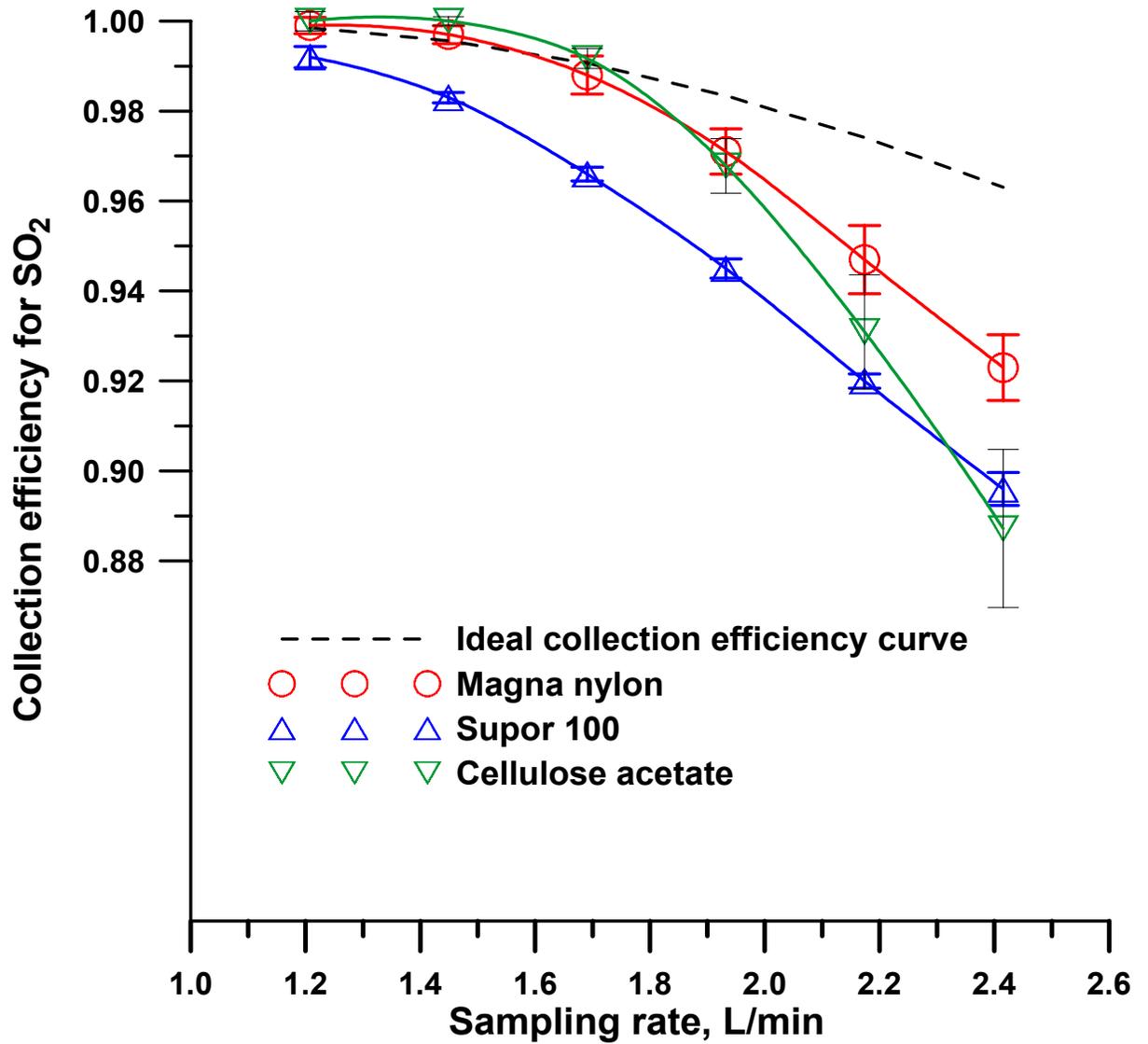


Figure 4.3. Gas collection efficiency as a function of sampling rate. The dashed line indicates the theoretical efficiency according to the Gormley-Kennedy Eqn. Note that the ordinate scale does not start at zero.

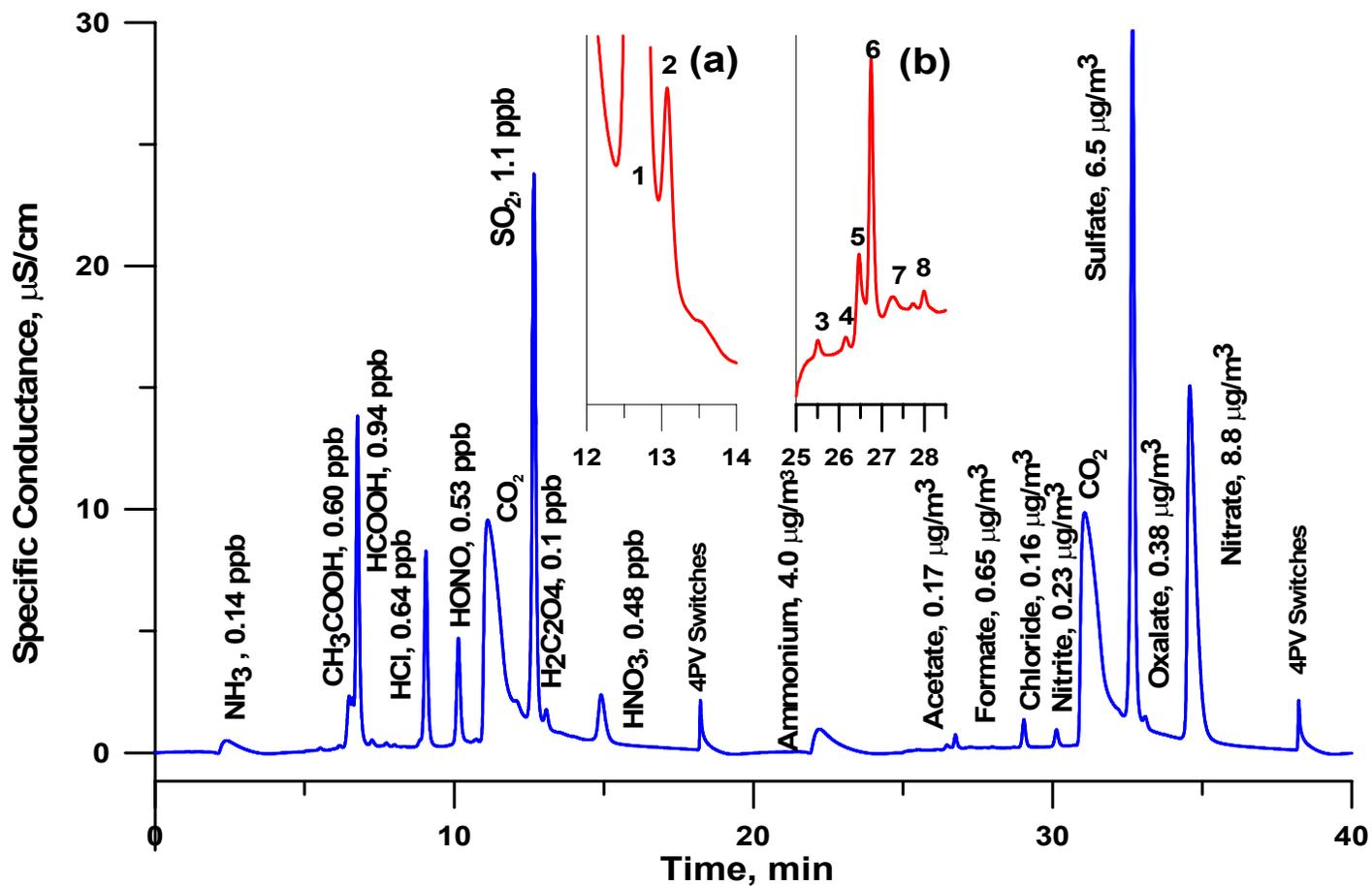


Figure 4.4. Typical instrument output for 40 min cycle, sampled 09/28/04, first half gas sample 7:39-8:19 am, second half particle sample 7:55-8:35 am. The second 20 min is for particle sample responses. When the 4PV switches for ammonia determination the accumulated liquid in the ATD produces a transient conductivity response, the switchback to anion determination does not register. Insets a and b shows the separation of (1) SO_2 and (2) $\text{H}_2\text{C}_2\text{O}_4$ and (5) acetate and (6) formate. See text for other details.

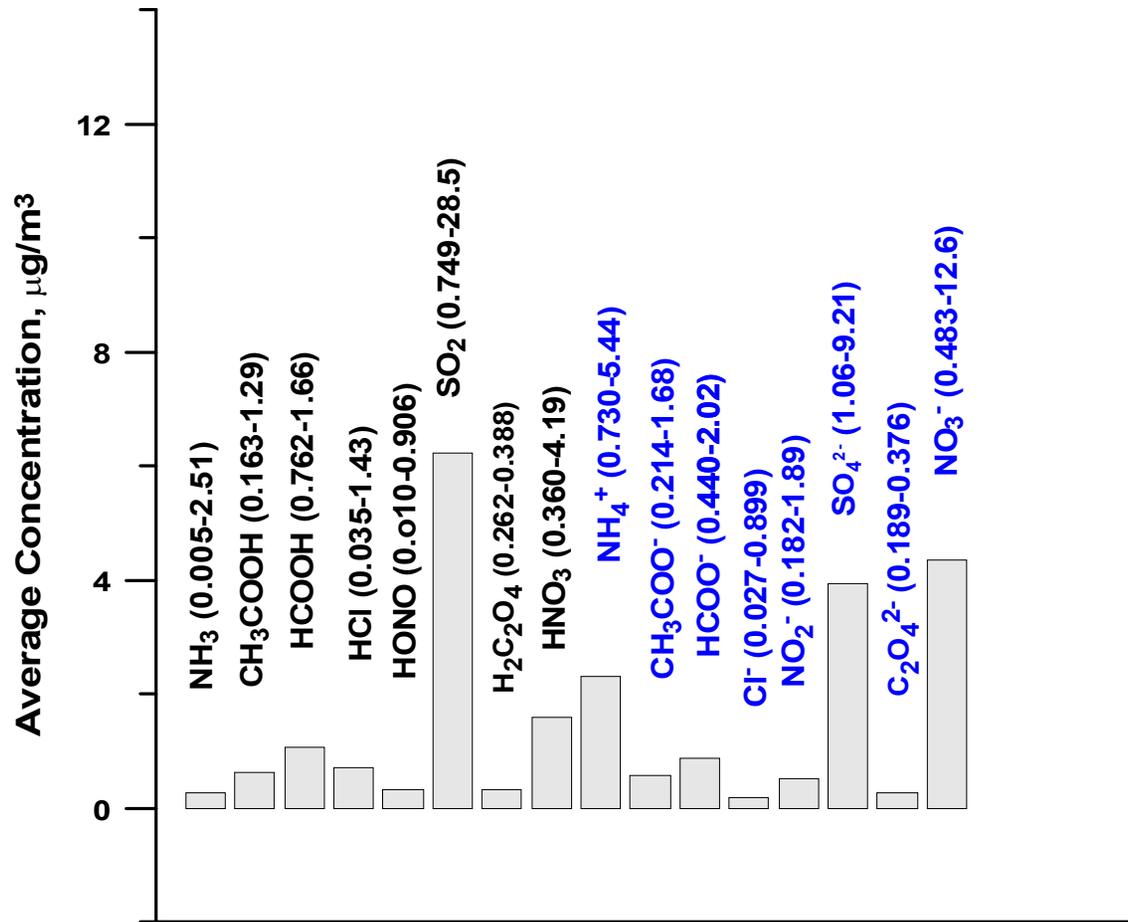


Figure 4.5. Average concentration of collected soluble gases and particulate species during October 10-16, 2004 at Bondville, IL. The parentheses represent the data range.

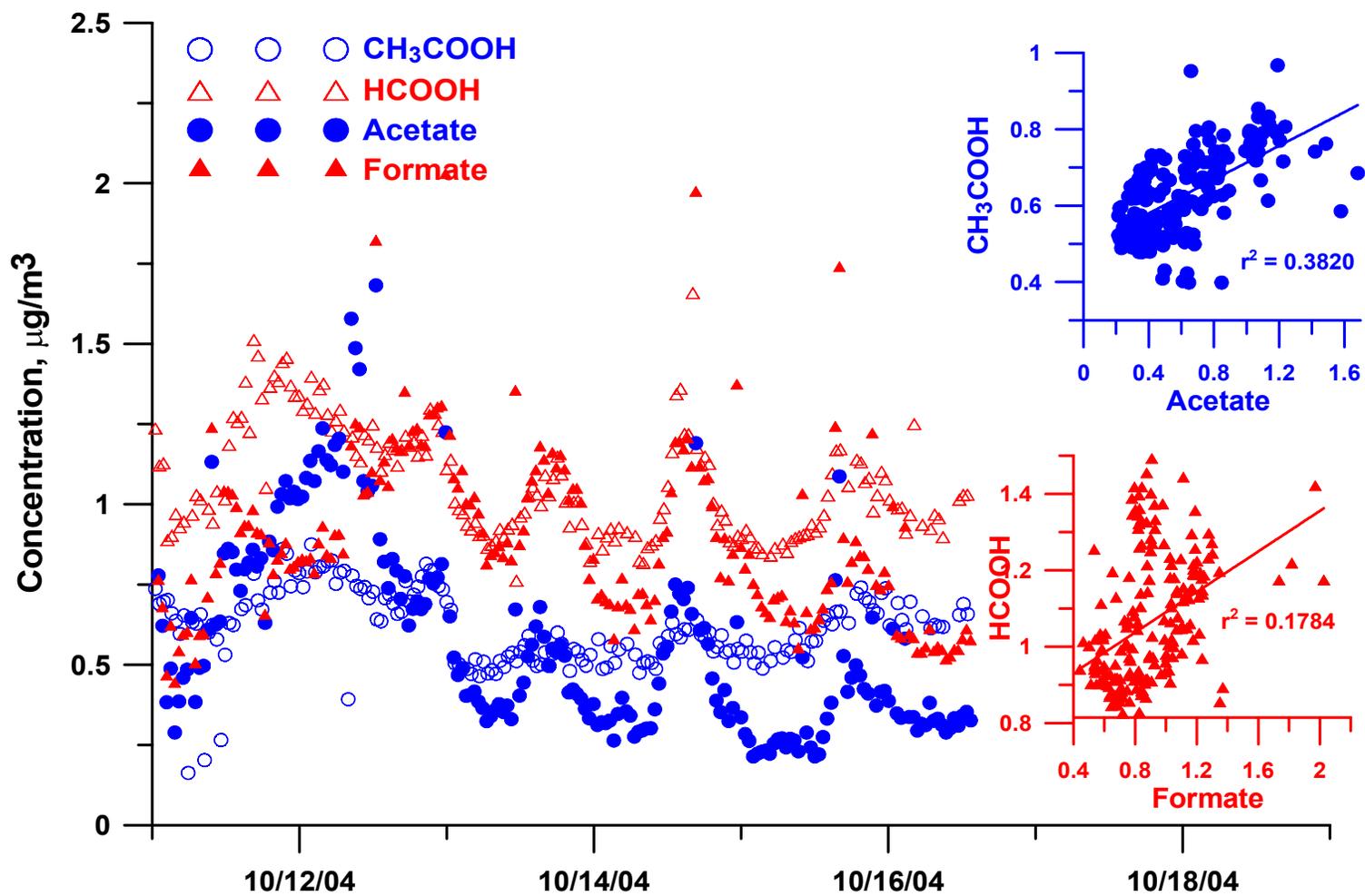


Figure 4.6. Diurnal behavior of HCOOH , CH_3COOH , formate and acetate. The insets show the correlations between individual gas and aerosol species.

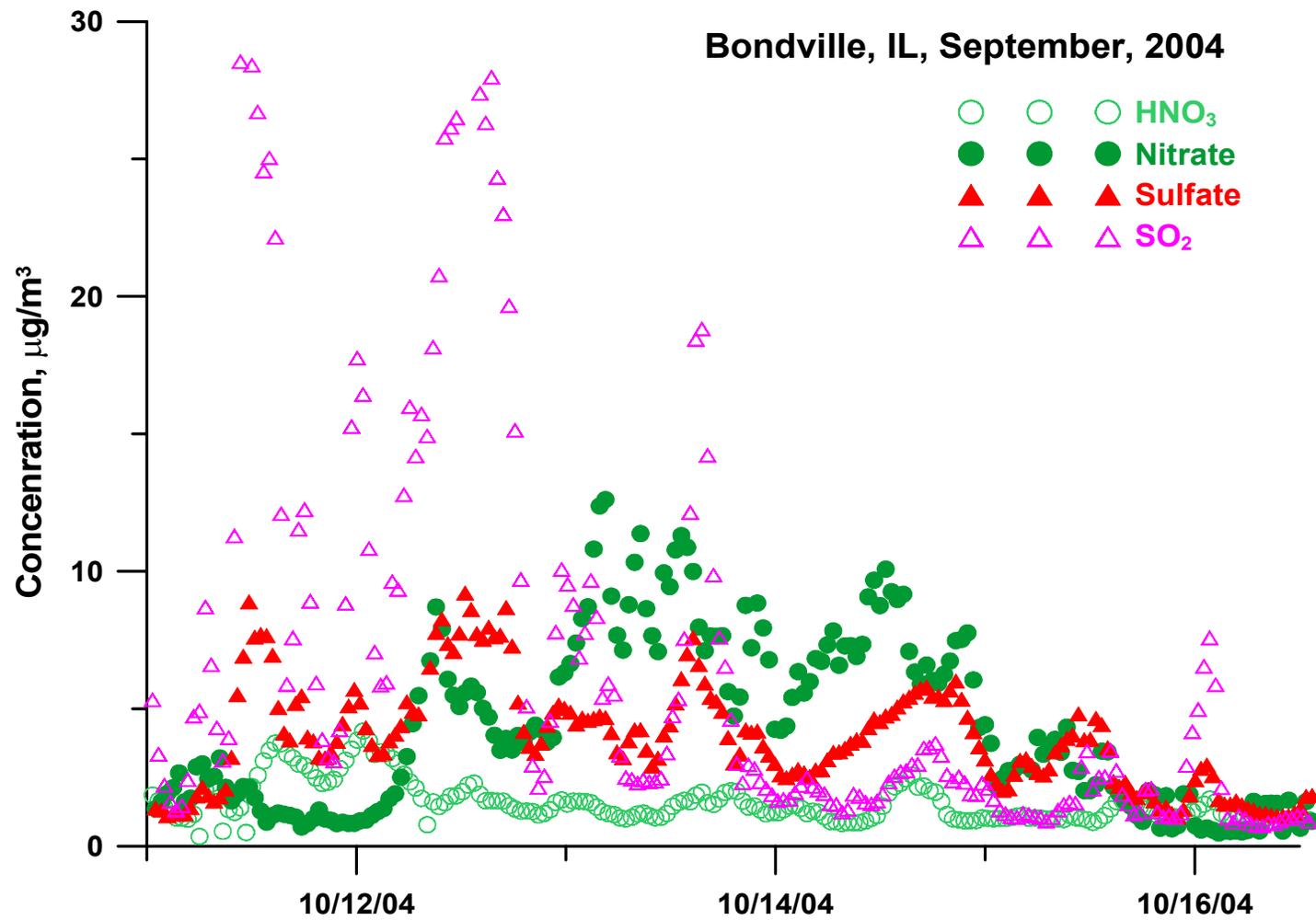


Figure 4.7. Concentrations of SO_2 , sulfate, HNO_3 , nitrate over a week long period.

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CHAPTER V

CONCLUSIONS

The epidemiological studies on the health effects of aerosols have led the United States Environmental Protection Agency (EPA) to add a fine particulate matter ($\text{PM}_{2.5}$ \equiv particulate matter $\leq 2.5 \mu\text{m}$ in size) standard. The EPA also established several PM health effect research centers and initiated “Supersites” research that attempts to characterize air quality in major urban areas by multi-investigation research initiatives. Particle toxicity is strongly dependent on chemical composition and physical properties. Atmospheric modeling is helpful in explaining or predicting atmospheric events but often it does so with a wide range of uncertainty in its output predictions and large number of assumption have to be made. These uncertainties can be resolved and some of the assumptions can be validated if real time phase-dependant chemical composition of pollutants are available.

The goal of this research was to develop tools that atmospheric scientists could use to measure species that contribute to atmospheric pollution. There is a great deal of interest on systems that can automatically measure chemical composition of PM and the precursor gases with high temporal resolution. Aside from providing a better understanding of the chemistry of gas and aerosol formation and transport processes; such measurement is also cost effective and does not suffer from analytical artifacts associated with long-term collection such as particle evaporation, gas-particle interaction, and particle-particle interaction on the collection media.

The development of a carbon dioxide removal device (CRD) for removing CO_2 in suppressed ion chromatography effluents is described in chapter II. With an appropriate

choice of the removal device and operating conditions, dissolved CO₂ can be essentially quantitatively (99+%) removed. This CRD thus facilitates the design and construction of the first gas particle ion chromatograph (GPIC1) that used easily prepared carbonate based eluent but provide the low background of a hydroxide eluent. In hydroxide eluent chromatography, the CRD largely removes the response from CO₂ present in the atmospheric samples that can cause problems in quantifying the nitrate or the sulfate peaks that elute in the vicinity of CO₂-induced carbonate peak; this greatly aids atmospheric trace gas analysis by IC. The CRD was of significant help to us for the measurement of nitric acid and nitrate using hydroxide eluent chromatography in State of Florida Department of Environmental quality sponsored field research in Tampa in 2003. The resulting data provide a wealth of information regarding to the nitrogen deposition in Tampa bay and the conversion of NaCl to NaNO₃.

The hydrophobic and hydrophilic filter-based particle collector (PC) devices are respectively described in chapters III and IV. Neither device uses steam, and also avoids problems associated with filter based collection i.e. fibrous filter leaching. These compact collectors permit automated collection and continuous extraction of soluble gases and soluble fractions of PM_{2.5}. The hydrophilic filter based particle collector made it possible to use lower air sampling flow rates while maintaining quantitative collection efficiency.

Both the gas particle ion chromatography (GPIC) systems described (in chapter III and IV) were fully automated and were adequately robust for long-term field deployment. For the GPIC1 system the measurement was based on a 30-min cycle for collection and analysis of particles and gases. Portability, cost-effectiveness, near reduced weight and field deployability were the main attracting features for the next

generation compact GPIC system as described in chapter IV (hence called GPIC2). Both systems are sensitive enough to detect the pollutant species of interest but were free of interferences or cross-talks from co-pollutants. In the GPIC2 system, the reported temporal resolution of 40 min was limited mainly by the sample processing time by the highly multi-tasking single syringe pump. Future efforts for the improvement of these systems will be focused on developing significantly faster analysis allowing for even higher temporal resolution while maintaining adequate sensitivity and limits of detection.

While this research constitutes meaningful contribution to atmospheric measurement of gases and particles, it was limited mainly to the measurement of soluble inorganic gases and inorganic ionic composition of particulate matter for GPIC1. The measurement of organic gases and organic species present in PM is a more challenging and interesting dimension of atmospheric analysis. Organic compounds constitute a large fraction of the total mass composition of atmospheric particles. Presently available methodologies and instrumentation are inadequate for such a task. In recent years, mass spectrometers with the ability to provide real time measurement of the chemical composition of a single particle have been developed. However, these instruments are expensive and currently not suitable for easy field deployment for reliable quantitative analysis. Moreover, they can only provide low resolution mass spectra that rarely allow identification of a specific compound. The development of the compact GPIC2 as a less expensive alternative instrument that can provide not only soluble inorganic gases and inorganic ionic composition of $PM_{2.5}$ but also more reliable quantitative real-time analysis of some important organic gases (acetic, formic and oxalic acid) and the corresponding organic ions in $PM_{2.5}$.

Although the only cation measured in this work is ammonium, the system can be configured with an additional ion chromatograph to measure other major soluble cations. In principle, a second IC can provide complete soluble cation analysis. However, it may be necessary to have respective preconcentrators in parallel, rather than in series, to avoid eluent counterion contamination between systems. The presently described GPIC instruments provide high sensitivity and allow analysis of ammonium plus anions in PM as well as ammonia plus acidic gases. They can do this in only a fraction of the time and cost of conventional techniques. Detection limits of low to subnanogram per cubic meter concentrations of most gaseous and particulate constituents were readily attained.

There is significant interest in developing systems with a capacity to detect bioagents for early detection of airborne bacterial and viral contamination. This year the U.S. government is proposing to spend billion of dollars for a bioshield program. A significant portion of it will undoubtedly be spent on developing necessary early detection technology. Again, The cost and complexity of mass spectrometry provide an opportunity for developing less expensive and more specific technology. Both the hydrophobic and hydrophilic filter based particle collectors can be of significant value in developing a bioagent collection system.

The loss of particles and gases in the inlet conduits of any air sampling system pose a constant challenge. The challenge remains even if the instrument was carefully characterized and calibrated with the appropriate gases or particles. This is because inlet losses depend on factors like humidity, temperature and other uncontrollable variables. In addition, the relative concentration of gases and density and composition of particles measured are often variable and hard to predict. Therefore, future work in this area

should certainly involve developing gas and particle system inlets that will have a high degree of flexibility, but will eliminate or at least decrease, the level of gas or particle loss in transit. Finally, it would be particularly interesting to develop miniaturized systems that can provide similar analysis, if possible.