

Versatile Gas/Particle Ion Chromatograph

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A new, compact gas/particle ion chromatograph has been developed for measuring ionic constituents in $PM_{2.5}$ (particulate matter of aerodynamic diameter $\leq 2.5 \mu m$) and water-soluble ionogenic gases. The instrument has separate sampling channels for gases and particles. In one, a membrane denuder collects soluble gases for preconcentration and analysis. In the other, a cyclone removes larger particles, a membrane denuder removes soluble gases, and a continuously wetted hydrophilic filter collects particles. A single, multiport, syringe pump handles liquid transport, and one conductivity detector measures anions and ammonium for both channels. Electrodealytically generated gradient hydroxide eluent permits 20 min chromatographic runs. Gas/particle samples are each collected for 40 min, but the sampling intervals are staggered by 20 min. Liquid samples from the gas denuder and particle collector are aspirated and preconcentrated on sequential cation and anion concentrators and transferred respectively to an ammonia transfer device and an anion separation column. 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, SO_2 , HNO_3 , and the corresponding ions in the aerosol phase. Low ng/m^3 to sub- ng/m^3 limits of detection (LODs) are attained for most common gases and particulate constituents, the LODs for gaseous SO_2 to NH_3 range, for example, from sub parts per trillion by volume (sub-pptv) to ~ 5 pptv.

Introduction

The measurements of aerosols and trace gases are important in many arenas. In particular, many epidemiologic studies associate exposure to ambient particulate matter (PM), especially fine particles, to increased mortality, morbidity, and increased risk of cardiovascular and respiratory illness.^{1–3} Such findings have led the U.S. Environmental Protection Agency to create a $PM_{2.5}$ (PM of aerodynamic diameter $\leq 2.5 \mu m$) standard, establish PM health effects centers, and initiate Supersites research.⁴

Most fine particles are secondary in nature; i.e., they are atmospherically formed via chemical reactions of gases, e.g., SO_2 , NO_x , NH_3 , volatile organic compounds, ozone, etc.⁵ Ammonia neutralizes various acidic gases to form NH_4^+ salts in the particle phase⁵ such that NH_4^+ , NO_3^- , and SO_4^{2-} are the dominant ionic species in $PM_{2.5}$.⁶ Physical, optical, and reactive properties of aerosols are dependent on their precise

composition.⁷ For human exposure, trace gas concentrations surrounding the particles may be very important. Sarnat et al. suggest that gaseous copollutants play an important role in the observed adverse health effects.⁸ Many atmospheric gases exist in reactive equilibrium with the aerosol phase.⁹ 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.⁹ Highly time resolved data can help carry out source apportionment as well.¹⁰

Measurement techniques used for various gaseous species have been reviewed by Parrish and Fehsenfeld¹¹ and by Sipin et al.¹² Differential optical absorption spectroscopy and tunable diode laser absorption spectroscopy permit direct measurement of several trace gases; many examples are in the recent literature.^{13,14} Direct spectroscopy is not a panacea. Spectral interferences are not unusual, and averaging over a long path may not always be desirable. Among thermal decomposition techniques, selective conversion of particulate sulfate and nitrate into specific gases^{15,16} cannot be extended to other species of potential interest. Ion chromatography (IC)-based systems offer the unique ability of performing simultaneous, multispecies analysis. Soluble gases can be collected/removed using diffusion-based collectors without affecting particles. Dasgupta^{17,18} and Toda¹⁹ have reviewed methods for diffusion-based collection and analysis of atmospheric gases, specifically automated IC-based systems for the rapid determination of gaseous constituents using a wet denuder, or a diffusion scrubber.

Particle mass spectrometry (MS) can characterize particle composition;²⁰ recent research focus has largely been on single-particle MS.²¹ 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, does not provide enough temporal resolution or real-time data, and is subject to many artifacts. Automation of collection/analysis and a reduced sampling period can potentially eliminate many of these artifacts. Automated particle collection and on-line analysis approaches have been reviewed by Dasgupta and Poruthoor,²² including their own work on collection after steam-induced particle growth^{23,24} and much other related significant work,^{25–29} summarized elsewhere.³⁰ We have been developing simpler, steamless particle collectors (PCs) that have less artifact nitrite and nitrate formation from NO_2 –steam reactions.^{31,32} The goal is to make smaller, hardened, more affordable systems while improving their analytical capabilities. The first step was an orientation-insensitive membrane-based parallel plate denuder (MPPD) operating at 1.5 L/min.³³ The MPPD has an internal holding capacity where liquid can remain stationary but the liquid volume is small and permits rapid washout/replenishment. The second step was a wetted hydrophilic filter-based PC that ideally complemented the MPPD in size and sampling rate. This PC efficiently collects small particles (98% of $0.3 \mu m$ particles) with a $5 \mu m$ pore size filter; the effective pore size decreases greatly by flowing water. No filter replacement is needed for month-long periods.

Presently, we combine these elements toward a complete compact IC-based system that uses a single conductivity detector for gas- or particle-derived anions and ammonia/ammonium. It produces a single chromatogram by placing the ammonia peak at the beginning of a gradient anion chromatogram. The system provides information not only

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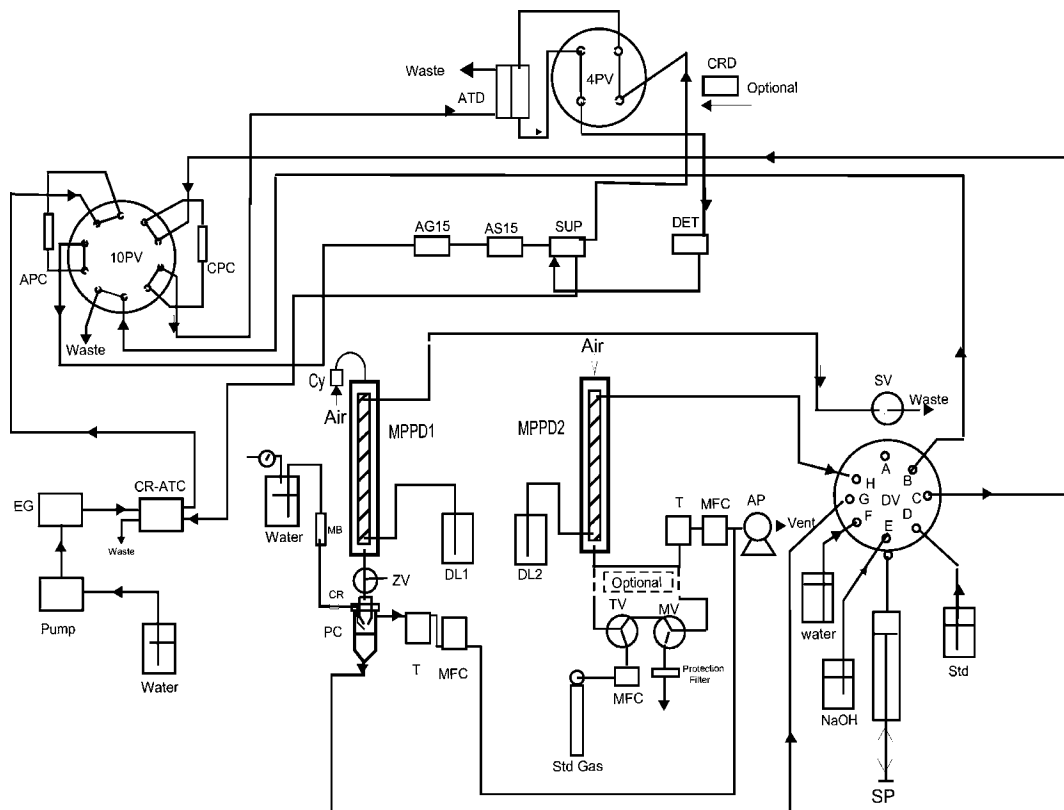


FIGURE 1. Instrument schematic for the gas/particle ion chromatography system. Key: SP, syringe pump; Std, standard solution; SV, three-way selector valve; 6PV, six-port valve; ATD, ammonia transfer device; CRD, carbon dioxide removal device, optional; 10PV, 10-port high-pressure valve; CPC, cation preconcentrator; APC, anion preconcentrator; AG, anion guard column; AS, anion separation column; SUP, anion suppressor; DET, conductivity detector; EG, anion eluent generator; CR-ATC, continuously regenerated anion trap column; Cy, cyclone for the $PM_{2.5}$ cut point; MPPD1, membrane-based parallel plate denuder for removing gas; PC, particle collector; MPPD2, membrane-based parallel plate wet denuder for the gas sample; DL1 and DL2, denuder liquids (0.5 mM H_2O_2 solution); MB, mixed bed resin column; CR, capillary restrictor; ZV, zero valve for zeroing particle collection (optional); TV, three-way solenoid valve (Teflon) for optional standard gas introduction; MV, metal valve, three-way; T, water trap column; MFC, mass flow controller; AP, air pump; Waste, waste line.

about sulfate and nitrate but also about organic ions such as acetate, formate, oxalate, etc.

Experimental Section

IC System. An ICS 2000 ion chromatograph (IC; Dionex Corp., Sunnyvale, CA; all chromatographic columns and hardware/software from this vendor) was used with AG15-5 μ m guard (3 \times 30 mm) and AS15-5 μ m separation (3 \times 150 mm) columns along with a 2 mm electrodyalytic suppressor (Ultra-II; SUP; Figure 1). An isocratic pump, a conductivity detector (DET), an electrodyalytic NaOH generator (EG; permits programmed gradients), and an electrodyalytically regenerated anion trap column (CR-ATC) constitute the IC. The NaOH linear gradient program (flow 0.60 mL/min) was as follows: 5–8 mM (0–3.5 min), 8–15 mM (3.5–5.0 min), 15–30 mM (5.0–7.9 min), 30–45 mM (7.9–11.4 min), 45–5 mM (11.4–16.5 min), hold at 5 mM till run ends (20 min), followed by a repeat over the next 20 min.

The columns and conductivity cell were maintained at 30 $^{\circ}$ C. The chromatographic cycles repeat every 40 min until a preprogrammed number of cycles have run. Acquisition of the detector signal, system automation, and valve control using relay/TTL outputs are all carried out under software control (Chromleon 6.6).

Gas Collection System (GCS). Water-soluble gas collection was accomplished with the previously described MPPD.³³ The cellulose acetate (CA) membranes previously used were replaced with hydrophilic nylon membranes (NYL; Magna nylon, Osmonics Inc.; 0.1 μ m pore size, \sim 100 μ m wet thickness). Briefly, the denuders consist of two parallel

membranes of active area 13 \times 220 mm held 2 mm apart by a spacer. Air enters the MPPD at the top and flows between the membranes, aspirated by a pump at 1.5 SLPM (standard liters per minute) and controlled by a mass flow controller (MFC). Gas-collection efficiency with the NYL membrane was measured as previously described with 100 ppbv (parts per billion by volume) SO_2 as the test gas in the 1.2–2.4 L/min flow rate range.

Particle Collection System (PCS). The PCS is designed to sample $PM_{2.5}$. Two separate channels are necessary because particles grow in size in the moist MPPD and a size cutoff device such as a cyclone cannot be installed after the MPPD because the post-MPPD size distribution no longer represents ambient distribution. Conversely, sampling integrity of sticky/reactive gases (e.g., HNO_3 , NH_3) is compromised with a cyclone ahead of the MPPD. A single-channel system where the same denuder both removes soluble gases for the PCS and supplies the collected gas for analysis is permissible if there are no PCS size-cut requirements. Sampling of $PM_{2.5}$ was desired here, and separate gas/particle sampling channels were needed. The PCS starts with a Triplex cyclone (SCC.062; D_{50} = 2.5 μ m at 1.5 LPM; BGI Inc., Waltham, MA) and is followed by an MPPD and a hydrophilic filter-based PC. Briefly, inlet air is brought in at 1.5 SLPM through a 6 cm long stainless steel inlet tube that is coupled directly to the denuder exit and terminates into a 75 $^{\circ}$ taper, 0.76 mm orifice nozzle. A peripheral capillary external and adjacent to the nozzle tip delivers water at 0.25 mL/min and produces a fine mist. The mist wets a pair of 25 mm filters (14 mm exposed diameter): a paper filter on top (Whatman no. 1) and a 5 μ m

pore polycarbonate filter (Millipore Isopore) on the bottom, placed 26 mm below the nozzle. Water and air simultaneously flow through the filter pair, and the flowing water effectively reduces the pore size of the filter. 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. The liquid is aspirated at the end of the desired collection period. With typical size distributions of sulfate and nitrate,⁵ the collection of PM_{2.5} mass with this PC is virtually quantitative (96+%).³⁰

Sample Processing Unit (SPU). A custom computer case (Lian Li, PC-6070; 21 (width) × 46 (height) × 52.5 (depth) cm) housed the following components: (i) a 48000-step V6 syringe pump (SP) with an eight-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 a power supply (C2-2340 EP, VICI), (iii) two MFCs (FC260, Tylan General, Torrance, CA) along with power supply/control/display modules made in-house, (iv) one glass-wool-filled liquid trap (T) each ahead of the two MFCs to protect them, (v) a three-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. Both MFC control/display modules, SP, and 10PV (fittings-end facing front) are mounted on the SPU front panel. This arrangement facilitates servicing/replacement of the syringe and cation/anion preconcentrator columns (CPC/APC). All other connections and electrical/fluid conduits were at the rear of the SPU. Flexible PVC tubing (³/₈ in. o.d., ¹/₄ in. i.d.) was 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. More frequently (dis-)assembled low-pressure connections were made with soft push-fit connecting tubes (Pharmed; 1.30 mm tube; Cole-Parmer). Liquid connections between the 10PV, SP, and the IC were made with ¹/₄-28 fittings from the front panel.

System Description. The complete system is shown in Figure 1. The capability of the eight-port DV was extended by connecting port A to the common port of the SV. Port A and the SV allow liquid withdrawal from MPPD1 (this liquid is not analyzed) and disposal of any liquid in the SP to waste. Port B allows loading of the liquid in the SP to the serial preconcentrators (CPC/APC) in the 10PV; this can involve either the sample or water as the wash liquid. As the CPC eluent, 15 mM NaOH is aspirated through port E and delivered via port C 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 is connected to an aqueous calibrant solution containing 12 μM NaNO₃ and 15 μM (NH₄)₂SO₄ (each milliliter corresponds to 9 μg/m³ NH₄⁺, 12.4 μg/m³ NO₃⁻, and 24 μg/m³ SO₄²⁻ for a 60 L air sample). Port F provides access to deionized (DI) water for washing. Port G allows the periodic withdrawal of the aqueous PM_{2.5} extract. Port H allows liquid withdrawal from and refilling of MPPD2 for soluble gas analysis.

Both MPPDs were fed from bottles (DL1.2; 0.5 mM H₂O₂) placed just below the denuder; the rationale for using H₂O₂ has been previously discussed. Water to the PC is supplied pneumatically via a mixed bed resin column (MB) through a capillary restrictor (CR). Air flows through the cyclone (Cy), down MPPD1 into the PC. 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 a liquid water trap (T) to the MFC and air pump (AP). In MPPD2, calibration/zero gas can be optionally introduced via a three-way Teflon solenoid valve (TV) while air aspiration by the AP continues via a protective filter and valve (MV).

TABLE 1. System Operating Sequence

<i>t</i> = 0 min	initialize syringe pump, simultaneously switch 4PV and 10PV to inject mode (black lines, Figure 1), begin ammonia elution and analysis, gas extract injected
<i>t</i> = 5 min	ammonia detection complete, switch 4PV, anion detection begins, switch 10PV to load mode (gray lines, Figure 1), wash CPC and APC with water
<i>t</i> = 8 min	aspirate PC sample and dispense to CPC and APC, follow with water wash
<i>t</i> = 18 min	switch 4PV to inject mode, system readied for ammonia analysis
<i>t</i> = 20 min	switch 10PV, particle extract injected, begin ammonia elution and analysis
<i>t</i> = 25 min	ammonia detection complete, switch 4PV, anion detection begins, switch 10PV to load mode (gray), wash CPC and APC with water, aspirate and refill MPPD1 and dispense to waste, wash syringe, wash CPC and APC
<i>t</i> = 32 min	aspirate MPPD2, load APC and CPC, follow with water wash
<i>t</i> = 38 min	switch 4PV to inject mode, system readied for ammonia analysis
<i>t</i> = 40 min	cycle complete, end and repeat

Sodium hydroxide eluent generated electrochemically by the EG passes through the CR-ATC to the 10PV. The CPC (5 × 35 mm) is filled with a 1:1 mixture (Dowex-50W×8 H⁺-form with chloromethylated poly(styrene-divinylbenzene), Bio-Beads S-X1; both 200–400 mesh; Bio-Rad Inc.). The APC (TAC-ULP1; 5 × 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 NH₃ across a membrane to a receptor stream was originally introduced by Carlson³⁴ and since followed by others.³⁵ In atmospheric samples, often the major non-H⁺ cationic species of interest is NH₄⁺. Ammonium preconcentrated on the CPC is eluted by NaOH as NH₃, and the effluent is made to pass through a high-permeability tubular membrane device that functions as the ATD. Receptor water carries the transferred NH₃ to a conductivity detector, and the receptor conductance is used to measure the original NH₃/NH₄⁺ content. The ATD is similar in principle to a recently reported CO₂ removal device (CRD)³⁶ but is constructed differently. A 400 × 450 μm (i.d. × o.d.), 30 cm long Celgard polypropylene tubular membrane is coated externally with silicone (~2 μm) and filled with a 200 μm diameter nylon monofilament. This is used for 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 thus the analyte dispersion small.

Ammonium measurement is done with the ATD in conjunction with the four-port valve (4PV; the six-port valve normally supplied with the chromatograph as the injector can serve this purpose and was used thus in our instrument). During normal anion chromatographic operation, the 4PV remains in the mode drawn with the lighter lines and the SUP is directly connected to the DET (via an optional CRD). Referring to Table 1, both the 10PV and 4PV are initially switched at the same time (*t* = 0 min) to the mode shown with heavy lines in Figure 1. The suppressor effluent, which at this time is pure water, is now routed via the ATD receiver channel to the DET. Eluted ammonia goes through the ATD and produces a detector response. At 5 min, the 4PV is switched back and regular anion detection proceeds.

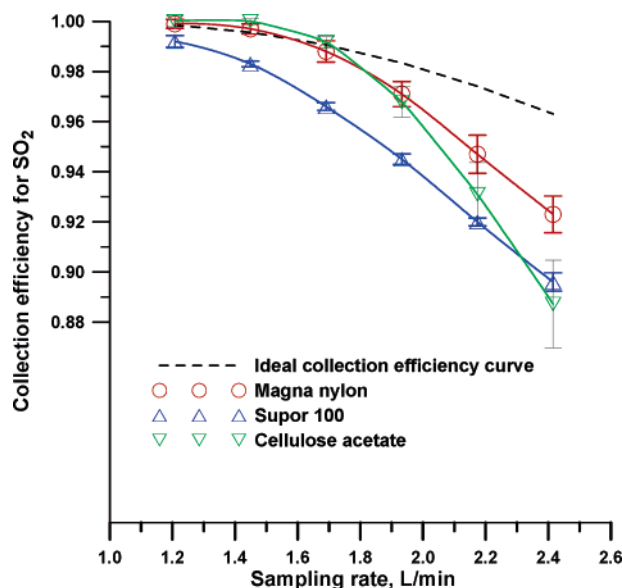


FIGURE 2. Collection efficiency for the test gas (100 ppbv SO_2) as a function of the sampling rate. The dashed line indicates the theoretical efficiency according to the Gormley–Kennedy equation. Note that the ordinate scale does not start at zero. Error bars represent ± 1 standard deviation ($n = 3$ each).

Each 40 min cycle consists of a gas sample analysis half (20 min) followed by an aerosol sample analysis half (20 min). Both are collected over 40 min periods but staggered 20 min apart. Table 1 lists the operational sequence. Washing steps are often critical and cannot be omitted (e.g., residual NaOH in the CPC will prevent collection of NH_4^+).

For liquid-phase calibration, multiple preprogrammed volumes (sub several milliliters) of the standard can be used to construct a multipoint calibration while air sampling is shut off. Standard loading is followed by DI water to ensure quantitative transfer. Both chromatographic halves of the 40 min cycle are used for calibration.

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 (4 ft above the roofline; the roofline is 10 ft from the ground) in a temperature-controlled (heated) insulated Plexiglas enclosure as some species such as HNO_3 cannot be effectively transmitted over significant lengths of tubing. Ambient winter temperatures at this location (latitude/longitude 40.113°/−88.369°) fall substantially below freezing. The enclosure temperature is just sufficient to keep the denuder and the particle collector liquid from freezing. Excessive heating must be avoided to avoid particle → gas transformation. The SPU and the IC were housed inside the trailer. The shortest possible lengths (ca. 5–10 cm) of PFA Teflon tubes (6.3 mm o.d., 4.8 mm i.d.) were used for air inlets for both MPPD2 and the Cy. The AP was located inside the shelter, but inside a compartment to reduce noise.

Results and Discussion

New Membrane for the Denuder. Gas Collection Efficiency (CE). CA membranes previously used are normally acceptable but generate an acetate background. With the present instrument, we wanted to measure CH_3COOH /acetate, and it was necessary to eliminate this background. Not only should the ideal membrane have low leachables, it should be highly wettable while having a very small pore size (to avoid significant seepage of liquid water). On the basis of initial findings on leachables, we chose poly(ether sulfone) (Supor) and nylon (Magna) sheet membranes with a 100 nm pore size. Figure 2 indicates the superior performance of NYL

compared to poly(ether sulfone), likely due to its greater wettability. Up to a flow rate of 1.5 L/min (ambient pressure and temperature in our laboratory are 680 mmHg and 296 K, respectively), the CE with this membrane is experimentally indistinguishable from unity. Up to 1.7 L/min, the observed CE is indistinguishable from the Gormley–Kennedy efficiency (calculated¹⁸ for a parallel plate denuder with an active area of 220×13 mm, spacing of 2 mm, and diffusion coefficient of SO_2 of $0.12 \text{ cm}^2/\text{s}$). It is only above this flow rate that the CE was subtheoretical, possibly due to the development of dry regions. These experiments were conducted with pure dry air. In more moist ambient air, theoretical behavior may extend to higher flow rates. As to the behavior of the three membranes, at low flow rates CA has the best efficiency, suggesting high wettability, but this performance falls off rapidly at higher flow rates because lower water transport through this membrane becomes a limiting factor. The poly(ether sulfone) membrane performs the poorest because of both lower wettability and a lower water transport rate.

Organic acid gases such as HCOOH or CH_3COOH , which are larger molecules with smaller diffusion coefficients and have lower Henry's law solubilities, are not likely to be collected as efficiently as SO_2 . The exact collection efficiency for these gases must be determined before use.

Optimization of Chromatographic Conditions. Previous chromatographic conditions elute the nitrate peak on the tail of the CO_2 peak,^{32,36} causing problems at very low nitrate levels. While this situation can be remedied with a CRD, the present chromatographic conditions have the elution order $t_{R,\text{sulfate}} < t_{R,\text{carbonate}} < t_{R,\text{nitrate}}$. Because sulfate/ SO_2 levels are often significant, the use of a CRD becomes optional.

The gradient program allows sufficient time in the beginning to park the ammonia response. The background-suppressed eluent is pure water; a low flow rate (0.60 mL/min) of this promotes ammonia detection sensitivity. The use of NaOH, instead of the more commonly used KOH, allows the CPC to remain in the Na form. This facilitates NH_4^+ 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 of the chromatographic time to 30 min from 20 min can be used to obtain even better separation of the early eluates while further increasing the ammonia response sensitivity. Fairly minor modifications of the system can increase the capabilities further: A second SP allows the gas and particle sampling times to be synchronous, rather than staggered, and/or allows calibration with 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.

Instrument Performance and Detection Limits. Typical output chromatograms (without a CRD) for real samples are shown in Figure 3. The LOD ($S/N = 3$, referring to the chromatographic baseline noise) for anions is 0.2–0.7 ng/ m^3 for a 60 L total sample volume (40 min at 1.5 L/min) using electroalytic eluent generation and suppression. This amounts to < 1 pptv (parts per trillion by volume) for SO_2 . Ammonium is measured as ammonium hydroxide, a weak base. A quadratic calibration equation must be used. The LOD for ammonium is 4 ng/ m^3 (~ 5 pptv). These LODs would be adequate, even for relatively unpolluted air. The concentrations of the major constituents appear in the chromatogram; the separation of (1) SO_2 and (2) $\text{H}_2\text{C}_2\text{O}_4$ and the region where (5) acetate and (6) formate elute are shown in magnified detail in insets a and b, respectively. Peak 3 corresponds to the retention time of fluoride; peaks 4, 7, and 8 are presently unidentified. We suggest that the real power

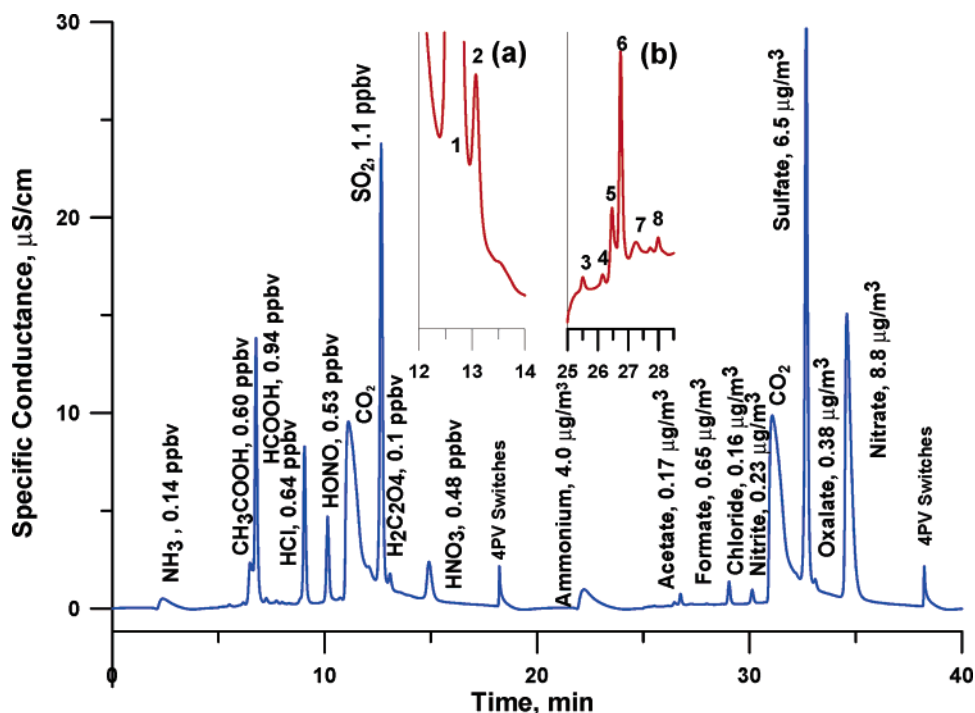


FIGURE 3. Typical instrument output for a 40 min cycle, sampled Sept 28, 2004, first half gas sample 7:39 to 8:19 a.m., second half particle sample 7:55 to 8:35 a.m. The second 20 min is for particle sample responses. When the 4PV switches for ammonia determination, the accumulated liquid in the ATD produces a transient conductivity response; the switch back to anion determination does not register. Insets a and b show the separation of (1) SO_2 and (2) $\text{H}_2\text{C}_2\text{O}_4$ and (5) acetate and (6) formate. See the text for other details.

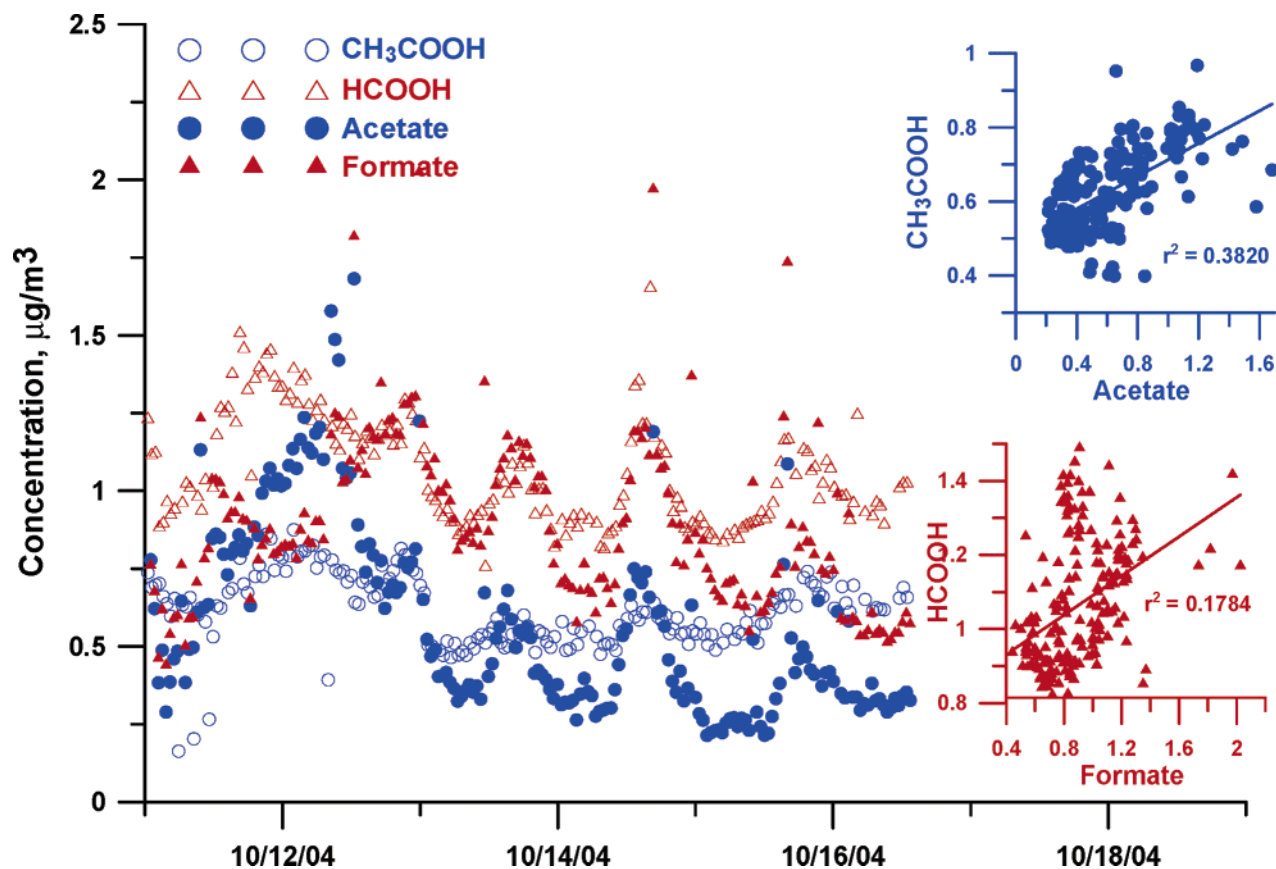


FIGURE 4. Diurnal behavior of HCOOH , CH_3COOH , formate, and acetate. The insets show the correlations between individual gas and aerosol species.

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 that the instrument offers.

System Maintenance. Continuous liquid flow was mandatory with our previous denuders. While syringe pumps are more robust than peristaltic pumps, it is difficult to maintain multiple continuous flow streams with syringe pumps. The

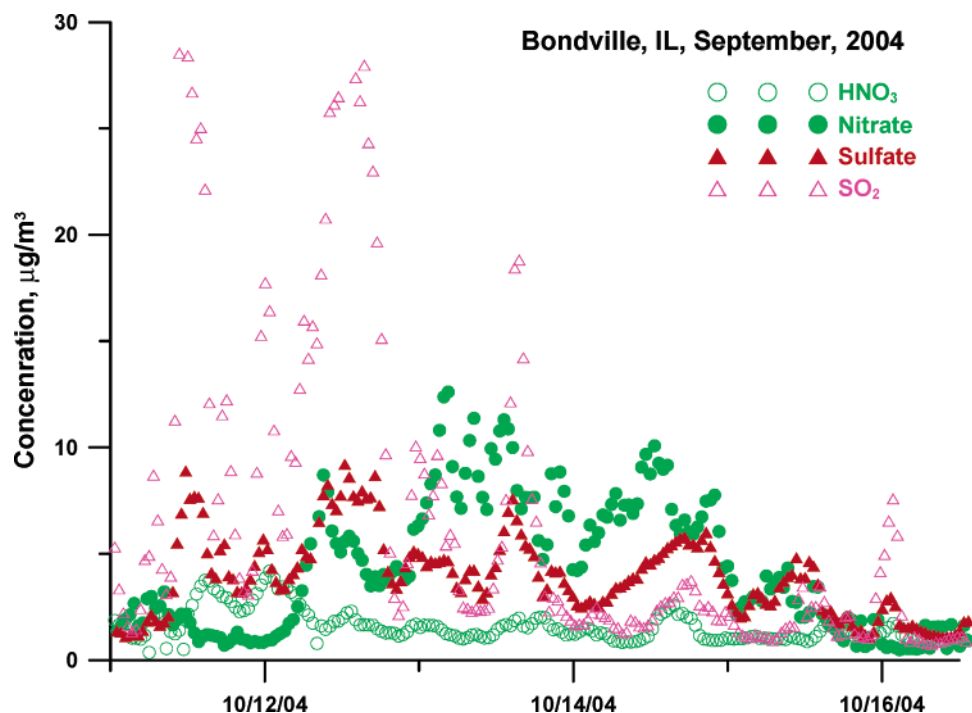


FIGURE 5. Concentrations of SO₂, sulfate, HNO₃, and nitrate over a week-long period.

present MPPD/PC can operate in either continuous or intermittent flow mode. The latter strategy is presently used with a single syringe pump. The biggest reservations on long-term deployment of wet instruments surround maintenance frequency. In the present instrument, a 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; the data from the two subsequent cycles are discarded. Both MPPDs and inlet tubes are washed thoroughly at this time with DI water to remove deposited particles. The longevity of the nylon membranes in the MPPDs is presently not known; replacement has not been needed in several months. The CPC inlet frit is inspected every two weeks and replaced if soiled. Our experience indicates that the 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.

Illustrative Field Data. The system has been deployed in Bondville, IL, with gaseous NH₃, CH₃COOH, HCOOH, HCl, HONO, SO₂, H₂, C₂O₄, and HNO₃ and particulate ammonium, acetate, formate, chloride, nitrite, sulfate, oxalate, and nitrate being monitored.

The present system has particular capabilities of monitoring organic acids in both the gas and particle phases. Although not commonly monitored and rarely with a high time resolution, organic acids often constitute a major fraction of gas-phase atmospheric acidity.^{37–39} Figure 4 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 is selectively displaced over HCOOH in a slightly acidic aerosol. Charge balance calculations do indicate that the Bondville aerosol is typically slightly acidic.

Figure 5 shows the behavior of SO₂, HNO₃, sulfate, and nitrate. The concentration of HNO₃ peaks during the

afternoon hours, and nitrate from semivolatile NH₄NO₃ is typically lower during the hotter part of the day. Sulfate levels are poorly correlated with those 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.

In summary, we have demonstrated here a versatile robust instrument for the facile automated analysis of the ionic/ionogenic constituents of atmospheric gases and soluble particles.

Acknowledgments

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