

Session AB-1c: Continuous Measurement Techniques for PM Components

Laboratory and Field Evaluation of Instrumentation for the Semi-Continuous Determination of Particulate Nitrate (and Other Water Soluble Particulate Components)

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Studies conducted at the EPA facility in Research Triangle Park, NC and at a field study in Southern California have demonstrated the capability for the semi-continuous determination of particulate nitrate (and other water soluble ionic species). Two instruments, a R&P 8400N particulate nitrate monitor and an ion chromatography (IC)-based prototype monitor developed at Texas Tech University (TTU), were evaluated both in the laboratory using a simulated ambient aerosol and in the field (Rubidoux, CA) during a three week joint ambient comparison study with Brigham Young University (BYU) and the South Coast Air Quality Monitoring District (SCAQMD). During the initial laboratory studies, both instruments were responsive to changes in the simulated aerosol concentration. However, potential problems were discovered involving both instruments during the laboratory based studies and these problems are currently being addressed. Both instruments were then transported to the SCAQMD Rubidoux field site and operated for a period of three weeks (July 1- 21, 2003). Due to manufacturer's quality assurance issues associated with IC components of the TTU prototype instrument, limited data were obtained from this instrument during the three week sampling period. Initial comparisons show general agreement between the R&P and IC-based prototype instruments for the semi-continuous determination of ambient particulate nitrate at lower nitrate concentrations ($<15 \mu\text{g}/\text{m}^3$) and an under determination by the R&P instrument at higher concentrations ($>15 \mu\text{g}/\text{m}^3$). During the three week study period, 15-minute average particulate nitrate concentrations approaching $30 \mu\text{g}/\text{m}^3$ were observed. Semi-continuous results obtained from the EPA-operated instruments were averaged and compared to integrated sampler results obtained by BYU and SCAQMD. Results of the laboratory and field studies will be addressed.

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ABSTRACT

Studies conducted at the EPA facility in Research Triangle Park, NC and at a field study in Southern California have demonstrated the capability for the semi-continuous determination of particulate nitrate (and other water-soluble ionic species). Two instruments, a R&P 8400N particulate nitrate monitor and an ion chromatography (IC)-based prototype monitor developed at Texas Tech University (TTU), were evaluated both in the laboratory using aqueous standards and a simulated ambient aerosol and in the field (Rubidoux, CA) during a three week joint ambient comparison study with Brigham Young University (BYU) and the South Coast Air Quality Monitoring District (SCAQMD). During the initial laboratory studies, both instruments were responsive to changes in the simulated aerosol concentration. However, potential problems were discovered involving both instruments during the laboratory based studies and these problems are currently being addressed. Both instruments were then transported to the SCAQMD Rubidoux field site near Riverside, CA and operated for a period of three weeks (July 1- 21, 2003). Due to malfunctioning IC components (concentrator columns) of the TTU prototype monitor, limited data were obtained from this instrument during the three week sampling period. Initial ambient comparisons show general agreement between the R&P and IC-based prototype instruments for the semi-continuous determination of ambient particulate nitrate at lower nitrate concentrations ($<15 \mu\text{g}/\text{m}^3$) and an under determination by the R&P instrument at higher concentrations ($>15 \mu\text{g}/\text{m}^3$). During the three week study period, 15-minute average particulate nitrate concentrations approaching $30 \mu\text{g}/\text{m}^3$ were observed. Semi-continuous results obtained from the EPA-operated instruments were averaged and compared to integrated sampler results obtained by BYU and SCAQMD.

INTRODUCTION

Human health endpoints associated with exposure to airborne particulate matter (PM) include increased mortality and morbidity from respiratory and cardiopulmonary disease.¹⁻³ The observed exacerbation of health problems is believed to be associated more closely with exposure to fine particles ($\text{PM}_{2.5}$) than coarse particles. As a result, in 1997, the U.S. Environmental Protection Agency (U.S. EPA) promulgated revised standards for PM, which establishes new annual and 24-hour fine particulate standards with $\text{PM}_{2.5}$ measured according to the Federal Reference Method ($\text{PM}_{2.5}$ FRM) as the indicator.⁴ However, ambient fine particulate matter is not a single pollutant, but a mixture of many chemical species, dominated by primary and

secondary aerosols from combustion emissions. Major components include: sulfate, nitrate, ammonium, and hydrogen ions; trace elements (including toxic and transition metals); organic material; and elemental carbon (EC). Stable species such as sulfate can be accurately measured by single filter samplers such as the PM_{2.5} FRM.⁴⁻⁵ Semi-volatile fine particulate species such as ammonium nitrate are not accurately determined by these techniques.⁶⁻⁹ As stated previously, the current national standard for PM_{2.5} is monitored using the PM_{2.5} FRM. This method provides a 24-hour averaged PM_{2.5} concentration. With the FRM, losses of semi-volatile ammonium nitrate from the particles can occur during sampling and equilibration¹⁰⁻¹² according to the following equation:



Filter samples collected over longer time periods, lack sufficient temporal resolution to track short-term diurnal events (i.e., impact of traffic and photochemistry events on particulate nitrate concentration).¹³ In addition, sampled filters require off-line analysis techniques which result in data availability delays. Therefore, it is desirable to obtain artifact free, PM chemical composition data with high temporal resolution. Short-term diurnal characterization of major PM_{2.5} components will provide previously unavailable information about changes in concentration, air mass movement and source contributions. This information benefits areas such as epidemiological and environmental studies, model development and evaluation, visibility degradation and climate change.¹³⁻¹⁴

This paper demonstrates the capability for the semi-continuous determination of particulate nitrate. Two instruments, a R&P 8400N particulate nitrate monitor and an ion chromatography (IC)-based prototype monitor developed at Texas Tech University (TTU), were evaluated. These evaluations were performed in the laboratory using standard injections and a simulated ambient aerosol, and also during a three week ambient comparison study in Rubidoux, CA.

EXPERIMENTAL METHODS

Sampling Sites

Laboratory Studies. Laboratory based evaluation of the R&P 8400N and the TTU prototype monitors was conducted at the new EPA campus located in Research Triangle Park, NC.

Summer 2003 Field Study. During the Summer 2003 field study both the R&P 8400N and the TTU prototype instruments were operated at the SCAQMD Rubidoux sampling site in Southern California. Rubidoux is a residential community on the east side of the L.A. Basin (near Riverside). In addition to local sources (mobile sources, stock yards, etc.), the Rubidoux site is frequently impacted by pollution transported from the L.A. metropolitan area by the prevailing wind (west to east) patterns associated with this area. PM_{2.5} composition at Rubidoux during summer months is expected to be dominated by organic material and ammonium nitrate.¹⁵⁻¹⁶ Average (24-hr) particulate nitrate concentrations observed in the Rubidoux/Riverside area are documented to be the highest in the State of California during summer months (>5 µg/m³).¹⁵⁻¹⁶ Thus the reason for choosing this site for study. Short term (10 min) nitrate concentrations have been reported to be in excess of 30 µg/m³.¹⁷

Sampling Periods

Laboratory Studies. Initial laboratory evaluation of both the R&P 8400N and the TTU prototype instrument began in February 2003. Upon completion of the Rubidoux, CA field study, both instruments were returned to the EPA facility in Research Triangle Park, NC where further laboratory-based evaluation is on-going.

Rubidoux, CA Field Study. Both instruments were transported to and operated at the SCAQMD Rubidoux sampling site during July 1- 21, 2003.

Sampling Methods

R&P Series 8400N Particulate Nitrate Monitor. The R&P Series 8400N Ambient Particulate Nitrate Monitor is composed of two components: (1) pulse generator and (2) pulse analyzer. Ambient air samples are pulled into the pulse generator through a sharp cut cyclone (SCC), operated at 5 L/min, to remove particles with diameters greater than 2.5 μm . Following the 2.5 μm cut, the flow is split into a 4 L/min bypass and a 1 L/min sample flow. The 1 L/min sample flow passes through an activated charcoal honeycomb denuder to remove potential gaseous interferences (i.e., HNO_3). The sampled particulate nitrate is collected by critical impaction onto a Ni-chrome impaction/flash strip mounted in a collection and vaporization cell. Prior to passing into the collection and vaporization cell, the particle containing sample stream is passed through a NafionTM humidifier. The humidifier increases the sample relative humidity (RH) above the deliquescence point¹⁸ of the nitrate salt (i.e., NH_4NO_3 , NaNO_3 and KNO_3) which causes the particles to grow thus achieving a higher collection (impaction) efficiency. In addition to increasing the collection efficiency, humidifying the sampled air stream also results in decreased evaporative losses of semi-volatile nitrate (i.e., ammonium nitrate).¹⁷ At the end of the sample collection phase, the monitor diverts the sample flow from the collection and vaporization cell, while maintaining flow through the sample line, denuder and humidifier, and purges the cell with nitrogen (N_2) gas. The nitrogen flows through the cell and into a nitrogen oxide NO_x analyzer (pulse analyzer). The impaction strip is then flash heated by current from a battery until reaching an infrared cutoff ($\sim 350^\circ\text{C}$). Typical heating times are 70-90 milliseconds (ms). The vaporization/decomposition process converts the particulate nitrate contained in the sample to NO_x (a combination of NO and NO_2). The evolved NO_x is transported by the nitrogen carrier gas into the pulse analyzer, where the NO_2 is subsequently reduced to NO by a heated molybdenum converter, and detected (along with the initial NO present) by chemiluminescence. The pulse analyzer output is integrated to yield the nitrate concentration. Additionally, the analyzer baseline is read prior to each analysis flash and subsequently subtracted from the integrated result, to yield the final, corrected pulse. At the end of the analysis period the system returns to sample collection. The pulse generator components (cyclone, denuder, humidifier and collection/vaporization cell) are housed in an enclosure which is ventilated with outside air to maintain sampling temperatures close to ambient. For the purpose of this paper the sampling (impaction) period was 13.5 min followed by a 1.5 min analysis period. This results in a new particulate nitrate measurement in $\mu\text{g}/\text{m}^3$ every 15 min. The above mentioned system is based on integrated collection and vaporization cell technology developed by Stolzenburg and Hering.¹⁷

Flow and span audits may be programmed into the monitors sampling program or performed manually. Analyzer flow audits are done during the sample collection step, without cycle interruption. The results of the flow audit are used to set the N_2 carrier gas flow during the

analysis phase of the 15 min cycle. Prior to sampling, the pulse analyzer is calibrated with 5.0 ppm NO in N₂ (O₂ free) span and N₂ (99.995%) zero gases. Daily span audits are used to monitor the calibration. Span audits were performed daily during the Rubidoux field study beginning at 12:00 AM each day. For the laboratory-based studies, span audits were performed at the beginning of each laboratory session. In addition, the system (pulse generator + pulse analyzer) is calibrated manually using aqueous standards applied directly to the collection substrate. The collection surface is then manually flashed and the instrument response recorded. Control standard injections were used to monitor the aqueous calibration.

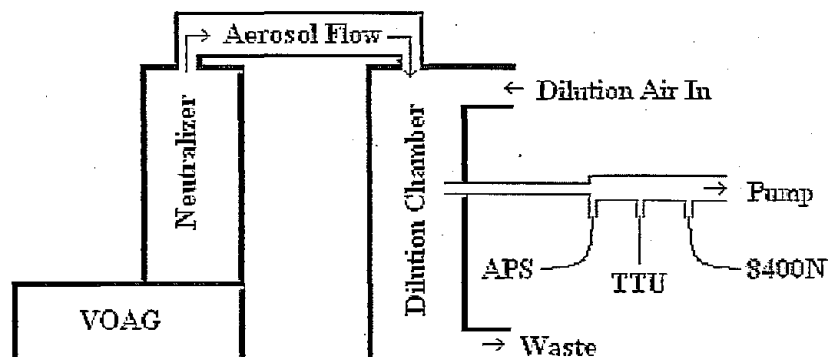
TTU IC-Based Soluble Particulate Component Monitor (prototype). The TTU prototype instrument consists of two main components: (1) particle collector with parallel plate denuder and peristaltic pump and (2) ion chromatograph (including concentrator columns, column switching valves, analytical columns and conductivity detector) for sample analysis. Ambient samples are pulled through a cyclone operated at 10 L/minute to remove particles above 2.5 μ m. After the cyclone inlet, the 10 L/minute flow is split with 5 L/minute going to waste. The remaining 5 L/minute sample flow passes through a wet-wall parallel plate denuder to remove potential gaseous interferences (positive artifacts). Ambient particles pass through the wet-wall, parallel plate denuder and into a cylindrical chamber through an orifice. A hydrophobic Teflon filter (Fluoropore, Millipore Corp., Billerica, MA) is placed at the chamber exit to prevent particles from escaping the chamber. At the chamber entrance orifice, the sampled air comes in contact with a stainless steel capillary tube through which de-ionized (DI) water is pumped. Acceleration of the sampled air through the orifice aspirates the water into a fine mist and places the sampled PM in a water matrix. Any nitrate (or other water soluble ion) contained in the particles goes into solution thus effectively reducing any evaporative losses (negative artifacts). The sample containing mist then continues through the chamber, encounters the hydrophobic filter, and condenses into droplets which then fall to the bottom of the chamber. The chamber bottom is cone shaped causing the water droplets to collect at a point. An additional stainless steel capillary is positioned at the cone point and extends through the chamber wall. The collected water is removed from the chamber bottom by means of the peristaltic pump and directed to the IC for subsequent analysis. Upon reaching the IC portion of the monitor, the ion containing water is pumped into a short concentrator column (TAC-ULP1, Dionex Corp., Sunnyvale, CA) filled with resin. The resin binds the nitrate and concentrates the sample over a period of 15 min. At the end of the 15 minute sampling period, the effluent from the mist chamber is switched to a second, alternate column of identical design. The original concentrator column is then back-flushed with IC eluent (~25 mM NaOH) causing the nitrate ions to be released to the analytical column for analysis. Thus, the two concentrators are alternately switched every 15 min for continual collection and analysis of nitrate. The IC analysis (including concentrator column switching) is automated under computer control through the use of an IBM Thinkpad™ computer and the standard Dionex software package (PeakNet™).

Calibration of the TTU prototype instrument is obtained by preparation of nitrate solutions of known and varying concentration. These solutions are subsequently injected into the sample loop (known volume) of the IC and analyzed. Using the injection loop volume and the calibration standard concentrations, the mass (μ g) of nitrate injected into the IC for analysis is calculated. Upon completion of the calibration standard analysis, the area count response is recorded and

plotted versus the corresponding injected nitrate mass in μg . After all calibration standards are injected and analyzed a calibration curve is plotted using linear regression analysis with independent variable μg nitrate. During ambient monitoring, an area count is obtained for each 15 minute cycle. The corresponding μg reading on the calibration curve can then be found and recorded. This mass of nitrate collected can then be divided by the total volume sampled (i.e., $5 \text{ lpm} \times 15 \text{ min} = 75 \text{ L} = 0.075 \text{ m}^3$) to give a 15 min nitrate concentration in $\mu\text{g}/\text{m}^3$. Calibration of the TTU prototype instrument was monitored by daily control standard injections. The TTU prototype instrument and its operation are described in Al-Horr *et al.*¹⁹ Instrumentation based on similar principles is described by Weber *et al.*²⁰ and Simon *et al.*²¹⁻²² Due to manufacturer's quality assurance issues associated with IC components of the TTU prototype instrument, limited data were obtained from this instrument during the three week Rubidoux field sampling period. However, these issues have been addressed and the prototype instrument has performed without incidence during post-Rubidoux laboratory evaluation.

Simulated Ambient Aerosol Generation System. A TSI (Shoreview, MN) Model 3941 Supermicrometer Monodisperse Aerosol Generation System was used to generate a simulated ambient aerosol of uniform size and shape (monodisperse). The complete Model 3941 System consists of a Model 3450 Vibrating Orifice Aerosol Generator (VOAG), a Model 3054 Aerosol Neutralizer, and a Model 3074B Filtered Air Supply. An HPLC solvent delivery system (pump) was used in conjunction with the TSI Model 3941 to facilitate longer operating periods than were normally obtainable with the system as configured from the manufacturer. In addition to the size and shape uniformity, the model 3941 allows the researcher to change and control the chemical composition and concentration of the generated aerosol. Both sodium nitrate and ammonium nitrate aerosols were produced by the Model 3941 and used in the laboratory evaluation of the previously described monitors. A TSI Model 3321 Aerodynamic Particle Sizer Spectrometer (APS) was used to characterize (particle size and concentration) the laboratory generated aerosol prior to sampling by the instruments being evaluated. Figure 1 shows a schematic representation of the overall simulated ambient aerosol generation system.

Figure 1. Schematic representation of the simulated ambient aerosol generation system used in the laboratory based studies.



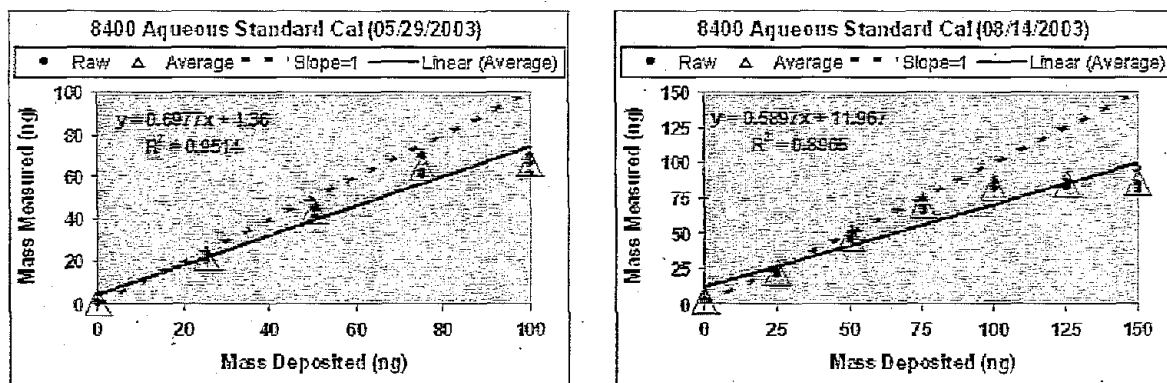
Integrated Filter Samples. During the Rubidoux field study, independent integrated nitrate filter samples (3-, or 24-hr) were collected by Brigham Young University using their PC-BOSS sampler.^{8, 10-12} In addition, 24-hr integrated nitrate filter samples were collected by the SCAQMD using a speciation sampler similar to the Met-One SASS. Nitrate in samples collected by both the PC-BOSS and SCAQMD sampler was determined by IC analysis in each corresponding lab.

RESULTS AND DISCUSSION

Laboratory Studies Results

8400N Laboratory-Based Evaluation. Prior to monitor comparisons, the R&P 8400N was evaluated using aqueous nitrate standards injected directly onto the collection/vaporization surface. Initial aqueous calibration studies involved the "One-drop, two-drop" method in which a single concentration standard (100 ng/ μ L NO_3) was used and the mass of nitrate deposited on the collection surface was varied by changing the injection volume. With this calibration method, both the amount of nitrate and water increase with an increase in injection volume. Typically, injection volumes ranged from 0.25 - 1.5 μ L (25-150 ng NO_3). This calibration method is analogous to that recommended by the manufacturer.²³ The zero point was obtained by injecting 0.5 μ L DI water. Figure 2 shows a comparison of mass deposited vs mass measured using the "One-drop, two-drop" method on two separate occasions. As indicated, a non-linear

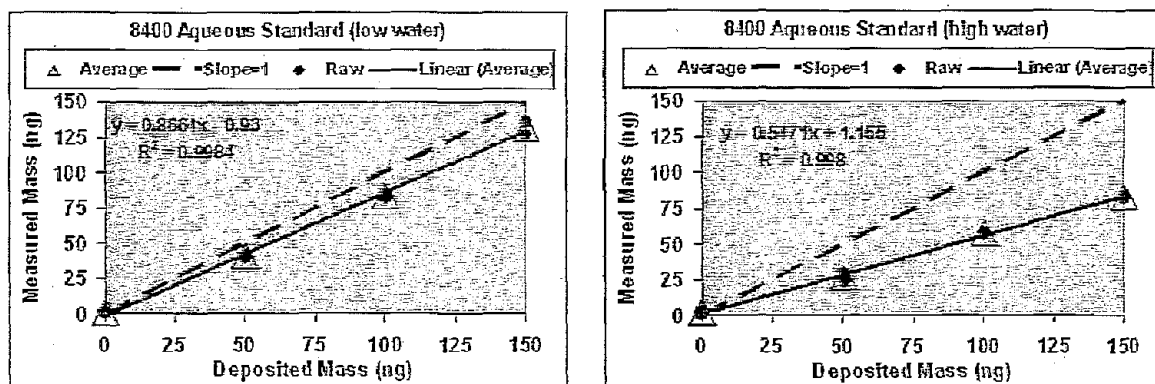
Figure 2. Comparison of Mass Deposited vs Mass Measured Using the "One-drop, two-drop" Method on Two Separate Occasions.



response was obtained when large injection volumes were used (i.e., $>0.75 \mu\text{L}$, corresponding to an ambient nitrate concentration of $5 \mu\text{g}/\text{m}^3$ for a 15-min average). This observation suggests two hypotheses (1) at high nitrate concentrations the instrument response is non-linear, or (2) the increase in the amount of water matrix results in the instrument response becoming non-linear. To test these hypotheses, a second calibration procedure (constant volume procedure) was used in which a constant volume (0.5 or 1.0 μL) of standard with varying concentrations was deposited on the collection surface. The concentration range of the standards used in this method was from 50-300 ng/ μL NO_3 . With this method, the deposited nitrate mass changes while the water amount remains relatively constant. Figure 3 shows a comparison of mass deposited vs mass

measured using the constant volume procedure. The figure on the left represents a low- water content calibration procedure in which masses of 0, 50, 100, and 150 ng of nitrate were deposited on the collection surface using 0.5 μL each of DI water (0 ng), and 100 ng/ μL (50 ng), 200 ng/ μL (100 ng), and 300 ng/ μL (150 ng NO_3 standards, respectively. The figure on the right

Figure 3. Comparison of Mass Deposited vs Mass Measured Using the Constant Volume Procedure.

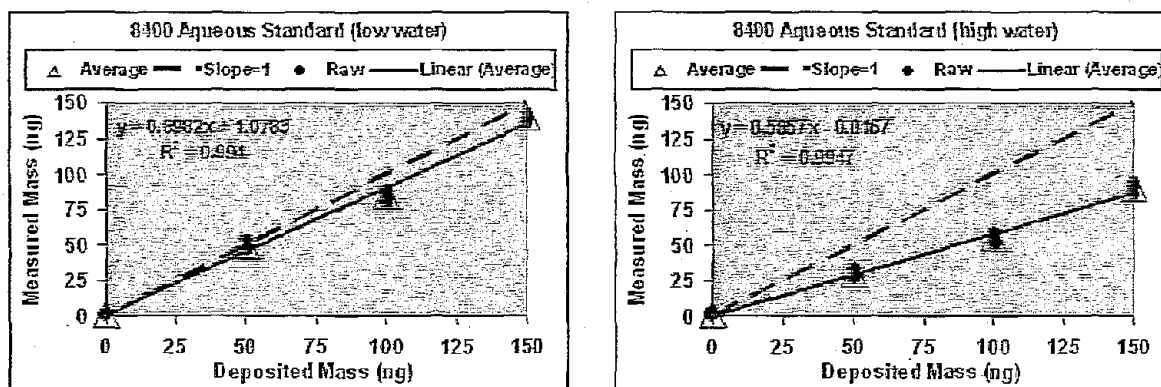


represents a high-water content calibration) procedure where identical masses were deposited using 1.0 μL ($2\times$ low-water injection volume) injection volumes and standards half as concentrated as those used in the low-water procedure. As indicated in both plots, a linear response is obtained for both the low- and high-water procedures. However, the response (calibration slope) is decreased when the high-water procedure is used as compared to that of the low-water. A factor of two increase in the amount of water injected onto the flash strip while holding the mass of nitrate injected constant, results in as much as a 35% decrease in the calibration slope. The linear response of both curves (even at high nitrate loading) and the decrease in instrument response associated with an increase in deposited water suggests that the previously observed non-linear response with the manufacture suggested calibration procedure is due to a matrix (water) interference.

Three hypotheses were proposed to explain the effect of the water matrix on the instrument response during the aqueous standard calibration studies. First, it was hypothesized that excess water on the collection surface could result in significant amounts of water vapor being transported to the chemiluminescence detector after flash vaporization. The evolved water vapor may then have a quenching effect on the chemiluminescence signal measured by the pulse detector. To test this hypothesis, a Nafion dryer (Perma Pure Inc., Toms River, NJ) was placed in line between the pulse generator and pulse analyzer. The presence of the drier will effectively remove any evolved water vapor from the sample stream prior to its entering into the chemiluminescence detector. The constant volume calibration procedure was then repeated with both the low and high water standards. Figure 4 shows the comparison of deposited nitrate mass vs measured mass for both the low- and high-water procedures. As indicated in the figure, the presence of the Nafion dryer in-line between the pulse generator and pulse analyzer did not

improve the slope degradation with increased water content. Therefore it is assumed that the decrease in instrument response in the presence of excess water is not due to quenching effects by water vapor in the pulse analyzer.

Figure 4. Comparison of Deposited Nitrate Mass vs Measured Mass for Both the Low- and High-Water Procedures with the Nafion Drier In-Line between the Pulse Generator and Pulse Analyzer.

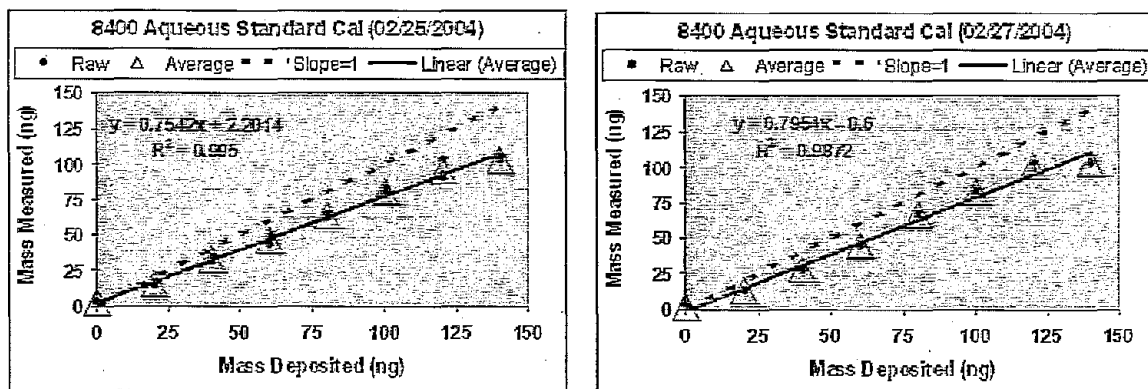


The second hypothesis was that the presence of water on collection surface (flash strip) results in a decreased NO_3 to NO conversion efficiency. Ideally, the flash vaporization process would result in complete conversion of the particulate nitrate to NO which is subsequently detected by the chemiluminescence analyzer. The presence of water on the flash strip will result in less energy being available during the vaporization process to quantitatively convert the nitrate to NO . This incomplete vaporization will result in the production of significant amounts of NO_2 . Under normal operating conditions, the presence and amount of NO_2 will not have an effect on the instrument response.²⁴ However, a reduced molybdenum converter efficiency (<95%) in converting NO_2 to NO in the pulse analyzer will result in under-determination of nitrate when the flash vaporization step results in a high NO_2/NO ratio. The molybdenum converter efficiency was determined by first spanning the pulse analyzer with a NIST traceable NO calibration gas of known concentration (5.01 ppm, Scott Specialty Gases, Plumsteadville, PA). A known concentration of NO_2 calibration gas was then passed through the pulse analyzer and the instrument response recorded. The above mentioned procedure resulted in a molybdenum converter efficiency of less than 50%. The decreased molybdenum converter efficiency may explain the non-linear response observed during the "One-drop, two-drop" calibration method (Figure 2). At higher injection volumes (i.e., >0.75 μL) the excess water present results in a higher NO_2/NO ratio where only a fraction of the NO_2 is converted to NO and detected. In addition, the decrease in slope associated with an increase in water during the constant volume procedures (Figures 3 and 4) can be attributed to a decreased molybdenum converter efficiency.

A new molybdenum converter (>95% efficiency, see procedure above) was installed in the instrument and the "One-drop, two-drop" calibration procedure repeated. Figure 5 shows the

results of this calibration on two separate occasions. As indicated in the figure, linearity of the calibration curve is improved with the new molybdenum converter installed in the 8400N pulse analyzer. A slight departure from linearity is still observed at high injection volumes. However,

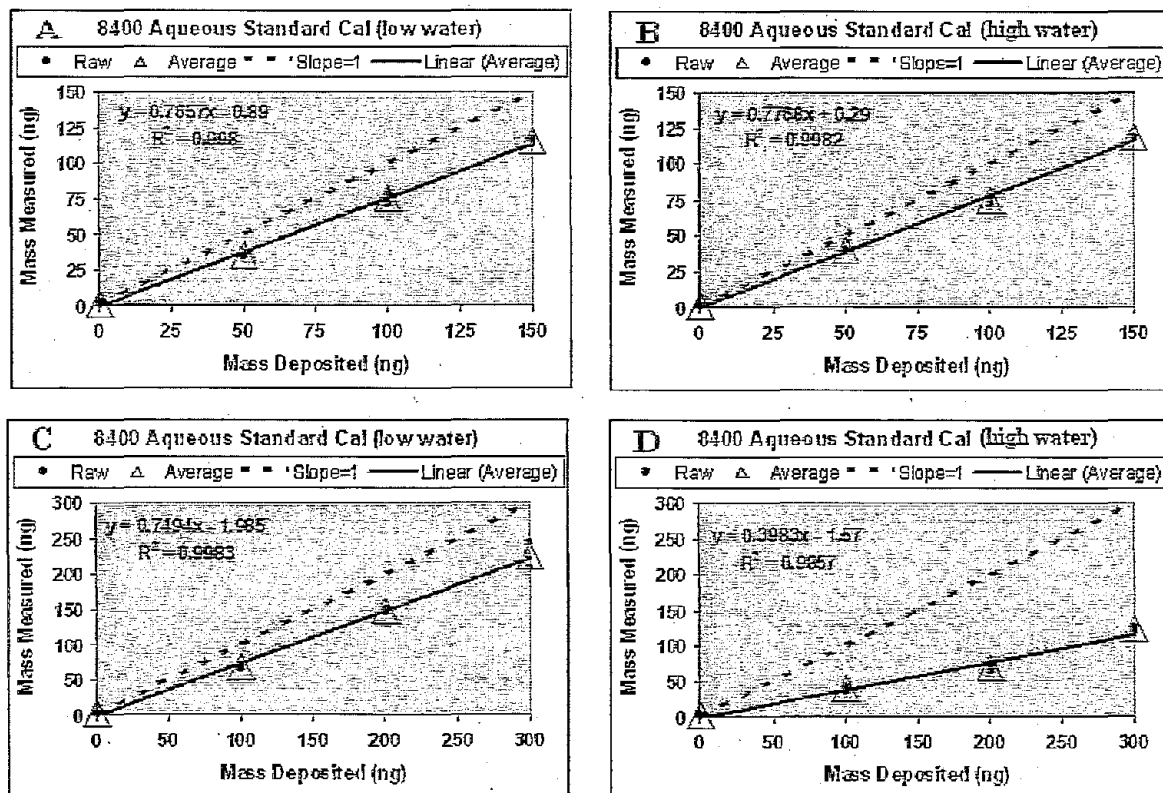
Figure 5. Comparison of Mass Deposited vs Mass Measured Using the “One-drop, two-drop” Method on Two Separate Occasions after Replacement of Pulse Analyzer Molybdenum Converter.



the volume required to produce a decrease in response is increased by a factor of 2 (i.e., ~150 μL) as compared to the volume required (i.e., ~75 μL) to produce a similar instrument response with use of the faulty molybdenum converter. The constant volume calibration procedure was repeated to determine the change in calibration slope with an increase in water on the flash strip with the new molybdenum converter installed in the pulse analyzer. As indicated in Figures 6A and 6B, no observable change in slope is observed in going from the low-water to the high-water procedure. Figures 6C and 6D illustrate an additional constant volume calibration procedure where both the deposited nitrate and water masses were increased by a factor of 2 by doubling the injection volumes (i.e., 1.0 and 2.0 μL for low- and high-water procedures, respectively). This procedure resulted in a decrease of the calibration slope by approximately 50 % when excess water was placed on the flash strip (see Figures 6C and 6D). The similarity of the calibration slope in Figure 6C (high-nitrate, medium-water) to those in Figures 6A (low-nitrate, low water) and 6B (low-nitrate, medium-water) further strengthen the assumption that high nitrate loading is not responsible for the decreased instrument response. Although improved with addition of a functioning molybdenum converter, a decrease in instrument response is still observed when excess water is placed on the flash surface (see Figures 5 and 6).

The third hypothesis investigated is that under conditions of heavy water loading, some but not all sampled nitrate is vaporized during the flash process. The residual nitrate remains in the particulate form and is removed from the sample stream by an in-line Teflon filter prior to entering the pulse analyzer. This assumption was tested by placing a 25 mm Teflo™ (Pall Corp. Ann Arbor, MI) filter in-line between the pulse generator and the pulse analyzer to collect any

Figure 6. Comparison of Deposited Nitrate Mass vs Measured Mass for Both the Low- and High-Water Procedures After Replacement of Pulse Analyzer Molybdenum Converter. In Figures C and D, Both the Deposited Nitrate and Water Mass Were Increased by a Factor of 2 by Doubling the Injection Volumes.



particulate nitrate remaining after the flash vaporization step. The filter can then be extracted and the deposited nitrate mass determined by IC analysis. Repeated 1.0 μL injections were made onto the collection surface using a concentrated (300 ng/ μL from NaNO_3) NO_3 standard solution. After each injection, the collection surface was flashed and the instrument response recorded. Upon completion of the final injection/flash step, the nitrate collected on the in-line filter was determined. The sum of the filter collected nitrate mass and the 8400N measured mass was then obtained and compared to the total mass deposited on the collection surface. The results of this comparison on two separate occasions are given in Table 1. The presence of nitrate on the in-line filter (up to 35% of the total mass deposited) suggests that the presence of excess water does have an effect on the NO_3 to NO conversion efficiency and hence the instrument response.

As stated previously, major components of ambient fine particulate matter include: sulfate, nitrate, ammonium, and hydrogen ions; trace elements (including toxic and transition

Table 1. R&P 8400N Aqueous Calibration Mass Recovery Results (Water Interference).

Date:	June 10, 2003	July 07, 2003
Deposited Mass (ng)	3600	6000
8400N Measured Mass (ng)	2057.9	4574
In-line Filter Mass (ng)	1253.5	1182.8
Measured + Filter Mass (ng)	3311.4	5756.8
% Mass Measured by 8400N	57.2%	76.2%
% Mass of Mass on Filter	34.8%	19.7%
% Mass Recovered (Measured + Filter Mass)	92%	95.9%

metals); organic material; and elemental carbon (EC). It is reasonable to assume that the presence of these other PM components, in addition to water, will also have an effect on the NO_3 to NO conversion efficiency and hence, instrument response. This assumption was investigated by again placing a 25 mm Teflo filter in-line between the pulse generator and the pulse analyzer to collect any residual particulate nitrate after the flash vaporization step. Repeated 1.0 μL injections were made onto the collection surface using a 250 $\text{ng}/\mu\text{L}$ NO_3 standard solution prepared from NH_4NO_3 . After each injection, the collection surface was flashed and the instrument response recorded. Upon completion of the final injection/flash step, the nitrate collected on the in-line filter was determined by IC analysis. The above process was then repeated using a 250 $\text{ng}/\mu\text{L}$ NO_3 + 250 $\text{ng}/\mu\text{L}$ SO_4 standard solution prepared from NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$, respectively. The results of this comparison for the two separate standard solutions are given in Table 2. The increased nitrate mass on the in-line filter for the NH_4NO_3 + $(\text{NH}_4)_2\text{SO}_4$ injections as compared to the single component NH_4NO_3 injections indicate that the presence of other PM components on the flash strip may result in a decreased instrument response. The low percentage of mass recovered for both the single- and double-component standards suggests additional loss mechanisms that warrant further evaluation.

In addition to effecting the slope and shape of the calibration curve (which may result in significant errors in ambient nitrate determinations), water has the potential to interfere with the actual ambient measurement. The hygroscopic nature of nitrate PM results in significant amounts of water being associated with the particles as they exist in the ambient air.¹⁸ In addition, the sample stream is humidified once inside the pulse generator resulting in even further hydration. Therefore, it is reasonable to assume that a situation similar to a "high-water" aqueous standard calibration may exist during periods of extremely high RH or high nitrate concentrations resulting in a decreased NO_3 to NO conversion efficiency and therefore an under determination of ambient nitrate concentrations by the 8400N. The presence of additional PM components may result in a similar decrease in instrument response under ambient conditions.

Table 2. R&P 8400N Aqueous Calibration Mass Recovery Results (PM Component Interference).

Standard:	NH_4NO_3	$\text{NH}_4\text{NO}_3 + (\text{NH}_4)_2\text{SO}_4$
Deposited Mass (ng)	8000	8000
8400N Measured Mass (ng)	3937.9	3026.1
In-line Filter Mass (ng)	690.8	2595.7
Measured + Filter Mass (ng)	4628.7	5621.8
% Mass Measured by 8400N	49.2%	37.8%
% Mass of Mass on Filter	8.6%	32.4%
% Mass Recovered (Measured + Filter Mass)	57.8%	70.2%

This decrease in response may be compounded further with multi-component aerosols such as exist in ambient air.

Comparison of 8400N and TTU Prototype Results (Simulated Nitrate Aerosol). The 15-min average TTU prototype and 8400N monitor nitrate results obtained while sampling a laboratory generated ammonium nitrate aerosol (1.2 μm average particle diameter) are given in Figure 7. Changes in aerosol concentration were obtained by adjusting the dilution air flow rate into the dilution chamber of the particle generation system (see Figure 1). During these laboratory studies, precautions were taken to provide a pure, dry ($\text{RH} < 20\%$) aerosol to the instruments for sampling to eliminate any potential matrix effects. Both monitors show general agreement with respect to changes in nitrate concentrations. However, the 8400N shows a more rapid response to increases and subsequent decreases in nitrate concentrations (see Figure 7, open circles). The slight delay in response associated with the TTU prototype monitor can be attributed to the time needed for droplet formation and dislocation in the TTU particle collector. In addition, a small portion of the dislodged droplets are held up on the chamber walls, thus adding to the delay. The residence time of the droplets on the chamber walls can be reduced considerably by treating the interior surface of the particle collector with a wetting agent (e.g., Rain-X). Figure 8 shows a comparison (with regression statistics) of TTU vs 8400N nitrate results obtained while sampling the laboratory generated ammonium nitrate aerosol. The highlighted data points (white circles, see Figure 8) represent samples taken immediately following dramatic increases or decreases in nitrate concentration (see Figure 7, open circles). During controlled laboratory conditions (low RH, single component monodisperse aerosol), similar results were obtained by both the TTU prototype and R&P 8400N particulate nitrate monitors with a regression slope near unity ($1.02x + 0.67$, $n=43$) and a R^2 value near 0.95.

Figure 7. TTU Prototype and 8400N Monitor Nitrate Results (15-min average) Obtained While Sampling a Laboratory Generated Ammonium Nitrate Aerosol. Open Circles Represent Time Periods Immediately Following Dramatic Changes in Nitrate Concentration.

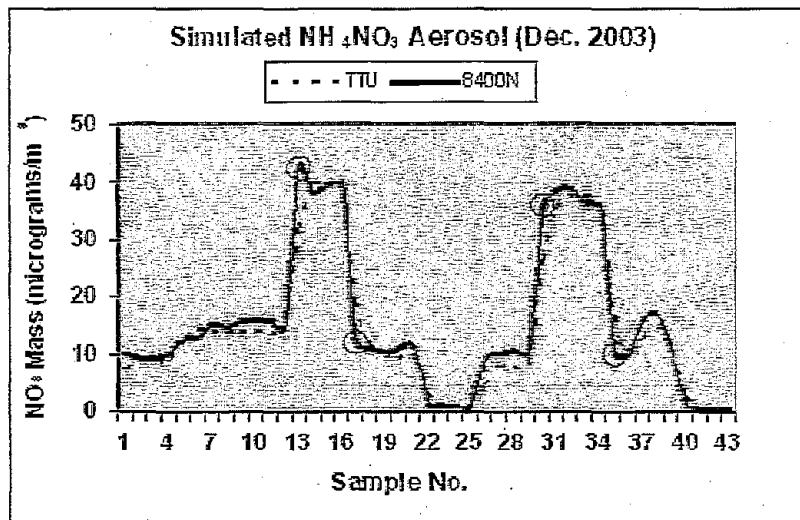
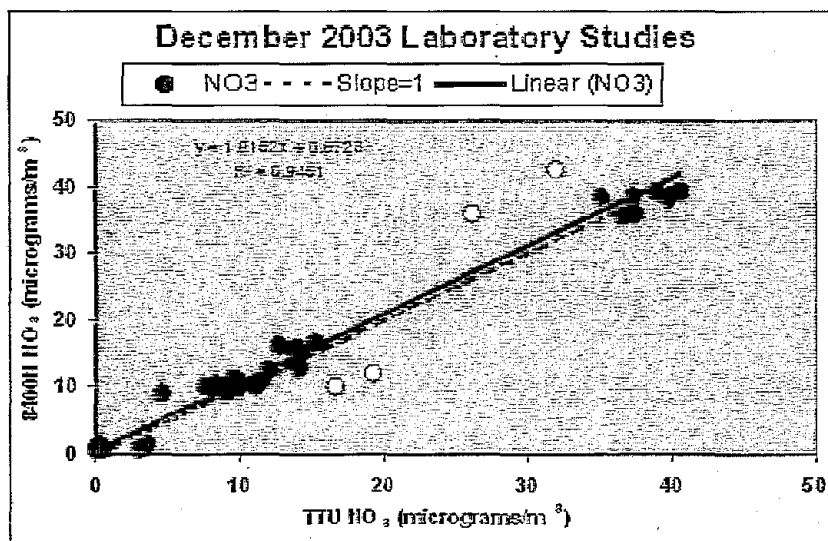


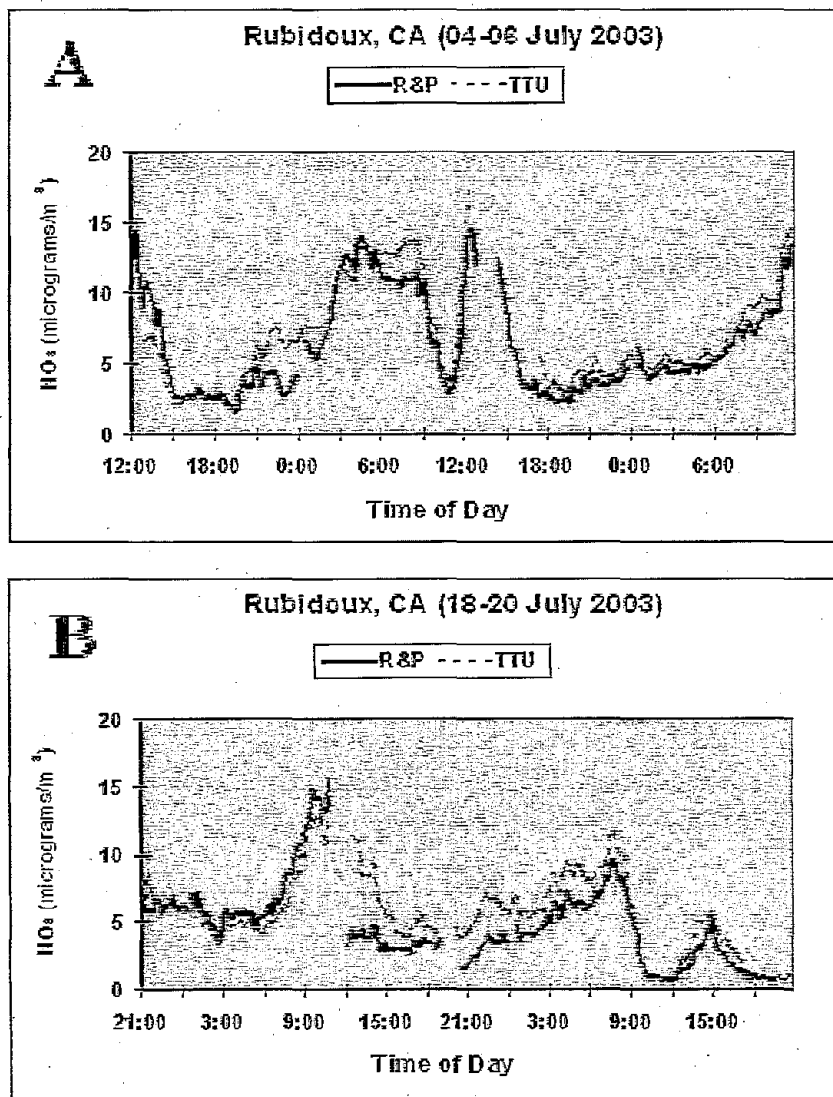
Figure 8. Comparison of TTU and 8400N Nitrate Results (15-min average) Obtained from Sampling a Laboratory Generated Ammonium Nitrate Aerosol. The Highlighted Data Points (white circles) are Due to Differences in Instrument Response Time to Changes in Nitrate Concentration.



Rubidoux, CA Field Study Results

Comparison of 8400N and TTU Prototype Results. The 15-min average TTU prototype and 8400N monitor nitrate results obtained during two, 2-day periods (12:00 July 4-12:00 July 6 and 21:00 July 18-21:00 July 20) from the July 2003 study at Rubidoux, CA are given in Figures 9A and 9B. These figures illustrate changing particulate nitrate concentrations during the respective

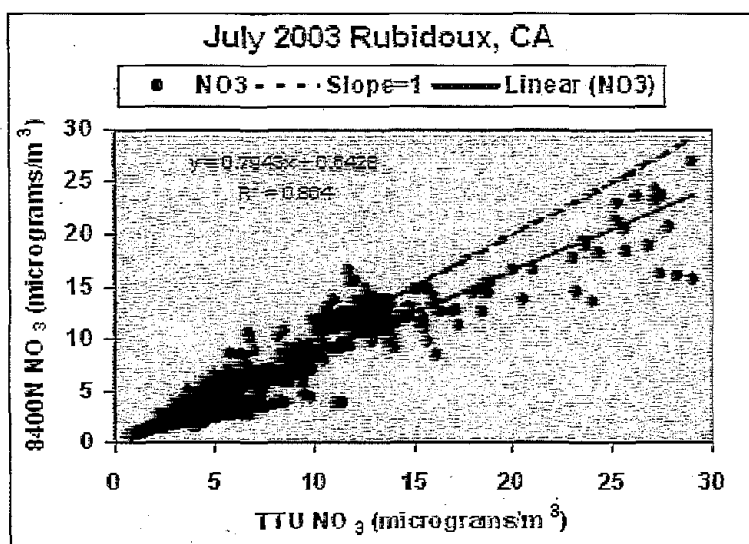
Figure 9. The TTU Prototype and 8400N Monitor Nitrate Results (15-min average) Obtained During: A) 12:00 July 4-12:00 July 6 and B) 21:00 July 18-21:00 July 20, from the July 2003 Study at Rubidoux, CA.



periods over the Rubidoux/Riverside area. Typically, peaks in particulate nitrate concentrations

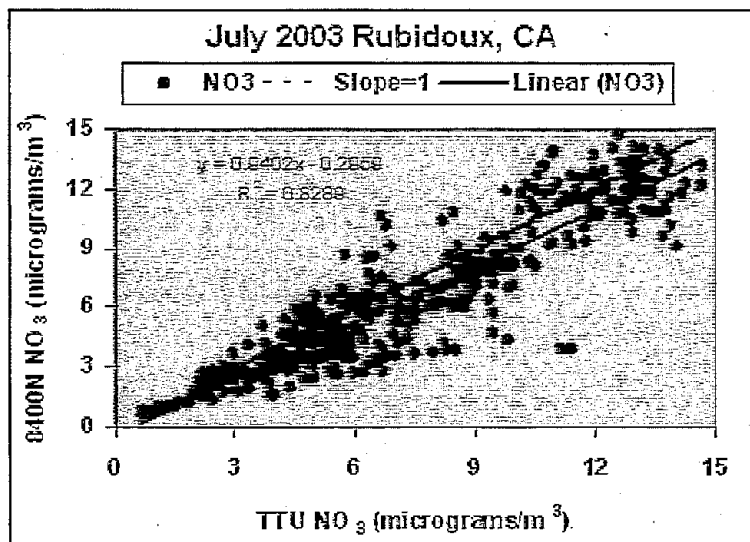
are observed around noon (12:00) each day. However, a large nitrate peak is observed beginning in the late evening on July 4 and extending to the early morning hours of July 5 (see Figure 9A). This peak is attributed to a local fireworks display and resulting brush fire near the Rubidoux site. The data shown in Figure 9 indicate that both instruments are capable of tracking rapid (i.e., 15-30 min) changes in ambient particulate nitrate concentrations. Figure 10 shows a comparison (with regression statistics) of TTU vs 8400N particulate nitrate results obtained during the Rubidoux, CA field study. As stated previously, limited data were obtained from the the TTU

Figure 10. Comparison (with regression statistics) of TTU vs 8400N Particulate Nitrate Results (15-min Average) Obtained During the Rubidoux, CA Field Study.



instrument due to IC component quality assurance issues. Therefore, this figure represents data obtained only during periods when both instruments were operating under control. The results obtained at Rubidoux show good agreement between the TTU and 8400N instruments at lower nitrate concentrations (i.e., <15 µg/m³). At higher nitrate concentrations (i.e., >15 µg/m³), the 8400N measures lower than the TTU instrument. Linear regression of TTU vs 8400N particulate nitrate results for the entire study period gives $y = 0.79x + 0.64$ ($n = 451$) with an R^2 value of 0.86. Limiting the data set to those values at or below 15 µg/m³ results in a regression slope closer to unity ($y = 0.94x - 0.30$, $n = 403$, $R^2 = 0.83$) as shown in Figure 11. As stated in the previous section, divergence at high nitrate concentrations was not observed when the TTU prototype and 8400N instruments were compared under controlled laboratory conditions (see Figure 7). It is therefore assumed that the divergence (under-measurement) of the 8400N at higher particulate nitrate concentrations is due to a matrix type interference (i.e., water, other particulate components, etc.) that exists under ambient conditions but is eliminated under controlled conditions.

Figure 11. Comparison (with regression statistics) of TTU vs 8400N Particulate Nitrate Results (15-min Average) $\leq 15 \mu\text{g}/\text{m}^3$ Obtained During the Rubidoux, CA Field Study.

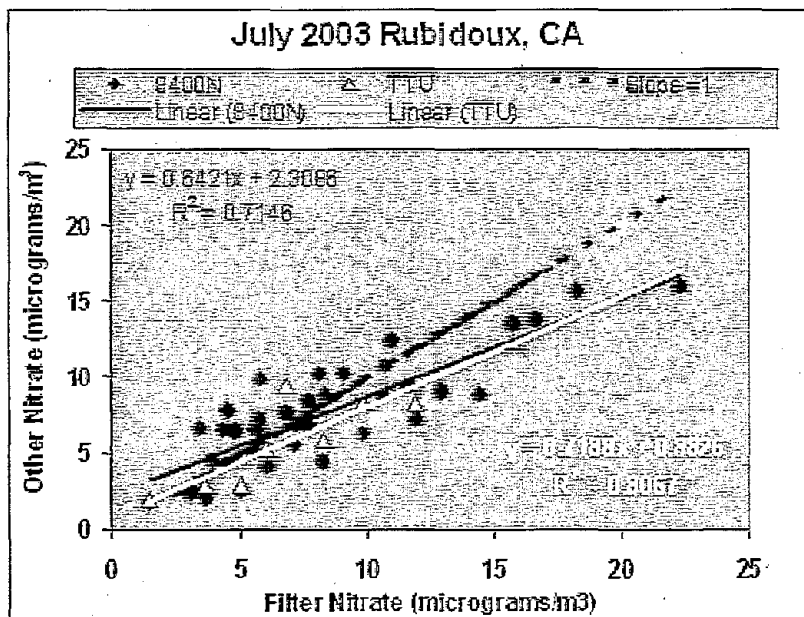


Comparison of Semi-continuous and Integrated Sampler Results. The results obtained by the 8400N and the TTU prototype for the semi-continuous determination of particulate nitrate were averaged (3-, or 24-hr) during the study period for comparison with results obtained from the PC-BOSS and SCAQMD samplers. The results of this comparison (with regression statistics) are given in Figure 12. The abscissa (filter nitrate data) in Figure 12 contains both PC-BOSS (3- and 24-hr) and SCAQMD (24-hr) results. Due to the previously mentioned IC associated issues with the TTU monitor, very limited data were obtained with this instrument for comparison with the integrated filter samples (Figure 12, white triangles). Al-Horr *et al.*, gives a more complete comparison of PC-BOSS and semi-continuous nitrate results obtained with a newly commercialized version of the TTU prototype instrument.²⁵ Comparison of filter based results with semi-continuous 8400N results show general agreement at concentrations at or below $10 \mu\text{g}/\text{m}^3$. Above this concentration, the 8400N measures lower than the filter based methods, possibly due to the previously described matrix effects.

SUMMARY

Studies conducted at the EPA facility in Research Triangle Park, NC and at a field study in Rubidoux, CA have demonstrated the capability for the semi-continuous determination of particulate nitrate. However, these studies have indicated that the presence of water and other matrix materials (i.e., other PM components) on the collection surface of the 8400N results in a decreased instrument response during both calibration procedures and ambient determinations.

Figure 12. Comparison (with regression Statistics) of Filter (3- and 24-hr average) vs Semi-continuous Particulate Nitrate Results Obtained During the Rubidoux, CA Field Study.



The decrease in instrument response can result in significant under-determination of particulate nitrate at higher concentrations. Comparison of TTU prototype and 8400N results obtained while sampling a laboratory generated nitrate aerosol show good agreement at both low and high nitrate concentrations. The response time to changes in nitrate concentration for the TTU prototype was delayed as compared to the 8400N. This delay is associated with the time needed for droplet formation and dislocation in the particle collection chamber of the TTU instrument. Treating the interior surface of the particle collection chamber with a wetting agent such as Rain-X was shown to reduce the delays associated with droplet hang-up on the chamber walls. During the Rubidoux field study, both instruments were capable of tracking short term changes in particulate nitrate concentrations. Data from the July 2003 study period show good agreement between the 8400N and TTU instruments at lower nitrate concentrations (i.e., $<15 \mu\text{g}/\text{m}^3$). At higher nitrate concentrations (i.e., $>15 \mu\text{g}/\text{m}^3$) the 8400N was observed to measure lower than the TTU instrument. Similarly, comparison of filter based and 8400N results show good agreement at nitrate concentrations at or below $10 \mu\text{g}/\text{m}^3$ and divergence (under-measurement by the 8400N) at concentrations above this level. The under-determination at higher nitrate levels under ambient conditions may reflect the matrix (water, other PM components) interference observed during the laboratory studies. Further investigation (laboratory and field) is needed to elucidate and eliminate the interference associated with the R&P monitor and to identify and address any problems associated with the IC based instrument (TTU prototype and Dionex commercial units). In addition, further comparison studies should be performed with both semi-continuous and filter

based methods. These studies are necessary to validate the semi-continuous methods for the determination of ambient particulate nitrate.

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DISCLAIMER

This paper has been reviewed in accordance with the United States Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Semi-Volatile Material

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