

Performance & Collection Efficiency

of the URG 9000 Ambient Ion Monitor System



URG 9000D Ambient Ion Monitor
with ICS-2100 Reagent Free IC[®]

Introduction

This technical document contains the information you need to better understand the URG 9000 Series Ambient Ion Monitor, specifically the URG-9000D model.

- Introduction of the Ambient Ion Monitor
- Gas & Particle Phase Collection Efficiency
- Ion Chromatograph Analysis Method
- Results
- Publications - Research Papers Documenting Use of URG-9000D Ambient Ion Monitor

Ambient Ion Monitor

The URG-9000D Ambient Ion Monitor (AIM) is a scientifically advanced multi-pollutant monitoring method which allows for continuous measurements of particle sulfate, nitrate, ammonium, chloride, potassium, magnesium, calcium and sodium. At the same time, the AIM provides time resolved gas measurements of sulfur-dioxide, nitric acid and ammonia. The Ambient Ion Monitor configuration detailed in this document includes two Thermo Scientific Dionex ICS-2100 Reagent Free Ion Chromatographs® for the analysis of both anions and cations.

What the AIM Measures:

Particles:

- Nitrate
- Sulfate
- Ammonium
- Nitrite
- Phosphate
- Chloride
- Fluoride
- Sodium
- Calcium
- Potassium
- Magnesium
- Formate
- Acetate

Gases:

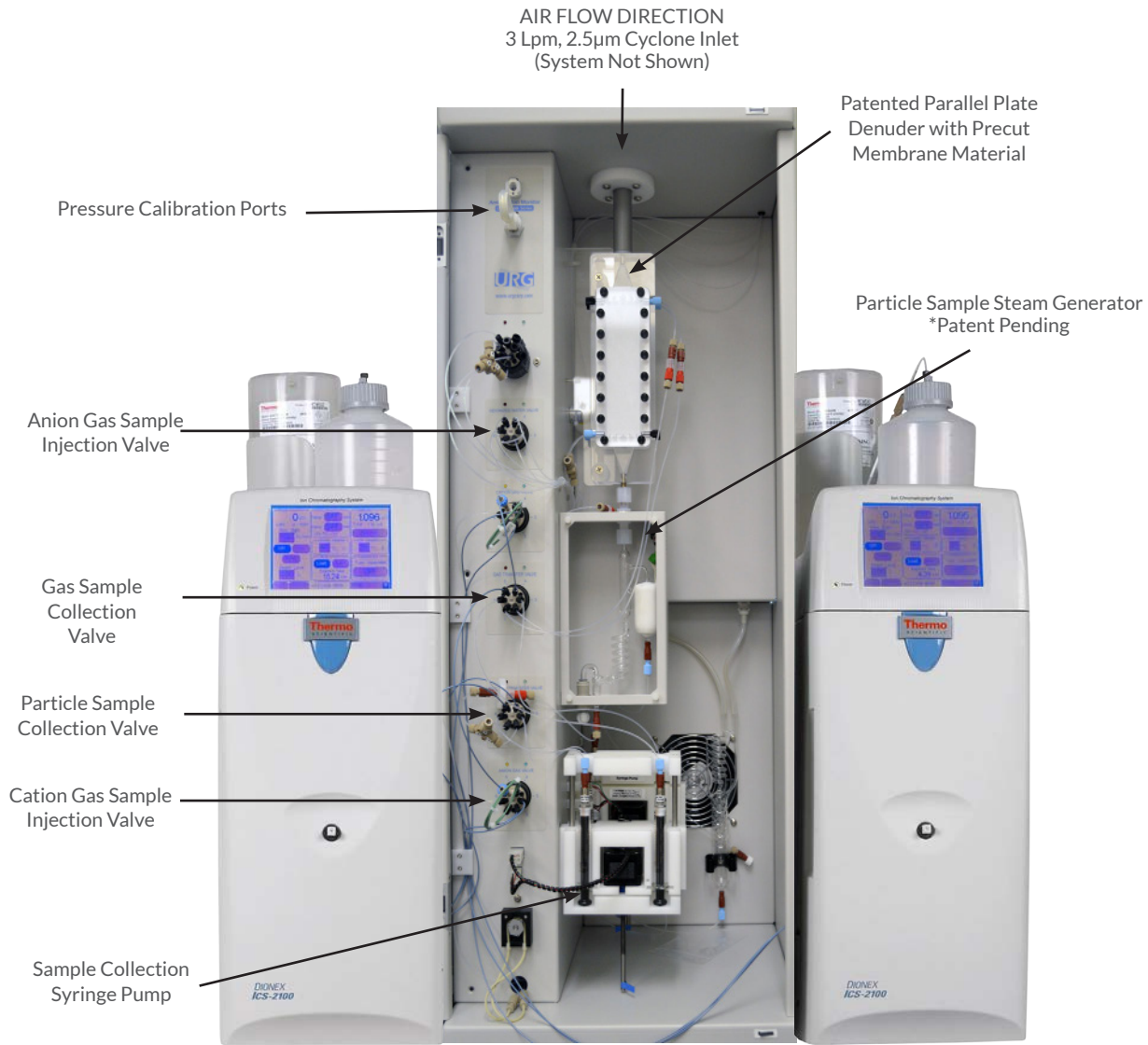
- Nitric Acid
- Sulfur Dioxide
- Ammonia
- Hydrogen Chloride
- Hydrogen Fluoride

IN THEORY

*If it is water-soluble
and can be analyzed by
Ion Chromatography
...The AIM can speciate it!*



Exhibit 1-1. Typical URG-9000D AIM Setup



ICS-2100 Reagent-Free Ion Chromatograph for Anion Gas and Particle Analysis
 8.5" w x 33" h x 20" d
 *with Deionized Water Reservoirs Installed

URG-9000D Ambient Ion Monitor
 19" w x 50" h x 16" d
 *with Standard Inlet Installed

ICS-2100 Reagent-Free Ion Chromatograph for Anion Gas and Particle Analysis
 8.5" w x 33" h x 20" d
 *with Deionized Water Reservoirs Installed

Gas Phase Collection Efficiency

A liquid denuder collection efficiency test was done with EPA certified SO₂ concentrations from 20-550ppb (parts per billion) of SO₂ gas produced with tanked SO₂, zero air and a dilution calibrator. A 5.5mM H₂O₂ denuder solution was used. Concentration measurements of SO₂ gas were taken both before the inlet and after the outlet of the denuder, using a “Thermo Environmental 43C SO₂ Analyzer.” Exhibit 1-3 and 1-4 illustrates the data from the denuder collection efficiency test. The denuder collection efficiency was found to remain at 99.8% for all concentrations.

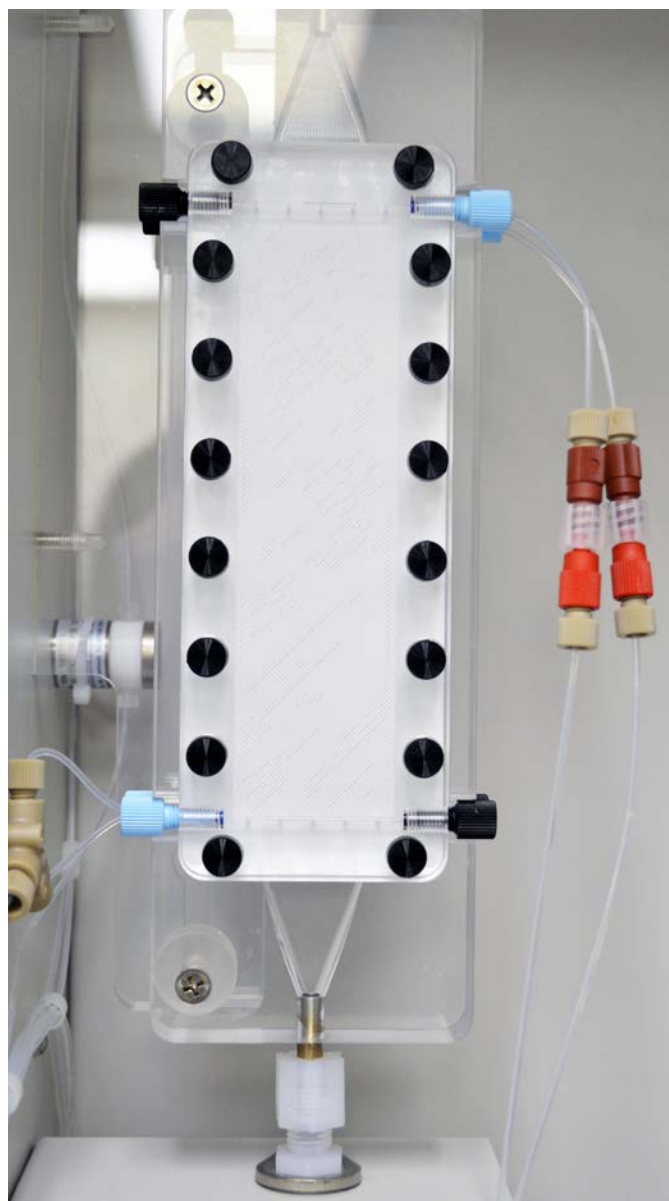


Exhibit 1-2. Patented Parallel Plate Denuder with Pre-cut Membrane

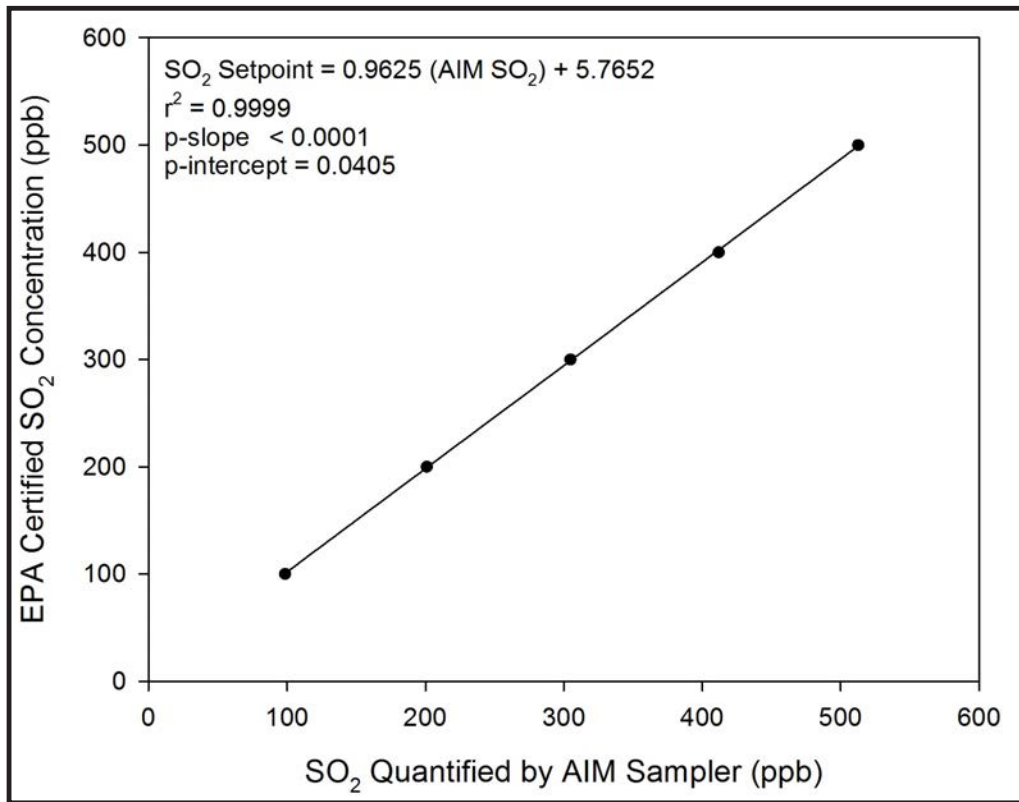


Exhibit 1-3. Comparison of Known SO₂ Concentrations to AIM Reported SO₂ Concentrations.

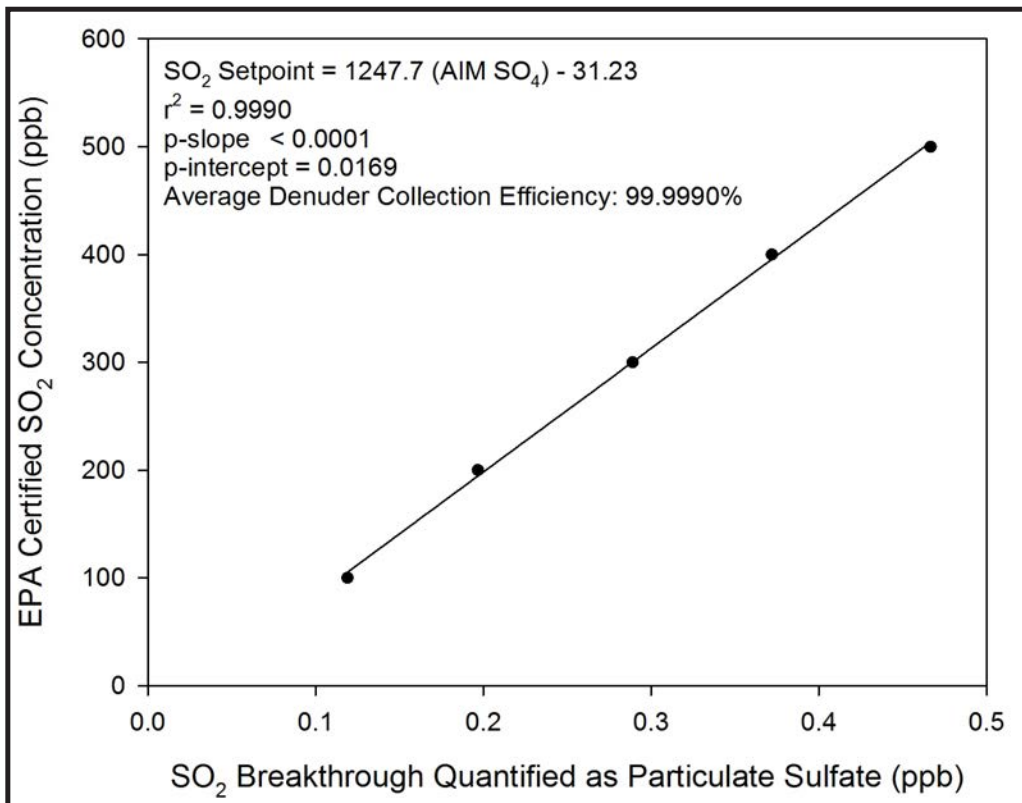


Exhibit 1-4. Comparison of Known Concentrations to AIM Reported Sulfate Concentrations (SO₂ Breakthrough).

Particle Phase Collection Efficiency

Water soluble particles are grown substantially in a patent pending super saturated steam environment. These “grown” particles are quantitatively (more than 99%) removed by an Inertial Particle Separator and injected into an ion chromatograph for analysis. Measurements of blank concentrations and measurements of the sampling efficiency with a back-up filter were made as detailed by Klystov et. al, 1992.

Measurements of Blank Concentrations in the AIM System

Zero air was introduced to the AIM to clean it completely. The AIM was operating normally to ensure that all components were cleaned with the zero air.

Measurements of Sampling Efficiency with a Back-up Filter

A QM-A filter was placed between the cyclone and condenser. After sampling, the filters were extracted and the extract was analyzed by Ion Chromatograph. During the tests, the collection efficiency was 99%.

The sampling efficiency was determined as the ratio of the aerosol mass collected by the AIM to the mass collected by both the AIM and the QM-A backup filter.

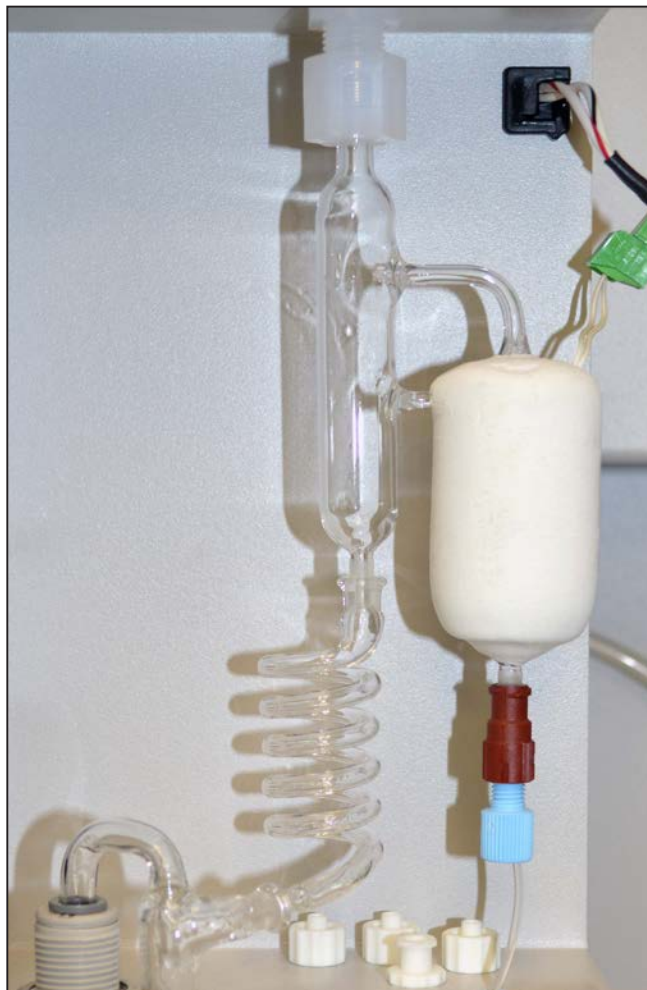


Exhibit 1-5. Super-Saturation Chamber
*Patent pending

Software

The Chromleon™ 7.2 software used by the AIM allows the users to easily QA data and automatically recalculate results. The sample volume, temperature and barometric pressure are reported in each of the analysis chromatograms so when the data is recalculated, the $\mu\text{g}/\text{m}^3$ for each ion is automatically reported. AIM and IC data are stored in a single database and can be exported using customizable report templates.

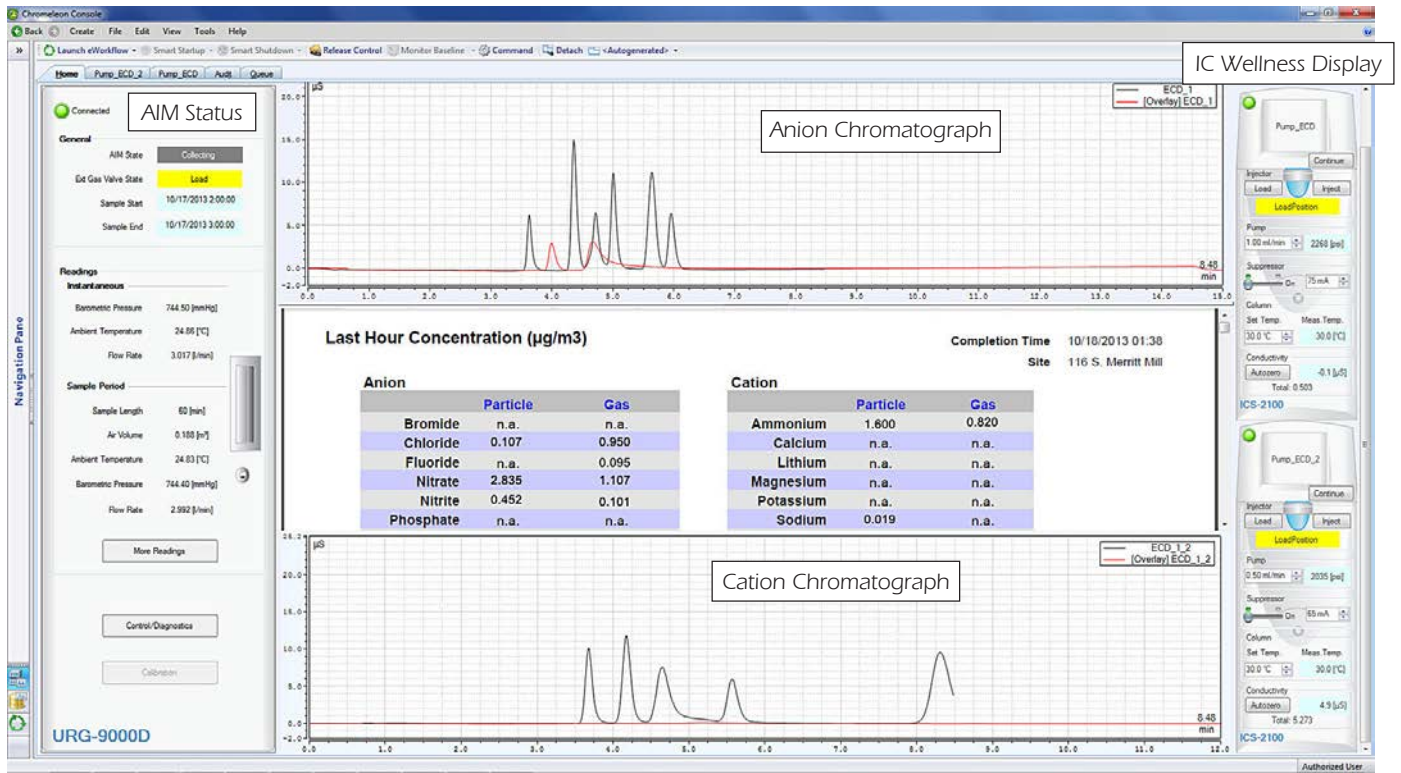


Exhibit 1-6. Results of the Ambient Ion Monitor System

IC Analysis Method

The URG-9000D AIM utilizes the proven measurement principle of ion chromatography (IC). The Dionex ICS-2100 is a reagent-free IC (RFIC™) that includes vacuum degas and column heaters that ensure consistent elution of peaks for every injection. RFIC™ eliminates operator error from reagent preparation; it requires only high-purity deionized water to operate. Also, by using an IC system that pumps only deionized water, you increase the lifetime of pump seals and pistons. From ordinary deionized water, RFIC™ generates high-purity eluents that perform superior separations and then neutralizes them back to plain water in the suppression step so there are no acidic or alkaline waste streams. There is little susceptibility to interferences present at monitoring sites. Losses due to volatilization are eliminated because the particles are collected in a solution and then analyzed by ion chromatography. The IC separates the nitrate and sulfate ions so that the measurements are not affected by other nitrogen-containing compounds.

The analytical sensitivity of the URG-9000D is equal to or better than 0.1µg/m³ for each of the required analytes and 0.08µg/m³ for ammonia. The URG-9000D collects 0.18m³/hour. Half of the collected sample is injected into and is analyzed with the Anion IC, while the other half is injected into and is analyzed with the Cation IC. Thus, to meet EPA's required instrument detection limits, the URG-9000D must collect a minimum sample of 0.009µg for each of the required analytes and 0.007µg for ammonia. The quantitative limits, as documented in Exhibit 1-7, are 0.005µg for anions and 0.0025µg for cations. These chromatographs (provided by the Dionex Corporation, the manufacturer of the ICs), show that the quantitative limits are lower than the required EPA specifications for the analytical sensitivity.

IonPac® concentrator columns for anions and cations are used to concentrate analytes, allowing determinations at µg/L (ppb) and sub-µg/L levels. Following concentration, anions and cations are analyzed using specific separation columns. Anion analysis is performed using the IonPac AS18 hydroxide-selective anion-exchange column, designed for the determination of inorganic anions and low-molecular weight organic acids including fluoride, acetate, formate, chloride, nitrite, bromide, nitrate, sulfate, and phosphate. The AS18 column can be used with isocratic hydroxide eluents or hydroxide gradients for the determination of inorganic anions.

Cation analysis is performed using the IonPac CS12 methanesulfonic acid-selective cation-exchange column. This column is designed to separate aliphatic amines and Group I and Group II cations such as lithium, sodium, ammonia, potassium, magnesium and calcium. The IonPac CS12 packing is functionalized with a unique carboxylate functional group that ensures long-term column stability. The column is compatible with acidic eluents and samples.

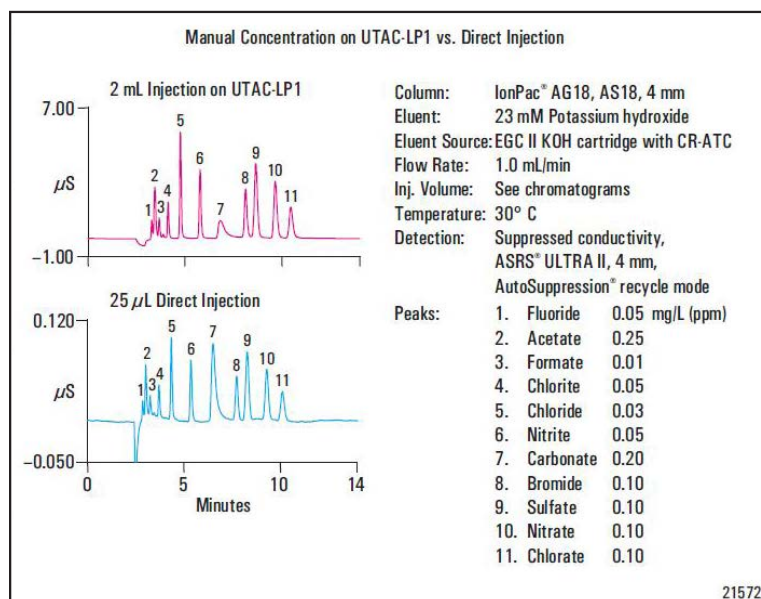


Exhibit 1-7. Quantitative Limits for Anions

Publications

Research Papers Documenting Use of URG-9000D Ambient Ion Monitor

2014

- Kuprov, R., Eatough, Delbert J., Cruickshank, T., Olson, N., Cropper, Paul M., Hansen, Jaron C. 2014. Composition and Secondary Formation of Fine Particulate Matter in the Salt Lake Valley: Winter 2009. *J. of the Air & Waste Management Association* 64(8): 957-969.
- Markovic, M. Z., VanderBoer, T. C., Baker, K. R., Kelly, J. T., Murphy, J. G. 2014. Measurements and modeling of the inorganic chemical composition of fine particulate matter and associated precursor gases in California's San Joaquin Valley during CalNex 2010. *Journal of Geophysical Research: Atmospheres* 119(11): 6853-6866.
- Wentworth, G. R., Murphy, J. G., Gregoire, P. K., Cheyne, C. A. L., Tevlin, A. G., Hems, R. 2014. Soil-atmosphere exchange of ammonia in a non-fertilized grassland: measured emission potentials and inferred fluxes. *Biogeosciences* (11): 5675-5686
- Moon, Kwang-Joo, Park, Jong-Sung, Park, Seung-Myeong, Song, In-Ho, Han, Jin-Seok. 2014. Evaluation of the Long-Range Transported PM_{2.5} at Seoul Supersite From 2010 to 2012. Presented at The 2014 International Aerosol Conference. Busan, Korea.

2013

- Hsu, Yu-Mei. 2013. Semi-Continuous Measurements of Inorganic Gases and PM_{2.5} Composition in the Athabasca Oil Sands Region (AOSR). Wood Buffalo Environmental Association. Presented at The A&WMA's 2013 Annual Conference & Exhibition in Chicago, IL.
- Pancras, J.P., Landis, M., Norris, G., Vedantham, R., Dvonch, J.T. 2012. Source apportionment of ambient fine particulate matter in Dearborn, Michigan, using hourly resolved PM chemical composition data. *Science of the Total Environment* 448 (2013) 2-13.

2012

- Markovic, M.Z., VandenBoer, T.C., Murphy, J.G. 2012. "Characterization and optimization of an online system for the simultaneous measurement of atmospheric water-soluble constituents in the gas and particle phases." *J. Environ. Monit.* 14, 1872
- Zhou, Y., Xue, L., Wang, T., Xiaomei, G., Wang, Z., Wang, X., Zhang, J., Zhang, Q., & Wang, W. 2012. "Characterization of aerosol acidity at a high mountain in central eastern China." *Atmospheric Environment* 51 (May 2012): 11-20.
- Gao, X., Xue, L., Wang, X., Wang, T., Yuan, C., Gao, R., Zhou, Y., Nie, W., Zhang, Q., & Wang, W. 2012. "Aerosol ionic components at Mt. Heng in central southern China: Abundances, size distribution, and impacts of long-range transport." *Science of the Total Environment* 433 (September 2012): 498-506.
- De Foy, B., Smyth, A., Thompson, S., Gross, D., Olson, M., Sager, N., & Schauer, J. 2012. "Sources of nickel, vanadium and black carbon in aerosols in Milwaukee." *Atmospheric Environment* 59 (November 2012): 294-301.
- Preunkert, S., Ancellet, G., Legrand, M., Kukui, A., Kerbrat, M., Sarda-Estève, R., Gros, V., & Jourdain, B. 2012. "Oxidant Production over Antarctic Land and its Export (OPALE project: An overview of the 2010-2011 summer campaign." *Journal of Geophysical Research* 117.
- Legrand, M., Gros, V., Preunkert, S., Sarda-Estève, R., Thierry, A., Pépy, G., & Jourdain, B. 2012. "A reassessment of the budget of formic and acetic acids in the boundary layer at Dumont d'Urville (coastal Antarctica): The role of penguin emissions on the budget of several oxygenated volatile organic compounds." *Journal of Geophysical Research* 117.
- Silva, P. 2012. "Measurement of Gas and Particulate Amines at Agricultural Facilities using an Ambient Ion Monitor." Presented at AAAR. Minneapolis, MN.
- Hsu, Y. 2012. "Application of Ambient Ion monitoring in the Athabasca Oil Sands Region." Presented at AAAR. Minneapolis, MN.

2011

- Gao, X., Yang, L., Cheng, S., Gao, R., Zhou, Y., Xue, L., Shou, Y., Wang, J., Wang, X., Nie, W., Xu, P., & Wang, W. 2011. "Semi-continuous measurement of water-soluble ions in PM_{2.5} in Jinan, China: Temporal variations of source apportionments." *Atmospheric Environment* 45 (July 2011): 6048-6056.
- Pathak, R., Wang, T., & Wu, W. 2011. "Nighttime enhancement of PM_{2.5} nitrate in ammonia-poor atmospheric conditions in Beijing and Shanghai: Plausible contributions of heterogeneous hydrolysis of N₂O₅ and HNO₃ partitioning." *Atmospheric Environment* 45 (July 2011): 1183-1191.
- VandenBoer, T.C., Petroff, A., Markovic, M.Z., & Murphy, J.G. 2011. "Size distribution of alkyl amines in continental particulate matter and their online detection in the gas and particle phase." *Atmospheric Chemistry and Physics* 11: 4319-4332
- Hsu, Y., 2011. "Application of Ambient Ion Monitor in Northeastern Alberta Canada at Wood Buffalo Environmental Association." Presented at The Seventh Asian Aerosol Conference. Xi'an, China.
- Wang, J. 2011. "On-line and Off-line Applications of Ion Chromatography in Atmospheric Environment. Presented at The Seventh Asian Aerosol Conference." Xi'an, China.
- Li, W., Zhou S., Wang, X. 2011. "Integrated Evaluation of Aerosols from Regional Brown Hazes over Northern China in Winter: Concentrations, Sources, Transformation, and Mixing States". Presented at The Seventh Asian Aerosol Conference. Xi'an, China.
- Long, R.W., Beaver, M., Krug, J., Lewandowski, M., Offenber, J., Kleindienst, T. 2011. "Determination of Organic Ions in Ambient Air and Atmospheric Smog Chamber Samples Using the Ion Chromatography Based URG Ambient Ion Monitor." Presented at the 30th Annual American Association for Aerosol Research. Orlando, Florida.

2010

- Nie, W., Wang, T., Gao, X., Pathak, R., Wang, X., Gao, R., Zhang, Q., Yang, L., & Wang, W. 2010. "Comparison among filter-based, Impactor-based and continuous techniques for measuring atmospheric fine sulfate and nitrate." *Atmospheric Environment* 44 (35): 4396-4403.
- Wang, T., Nie, W., Gao, J., Xue, L., Gao, X., Wang, X., Qiu, J., Poon, C., Meinardi, S., Blake, D., Ding, A., Chai, F., Zhang, Q., & Wang W. 2010. "Air quality during the 2008 Beijing Olympics: secondary pollutants and regional impact." *Atmospheric Chemistry and Physics* 10: 12433-12463.
- Maurizio, M., Abballe, F., Jack, R., & Avino, P. 2010. "Time-Resolved Measurement of the Ionic Fraction for Atmospheric Fine Particulate Matter." *Journal of Chromatographic Science* 48 (August 2010): 549-552.
- Long, R.W., Landis, M., Fortune, C., Stone, J., 2010. "High-Time Resolution Determination of Ions in Matrix Challenged Ambient Air Samples Using the Ion Chromatography Based URG Ambient Ion Monitor." Presented at AAAR. Portland, Oregon.
- Silva, P., 2010. "Adaptation of an Ambient Ion Monitor for Detection of Organic Ions in Particulate Matter from Agricultural Emissions." Presented at AAAR. Portland, Oregon.
- Hsu, Yu-Mei., Landis, Matthew S., 2010. "Application of Ambient Ion Monitor in Northeastern Alberta." Presented at AWMA Annual Conference, Calgary, Alberta, Canada.
- Long, R.W., Landis, M., Fortune, C., Stone, J., 2010. "High-Time Resolution Determination of Ions in Matrix Challenged Ambient Air Samples Using the Ion Chromatography Based URG Ambient Ion Monitor." Presented at Pittcon Conference and Expo, Orlando, Florida and Presented at AWMA International Specialty Conference: Leapfrogging Opportunities for Air Quality Improvement, May 2010. Xi'an, Shaanxi Province, China.

2009

- Zhou, Y., Wang, T., Gao, X., Xue, L., Wang, X., Wang, Z., Gao, J., Zhang, Q., & Wang, W. 2009. "Continuous observations of water-soluble ions in PM_{2.5} at Mount Tai (1534 m a.s.l.) in central-eastern China." *Journal of Atmospheric Chemistry* 64 (2): 107-127.

2008

- Long, R.W., Grover, B., Vanderpool, R., Landis, M., 2008. "Laboratory and Field Evaluation/Application of Methods Relevant to Reducing Uncertainty in Source Apportionment Modeling for Use in Residual Non-Attainment Area SIP Development." Presented at the Symposium on Air Quality Measurement Methods and Technology. November 3-6, 2008. Chapel Hill, North Carolina.
- Vandenboer, T.C., Markovic, M.Z., Czar, M., Murphy, J.G., 2008. "Characterization and Application of an Ambient Ion Monitor." Presented at American Geophysical Union, Fall Meeting.

2007

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- Wu, W. S., Wang, T., 2007. "On the performance of a semi-continuous PM_{2.5} sulphate and nitrate instrument under high loadings of particulate and sulphur dioxide." *Atmospheric Environment* 41: 5442-5451.
- Long, R., Grover, B., Landis, M., Vanderpool, R., Kronmiller, K., Murdoch, R., Eatough, D., Stevens, R., 2007. "Evaluation and Comparison of High Time Resolution Wetted Denuder-Ion Chromatography Methods for the Determination of PM Ion and Gaseous Precursor Concentrations During Controlled Laboratory and Field Intensive Studies." Presented at the 2007 American Association of Aerosol Research Conference, Reno, Nevada.

2006

- Han, J.S., Moon, K.J., Jung, I.R., Kondo, Y., Miyazaki, Y., 2006. "Evaluation of a URG Ambient Ion Monitoring System (AIM) for Measuring Water-Soluble Ion Components of Ambient PM_{2.5}: Intercomparison with PILS-IC Monitor." Presented at the 2006 International Aerosol Conference, St. Paul, Minnesota.
- Han, J.S., Moon, K.J., Kong, B.J., 2006. "Characterization of Physical, Chemical and Optical Properties of Ambient Aerosol as a Function of Relative Humidity at Gosan, Korea During ABC-EAREX 2005." Presented at the 2006 International Aerosol Conference, St. Paul, Minnesota.



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