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## **Particle-into-Liquid Sampler Instrument Handbook**

TB Watson

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## Acronyms and Abbreviations

AAF	ARM Aerial Facility
ARM	Atmospheric Radiation Measurement Climate Research Facility
BDL	data descriptor indicating “Below Detection Limit”
G-1	Gulfstream-1 aircraft
IC	ion chromatographs
IOP	intensive operational period
MAOS	Mobile Aerosol Observing System
M-ohm	mega-ohm
NG	data descriptor indicating “No Good”
PILS	Particle-into-Liquid Sampler
TOC	total organic carbon

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## **1.0 Instrument Title**

Particle-into-Liquid Sampler

## **2.0 Mentor Contact Information**

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## **3.0 Vendor/Developer Contact Information**

### **3.1 PILS Extraction Unit**

Applikon Analytical B.V.  
De Brauwweg 13, P.O. Box 149,  
3100 AC Schiedam  
The Netherlands  
Phone: +31 10 298 35 55  
Fax: +31 10 437 96 48  
E-mail: [analyzers@applikon.com](mailto:analyzers@applikon.com)

### **3.2 Ion Chromatographs**

Metrohm  
6555 Pelican Creek Circle  
Riverview, FL 33578  
Phone: (866) 638-7646  
<http://www.metrohmusa.com/en-us>

### 3.3 Total Organic Carbon Analyzer

GE Power and Water Process Technologies

6060 Spine Road

Boulder, CO 80301

Main: (303) 444-2009

Main (toll-free): (800) 255-6964

Technical Support: (888) 245-2595

Main: (303) 444-9543

Sales: (303) 444-9543

Orders: (303) 527-1797

Service: (303) 444-6272

[geai@ge.com](mailto:geai@ge.com)

## 4.0 Instrument Description

The Particle-into-Liquid Sampler (PILS) is an aqueous-solution-based online technique for determining bulk chemical composition of ambient aerosol particles. As shown in Figure 1, the instrument consists of two units, briefly described below:

1. An aerosol extraction unit where particles are passed through a growth chamber saturated with water vapor, liquid droplets are grown, and the resulting liquid collected and transferred to the detection system.
2. The detection system that includes ion chromatographs (IC) or a total organic carbon detector (TOC).



**Figure 1.** PILS aerosol extraction unit.



Ion chromatography is performed using two Metrohm ICs—one for positive ions and one for negative ions—with conductivity detectors.

The TOC is detected using a GE TOC analyzer.

The instrument can be run in either the ion detection mode or the TOC mode.

## 5.0 Measurements Taken

### 5.1 Inorganic Ionic Species

The PILS measures the following particulate ionic inorganic species:  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{H}_2\text{PO}_4^{3-}$ .

### 5.2 Organic Ionic Species

The PILS measures the following particulate ionic organic species:  $\text{HCO}_2^-$ ,  $\text{CH}_3\text{CO}_2^-$ ,  $\text{CH}_3\text{SO}_3^-$ , and  $\text{C}_2\text{O}_4^{2-}$ .

The ions and their approximate retention times detected by the PILS using the Metrohm ICs are given in Table 1.

**Table 1.** Ions detected by the PILS

Ion	Retention Time
Li	0.80
Na	1.83
$\text{NH}_4$	2.36
K	3.98
Mg	12.60
Ca	13.20
Cl	1.91
Br	4.26
$\text{NO}_3$	9.04
$\text{PO}_4$	9.04
$\text{SO}_4$	11.16
Oxalate	13.17

### 5.3 Total Organic Carbon

The PILS measures particulate TOC when used with the GE TOC detector.

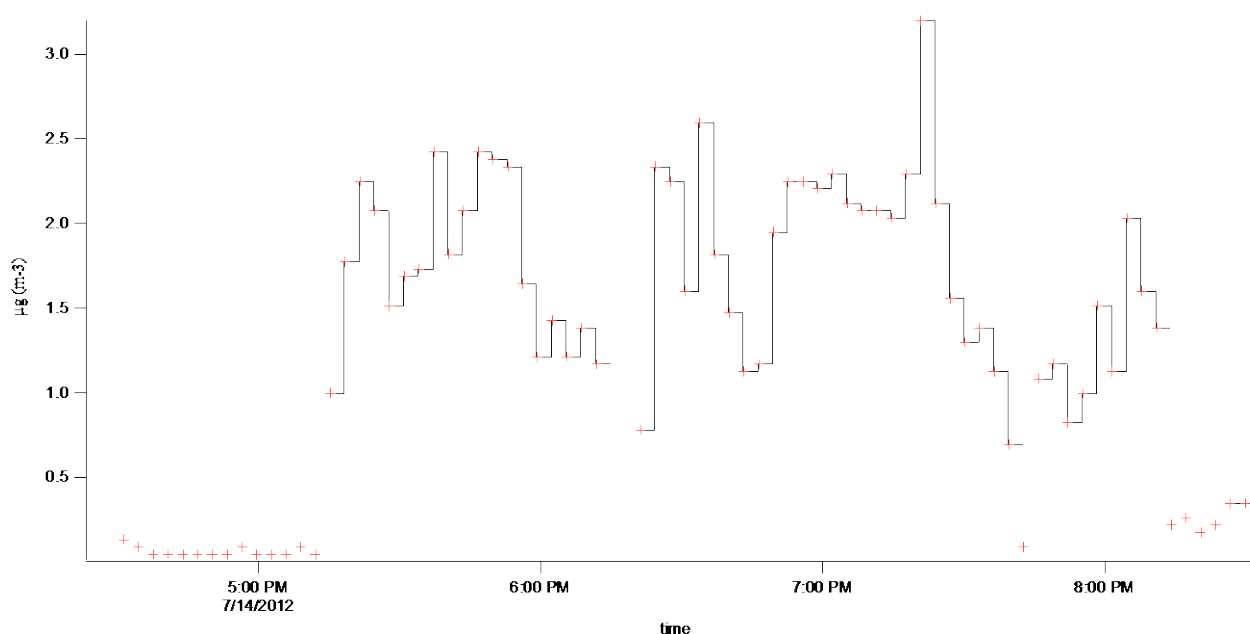
## 6.0 Data Object Description

Data are presented in text files in the following formats:

Column 1:	UTC Time	yyyy/mm/dd hh:mm:ss
Column 2–24:	Ion_flag	Data descriptor indicating below detection limit (BDL) or no good (NG) or text concentration value in $\mu\text{g}/\text{m}^3$ with all calculated digits (not all significant)
Column 3–25:	Ion_conc	Concentration value in $\mu\text{g}/\text{m}^3$ with all digits significant. Blanks where data are BDL or NG

The reported time is corrected for the sample delay time. Even columns are in text format and contain data flags and numerical data that are not rounded to reflect significant figures. Odd columns contain ion concentration data in  $\mu\text{g}/\text{m}^3$  and are rounded to reflect significant figures. All concentrations are reported at ambient temperature and pressure.

Data are reported at 1-s intervals, but because there is only one data point taken by the PILS every 3 min in the aircraft and every 15 min for the ground-based instrument, the reported data are padded so the time between every data point is filled with the same value. An example of this is given in Figure 2, which shows the individual data points and the padded data.



**Figure 2.** Individual data points (red crosses) and the padded (black line) data for  $\text{SO}_4$  data during Flight 3 on July 14, 2012.

## 6.1 Mass Calculation

The concentration data determined from the chromatograms are converted into mass concentration of the aerosol at ambient pressure and temperature using the following expression.

$$[X]_m = [X]_{liq} \times F_{liq} \times M_w \div F_{air}$$

where:

$[X]_m \equiv$  ion concentration in ( $\mu\text{g}/\text{m}^3$ )

$[X]_{liq} \equiv$  molar ion concentration

$F_{liq} \equiv$  PILS carrier solution flow rate (L/min)

$M_w \equiv$  molecular weight ( $\mu\text{g}/\text{mole}$ )

$F_{air} \equiv$  flow rate of sample air through the PILS body (15 L/min at ambient conditions).

## 6.2 Data Ordering

Data ordering is addressed at <http://www.arm.gov/xdc>.

## 7.0 Technical Specification

### 7.1 Ion Chromatographs

- Time resolution
  - 15min in the ground-based configuration
  - 3 min in the aircraft-based configuration.
- Analysis time
  - 14.5 min
- Aerosol particle diameter size range
  - Approximately 70 nm to 2.5  $\mu\text{m}$

### 7.2 Total Organic Carbon

- Analysis time
  - 4 min
- Range
  - 0.03 ppb to 50 ppm

### 7.3 Units

$\mu\text{g}/\text{m}^3$

## 7.4 Accuracy

### 7.4.1 Ion Chromatographs

The uncertainty associated with the mass measurements was estimated by combining the uncertainties in flow rates and IC calibrations. Uncertainties of both liquid and air flow rates are approximately 4%. Uncertainties in the IC calibration for sulfate, nitrate, and ammonium were determined by comparisons with measurements of independent traceable standards from the National Institute of Standards and Testing. Comparisons immediately following IC calibrations were within 3 to 5% and 5 to 10% after running for an extended period. The overall uncertainty of the measured ionic species is estimated to be approximately 10% (Orsini et al. 2003).

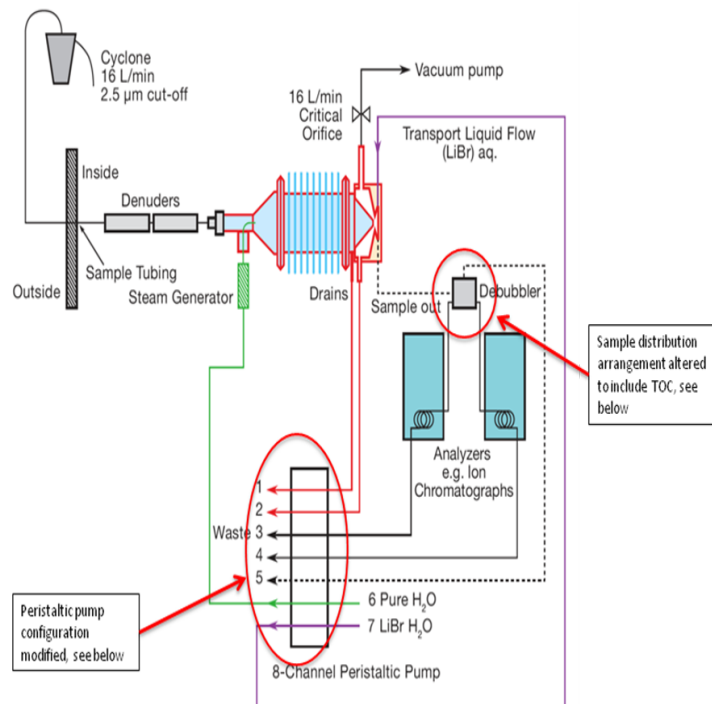
### 7.4.2 Total Organic Carbon Detector

The Seivers TOC detector has an accuracy of  $\pm 2\%$ .

## 7.5 Limits of Detection

- Anions:  $\sim 0.05 \mu\text{g}/\text{m}^3$
- Cations:  $\sim 0.1 \mu\text{g}/\text{m}^3$
- TOC:  $\sim 0.5 \mu\text{g}/\text{m}^3$

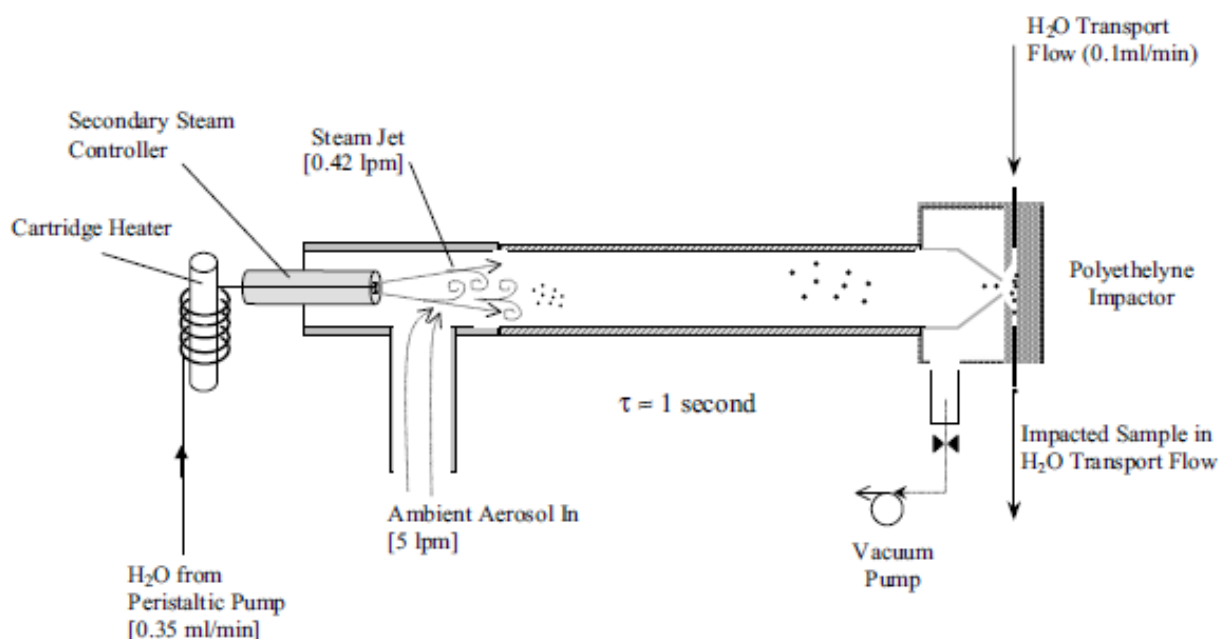
## 8.0 Instrument System Functional Diagram



**Figure 3.** Schematic of the instrument configured to measure ions.

## 9.0 Instrument/Measurement Theory

Ambient air containing aerosol is drawn into the PILS growing chamber at approximately 15 L/min. There, the sample is mixed with a smaller, approximately 1.5 L/min, turbulent flow of 100°C steam. The steam is cooled by mixing with the sample flow to create a condition in which the chamber is supersaturated with water vapor. In the supersaturated conditions, aerosol particles are activated and grow into droplets approximately 1  $\mu\text{m}$  and larger in diameter. The droplets are collected on a single-orifice impactor. The liquid sample collected on the impactor surface is removed using a small, constant flow of purified water that also contains an internal standard (Figure 4). This liquid sample is then analyzed using IC or TOC techniques to quantify the ionic species or TOC contained in aerosol particles. Because gas-phase compounds also are present in ambient air samples, gas-phase denuders are placed in the sample line upstream of the PILS aerosol extraction unit.



**Figure 4.** Schematic of the aerosol extraction unit (taken from Orsini et al. 2003).

## 10.0 Operation of Instrument

Currently, two PILS systems are operating at ARM facilities. One is located at the in the Mobile Aerosol Observing System (MAOS) (Figure 5), and the other is used as needed on the Gulfstream-1 (G-1) aircraft in support of field programs of the ARM Aerial Facility (AAF).

## 11.0 Software

The ICs are controlled by proprietary software, Magicnet IC, developed by Metrohm. This software is used to control the operation of the chromatographs and in data processing.

## 12.0 Calibration

### 12.1 Ion Chromatography

Calibration of the ICs is performed using standard solutions made from serial dilution of primary standards. The primary standards are made gravimetrically. Stock solutions are prepared at 0.1 or 0.05 M ( $\pm 1\%$ ) using 18 M-ohm purified H<sub>2</sub>O in plastic 100-mL volumetric flasks. The compounds used for calibrating the ICs are given in Table 2. Serial dilution is then used to produce intermediate and final calibration standards. Concentrations of the final standard are given in Table 3. Intermediate and final calibration standards must be prepared immediately prior to each calibration to ensure accurate concentrations. The chemical degradation of low concentration solutions can occur if they are not used immediately. An example of a calibration curve is given in Figure 6.

## MAOS C Aerosol and Trace Gas Inlets

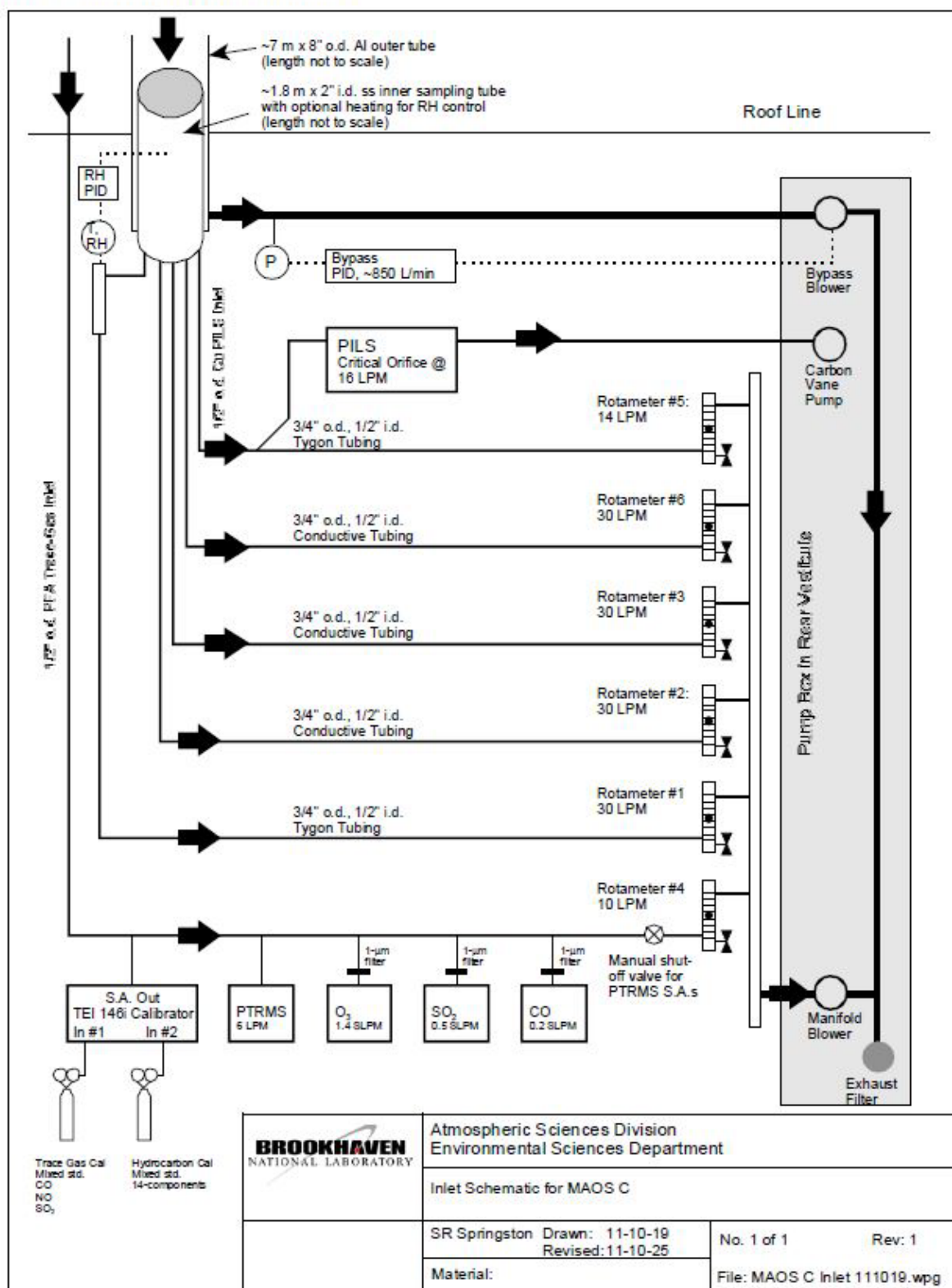


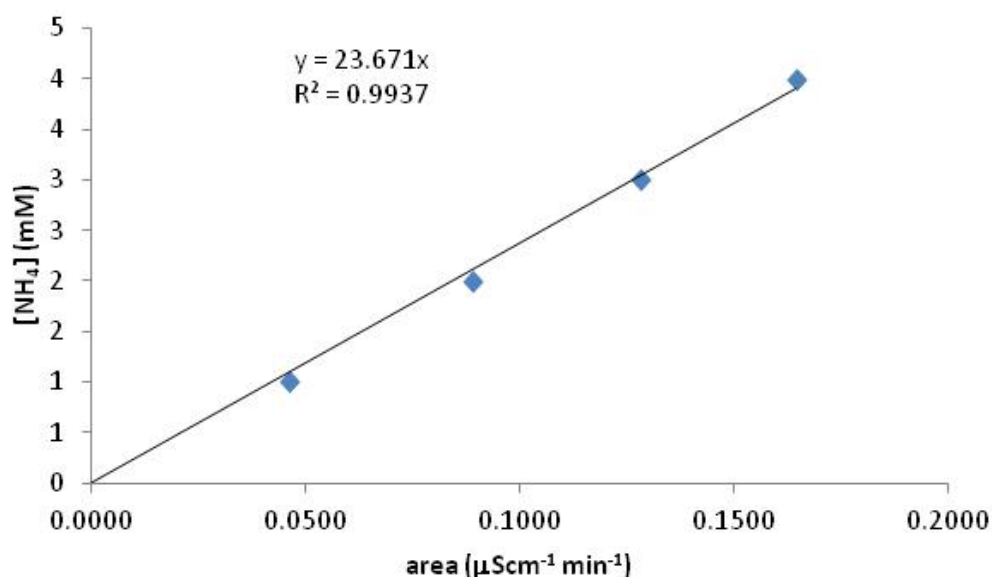
Figure 5. Schematic of MAOS C inlet system including the sample line supplying the PILS.

**Table 2.** Compounds used to calibrate the ICs, their molecular weights, and the masses used in preparation of the primary standards at 100 and 50 mM.

Chemical	M. W.	For 0.100 M, gm	For 0.05 M, gm
LiClO <sub>4</sub> •3H <sub>2</sub> O	160.4	1.60	0.80
NaAct	82.0	0.82	0.41
CaCl <sub>2</sub>	111	1.11	0.55
KBr	119	1.19	0.60
NH <sub>4</sub> NO <sub>3</sub>	80	0.80	0.40
KH <sub>2</sub> PO <sub>4</sub>	136	1.36	0.68
MgSO <sub>4</sub> •7H <sub>2</sub> O	246.5	2.47	1.24
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	134	1.34	0.67

**Table 3.** Nominal concentrations of final ion standards and volume of intermediate standard used.

Final Nominal Concentration, $\mu\text{M}$	Volume, $\mu\text{L}$
0.5	10
1	20
2	40
3	60

**Figure 6.** Calibration curve for  $\text{NH}_4$  determined from averages of a total of 61 points at concentrations of 1, 2, 3, and 4 mM.

## 12.2 Total Organic Carbon

The total organic carbon detector is calibrated using certified reference materials containing potassium hydrogen phthalate and sodium carbonate. These standards are supplied by the instrument manufacturer.



## 12.3 Calibration Frequency

### 12.3.1 Ion Chromatographs

The ground-based ICs and TOC detector should be calibrated with a full range of standards at least once a week. The PILS operated on the aircraft should be calibrated at the end of every flight with at least one standard concentration.

### 12.3.2 Total Organic Carbon

The TOC should be calibrated before and after every intensive operational period (IOP) or once a month.

## 13.0 Inlet System

Ambient aerosol-laden air is brought to the instruments at 800 L/min through an 8-in. diameter external stack extending nominally 10 ft above the roof (Figure 7) of the enclosure. Inside the stack, sample air flows through a 2-in. diameter stainless-steel pipe in the center of this larger flow at 120 L/min. This flow is split inside the enclosure into four, 30-L/min sample lines, one of which supplies the PILS as well as other instruments. The proton transfer reaction mass spectrometer is connected to this line with a tee fitting. This line is insulated to prevent condensation in the line in the air-conditioned interior of the instrument enclosure.



**Figure 7.** AOS instrument enclosure with 10-m sampling stack.

## 14.0 Maintenance

### 14.1 Solutions

Solutions necessary for operation of the PILS in the ionic measurement mode are given in Table 4. These solutions must be prepared with ultra-pure deionized water with a conductivity of 18 M-ohm.

**Table 4.** Solutions needed to operate the ion chromatographs.

	<b>Solution</b>	<b>Use</b>	<b>Content</b>	<b>Flow Rate mL/min</b>	<b>Preparation<sup>a</sup></b>
1	Purified H <sub>2</sub> O	Steam H <sub>2</sub> O supply and TOC background	Purified H <sub>2</sub> O (18 M-ohm cm TOC <50 ppb)	1.5	18 M-ohm H <sub>2</sub> O from EasyPure II
2	Carrier solution	For washing off aerosol sample from impactor	2 $\mu$ M LiClO <sub>4</sub> (internal standards)	0.86	
3	Anion IC eluent	For anion column elution	1.0 mM NaHCO <sub>3</sub> 3.2 mM Na <sub>2</sub> CO <sub>3</sub>	0.7	One sachet of stock into 800 mL H <sub>2</sub> O
4	Cation IC eluent	For cation column elution	2.5 mM oxalate	0.7	
5	Anion IC suppressor solution 1	For suppressing anion IC background signal	100 mM H <sub>2</sub> SO <sub>4</sub>	0.06@ setting = 1	available from Metrohm
6	Anion IC suppressor solution 2	For suppressing anion IC background signal	Purified H <sub>2</sub> O	0.06@ setting = 1	Purified H <sub>2</sub> O
7	Calibration standards	For calibrating the ICs	0.5-3.0 $\mu$ M		Prepared from 1 mM intermediate standards

<sup>a</sup> All solutions prepared from purified H<sub>2</sub>O (ASTM Type 1)

### 14.2 Peristaltic Pump Tubing

Peristaltic pump tubing should be replaced before every IOP, or after 1 month of semi-continuous operation.

### 14.3 Columns

Columns should be replaced before every IOP or when they show signs of degradation. Symptoms of degradation are the appearance of spurious peaks or inadequately separated peaks when running calibration standards.

## 14.4 Denuders

The Honeycomb denuders are applied to remove acid and base gas species, including SO<sub>2</sub>, HNO<sub>3</sub>, and NH<sub>3</sub>, to eliminate positive concentration biases of these soluble species to aerosol SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>. Two denuders are used in series to eliminate gas-phase compounds. The denuders are coated with:

- 1% (by weight) Na<sub>2</sub>CO<sub>3</sub> in a solution of 1% glycerol in a 50% methanol/50% water mixture
- 2% citric acid in 1% glycerol in methanol.

## 15.0 Safety

Safety glasses, gloves, and lab coats should be used in the preparation of all operational and calibration solutions.

## 16.0 Citable References

Orsini, DA, Y Ma, A Sullivan, B Sierau, K Baumann, and RJ Weber. 2003. "Refinements to the particles into water sampler (PILS) for ground and airborne measurements of water soluble aerosol composition." *Atmospheric Environment* 37(9-10):1243-1259, [doi:10.1016/S1352-2310\(02\)01015-4](https://doi.org/10.1016/S1352-2310(02)01015-4).

Watson, TB. "TCAP 1 and 2 Particle-into-Liquid Sampler aircraft data." Data report prepared for the TCAP program. Slide available at [http://asr.science.energy.gov/meetings/stm/posters/poster\\_pdf/2013/P000998.pdf](http://asr.science.energy.gov/meetings/stm/posters/poster_pdf/2013/P000998.pdf).



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