

Introduction

anions:

The Particle-into-Liquid Sampler (PILS) is used to determine the bulk chemical composition of water soluble aerosol particles. The PILS samples particles in the size range from approximately 60 nm to 2.5 μm in diameter with collection efficiency greater than 97%. The chemical components are determined using ion chromatography. The species normally reported are: cations:

Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺

Cl⁻, Br⁻, NO₃⁻, H₂PO₄⁻ SO₄²⁻, and C₂O₄²⁻ (oxalate).

The instrument as it is configured to operate on the DOE G-1 collects a 3 min integrated sample every 3 min. The nominal limits of detection (LOD) are approximately 0.1 µg m⁻³ for anions and 0.2 µg m⁻³ for cations. The LOD by species determined during the operation of the instrument during TCAP 1 are given below. An ion mixture of concentrations of nominal 1, 2, 3 mM is run as a calibration standard at the end of every flight

Chromatogram evaluation

The data processing begins with a visual inspection of each chromatogram to make sure that the peak identification is accurate and that the baselines are reasonable. Chromatograms are reprocessed using the MagicNet software to correct discrepancies and converted into text files. The text files are processed using Excel or Igor software.

Calibration

Calibration curves are calculated from the calibration data collected at the end of each flight. Data from all 10 flights was combined and the instrument response was found to be consistent across the entire 16 days of aircraft operations. The standard deviation of the mean of the instrument response to each level of ion concentration was 7% or less for all ion species. A example calibration curve is given in Figure 1 and calibration data for all ions are given in Table 1 and Table 2.



Calibration curve for SO₄ determined from averages of a minimum of 19 points at each concentration of 1, 2, and 3 mM.

Calibration factors including slope (m), standard error in the slope (d m, coefficient of determination (r²), standard error in the millimolar concentration, d y (mM), and standard error in micro gram per cubic meter concentration d y (μ g m⁻³).

	Li	Na	NH_4	K	Mg	Ca
m	23.4	25.3	23.7	26.5	12.7	16.0
δm	0.15	0.46	0.38 0.24		0.23	0.40
r^2	0.9999	0.9990	0.9990	0.9996	0.9990	0.9982
δ y (mM)	0.02	0.14	0.09	0.07	0.07	0.09
δ y (μg m ⁻³)	0.01	0.14	0.07	0.13	0.07	0.16

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TCAP 1 Particle-into-Liquid Sampler Aircraft Data Thomas B. Watson (twatson@bnl.gov) Atmospheric Sciences Division/Brookhaven National Laboratory

Limits of Detection



 NH_4 .

Data used to determine limits of detection. The values in mM were determined from the standard error in the intercept of a plot of instrument response versus standard concentration.

	Li	Na	NH_4	K	Mg	Ca
mM	0.011	0.0013	0.07	0.08	0.03	0.09
µg m ⁻³	0.004	0.0013	0.05	0.07	0.02	0.07
LOD	0.011	0.004	0.16	0.20	0.07	0.20
µg m ⁻³						
	Cl	Br	NO ₃	H_2PO_4	SO_4	Oxt
mM	0.007	0.05	0.05	0.10	0.05	0.08
µg m ⁻³	0.006	0.04	0.04	0.08	0.23	0.04
LOD	0.02	0.11	0.12	0.23	0.3	0.11

TCAP 1, Flight 1 Results



Plot of horizontal flight legs showing altitude. Profile on the right hand side is over the ground station. Profile on the left hand side is over the ocean. Red circle indicates the location of the ground site.



Plot of selected ion concentrations versus time for flight 1, 2012 07 09.



Plot of dew point versus altitude for two profiles. Black is profile over the ground station. Red Is profile over the ocean.



Plot of average SO₄ concentration versus altitude for each leg of flight 1.



Plot of average NH₄ concentration versus altitude for each leg of flight 1.



Average concentration of Na, NH4, and SO4 ions and altitude during the 12 flight legs on 2102 07 09 t. The blue high lights are the tracks in the marine profile. The Pink high lights are the tracks in the profile over the ground station.

track	Na	σNa	NH4	σNH4	SO4	σSO4	alt
0	0.7	0.13	0.4	0.06	0.8	0.45	590
1	0.4	0.02	0.5	0.08	0.5	0.11	96
2	0.6	0.22	0.4	0.11	0.6	0.27	305
3	0.4	0.02	0.6	0.01	1.0	0.13	97
4	0.5	0.23	0.5	0.07	0.7	0.14	318
5	0.5	0.26	0.5	0.05	0.7	0.09	2150
6	0.6	0.07	0.2	0.00			3685
7	0.3	0.05	0.6	0.06	1.4	0.48	104
8	0.3	0.15	0.4	0.07	0.4	0.08	318
9	0.2	0.01	0.4	0.03	0.4	0.07	591
10	0.3	0.11	0.2	0.00			2112
11	0.3	0.12					3640

Recommendations



Plot of average Na concentration versus altitude for each leg of flight 1.

Preliminary conclusions

 Instrument performance was within expected ranges as determined by evaluation of calibration standards. • The limits of detection for all ions were within expected ranges.

• There were some problems with the in-flight performance of the anion IC resulting in limited useable CI data and the appearance of periodic noise, perhaps related to the CO₂ suppressor module and

altitude. • The eluant solutions began to degas at altitudes

above 3000 m causing the peristaltic pumps in the ICs to loose prime.

• The CO₂ suppressor unit was turned off during TCAP2 to attempt to eliminate the periodic noise in the anion IC.

• Br was added to the carrier solution in addition to Li to give an internal standard in the anion channel.







