QUALITY ASSURANCE PROJECT PLAN (QAPjP)
And QA Report for Pacific 2001

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Date: June 18 2001

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1. **Principal Investigator**
   Geoff Harris
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2. **Team Members**
   Corinne Schiller – York University
   Jean Francois Gouin – York University

3. **Measurement Program**
   Tropospheric gas phase ammonia, nitrous acid and/or hydrogen peroxide

4. **Measurement Species and Units**
   NH_3 (ammonia) – ppbv
   HONO (nitrous acid) – ppbv
   H_2O_2 (hydrogen peroxide – ppbv

5. **Representative Size Range (if PM)**
   N/A

6. **Measurement Platform (surface, airborne)**
   Tunable Diode Laser Spectroscopy ~ 5 m above ground on trailer

7. **Measurement Sites (surface only)**
   Langley

8. **Measurement Objective(s)**
   Tropospheric gas phase Ammonia, nitrous acid and/or hydrogen peroxide using tunable diode laser absorption spectroscopy

9. **Measurement Details**
   9.1. Field Measurements
   9.1.1. Measurement Principle
   Tunable Diode Laser Spectroscopy
   HONO ~1280 cm^{-1}
   NH_3 ~ 950 cm^{-1}
   H_2O_2 ~ 1280 cm^{-1}

   9.1.2. Instrumentation (Manufacturer/Model)
   The tunable diode laser spectrometer was originally a TAMS 150 built by Unisearch, which has since been modified by Corinne Schiller and Jean Francois Gouin at York University. The White cell incorporates 2 vertical corner cubes, resulting in 8 rows and thereby doubling the path length.

The White cell mirrors have been recoated with super silver resulting in a reflectance greater than 99.8%. The program has been completely rewritten in Labview with a Real Time data acquisition board. The electronics have incorporated a Profile temperature/laser controller as well as new GE lock in amplifiers.

9.1.3. Flow System

Air will be sampled from a manifold starting approximately 2 m above the trailer. The manifold has an internal diameter of approximately 2 inches. The air will be drawn down the manifold at a flow rate of approximately 50 l/min. The flow through the manifold should be laminar with a Reynolds number of approximately 1350. From the center of this flow, ~ 10 l/min will be sampled into the White cell through a glass inlet with aperture. A short length of Teflon tubing will be located on the low-pressure side to relieve tension.

9.1.4. Inlet Height Above Ground (if surface)

~ 2 meters above trailer therefore about 5 meters above the ground

9.1.5. Nominal Flow Rate

Flow down manifold ~ 50 l/min
Flow into White Cell ~ 10 l/min

9.1.6. Flow Measurement/Control

The flow through the manifold will be controlled by a 50 l/min mass flow controller, while the flow through the white cell will be controlled by an aperture in the glass inlet. The zero air for calibrations and backgrounds will be controlled with a 20 l/min flow controller. The flow through the permeation devices will be controlled by rotometers and the flow of HCl for HONO calibration will be controlled with a 50 ml/min flow controller.

9.1.7. Flow Temperature and Pressure

The flow controllers will be calibrated with a Gillian Flow measurement system to STP.

9.1.8. Sampling Times/Period/Frequency

The tunable diode laser will operate continuously, obtaining 1 minute averages of 2 species. Backgrounds will be taken every 3 minutes and calibrations once per hour

9.1.9. Sampling Methods

N/A

9.1.10. Filter Type/Coating Type/Reagent Type

N/A

9.1.11. Planned Changes to Instruments or Methods During Study

N/A

9.2. Laboratory Measurements (If Applicable)

9.2.1. Laboratory Name and Address

York University – Geoff Harris Lab

9.2.2. Analytical Method(s)

For periodic verification of our calibration standards

Nitrous Acid: Bubble gas sample through 10^{-5} NaOH solution
Analyze using Ion Chromatography

Ammonia: Bubble gas sample through 10^{-5} HCl solution
Analyze using Ion Chromatography

H_2O_2 Bubble solution through titanium tetrachloride
Measure color change with a Spec 20.

9.2.3. Sample Extraction or Work-up

N/A

9.2.4. Analytical Detection Limits

Laboratory
NO_2^- by IC = <1 nmoles/ml (do not require better)
NH_4^+ by IC = <1 nmoles/ml (do not require better)
H_2O_2 by titanium tetrachloride = 4×10^{-5} g (~ 2% absorbance by spectrometer)

10. Quality Assurance/Quality Control

10.1. Field Quality Assurance/Quality Control

10.1.1. Traceability

Nitrite –volumetric dilution of a primary standard dried $NaNO_2$ (purity >99.99%) – Sigma Aldrich
Ammonium – volumetric dilution of a primary standard of ammonium sulfate – purity >99.99% - Sigma Aldrich H_2O_2 - Quantitative reaction with titanium tetrachloride resulting in a colored product whose extinction coefficient has been determined quantitatively. [W. Pilz, I. Johann; J. Environ. Chem., 3, 257, 1974. – Extinction Coefficient of 735 M^{-1} cm^{-1})]

10.1.2. Calibration

Calibration of the TDLAS will be carried out by the addition of the molecule of interest from a permeation device being diluted into zero air very near where the air is drawn off the manifold.
Calibration of the permeation devices has been described in section 10.2.2

10.1.3. Zeros and spans

Zero air will be used for the zero on the TDLAS

10.1.4. Blanks

Verifying calibration concentrations will result in 2 blanks used to determine possible contamination of the samples with shipping.

10.1.5. Field Quality Control procedures

Calibration of permeation devices will be sampled into pre-pipetted sealed vials.

10.1.6. Precision determination

Precision will be determined by the variability of subsequent measurements of known concentrations of calibration gas in zero air introduced to the instrument.

10.1.7. Comparison with other measurements

No other ammonia measurements will be made at the Langley site. There may be a chemical method for HONO measurement by the AES group. No other measurements of H_2O_2 are expected to be made at the Langley site.

10.1.8. Inspections and Audits

No external audits will be carried out.

10.2. Laboratory Quality Assurance/Quality Control

10.2.1. Traceability

Nitrite –volumetric dilution of a primary standard dried $NaNO_2$ (purity >99.99%) – Sigma Aldrich

Ammonium Chloride – volumetric dilution of a primary standard – purity >99.999% - sigma Aldrich

H_2O_2 a spectroscopic method – (W. Pilz, I. Johann; J. Environ. Chem., 3, 257, 1974. – Extinction Coefficient of 735 M^{-1} cm^{-1})

10.2.2. Calibration procedures

A 5 - point calibration in duplicate will be run for every 20 samples for both anions and cations measured by IC

10.2.3. Blanks

2 types of blanks will be run

Calibration blank – run from the same water that the calibration standards were made with

Collection Blank – a blank of the material samples were collected in will be returned from the field and analyzed the same as a sample

10.2.4. Other lab QC

Latex gloves will be worn while for standard generation. Weights of dried primary standards will be determined with a calibrated analytical balance with an accuracy of 0.0001 g. New volumetric glassware that has never

been dried will be used for calibration standards. Disposable tip pipettes will be used to measure 15 ml into sterile clean disposable vials for collection in the field.

10.2.5. Precision determination

Standards and samples will be run in triplicate to determine reproducibility and minimize error

10.2.6. Comparison with other methods

IC determinations of nitrite and ammonia are standard procedures. Determination of hydrogen peroxide by reaction with titanium tetrachloride is the accepted technique for low concentration determination of hydrogen peroxide. [Reference]

10.2.7. Audits

No external audits will be carried out

11. Data Management and Quality Control

11.1. Raw Data Recording

Raw 1 - minute spectra from the TDLAS will be recorded on computer as well as a calculated concentration from a fit with the previous calibration.

11.2. Final Data Reporting

1 minute data will be recorded, but data will be presented as either 10, 30 or 60 minute data

11.3. Data Quality Control and Validation

Only Valid Data will be reported.

11.4. Validity Flags

The following NARSTO flags will be used:

V0	Valid value
V1	Valid value but comprised wholly or partially of below-MDL data
M1	Missing value because no value is available
M2	Missing value because invalidated by data originator

11.5. Below Method Detection Limit Values

A macro will be written to flag values that are below the determined detection limit

11.6. Derived Parameters

N/A

11.7. Explanation of Zero or Negative Data

Data below the detection limit will be flagged with V1

12. Data Quality Objectives (Pre-Study)

12.1. Accuracy

The accuracy has yet to be determined. Accuracies of about 2% should be attainable.

12.2. Precision

Precisions of better than 5% are expected

12.3. Comparability

Since we do not expect very well mixed air masses for HONO and ammonia, there may be some spatial variability associated with these measurements, however this variability should be within ~10%

12.4. Representativeness

The measurements at the Langley site will be representative of processed air pollution in which secondary pollutants, such as hydrogen peroxide, will have formed. We are close to the source region for ammonia, so there may be large variability in this point source measurement. HONO is produced on black carbon particles in the presence of NO_2 and water, and is lost through both wet and dry deposition; therefore the concentration is likely to relate to local conditions only.

12.5. Completeness

Following the initial start up period, we expect between 22 and 23 hours per day coverage.

12.6. Other Quality Information

Unaware of any qualifiers at this time

End of Pre-Study QAPjP

Start of Post-Study QA Report

13. Significant Changes to Site, Instruments or Methods During Study

14. Post-study Data Quality Indicators (DQIs)

    14.1.1. Accuracy

    14.1.2. Precision

    14.1.3. Comparability

    14.1.4. Representativeness

    14.1.5. Completeness

    14.2. Blank correction (describe whether done and method used):

    14.3. Other Quality Information

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