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

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3. **Measurement Program**
   Hivol Particle Chemical Characterization Measurements

4. **Measurement Species and Units**
   Hivol: PM 2.5 Aerosol SO_4^{2-}, μgm^{-3} at 0^oC and 1 atm.
   Gas: (possibly SO_2), ppbv

5. **Representative Size Range (if PM)**
   Hivol PM < 2.5 µm

6. **Measurement Platform (surface, airborne)**
   Hivol: Surface - 2m above ground level on trailer

7. **Measurement Sites (surface only)**
   Cassier Tunnel, Langely and Burnaby South High School.

8. **Measurement Objective(s)**
   Hivol: Determine the amount of SO_4^{2-} (and SO_2), and determine their isotopic ratios to assist with aerosol sulphate source identification and formation mechanisms prior to and after fine aerosol formation.

9. **Measurement Details**
   9.1. Field Measurements
      9.1.1. Measurement Principle
      Filtration

      9.1.2. Instrumentation (Manufacturer/Model)
      Sierra Miscu (1970's version no model numbers available) with a WSAG1200 PM2.5 conversion kit.

9.1.3. Flow System

The flow inlet contains an impactor plate to intercept particles above PM 2.5 followed by a filter pack to collect the aerosols of interest. The sampler head is connected to a vacuum motor in series with a mechanical Sierra Miscu flow control system adjusted to operate at a constant flow of 40 scfm. The exhaust from the motor is shunted downwind of the samplers through 20 ft of pipe.

9.1.4. Inlet Height Above Ground (if surface)

Hivol: 2m above ground level on top of platform.

9.1.5. Nominal Flow Rate

40 scfm (standard cubic feet per minute)

9.1.6. Flow Measurement/Control

Kurz model 341 calibrator, serial # 032, 15-60 scfm using mass flow measurements is used to set flow prior to sample program, after motor brushes have been changed, and at the end of the sampling program.

9.1.7. Flow Temperature and Pressure

25 degrees C and 1 atmosphere

9.1.8. Sampling Times/Period/Frequency

Continuous sampling every 24 hours.

9.1.9. Sampling Methods

HVS protocol.

9.1.10. Filter Type/Coating Type/Reagent Type

Particulate: Glass fibre.

Sulphur Dioxide: K_2CO_3 impregnated cellulose nitrate filters.

9.1.11. Planned Changes to Instruments or Methods During Study

None.

9.2. Laboratory Measurements (If Applicable)

9.2.1. Laboratory Name and Address

Isotope Science Laboratory
University of Calgary
University Dr. NW
Calgary AB
T2N 1N4

9.2.2. Analytical Method(s)

IRMS analysis of $^{34}S/^{32}S$ in SO_2 and SO_4^{2-} and $^{18}O/^{16}O$ in SO_4.

9.2.3. Sample Extraction or Work-up

Sonication in deionized, distilled water followed by filtration and

precipitation as $BaSO_4$.

9.2.4. Analytical Detection Limits

10 μg S, 20 μg O.

10. Quality Assurance/Quality Control

10.1. Field Quality Assurance/Quality Control

10.1.1. Traceability

Flow rate calibrations are traceable to NIST Test numbers 213-21/190522.

10.1.2. Calibration

Calibration in the field is performed using the Kurz flow calibrator and logged prior to and after the sampling program at each site. Also a recalibration is performed after motor brushes are changed.

10.1.3. Zeros and spans

N/A

10.1.4. Blanks

As per HVS protocol.

10.1.5. Field Quality Control procedures

Disposable gloves will be worn and filters will be in contact with clean tweezers only. Filters will be inspected for holes and contamination such as grass, insects, etc. which will be removed prior to analysis. Filters will be placed in clean tinfoil and placed in labelled ziplock bags. HVS and head cleaned with distilled, deionized water prior to operation and if contaminated (eg. After grass cutting is observed).

10.1.6. Precision determination

Precision determinations will be assessed prior to the field study by operating duplicate instruments simultaneously for 24 hours.

10.1.7. Comparison with other measurements

The Hivol PM2.5 sulphate concentrations for the isotope samples will be cross-checked with those from similar filtration sampling programs.

10.1.8. Inspections and Audits

Instruments and filters to be inspected daily. Anomalies such as motor noise, filter tear and other flags will be recorded in a daily log book. Flow rate calibration and inspection to be performed a) upon Hivol setup, b) when brushes are changed, c) prior to Hivol takedown.

10.2. Laboratory Quality Assurance/Quality Control

10.2.1. Traceability

Sulphur isotopes are measured against an internal laboratory reference SO_2 (Quemont) similar to, and calibrated to the isotope composition of the international standard, V-CDT. The calibration takes place daily using internal laboratory standards that bracket the isotope composition of the sample material (SW and STB) that are calibrated on a nominal biannual basis to the international reference materials NBS-127, NZ-1 and Zero.

Oxygen isotopes are measured relative to a reference gas CO and calibrated relative to the international standard V-SMOW. The calibration is performed daily using an internal laboratory isotope $BaSO_4$ standard (Fisher-Old) the ratios for which have been determined relative to V-SMOW by a disproportionation technique (Ph.D. thesis Shakur).

10.2.2. Calibration procedures

Six initial standards are run at the start of each day followed by two (or more) calibration standards every ten samples. The isotope composition and amount of standard brackets the ratio and size of the samples analyzed. Standards calibrated to international standards VCDT and VSMOW.

10.2.3. Blanks

Laboratory filter blanks are performed for each sample preparation batch and include the multiple sources of contamination including reagent blank, DD water blanks, glassware blanks, and filter handling contamination.

10.2.4. Other lab QC

Calibration check solutions have been used to assess the quality of the analysis procedures. Duplicate sulphate solutions across a range of concentrations have been prepared and analyzed in an identical manner to samples to ensure quality control.

10.2.5. Precision determination

Gravimetric precision determined by creating replicate solutions of known SO_4^2 concentration, then precipitating SO_4^{2-}, and weighing the resulting $BaSO_4$. ±0.02 mg.

Isotope ratio precision is determined from the standard deviation of replicate measurements of samples: ± 0.5 ‰ for sulphur isotopes, ±1 ‰ for oxygen isotopes.

10.2.6. Comparison with other methods

If SO_2 concentration samples are collected then they will be compared to SO_2 concentration measured by pulse-fluorescence and K_2CO_3 impregnated filters at the same sites.

10.2.7. Audits

No independent audits of the laboratory will be performed specifically for this study. However, the laboratory is the source of several International Atomic Energy Association standards for sulphur isotopes and has undergone numerous intercomparison programs with NIST and other calibration materials.

11. Data Management and Quality Control

11.1. Raw Data Recording

Once daily entry into lab-book and log files including:
Sample Name (e.g. GVRD - CasT)
Start Date (e.g. 25/08/01) time (10:45)
Stop Date (e.g. 26/08/01) time (8:50)
Flow rate: 40 scfm
Sampling time recorded by HVS timer. (x minutes)
Sampling time recorded by operator (y minutes =Start to Stop time)

11.2. Final Data Reporting

24 hour data will be recorded and reported.

11.3. Data Quality Control and Validation

All filter samples will be flagged as either valid (V) or invalid (I). Raw data will be inspected by the PI and all samples containing <24 hours of sampling will be flagged as invalid. Sample identifier tags, and times recorded on sample zip-lock storage bags to be checked against the spreadsheet information prior to sample processing.

11.4. Validity Flags

OK	Valid data
TF	Torn Filter
VC	Visible Contamination (with descriptor)
WB	Worn Brushes (Hivol sampling interrupted)
PNF	Protocol Not Followed (and descriptor)
RN	Raining during sampling (and descriptor: sprinkle, drizzle, shower, downpour)

11.5. Below Method Detection Limit Values

Samples below detection limits will be corrected and evaluated using a series of standards bracketing the sample size. Replicates of a laboratory reference will be used to identify the precision of the measurements.

11.6. Derived Parameters

Non-sea-salt sulphate isotope ratios will be calculated using sulphate to sodium ratios for sea water (0.252) and isotope mass balance calculations.

11.7. Explanation of Zero or Negative Data

In the event of a Hivol motor failure no sample data will be recorded. Below detection limit or blank corrections may produce zero or negative values in the data set.

12. Data Quality Objectives (Pre-Study)

12.1. Accuracy

The accuracy of the isotope measurements for particles between 0.03 μm to 2.5 μm cannot be ascertained at this time.

12.2. Precision

Measurement precision for replicate gravimetric determinations < ±15%.
δ-value replicate measurements < ± 1.

12.3. Comparability

Measurements for concentration using Filtration techniques are expected to compare within ± 15% with other techniques.
Isotope measurements are expected to compare within ± 1 ‰.

12.4. Representativeness

Samples collected on days when RH (relative humidity) < 98% are expected to be representative for the approximate size range 0.03 μm to 2.5 μm.

12.5. Completeness

Completeness objective = 80 % calculated as the number of 24 hour periods with valid data (including periods of instrument failure, power failure, contamination etc.).

12.6. Other Quality Information

End of Pre-Study QAPjP