

## **Section G**

# **AIR CONSTITUENTS - INORGANIC**

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## Particulate - Total

|   |  |
|---|--|
| <b>Parameter</b>                        | Particulate – Total: Gravimetric   |
| <b>Analytical Method and EMS Code</b>   | a) Gravimetric intermediate results <b>TP-T X484</b><br>b) Loading results <b>TP-T CAL1</b>  |
| <b>Introduction</b>                     | A 10.4 cm (4.1") diameter polyethylene canister containing a collection medium is exposed to the ambient air for a period of approximately 30 days. The sample subsequently undergoes gravimetric and/or chemical analysis in the laboratory plus loading calculation.   |
| <b>Method Summary</b>                   | The Total Particulate is the sum of Insoluble Particulate and the Soluble Particulate.   |
| <b>MDL</b>                              | 0.1 mg for intermediate result   |
| <b>Units</b>                            | a) Intermediate results: mg<br>b) Loading results: mg/dm <sup>2</sup> /d   |
| <b>Matrix</b>                           | Particulate  |
| <b>Sample Handling and Preservation</b> | If the temperature during the sampling period is below 0°C, either isopropanol or 50% V/V isopropanol/water is used as the solution in the canister.   |
| <b>Principle or Procedure:</b>          | Gravimetric, 550°C   |
| <b>Field Preparation</b>                | a) Add 500 mL of the collection medium to the 10.4 cm diameter polyethylene canister (canister must have a tight fitting, waterproof lid). Usually deionized water, to which 2.0 mL diluted algae inhibitor has been added, is used. However, if the temperature during the sampling period is below 0°C, either isopropanol or 50% V/V isopropanol/water is used. The algae inhibitor is obtained commercially and diluted 1:100 before use (Note: algae inhibitor must be added to all analytical blanks).<br><br>b) Ship the prepared canisters to the field. |
| <b>Laboratory Preparation</b>           | a) Transfer the sample quantitatively to a 2 litre beaker, filtering through a 20 mesh sieve to remove extraneous materials such as leaves, twigs and bugs. If the collection medium was isopropanol, use 50 to 100 mL deionized water in the transfer process.<br><br>b) Reduce the sample volume to about 200 mL by evaporating on a hot plate.<br><br>c) Allow the sample to cool, proceed to further analyses of the requested parameters i.e., step 4 of Particulate Soluble and/or Particulate Insoluble procedures.                                       |
| <b>Calculation</b>                      | Total Particulate, mg = P <sub>1</sub> + P <sub>2</sub><br><br>where:                      P <sub>1</sub> = Insoluble Particulate in mg<br>P <sub>2</sub> = Soluble Particulate in mg  |
| <b>Quality Control</b>                  | Retain at least four of the canisters so that they may subsequently be used in the determination of the various blank values.  |
| <b>References</b>                       | a) American Society of Testing and Materials. <u>Annual Book of ASTM Standards; Part 26</u> . Philadelphia, (1974).  |

## Revision History

April 1, 1996: Initial draft.

October 29, 1996: Procedure vetted by private sector laboratories.

July 9, 1997: Conversion to EMS code; unit correction as confirmed by E. Tradewell and N. Peppin.

July 14, 1997: Term "Dustfall" replaced by "Particulate" on request of E. Tradewell.

January 5, 1998: EMS codes confirmed.

December 31, 2000: Minor editing; Supplement #2 merged into main Lab Manual.

## Particulate - Total Ashed

|                                       |  |   |
|---------------------------------------|--|---|
| <b>Parameter</b>                      | Particulate - Total Ashed  |   |
| <b>Analytical Method and EMS Code</b> | a) Gravimetric intermediate result<br>b) Loading result  | <b>ASHT X484</b><br><b>ASHT CAL1</b>                                    |
| <b>Introduction</b>                   | A 10.4 cm (4.1") diameter polyethylene canister containing a collection medium is exposed to the ambient air for a period of approximately 30 days. The sample subsequently undergoes gravimetric and/or chemical analysis in the laboratory plus loading calculation. |   |
| <b>Method Summary</b>                 | The Total Ashed Particulate is the sum of the Insoluble Ashed and Soluble Ashed Particulate.   |   |
| <b>MDL</b>                            | 0.1 mg for intermediate results  |   |
| <b>Units</b>                          | a) Intermediate results: mg<br>b) Loading results: mg/dm <sup>2</sup> /d   |   |
| <b>Matrix</b>                         | Particulate  |   |
| <b>Principle or Procedure:</b>        | Gravimetric, 550°C   |   |
| <b>Calculation</b>                    | Total Ashed Particulate = $P_1 + P_2$<br>where: $P_1$ = Insoluble Ashed Particulate<br>$P_2$ = Soluble Ashed Particulate   |   |
| <b>Quality Control</b>                | A blank should be carried through all steps of the procedure.  |   |
| <b>References</b>                     | a) American Society of Testing and Materials. <u>Annual Book of ASTM Standards; Part 26</u> . Philadelphia, (1974).  |   |
| <b>Revision History</b>               | April 1, 1996:   | Initial draft.  |
|                                       | October 29, 1996:  | Procedure vetted by private sector laboratories.                        |
|                                       | July 9, 1997:  | SEAM code replaced by EMS code; units correction.                       |
|                                       | July 14, 1997:   | Term "Dustfall" replaced by "Particulate" on request from E. Tradewell. |
|                                       | January 5, 1998:   | EMS codes confirmed.  |
|                                       | December 31, 2000:   | Minor editing; Supplement #2 merged into main Lab Manual.               |

## Particulate - Total Combustible

|                                       |  |   |
|---------------------------------------|--|---|
| <b>Parameter</b>                      | Particulate - Total Combustible  |   |
| <b>Analytical Method and EMS Code</b> | a) Gravimetric intermediate result<br>b) Loading result  | <b>CP-T X484</b><br><b>CP-T CAL1</b>                                    |
| <b>Introduction</b>                   | A 10.4 cm (4.1") diameter polyethylene canister containing a collection medium is exposed to the ambient air for a period of approximately 30 days. The sample subsequently undergoes gravimetric and/or chemical analysis in the laboratory plus loading calculation. |   |
| <b>Method Summary</b>                 | The Total Combustible Particulate is the difference between the Total Particulate and the Total Ashed Particulate.   |   |
| <b>MDL</b>                            | 0.1 mg for intermediate results  |   |
| <b>Units</b>                          | a) Intermediate results: mg<br>b) Loading results: mg/dm <sup>2</sup> /d   |   |
| <b>Matrix</b>                         | Particulate  |   |
| <b>Principle or Procedure:</b>        | Gravimetric, 550°C   |   |
| <b>Calculation</b>                    | Total Combustible Particulate = $P_1 - P_2$<br>where: $P_1$ = Total Particulate<br>$P_2$ = Total Ashed Particulate   |   |
| <b>Quality Control</b>                | A blank should be carried through all steps of the procedure.  |   |
| <b>References</b>                     | a) American Society of Testing and Materials. <u>Annual Book of ASTM Standards; Part 26</u> . Philadelphia, (1974).  |   |
| <b>Revision History</b>               | April 1, 1996:   | Initial draft.  |
|                                       | October 29, 1996:  | Procedure vetted by private sector laboratories.                        |
|                                       | July 9, 1997:  | SEAM code replaced by EMS code; units correction.                       |
|                                       | July 14, 1997:   | Term "Dustfall" replaced by "Particulate" on request from E. Tradewell. |
|                                       | January 5, 1998:   | EMS codes confirmed.  |
|                                       | December 31, 2000:   | Minor editing; Supplement #2 merged into main Lab Manual.               |

## Particulate - Insoluble

|                                       |   |
|---------------------------------------|---|
| <b>Parameter</b>                      | Particulate Insoluble   |
| <b>Analytical Method and EMS Code</b> | a) Gravimetric intermediate results <b>TP-I X484</b><br>b) Loading results <b>TP-I X175</b>   |
| <b>Introduction</b>                   | A 10.4 cm (4.1") diameter polyethylene canister containing a collection medium is exposed to the ambient air for a period of approximately 30 days. The sample subsequently undergoes gravimetric and/or chemical analysis in the laboratory plus loading calculation.  |
| <b>Method Summary</b>                 | The prepared sample (see Particulate-Total procedure) is passed through a 0.45 $\mu\text{m}$ membrane filter. The residue retained by the filter after drying to a constant weight at 105°C constitutes the insoluble particulate intermediate results with units of mg. This value is then converted to a loading unit of mg/dm <sup>2</sup> /d.   |
| <b>MDL</b>                            | 0.1 mg for intermediate results   |
| <b>Units</b>                          | a) Intermediate results: mg<br>b) Loading results: mg/dm <sup>2</sup> /d  |
| <b>Matrix</b>                         | Particulate   |
| <b>Principle or Procedure:</b>        | Gravimetric, 105°C  |
| <b>Apparatus</b>                      | a) Filtration apparatus, one litre vacuum flask fitted with a filtration assembly<br>b) Porcelain crucibles, 35 mL<br>c) Drying oven<br>d) Muffle furnace<br>e) Desiccator with desiccant<br>f) Analytical balance  |
| <b>Procedure</b>                      | a) Ignite a clean porcelain crucible at 550°C in the muffle furnace for 1 hour; cool for 3 hours in a desiccator, then weigh.<br>b) Weigh a 0.45 $\mu\text{m}$ filter (Gelman HT 450, 47 mm diameter). Place filter in desiccator.<br>c) Carefully place the 0.45 $\mu\text{m}$ filter in the filtration apparatus.<br>d) Filter the prepared sample (see Particulate-Total). Note: Wash the sample container with deionized water to ensure all the sample is passed through the filter.<br>e) Transfer the filtrate quantitatively to a 500 mL bottle, dilute to volume, and then transfer to a polyethylene container for further analysis.<br>f) Return the filter and retained residue to the porcelain crucible; dry for 3 hours in an oven at 105°C; cool in desiccator and weigh. |

**Calculations**

Insoluble Particulate, mg =  $\{(W_1 - W_2) - C\}$

where  $W_1$  = weight of filter + crucible + residue in mg  
 $W_2$  = weight of filter + crucible in mg  
C = weight contribution from blank in mg

Loading calculation: units of mg/dm<sup>2</sup>/d

**Quality Control**

A blank should be carried through all steps of the procedure.

**References**

a) American Society of Testing and Materials. Annual Book of ASTM Standards; Part 26. Philadelphia, (1974).

**Revision History**

April 1, 1996: Initial draft.  
October 29, 1996: Procedure vetted by private sector laboratories.  
July 14, 1997: SEAM code replaced by EMS code; units; minor editing revisions; term "Dustfall" replaced by "Particulate" on request of E. Tradewell.  
January 5, 1998: EMS codes confirmed.  
December 31, 2000: Minor editing; Supplement #2 merged into main Lab Manual.



## Particulate - Insoluble Ashed

|                                       |  |                  |
|---------------------------------------|--|------------------|
| <b>Parameter</b>                      | Particulate – Insoluble Ashed  |                  |
| <b>Analytical Method and EMS Code</b> | a) Gravimetric Intermediate results  | <b>AP-I X484</b> |
|                                       | b) Loading results   | <b>AP-I X175</b> |
| <b>Introduction</b>                   | A 10.4 cm (4.1") diameter polyethylene canister containing a collection medium is exposed to the ambient air for a period of approximately 30 days. The sample subsequently undergoes gravimetric and/or chemical analysis in the laboratory plus loading calculation. |                  |
| <b>Method Summary</b>                 | The prepared sample (see Particulate-Total procedure) is passed through a 0.45 µm membrane filter. The residue after ignition at 550°C constitutes the ashed insoluble particulate.  |                  |
| <b>MDL</b>                            | 0.1 mg for intermediate result   |                  |
| <b>Units</b>                          | a) Intermediate results: mg  |                  |
|                                       | b) Loading results: mb/dm <sup>2</sup> /d  |                  |
| <b>Matrix</b>                         | Particulate  |                  |
| <b>Principle or Procedure:</b>        |  |                  |
| <b>Apparatus</b>                      | a) Filtration apparatus, one litre vacuum flask fitted with a filtration assembly  |                  |
|                                       | b) Porcelain crucibles, 35 mL  |                  |
|                                       | c) Muffle furnace  |                  |
|                                       | d) Desiccator with desiccant   |                  |
|                                       | e) Analytical balance  |                  |
| <b>Procedure</b>                      | a) Ignite a clean porcelain crucible at 550°C in the muffle furnace for 1 hour; cool for 3 hours in a desiccator, then weigh.  |                  |
|                                       | b) Weigh a 0.45 µm filter (Gelman HT 450, 47 mm diameter). Place filter in desiccator.   |                  |
|                                       | c) Carefully place the 0.45 µm filter in the filtration apparatus.   |                  |
|                                       | d) Filter the prepared sample (see Particulate-Total procedure). Note: Wash the sample container with deionized water to ensure all the sample is passed through the filter.   |                  |
|                                       | e) Return the filter and retained residue to the porcelain crucible; dry for 3 hours in an oven at 105°C; cool in desiccator and weigh.  |                  |
|                                       | f) Transfer the crucible and filter to a muffle furnace.   |                  |
|                                       | g) Heat at 550°C for 1 hr, cool for 3 hr in a desiccator and then weigh, W <sub>1</sub> .  |                  |
| <b>Calculations</b>                   | Ashed Insoluble Particulate = $\{(W_1 - W_2) - C\}$  |                  |
|                                       | where $W_1$ = weight of filter + crucible + residue in mg, ( after ashing)   |                  |
|                                       | $W_2$ = weight of filter + crucible in mg, (after ashing)  |                  |
|                                       | C = weight contribution from blank in mg   |                  |
|                                       | This is followed by a loading calculation to units of mg/dm <sup>2</sup> /d  |                  |

**Quality Control**

A blank should be carried through all steps of the procedure.

**References**

- a) American Society of Testing and Materials. Annual Book of ASTM Standards; Part 26. Philadelphia, (1974).

**Revision History**

- April 1, 1996: Initial draft.
- October 29, 1996: Procedure vetted by private sector laboratories.
- July 15, 1997: SEAM code replaced with EMS code; units correction; minor editing corrections; term "Dustfall" replaced by "Particulate" on request of E. Tradewell.
- January 5, 1998: EMS codes confirmed.
- December 31, 2000: Minor editing; Supplement #2 merged into main Lab Manual.

## Particulate - Soluble

|                                       |  |                  |
|---------------------------------------|--|------------------|
| <b>Parameter</b>                      | Particulates, Soluble  |                  |
| <b>Analytical Method and EMS Code</b> | a) Gravimetric intermediate results  | <b>TP-S X484</b> |
|                                       | b) Loading results   | <b>TP-S X175</b> |
| <b>Introduction</b>                   | A 10.4 cm (4.1") diameter polyethylene canister containing a collection medium is exposed to the ambient air for a period of approximately 30 days. The sample subsequently undergoes gravimetric and/or chemical analysis in the laboratory plus loading calculation.   |                  |
| <b>Method Summary</b>                 | The prepared sample (see Particulate Total procedure) is passed through a 0.45 $\mu\text{m}$ membrane filter. A portion of the filtrate is then evaporated on an oven; the portion which dries to constant weight at 105°C constitutes the soluble particulate.  |                  |
| <b>MDL</b>                            | 0.1 mg for intermediate results  |                  |
| <b>Units</b>                          | a) Intermediate results: mg  |                  |
|                                       | b) Loading results: mg/dm <sup>2</sup> /d  |                  |
| <b>Matrix</b>                         | Particulates   |                  |
| <b>Principle or Procedure:</b>        | Gravimetric  |                  |
| <b>Apparatus</b>                      | a) Inert crucibles, 100 mL (e.g. nickel, porcelain, platinum)<br>b) Drying oven<br>c) Steam Bath<br>d) Desiccator with desiccant<br>e) Analytical balance  |                  |
| <b>Procedure</b>                      | a) Ignite a clean porcelain crucible at 550°C in the muffle furnace for 1 hour; cool for 3 hours in a desiccator, then weigh.<br>b) Weigh a 0.45 $\mu\text{m}$ filter (Gelman HT 450, 47 mm diameter). Place filter in desiccator.<br>c) Carefully place the 0.45 $\mu\text{m}$ filter in the filtration apparatus.<br>d) Filter the prepared sample (see Particulate-Total procedure). Note: Wash the sample container to ensure all the sample is passed through the filter.<br>e) Return the filter and retained residue to the porcelain crucible; dry for 3 hours in an oven at 105°C; cool in desiccator and weigh.<br>f) Transfer the filtrate quantitatively to a 500 mL beaker, dilute to volume, and then transfer to a polyethylene container.<br>g) Dry a clean platinum crucible to constant weight at 550°C; cool in a desiccator and then weigh.<br>h) Measure 2 x 50 mL of the prepared filtrate into the crucible.<br>i) Evaporate overnight (24-48 hours) in an oven at 105°C; cool in a desiccator and weigh. |                  |

**Calculations**

$$\text{Soluble particulate, mg} = \frac{V_1}{V_2} \{(W_1 - W_2) - C\}$$

where  $V_1$  = mL filtrate diluted (at step 6)  
 $V_2$  = mL filtrate evaporated  
 $W_1$  = weight of crucible + residue in mg  
 $W_2$  = weight of crucible in mg  
 $C$  = weight contribution from blank in mg

This is followed by a loading calculation to units of mg/dm<sup>2</sup>/d.

**Quality Control**

A blank should be carried through all steps of the procedure.

**References**

- a) American Society of Testing and Materials. Annual Book of ASTM Standards; Part 26. Philadelphia, (1974).

**Revision History**

- April 1, 1996: Initial draft.
- October 29, 1996: Procedure vetted by private sector laboratories.
- July 15, 1997: SEAM code replaced with EMS code; units correction; minor editing corrections; term "Dustfall" replaced by "Particulate" at request of E. Tradewell.
- January 5, 1998: EMS codes confirmed.
- December 31, 2000: Minor editing; Supplement #2 merged into main Lab Manual.

## Particulate - Soluble Ashed

|                                       |   |  |
|---------------------------------------|---|--|
| <b>Parameter</b>                      | Particulate - Soluble Ashed   |  |
| <b>Analytical Method and EMS Code</b> | a) Gravimetric intermediate results   | <b>AP-S X484</b>   |
|                                       | b) Loading results  | <b>AP-S X175</b>   |
| <b>Introduction</b>                   | A 10.4 cm (4.1") diameter polyethylene canister containing a collection medium is exposed to the ambient air for a period of approximately 30 days. The sample subsequently undergoes gravimetric and/or chemical analysis in the laboratory followed by loading calculation.   |  |
| <b>Method Summary</b>                 | The prepared sample (see Particulate-Total procedure) is passed through a 0.45 µm membrane filter. A portion of the filtrate is then evaporated in an oven; the portion which ignites to constant weight at 550°C constitutes the ashed soluble particulate. It should be noted that if the ashed soluble particulate procedure is completed, this will preclude phosphorus and metal analysis. |  |
| <b>MDL</b>                            | 0.1 mg particulate  |  |
| <b>Units</b>                          | a) Intermediate results: mg   |  |
|                                       | b) Loading results: mg/dm <sup>2</sup> /d   |  |
| <b>Matrix</b>                         | Particulate   |  |
| <b>Principle or Procedure:</b>        |   |  |
| <b>Apparatus</b>                      | a) Inert crucibles, 100 mL (e.g. nickel, porcelain)   |  |
|                                       | b) Muffle Furnace   |  |
|                                       | c) Desiccator with desiccant  |  |
|                                       | d) Analytical balance   |  |
| <b>Procedure</b>                      | a) After completing step 9 in the Particulate Soluble procedure transfer the crucible to a muffle furnace.  |  |
|                                       | b) Heat at 550 °C for 1 hr; cool for 3 hr in a desiccator and then weigh.   |  |
| <b>Calculation</b>                    | Soluble Ashed Particulate, mg = $\frac{V_1 \{(W_1 - W_2) - C\}}{V_2}$   |  |
|                                       | where:  | $V_1$ = mL filtrate diluted<br>$V_2$ = mL filtrate evaporated<br>$W_1$ = weight of platinum crucible + residue, mg<br>$W_2$ = weight of platinum crucible, mg<br>$C$ = weight of contribution from blank, mg |
|                                       | This is followed by a loading calculation.  |  |
| <b>Quality Control</b>                | A blank should be carried through all steps of the procedure.   |  |
| <b>References</b>                     | a)  | American Society of Testing and Materials. <u>Annual Book of ASTM Standards; Part 26</u> . Philadelphia, (1974).   |

## Revision History

April 1, 1996: Initial draft.

October 29, 1996: Procedure vetted by private sector laboratories.

July 23, 1997: SEAM code replaced with EMS code; units correction; minor editing corrections; term "Dustfall" replaced by "Particulate" on request of E. Tradewell.

January 6, 1998: EMS codes confirmed.

December 31, 2000: Minor editing; Supplement #2 merged into main Lab Manual.

## Particulate - Soluble – Anions and Cations by Ion Chromatography

|                                |  |  |
|--------------------------------|--|--|
| <b>Parameter</b>               | NO <sub>3</sub> -: Nitrate-Soluble<br>SO <sub>4</sub> -: Sulphate-Soluble<br>Cl-S: Chloride-Soluble  | Na-S: Sodium-Soluble<br>NH <sub>4</sub> -: Ammonium-Soluble<br>K--S: Potassium Soluble |
| <b>Analytical Method</b>       | Ion Chromatography-Anion   |  |
| <b>EMS codes</b>               | <u>Intermediate Results</u>  | <u>Loading Results</u>   |
|                                | NO <sub>3</sub> - 5068   | NO <sub>3</sub> - 5049   |
|                                | SO <sub>4</sub> - 5068   | SO <sub>4</sub> - 5049   |
|                                | Cl-S 5068  | Cl-S 5049  |
|                                | Ca-S 5070  | Ca-S 5061  |
|                                | Na-S 5071  | Na-S 5061  |
|                                | K--S 5071  | K--S 5061  |
|                                | NH <sub>4</sub> - 5071   | NH <sub>4</sub> - 5061   |
|                                | Mg-S 5070  | Mg-S 5061  |
| <b>Introduction</b>            | A 10.4 cm (4.1") diameter polyethylene canister containing a collection medium is exposed to the ambient air for a period of approximately 30 days. The sample subsequently undergoes gravimetric and/or chemical analysis in the laboratory, followed by a loading calculation. |  |
| <b>Method Summary</b>          | A portion of filtrate from the Particulate-Total procedure made up to 500 mL is analyzed by Ion Chromatography, then converted to loading units.   |  |
| <b>MDL</b>                     | 0.1 mg/L for intermediate results  |  |
| <b>Units</b>                   | a) Intermediate results: mg/L<br>b) Loading results: mg/dm <sup>2</sup> /d   |  |
| <b>Matrix</b>                  | Particulate  |  |
| <b>Principle or Procedure:</b> |  |  |
| <b>Procedure</b>               | Analyze an aliquot of prepared sample (see Particulate-Total) by Ion Chromatography in accordance with the procedures for Anions - Ion Chromatography - Precipitation <b>or</b> Cations - Ion Chromatography-Precipitation.  |  |
| <b>Quality Control</b>         | A blank should be carried through all steps of the procedure.  |  |
| <b>Revision History</b>        | April 30, 1996: Initial draft.   |  |
|                                | October 29, 1996: Procedure vetted by private sector laboratories. Note regarding alternative methods added.   |  |
|                                | July 11, 1997: SEAM codes replaced by EMS codes; units correction; term "Dustfall" replaced by "Particulate" on request of E. Tradewell.   |  |
|                                | January 8, 1998: EMS codes verified; magnesium added.  |  |
|                                | December 31, 2000: Minor editing; Supplement #2 merged into main Lab Manual. Also reference in Note 2 changed to current edition of Lab Manual.  |  |

**Note 1: While anions and cations are usually reported for water samples on an elemental basis, for air samples, the convention is to report on an ion weight basis. Thus, ammonia is reported as mg/L and mg/dm<sup>2</sup>/d as NH<sub>4</sub> and nitrate is reported as mg/L and mg/dm<sup>2</sup>/d as NO<sub>3</sub>.**

**Note 2: Note that the listed anions and cations may alternatively be analyzed according to any relevant procedure specified in this edition of the BC Environmental Laboratory Manual.**



## Particulate - Metals - ICP

|                                      |   |
|--------------------------------------|---|
| <b>Parameters</b>                    | Arsenic, Cadmium, Copper, Lead, Zinc  |
| <b>Analytical Method</b>             | Acid Digestion - ICP Analysis   |
| <b>EMS Code</b>                      | See following page  |
| <b>Introduction</b>                  | An aliquot of prepared air particulate sample (see the Particulate-Total procedure) is digested by nitric perchloric acid digestion procedure.  |
| <b>Method Summary</b>                | Following acid digestion, aqueous solutions of metals are converted to aerosols in the nebulizer of the ICP and injected directly into a high temperature plasma (6000 to 8000°K). This highly efficient ionization produces ionic emission spectra at wavelengths specific to the elements of interest which can be monitored either simultaneously or sequentially.   |
| <b>MDL</b>                           | The following MDL concentrations (see table) are extrapolated from aqueous solutions. For instrument and analytical method MDL values, see Section C – Metals. A constant ratio (within rounding) of 11.77 has been used to convert mg/L to mg/dm <sup>2</sup> /d.  |
| <b>Matrix</b>                        | Ambient Air Particulates  |
| <b>Interferences and Precautions</b> | See Section C – Metals, paragraph 2.4.4.  |
| <b>Stability</b>                     | Samples are stable.   |
| <b>Reagents</b>                      | a) Nitric Acid, Concentrated, analytical<br>b) Perchloric acid, 70%, analytical   |
| <b>Procedure</b>                     | a) Place an aliquot of prepared sample (see Particulate-Total, Particulate-Insoluble, and Particulate-Soluble procedures) into a calibrated 75 mL digestion tube, add two mL HNO <sub>3</sub> and heat cautiously to oxidize any organic matter; do not take to dryness.<br>b) Cool, then add 3.75 mL HClO <sub>4</sub> . Heat until dense white fumes are present. Final conditions are 5% HClO <sub>4</sub> .<br>c) Cool and make up to 75 ml with deionized water.<br>d) Filter through Whatman #41 filter paper and collect the filtrate in a 250 mL polyethylene bottle, and bring to volume (record this volume for calculations).<br>e) Analyze for As, Cd, Cu, Pb, Zn by ICP by procedures given in Section C - Metals.<br>f) For particulate metals soluble only step 5 is required. |

## EMS Codes

| Element             |              | EMS Code<br>(nitric/perchloric<br>acid digestion) | EMS Code<br>(aqua regia<br>digestion) | MDL                          |
|---------------------|--------------|---|---------------------------------------|------------------------------|
| Arsenic - Soluble   | Intermediate | <b>AS-S 5038</b>                                  | <b>AS-S 6038</b>                      | 0.08 mg/L                    |
|                     | Loading      | <b>AS-S 5039</b>                                  | <b>AS-S 6039</b>                      | 0.005 mg/dm <sup>2</sup> /d  |
| Arsenic - Insoluble | Intermediate | <b>AS-I 5038</b>                                  | <b>AS-I 6038</b>                      | 0.08 mg/L                    |
|                     | Loading      | <b>AS-I 5039</b>                                  | <b>AS-I 6039</b>                      | 0.005 mg/dm <sup>2</sup> /d  |
| Arsenic – Total     | Intermediate | <b>AS-T 5038</b>                                  | <b>AS-T 6038</b>                      | 0.08 mg/L                    |
|                     | Loading      | <b>AS-T 5039</b>                                  | <b>AS-T 6039</b>                      | 0.005 mg/dm <sup>2</sup> /d  |
| Cadmium - Soluble   | Intermediate | <b>CD-S 5038</b>                                  | <b>CD-S 6038</b>                      | 0.004 mg/L                   |
|                     | Loading      | <b>CD-S 5039</b>                                  | <b>CD-S 6039</b>                      | 0.0001 mg/dm <sup>2</sup> /d |
| Cadmium - Insoluble | Intermediate | <b>CD-I 5038</b>                                  | <b>CD-I 6038</b>                      | 0.004 mg/L                   |
|                     | Loading      | <b>CD-I 5039</b>                                  | <b>CD-I 6039</b>                      | 0.0001 mg/dm <sup>2</sup> /d |
| Cadmium - Total     | Intermediate | <b>CD-T 5038</b>                                  | <b>CD-T 6038</b>                      | 0.004 mg/L                   |
|                     | Loading      | <b>CD-T 5039</b>                                  | <b>CD-T 6039</b>                      | 0.0001 mg/dm <sup>2</sup> /d |
| Copper - Soluble    | Intermediate | <b>CU-S 5038</b>                                  | <b>CU-S 6038</b>                      | 0.004 mg/L                   |
|                     | Loading      | <b>CU-S 5039</b>                                  | <b>CU-S 6039</b>                      | 0.0005 mg/dm <sup>2</sup> /d |
| Copper - Insoluble  | Intermediate | <b>CU-I 5038</b>                                  | <b>CU-I 6038</b>                      | 0.004 mg/L                   |
|                     | Loading      | <b>CU-I 5039</b>                                  | <b>CU-I 6039</b>                      | 0.0005 mg/dm <sup>2</sup> /d |
| Copper - Total      | Intermediate | <b>CU-T 5038</b>                                  | <b>CU-T 6038</b>                      | 0.004 mg/L                   |
|                     | Loading      | <b>CU-T 5039</b>                                  | <b>CU-T 6039</b>                      | 0.0005 mg/dm <sup>2</sup> /d |
| Lead - Soluble      | Intermediate | <b>PB-S 5038</b>                                  | <b>PB-S 6038</b>                      | 0.06 mg/L                    |
|                     | Loading      | <b>PB-S 5039</b>                                  | <b>PB-S 6039</b>                      | 0.01 mg/dm <sup>2</sup> /d   |
| Lead - Insoluble    | Intermediate | <b>PB-I 5038</b>                                  | <b>PB-I 6038</b>                      | 0.06 mg/L                    |
|                     | Loading      | <b>PB-I 5039</b>                                  | <b>PB-I 6039</b>                      | 0.01 mg/dm <sup>2</sup> /d   |
| Lead - Total        | Intermediate | <b>PB-T 5038</b>                                  | <b>PB-T 6038</b>                      | 0.06 mg/L                    |
|                     | Loading      | <b>PB-T 5039</b>                                  | <b>PB-T 6039</b>                      | 0.01 mg/dm <sup>2</sup> /d   |
| Zinc - Soluble      | Intermediate | <b>ZN-S 5038</b>                                  | <b>ZN-S 6038</b>                      | 0.01 mg/L                    |
|                     | Loading      | <b>ZN-S 5039</b>                                  | <b>ZN-S 6039</b>                      | 0.001 mg/dm <sup>2</sup> /d  |
| Zinc - Insoluble    | Intermediate | <b>ZN-I 5038</b>                                  | <b>ZN-I 6038</b>                      | 0.01 mg/L                    |
|                     | Loading      | <b>ZN-I 5039</b>                                  | <b>ZN-I 6039</b>                      | 0.001 mg/dm <sup>2</sup> /d  |
| Zinc - Total        | Intermediate | <b>ZN-T 5038</b>                                  | <b>ZN-T 6038</b>                      | 0.01 mg/L                    |
|                     | Loading      | <b>ZN-T 5039</b>                                  | <b>ZN-T 6039</b>                      | 0.001 mg/dm <sup>2</sup> /d  |

|                         |  |
|-------------------------|--|
| <b>Calculation</b>      | <p>From the results obtained in mg/L from the ICP analysis, select the calculation method appropriate to the reporting requirements.</p> <p>mg Metal = CV</p> <p>where: C = mg/L Metal in sample<br/>V = sample volume in liters</p>   |
| <b>Quality Control</b>  | <p>To ensure accuracy and precision, quality control blanks, duplicates, and spikes must be incorporated into the analysis scheme. It should be noted that a wide variety of certified reference materials for water are available and are appropriate for soluble particulate metals analysis. Suitable reference materials for insoluble particulates are less available.</p>  |
| <b>References</b>       | <p>None listed.</p>  |
| <b>Revision History</b> | <p>April 1, 1996: Initial draft.</p> <p>October 29, 1996: Procedure vetted by private sector laboratories; and at their request, a note was added regarding substitution of aqua regia digestion for perchloric acid digestion procedure.</p> <p>January 8, 1998: SEAM code replaced with EMS code; term "Dustfall" replaced with "Particulate" on request of E. Tradewell; EMS codes confirmed.</p> <p>February 17, 1998: EMS code for intermediate results revised to eliminate redundant variables; revised MDLs per Dr. D. Jeffery.</p> <p>December 31, 2000: Minor editing; Supplement #2 merged into main Lab Manual. Reference to 1994 Manual deleted. Also preference for aqua regia digestion over perchloric acid digestion noted.</p> |

|  |
|--|
| <p><b>Note: Aqua regia digestion is preferred in place of the nitric/perchloric acid digestion procedure. Note that these different procedures have been assigned different EMS codes.</b></p> |
|--|

## Particulate - Phosphate

|                                      |   |                        |                             |                        |           |                  |                  |         |                  |                  |
|--------------------------------------|---|------------------------|-----------------------------|------------------------|-----------|------------------|------------------|---------|------------------|------------------|
| <b>Parameter</b>                     | Phosphate Total Insoluble<br>Phosphate Total Soluble  |                        |                             |                        |           |                  |                  |         |                  |                  |
| <b>Analytical Method</b>             | Dig: Auto Color Ascorbic Acid   |                        |                             |                        |           |                  |                  |         |                  |                  |
| <b>EMS Code</b>                      | <table border="0" style="width: 100%;"> <tr> <td></td> <td style="text-align: center;"><u>Intermediate Results</u></td> <td style="text-align: center;"><u>Loading Results</u></td> </tr> <tr> <td>Insoluble</td> <td style="text-align: center;"><b>PP-I 5139</b></td> <td style="text-align: center;"><b>PP-I 5132</b></td> </tr> <tr> <td>Soluble</td> <td style="text-align: center;"><b>PP-S 5139</b></td> <td style="text-align: center;"><b>PP-S 5135</b></td> </tr> </table>  |                        | <u>Intermediate Results</u> | <u>Loading Results</u> | Insoluble | <b>PP-I 5139</b> | <b>PP-I 5132</b> | Soluble | <b>PP-S 5139</b> | <b>PP-S 5135</b> |
|                                      | <u>Intermediate Results</u>   | <u>Loading Results</u> |                             |                        |           |                  |                  |         |                  |                  |
| Insoluble                            | <b>PP-I 5139</b>  | <b>PP-I 5132</b>       |                             |                        |           |                  |                  |         |                  |                  |
| Soluble                              | <b>PP-S 5139</b>  | <b>PP-S 5135</b>       |                             |                        |           |                  |                  |         |                  |                  |
| <b>Introduction</b>                  | A 10.4 cm (4.1") diameter polyethylene canister containing a collection medium is exposed to the ambient air for a period of approximately 30 days. The sample subsequently undergoes gravimetric and/or chemical analysis in the laboratory.   |                        |                             |                        |           |                  |                  |         |                  |                  |
| <b>Method Summary</b>                | The prepared sample (see Particulate-Total procedure) is passed through a 0.45 µm membrane filter. The organic material in the sample undergoes a sulfuric acid persulfate digestion. This oxidizes the organically bound phosphorus to phosphate. The digestion with acid also hydrolyses polyphosphates to ortho phosphate. The ortho phosphate released by digestion and hydrolysis plus the ortho phosphate originally present in the sample is then reacted with ammonium molybdate to form heteropoly molybdophosphoric acid. Finally, the molybdophosphoric acid is reduced by ascorbic acid to a blue coloured complex which is measured colorimetrically at 880 nm. It is to be noted that at the concentration sulfuric acid used in the method, silica does not interfere. |                        |                             |                        |           |                  |                  |         |                  |                  |
| <b>MDL</b>                           | 0.003 mg/L P for intermediate results   |                        |                             |                        |           |                  |                  |         |                  |                  |
| <b>Units</b>                         | a) Intermediate results: mg/L<br>b) Loading results: mg/dm <sup>2</sup> /d  |                        |                             |                        |           |                  |                  |         |                  |                  |
| <b>Matrix</b>                        | Particulate   |                        |                             |                        |           |                  |                  |         |                  |                  |
| <b>Interferences and Precautions</b> | a) Arsenic at levels above 0.10 mg/ L interferes by producing a blue colour.<br>b) Mercury (II) at levels above 1.0 mg/ L interferes by giving a precipitate in the reducing step.  |                        |                             |                        |           |                  |                  |         |                  |                  |
| <b>Principle or Procedure</b>        |   |                        |                             |                        |           |                  |                  |         |                  |                  |
| <b>Apparatus</b>                     | a) Culture tubes , 50 mL<br>b) Autoclave<br>c) An automated system (Technicon TrAAcs, or equivalent) consisting of <ol style="list-style-type: none"> <li>1) sampler</li> <li>2) manifold</li> <li>3) proportioning pump</li> <li>4) heating bath set at 37° C</li> <li>5) colorimeter equipped with 30 mm flow cell and 880 nm filters</li> <li>6) data collection system</li> </ol>   |                        |                             |                        |           |                  |                  |         |                  |                  |

## Reagents

- a) Strong Acid solution: To 600 mL Deionized water, add 150 mL conc  $\text{H}_2\text{SO}_4$ . Cool and add 2 mL conc  $\text{HNO}_3$  and dilute to one litre.
- b) Potassium Persulfate; reagent grade.
- c) Ammonium Molybdate solution: Dissolve 10g ammonium molybdate,  $(\text{NH}_4)_6\text{MO}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , in one litre Deionized water. Add 120 mL conc  $\text{H}_2\text{SO}_4$  a little at time with mixing; cool. Add 0.6 g potassium antimonyl tartrate,  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2} \text{H}_2\text{O}$ , after first dissolving it in about 30 mL Deionized water. Finally, dilute to 2 litres with Deionized water.
- d) Stock Ascorbic Acid solution: Dissolve 4.0 g ascorbic acid,  $\text{C}_6\text{H}_8\text{O}_6$ , in a mixture of 100 mL acetone and 100 mL Deionized water. Add 4 mL of wetting agent (Levor IV). Store at  $4^\circ\text{C}$  and prepare monthly or if signs of discoloration appear.
- e) Working Ascorbic Acid solution: Add 20 mL of stock ascorbic acid solution to 100 mL Deionized water. Prepare daily.
- f) Background Matrix Solution: Add 30 ml of the strong acid solution to approximately 1.5 L.
- g) Stock Phosphate solution (1000 mg/L P): Dissolve 4.393 g pre-dried potassium dihydrogen phosphate,  $\text{KH}_2\text{PO}_4$ , in Deionized water and dilute to one litre.
- h) Working Phosphate solution (10 mg/L P): Dilute 10 ml stock phosphate solution to one litre with Deionized water. Preserve by adding 2 mL chloroform and store at  $4^\circ\text{C}$ .
- i) Standards Phosphate solutions: Suitable aliquots of the working solution are diluted to prepare the appropriate standards (0.02, 0.05, 0.1, 0.25, and 0.5 mg/L P).

## Procedure

- a) 1) Phosphate Total :  
Total phosphate samples are diluted 2:1 just before loading them onto autoanalyzer.  
2) Phosphate Total Soluble:  
A 50 mL aliquot of the sample from step 6 of procedure TP-S5040 is digested by the total phosphorus digest method. No additional blanks are required here.
- b) Regular blanks, standards and quality control samples are digested with these samples.
- c) Add 25 mL of sample and standards to 50 mL test tubes.
- d) To each add 0.5 mL strong acid solution and 0.1 g potassium persulfate.
- e) Autoclave each at 15 psi ( $121^\circ\text{C}$ ) for 30 min. Allow the chamber pressure to drop to atmospheric pressure (without the aid of venting) before removing the samples.
- f) Allow to cool and filter, unless the sample is clear.
- g) Establish a baseline after all reagents have pumped through and the system is stable.
- h) Adjust the gain so that the top standard (0.50 mg/L P) gives a peak height of 80%-95% full scale.
- i) Run the sample and standards at 95 per hour on a TrAAcs 800 and

60/hr on an AAll ( or equivalent equipment).

- j) Monitor baseline drift, sensitivity drift, and carryover, and correct if necessary.

**Calculation**

The total phosphate concentrations are read directly from the printout, after a calibration curve is prepared from the peak heights obtained with the standard solutions. The sample concentrations are then determined by comparing the sample peak heights with the calibration curve. Baseline drift, sensitivity drift, and carryover corrections are made on the TrAAcs 800 computer system. The final step is a loading calculation.

**Precision**

Authentic samples at concentrations of 0.1403 and 0.4321 mg/ L P gave coefficients of variation of 1.0 and 1.6% respectively.

**Accuracy**

An authentic sample at a concentration of 0.3390 mg/ L P gave a relative error of -1.6%.

**Quality Control**

Each batch should contain a 10% level each of blank and duplicate samples with a minimum of one each per batch.

**References**

- a) J. Murphy and J.P. Riley. Anal. Chim. Acta 27;31 (1962).

**Revision History**

- April 1, 1996: Initial draft.
- October 29, 1996: Procedure vetted by private sector laboratories.
- January 8, 1998: SEAM code replaced by EMS code: term "Dustfall" replaced by "Particulate" on request of E. Tradewell; EMS codes confirmed; unavailable reference deleted.
- February 16, 1998: EMS code for intermediate results revised to eliminate redundant variables.
- December 31, 2000: Minor editing; Supplement #2 merged into main Lab Manual. Reference to out-of-print 1994 Manual deleted.

## Precipitation - Acidity, Alkalinity, pH

|   |  |                  |
|---|--|------------------|
| <b>Parameters and EMS Codes</b>         | Acidity: Free  | <b>AC-F 5063</b> |
|   | Acidity to pH 8.3  | <b>AC83 5062</b> |
|   | Alkalinity Total   | <b>AK-T 5062</b> |
|   | pH (Rain)  | <b>pH-- 5065</b> |
| <b>Analytical Method</b>                | Electrometer/Grans Plot  |                  |
| <b>Introduction</b>                     | The sample is first titrated for acidity and alkalinity, the Gran's function is calculated, then this procedure is followed by the measurement of several anions and cations by ion chromatography.  |                  |
| <b>Method Summary</b>                   | A glass electrode, calibrated with a pH 4.10 H <sub>2</sub> SO <sub>4</sub> buffer, is used with a digital pH/mV meter to measure sample pH. Acidity is then determined on the same aliquot by titration with $\mu$ L increments of 0.01 N NaOH. The volume of NaOH added to the sample is plotted against the Gran's function, calculated from the readings obtained during the titration (see examples on following pages). Equivalence point for strong acidity is obtained by extrapolating the Gran's functions to the volume axis. Total alkalinity is determined in a similar manner using 0.01N H <sub>2</sub> SO <sub>4</sub> . |                  |
| <b>MDL</b>                              | Acidity free   | 0.1 $\mu$ eq/L   |
|   | Acidity to pH 8.3  | 0.1 $\mu$ eq/L   |
|   | Alkalinity total   | 0.1 $\mu$ eq/L   |
| <b>Matrix</b>                           | Precipitation (fog, rain, snow, surface water)   |                  |
| <b>Interferences and Precautions</b>    | Coating of the electrode with oily or particulate matter and temperature effects are interferences.  |                  |
| <b>Sample Handling and Preservation</b> | Samples are collected with a rain sampler*, and submitted unfiltered and unpreserved. An additional pH sample drawn in a 60 mL syringe may be collected. Sample bottles should be filled leaving no head space, if sample collected from a water body. Samples should be kept at 4°C until analyzed.   |                  |
|   | <b>*Note: Precipitation depth has EMS code PRED 5066 and MDL 0.0001 m.</b>   |                  |
| <b>Stability</b>                        | Samples are unstable due to loss of gases or absorption of atmospheric gases. Titrations should be completed within 72 hours of sampling and as soon as possible after the sample container has been opened.   |                  |
| <b>Principle or Procedure:</b>          |  |                  |
| <b>Apparatus</b>                        | a) Digital pH meter, with MV scale, readable to at least the second decimal place in the pH mode.<br>b) Glass electrode, currently using a "low ionic strength" electrode (Radiometer PHC 2701). An equivalent electrode may be used.<br>c) Magnetic stirrer and stirring bar.<br>d) Microliter pipettes (e.g. Eppendorf) in sizes 10, 20, 50, 100 $\mu$ L fixed volumes.  |                  |
| <b>Reagents</b>                         | a) Standard reference buffers of pH 4.10 and 6.97, low ionic strength buffers from Orion or equivalent buffers.  |                  |

- b) Deionized water, boiled to remove carbon dioxide, and kept covered with limited headspace, as much as possible. Boiled deionized water should be freshly prepared each week and be used for all reagents.
- c) Potassium biphthalate solution (0.005 N) - dry 15 to 20 g of primary standard,  $\text{KHC}_8\text{H}_4\text{O}_4$  (100 mesh) at 120°C. Cool in a desiccator. Weigh accurately 1 g to the nearest mg, transfer to a 1 L flask, and dilute to volume with deionized water.
- d) Sodium hydroxide (0.01 N) - dissolve 0.4 g NaOH in 1 L distilled water, cool, and filter. Store protected from  $\text{CO}_2$ . Standardize by differential titration of 40.00 mL  $\text{KHC}_8\text{H}_4\text{O}_4$  solution to the inflection point.

Calculate the normality of the NaOH as follows:

$$\text{Normality} = \frac{A \times B}{204.2 \times C}$$

where  $A = \text{weight of } \text{KHC}_8\text{H}_4\text{O}_4 \text{ in } 1 \text{ L}$

$B = \text{mL } \text{KHC}_8\text{H}_4\text{O}_4 \text{ in the titration}$

$C = \text{mL NaOH used}$

## Procedure

- a) Allow all samples and buffers to reach laboratory temperature within 0.5°C, before analysis. Record laboratory temperature on datasheet.
- b) Set the temperature compensator to the temperature of the samples.
- c) Make all pH measurements as follows:
  - 1) Pipette a 40.00 mL aliquot of pH 6.97 buffer solution/or sample into a 50 mL beaker.
  - 2) Place a magnetic stir bar, carefully cleaned, into the beaker and place the beaker on a magnetic stirring apparatus. Insert the pH electrode into the sample.
  - 3) Stir the sample slowly for approximately 15 sec.
  - 4) Turn the stirrer off, allow the pH reading to stabilize (1 min) and record the reading (or make the appropriate adjustment).
- d) Set the calibration control with the pH 6.97 reference buffer.
- e) Rinse the electrode thoroughly in deionized water.
- f) Adjust the slope control using the standard reference buffer pH 4.10.
- g) Rinse the electrode thoroughly with deionized water.
- h) Measure the pH of a rainfall sample using the procedure in (3) above.
- i) Measure the acidity as follows:
  - 1) Stir sample for 15 sec.
  - 2) Turn stirrer off, allow pH reading to stabilize (45 sec) and record reading.
  - 3) Use an Eppendorf pipette to add 10 $\mu$ l standard 0.01 N NaOH; repeat steps (1) and (2).
  - 4) Continue incremental additions of 0.01 N NaOH to establish required titration curves. The capacity of the Eppendorf pipette may be varied as required.



## Calculations

j) After all analyses are completed, store the electrode immersed in pH 4.10 buffer.

a) Calculate Gran's functions ( $\Phi$ ) for each point as follows.

### Strong Acidity

$$\Phi = (V_0 + V) 10^{-\text{pH} + C} = (V_{e'} - V) K_1$$

where  $V_0$  = initial sample vol (40.00 mL)  
 $V$  = mL 0.01 N NaOH added  
 $C$  = arbitrary constant (7)  
 $V_{e'}$  = equivalence point (strong acidity)

### Free Acidity

$$= 10^{-\text{pH}}$$

b) Plot Gran's function vs. volume of NaOH added (mL). Extrapolate data points representing strong acidity component to the volume axis. Note that a minimum of three points and a correlation coefficient of at least 0.9995 is required for extrapolation.

c) Calculate the strong acidity component as follows:

$$\text{Strong Acidity } (\mu\text{eq/L}) = \underline{N} \cdot (V_{e'}/40.00) \times 10^6$$

where:  $V_{e'}$  = volume axis intercept (mL)  
 $\underline{N}$  = normality of the NaOH.

**Total Alkalinity** is determined by carrying out a procedure which is a mirror image of the procedure for total acidity. Gran's titration is carried out using standard 0.01N  $\text{H}_2\text{SO}_4$  instead of 0.01N NaOH. Prepare the standard 0.01 N  $\text{H}_2\text{SO}_4$  as follows:

a) Sodium carbonate solution (0.05 N) - dry 3 to 5 g primary standard  $\text{Na}_2\text{CO}_3$  at 250°C for 4 hours and cool in a desiccator. Weigh accurately 0.1 g to the nearest mg, transfer to a 500 mL volumetric flask, and dilute to volume with deionized water.

b) Standard sulfuric acid (0.01 N) - dilute an ampoule of analytical concentrate to 1 N with deionized water, then further dilute to 0.01 N. Standardize by potentiometric titration of 20.00 mL 0.05 N  $\text{Na}_2\text{CO}_3$  solution to the inflection point. Calculate the normality of the  $\text{H}_2\text{SO}_4$  as follows:

$$\text{Normality} = \frac{A \times B}{53.00 \times C}$$

Where  $A$  = weight of  $\text{Na}_2\text{CO}_3$  in one litre  
 $B$  = mL  $\text{Na}_2\text{CO}_3$  used in the titration  
 $C$  = mL  $\text{H}_2\text{SO}_4$  used

**Precision and Accuracy**

The precision and accuracy of the pH measurement is  $\pm 0.01$  pH unit. The acidity procedure yielded mean precision values (expressed as relative standard deviations) of 1.4% for strong acidity on the intervals 24–97  $\mu\text{eq H}^+/\text{L}$ .

**Quality Control**

Determine electrode precision by making 10 replicate measurements of a known reference solution. The average of these ten measurements must be within 0.1 pH units of the reference value. The standard deviation of these measurements should be less than 0.03 pH units. Record this data along with electrode reference number in an accumulating database. This test of precision should be carried once every three months, or whenever a new electrode is introduced.

**References**

- a) Standard Methods for the Examination of Water and Wastewater, 18th ed., APHA, AWWA, WPCF, Washington, DC (1992).
- b) McQuaker Neil R., Paul D. Kluckner and Douglas K. Sandberg. 1983. "Chemical analysis of acid precipitation: pH and acidity determinations", Environmental Science and Technology 17;7, July 1983, p. 431 - 435.

**Revision History**

- April 30, 1997: Initial draft.
- October 29, 1996: Procedure vetted by private sector laboratories.
- July 9, 1997: SEAM codes converted to EMS codes; out-of-print references deleted.
- January 9, 1998: EMS codes confirmed; edit changes confirmed with E. Tradewell.
- December 31, 2000: Minor editing; Supplement #2 merged into main Lab Manual. Reference to out-of-print manual deleted.

**ACIDITY TITRATION EXAMPLE and  
GRAN FUNCTION CALCULATION**

Sample #: #####

Conc. of base: 0.0103 N

Volume titrated 40.0 ml

Total Point: 13

| Point | Vol. added | pH     | Gran's function |
|-------|------------|--------|-----------------|
| 1     | 0.00       | 4.780  | 0.664D+04       |
| 2     | 0.02       | 4.920  | 0.481D+04       |
| 3     | 0.04       | 5.120  | 0.304D+04       |
| 4     | 0.06       | 5.410  | 0.156D+04       |
| 5     | 0.08       | 5.770  | 0.681D+03       |
| 6     | 0.10       | 6.070  | 0.341D+03       |
| 7     | 0.15       | 7.200  | 0.636D+02       |
| 8     | 0.19       | 8.640  | 0.175D+04       |
| 9     | 0.21       | 8.530  | 0.136D+04       |
| 10    | 0.23       | 8.870  | 0.298D+04       |
| 11    | 0.25       | 9.080  | 0.484D+04       |
| 12    | 0.50       | 10.030 | 0.434D+05       |
| 13    | 0.75       | 10.310 | 0.832D+05       |

**Tritration Results**

Strong acidity = 19.0  $\mu\text{eq/L}$

Equivalence point Vol = 0.07

Equivalence point pH = 5.62

$d[\text{H}^+]/d\text{Cb} = -0.875$

Free Acidity = 16.6  $\mu\text{eq/L}$

Free/Strong acidity: 0.875

Acidity to pH 8.3 = 43.1  $\mu\text{eq/L}$

Eq. Vol. @ pH 8.3 = 0.17 ml

Weak acidity = 26.5  $\mu\text{eq/L}$

**EXAMPLE OF ALKALINITY TITRATION and  
GRAN FUNCTION CALCULATION**

Sample #: #####

Conc. of acid: 0.0102 N

Volume titrated 40.0 ml

Total Point: 21

| Point | Vol. added | pH    | Gran's function |
|-------|------------|-------|-----------------|
| 1     | 0.00       | 7.570 | 0.607D+02       |
| 2     | 0.02       | 7.560 | 0.000D+00       |
| 3     | 0.04       | 7.380 | 0.000D+00       |
| 4     | 0.06       | 7.300 | 0.000D+00       |
| 5     | 0.08       | 7.250 | 0.000D+00       |
| 6     | 0.10       | 7.180 | 0.000D+00       |
| 7     | 0.20       | 6.960 | 0.441D+02       |
| 8     | 0.40       | 6.640 | 0.926D+02       |
| 9     | 0.60       | 6.360 | 0.177D+03       |
| 10    | 0.80       | 6.090 | 0.332D+03       |
| 11    | 0.90       | 5.920 | 0.492D+03       |
| 12    | 0.95       | 5.820 | 0.620D+03       |
| 13    | 1.00       | 5.720 | 0.781D+03       |
| 14    | 1.05       | 5.590 | 0.106D+04       |
| 15    | 1.10       | 5.450 | 0.146D+04       |
| 16    | 1.15       | 5.270 | 0.221D+04       |
| 17    | 1.20       | 5.070 | 0.351D+04       |
| 18    | 1.25       | 4.880 | 0.544D+04       |
| 19    | 1.75       | 4.030 | 0.390D+05       |
| 20    | 2.25       | 3.740 | 0.769D+05       |
| 21    | 2.75       | 3.570 | 0.115D+06       |

Titration Results

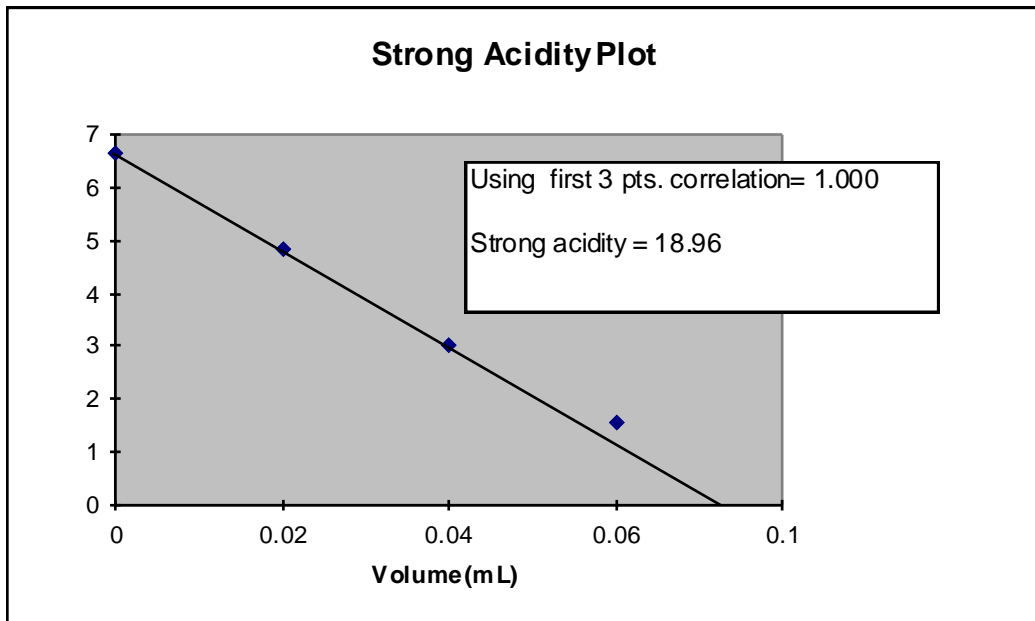
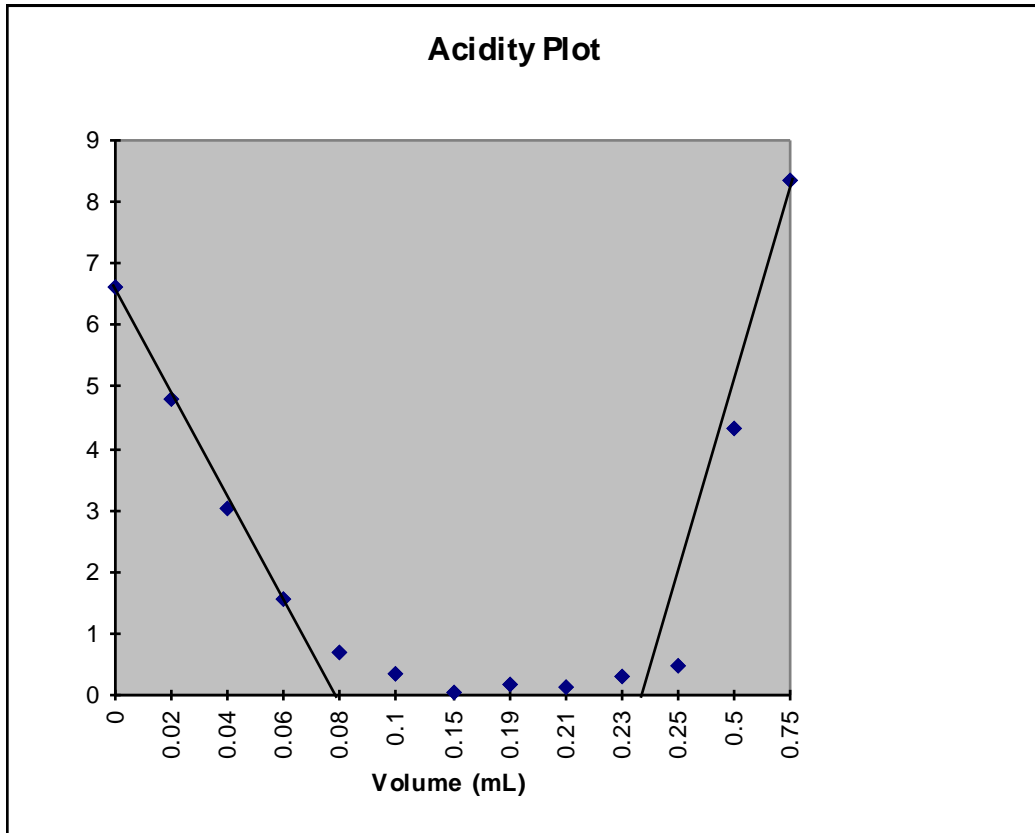
Alkalinity = 304.6  $\mu\text{eq/L}$

Equivalence point Vol = 1.19

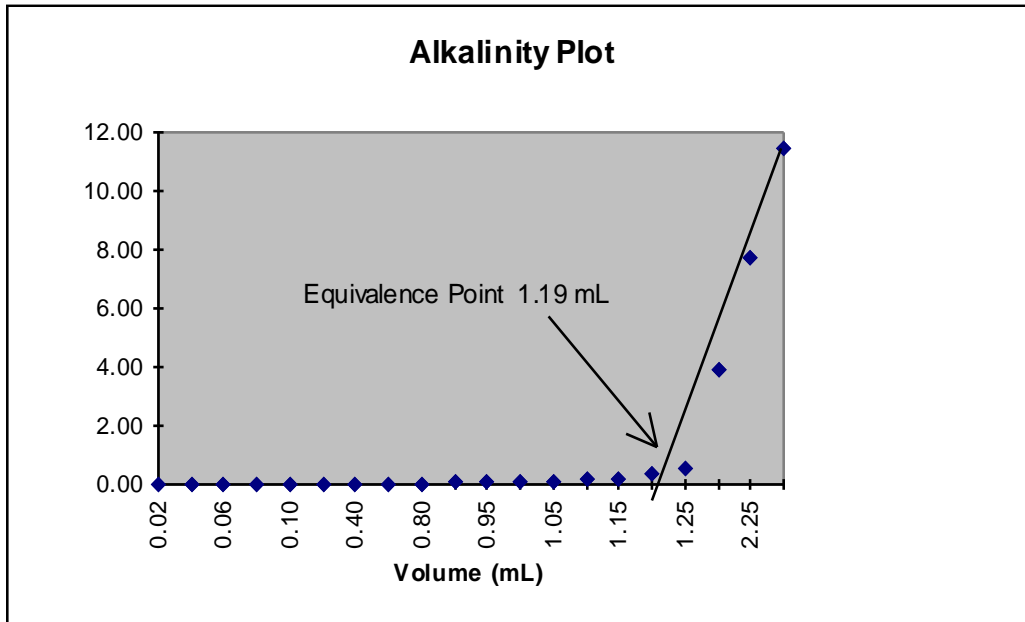
Equivalence point pH = 5.09

$d[\text{H}^+]/d\text{Ca} = 0.703$

ACIDITY PLOT FROM EXAMPLE DATA



ALKALINITY PLOT FROM EXAMPLE DATA



**PRECIPITATION CHEMISTRY EXAMPLE REPORT**

LABORATORY NAME

LABORATORY ADDRESS

TELEPHONE: (XXX) XXX-XXXX FAX: (XXX) XXX-XXXX

**LRTAP MONITORING REPORT: PRECIPITATION**

REPORT DATE: Dec 16/94

FORM NUMBER: 0 Sampling Time (Start): Dec 16/94-0000

SAMPLE NUMBER: 94000000 Sampling Time (End): Dec 16/94-0000

Site: MDC

| <b>CATIONS</b> | <b>mg/L</b> | <b>ueq/L</b> | <b>ANIONS</b> | <b>mg/L</b> | <b>ueq/L</b> | <b>OTHER</b> | <b>mg/L</b> |
|----------------|-------------|--------------|---------------|-------------|--------------|--------------|-------------|
| AMMONIUM       | <0.01       | <0.6         | NITRATE       | <0.01       | <0.2         | PHOSPHATE    | <0.009      |
| SODIUM         | <0.01       | <0.4         | CHLORIDE      | <0.01       | <0.3         | ALUMINUM     | <0.02       |
| POTASSIUM      | <0.01       | <0.3         | FLUORIDE      | <0.04       | <2.1         |              |             |
| CALCIUM        | <0.02       | <1.0         | SULPHATE      | <0.02       | <1.6         |              |             |
| MAGNESIUM      | <0.02       | <1.6         | ALKALINITY    | -           | -            |              |             |
| FREE ACIDITY   | 0.1         |              |               |             |              |              |             |
| TOTAL          | 0.1         |              |               |             |              |              |             |
| SUM+ / SUM-    |             |              |               |             |              |              |             |

---

|                  | <b>ueq/L</b>           | <b>mg/L CaC03</b> | <b>Approximate pH</b> |
|------------------|------------------------|-------------------|-----------------------|
|                  | <b>at equiv. point</b> | <b>equiv.</b>     |                       |
| STRONG ACIDITY   | -                      | -                 | -                     |
| pH 8.3 ACIDITY   | 0.0                    | 0.0               | -                     |
| TOTAL ALKALINITY | -                      | -                 | -                     |
| pH MEASURED      | 7.00                   | -                 | -                     |

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|                           | <b>SAMPLERMOE</b> | <b>AES</b> |     |
|---------------------------|-------------------|------------|-----|
|                           | <b>GAUGE</b>      |            |     |
| PRECIPITATION DEPTH (mm)  | 0.0               | -          | 0.0 |
| COLLECTION EFFICIENCY (%) | -                 | -          | -   |

COMMENTS:

## Precipitation - Anions - Ion Chromatography

|                                     |                  |                  |
|-------------------------------------|------------------|------------------|
| <b>Parameters<br/>and EMS Codes</b> | Nitrate-Soluble  | <b>NO3- 5068</b> |
|                                     | Sulphate-Soluble | <b>SO4- 5068</b> |
|                                     | Chloride-Soluble | <b>Cl-S 5068</b> |

**Analytical Method** Ion Chromatography-Anion

**Introduction** Precipitation samples are collected and shipped to the laboratory unpreserved. The sample is first titrated for acidity and alkalinity, the Gran's function is calculated, then several anions and cations are measured. Ion balance is also calculated.

**Method Summary** An ion chromatograph equipped with a conductivity detector is used to determine several common anions from a single sample injection. Samples and standards are "spiked" with concentrated carbonate / bicarbonate solution to give the sample the same background as the eluent used (avoiding a "water dip" effect). The anions of interest are separated through an anion "guard" and anion "separator" column. An anion micro membrane suppressor following the separator columns is used to reduce the background eluent conductivity by converting the carbonate and bicarbonate species to carbonic acid, while enhancing the conductivity of the ions of interest by converting these ions to their corresponding acids. A conductivity detector senses the sample species in direct proportion to their initial concentration. Note that nitrate is reported as mg NO<sub>3</sub>/L and sulphate as mg SO<sub>4</sub>/L.

**MDL** 0.01 mg/L Nitrate  
0.01 mg/L Chloride  
0.01 mg/L Sulphate

**Matrix** Water

**Interferences and Precautions** Interferences can be caused by substances with retention times similar to overlapping those of the ion of interest. Large amounts of an anion can interfere with peak resolution of an adjacent anion. The most common interference is due to extremely high concentrations of dissolved carbonate or weak organic acid.

### Principle or Procedure:

- Apparatus**
- a) An ion chromatography system consisting of:
    - 1) selectable eluent supply
    - 2) high pressure, pulseless pump
    - 3) sample injection port and sample loop
    - 4) anion guard and separator columns
    - 5) anion micro membrane suppressor
    - 6) conductivity detector
    - 7) data station
    - 8) auto sampler



## Reagents

- a) Concentrated Stock Eluent: Dissolve 15.12 g sodium bicarbonate ( $\text{NaHCO}_3$ ) and 18.02 g sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) with deionized water into a 1 L flask. Dilute to volume and store in a 1 litre poly bottle.
- b) Working Eluent Solution: Dilute 10.0 mL of concentrated stock eluent to 1L in a volumetric flask. ( $1.8 \text{ mM NaHCO}_3 / 1.7 \text{ mM Na}_2\text{CO}_3$ ) Filter before use.
- c) Regenerent Solutions:  $0.025 \text{ N Sulphuric acid (H}_2\text{SO}_4)$  - Dilute 26.8 mL concentrated sulphuric acid to one liter to prepare a  $1.00 \text{ N H}_2\text{SO}_4$  solution. Dilute 25.0 mL of this solution to one liter.
- d) Stock Chloride Standard Solution: Dry 2 to 3 g of sodium chloride ( $\text{NaCl}$ ) at  $120^\circ\text{C}$  for 2 hours and cool in a desiccator. Dissolve 1.648 g  $\text{NaCl}$  in deionized water and dilute to 1.0 liter ( $1.00 \text{ mL} = 1.00 \text{ mg Cl}$ ). Store in a poly bottle under refrigeration.
- e) Stock Nitrate Standard Solution: Dissolve 1.630 g anhydrous potassium nitrate ( $\text{KNO}_3$ ) in deionized water and dilute to 1 liter ( $1.00 \text{ mL} = 1.00 \text{ mg NO}_3$ ). Store in a poly bottle under refrigeration.
- f) Stock Sulphate Standard Solution: Dissolve 1.479 g anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) in deionized water and dilute to 1 liter ( $1.00 \text{ mL} = 1.00 \text{ mg SO}_4$ ). Store in a poly bottle under refrigeration.

## Procedure

- a) Allow all samples and standards to reach laboratory temperatures before analysis.
- b) Establish a constant background conductivity using the following instrument conditions:

|                     |  |
|---------------------|--|
| Eluent:             | $0.0018 \text{ M NaHCO}_3 / 0.0017 \text{ M Na}_2\text{CO}_3$  |
| Separator:          | 4 x 50 Anion Precolumn (Guard)<br>Dionex IONPac®-AG4-SC<br>4 x 250 Anion Separator Column<br>Dionex IONPac®-AS4-SC |
| Suppressor:         | Anion Micro Membrane Suppressor<br>Dionex AMMS-1   |
| Eluent Flow :       | 2.0 mL/min.  |
| Operating Pressure: | 900 psi  |
| Regenerent:         | $0.025 \text{ N H}_2\text{SO}_4$   |
| Regenerent Flow :   | 2.0 - 3.0 mL/min.  |
| Backgrd. Conduct.   | 12 - 16 $\mu\text{S}$  |
| Injection Volume:   | 25 $\mu\text{L}$   |
| Detector Range:     | Auto-range   |

- c) Pipette 5.0 mL of each sample or standard solution into a 5 mL autosampler vial (Dionex Polyvial™), then add 50  $\mu\text{L}$  of concentrated stock eluent. Cap vial with a  $0.22 \mu\text{m}$  filter cap and shake. Load into an autosampler.
- d) Run a blank and at least a four point calibration curve of composite standards for each detector range. The calibration curve should include at least one calibration point for each decade of the concentration range. Calibration should be run daily when the analysis is run.
- e) Run samples through the chromatograph with standards after every five samples.

|                         |  |
|-------------------------|--|
| <b>Calculations</b>     | Calibration curves are programmed into the data station to be read directly off the chromatogram in terms of peak heights and in units of mg/L of anions in the filtrate.  |
| <b>Precision</b>        | RSD           = 1.18% at 31.0 mg NO <sub>3</sub> -N/L (water)<br>= 1.49% at 98.5 mg SO <sub>4</sub> /L (water)<br>= 2.89% at 10.0mg Cl/L (water)   |
| <b>Accuracy</b>         | 100.7% at 31.0 mg NO <sub>3</sub> -N/L (water)<br>104% at 98.5 mg SO <sub>4</sub> /L (water)<br>98.2% at 10.0 mg Cl/L (water)  |
| <b>Quality Control</b>  | <p>a) Record the old and new standard concentrations, along with preparation dates, in a QC record sheet. New standards should be within 5% of old standards, unless previous information suggests old standards have deteriorated. Record this information on QC record sheet as a comment.</p> <p>b) Record and plot the mid-range check standard run between every fifth sample. Maintain this record in such a manner to allow comparison between runs. If limiting the ions to record, do at least Cl. When sufficient data is recorded, determine control limits. For the interim, control limits of ± 10% should be used.</p> <p><b>Note:</b> This is not an independent reference standard. This check is to monitor within run drift.</p> <p>c) Run an independent reference standard prepared from an alternate salt with addition of flouride, nitrite, bromide, phosphate to check peak resolution and column integrity.</p> |
| <b>References</b>       | <p>a) J.P. Smith, D. Grodjean and J.N. Pitts, J.Air Pollut. Contr. Assoc. 28;930 (1978).</p> <p>b) Dionex Corporation, <u>Basic Ion Chromatography</u>. 1228 Titan Way, Sunnyvale, CA. 94088-3603, U.S.A.</p> <p>c) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992.</p>   |
| <b>Revision History</b> | <p>April 1, 1996:           Initial draft.</p> <p>October 29, 1996:      Procedure vetted by private sector laboratories. Note regarding alternative methods added.</p> <p>July 11, 1997:         Minor editing; replace SEAM code with EMS code.</p> <p>January 9, 1998:        EMS codes confirmed.</p> <p>December 31, 2000:    Minor editing; Supplement #2 merged into main Lab Manual. Reference to out-of-print manual deleted.</p>   |

|  |
|--|
| <p><b>Note 1: While anions and cations are usually reported for water samples on an elemental basis, for air samples, the convention is to report on an ion weight basis. Thus, ammonia is reported as mg/L as NH<sub>4</sub> and nitrate is reported as mg/L as NO<sub>3</sub>.</b></p> |
|--|

|  |
|--|
| <p><b>Note 2: Note that the listed anions and cations may alternatively be analyzed according to any relevant procedure specified in this edition of the BC Environmental Laboratory Manual.</b></p> |
|--|

## Precipitation - Cations - Ion Chromatography

|                                      |  |                  |
|--------------------------------------|--|------------------|
| <b>Parameters and EMS Codes</b>      | Sodium   | <b>Na-S 5071</b> |
|                                      | Ammonium   | <b>NH4- 5071</b> |
|                                      | Potassium  | <b>K--S 5071</b> |
|                                      | Magnesium  | <b>Mg-S 5070</b> |
|                                      | Calcium  | <b>Ca-S 5070</b> |
| <b>Analytical Method</b>             | Ion Chromatography-Cation  |                  |
| <b>Introduction</b>                  | Precipitation samples are collected and shipped to the laboratory unpreserved. The sample is first titrated for acidity and alkalinity, the Gran's function is calculated, then several anions and cations are measured. Ion balance is also calculated.   |                  |
| <b>Method Summary</b>                | An ion chromatograph equipped with a conductivity detector is used to determine several cations from a single sample injection. All samples are filtered through a 0.22 µm fritted glass filter prior to injection. The cations of interest are separated through a cation "guard" and cation "separator" column with a methane sulphonic acid eluent. After the cations are separated they exit at various times from the column in a background of eluent. A self-regenerating membrane suppressor is attached to the end of the column to neutralize the acid before detection and form the corresponding hydroxide. Note that ammonium is reported as mg NH <sub>4</sub> /L. |                  |
| <b>MDL</b>                           | 0.01 mg/L Na<br>0.01 mg/L NH <sub>4</sub><br>0.01 mg/L K<br>0.01 mg/L Mg<br>0.01 mg/L Ca   |                  |
| <b>Matrix</b>                        | Water  |                  |
| <b>Interferences and Precautions</b> | Interferences can be caused by substances with retention times similar to overlapping those of the ion of interest. Significant concentrations of previously eluted cations may cause masking problems.  |                  |
| <b>Principle or Procedure:</b>       |  |                  |
| <b>Apparatus</b>                     | a) An ion chromatograph consisting of: <ol style="list-style-type: none"><li>1) selectable eluent supply</li><li>2) high pressure, pulseless pump</li><li>3) chromatography module</li><li>4) cation guard and separator columns</li><li>5) cation membrane suppressor</li><li>6) conductivity detector</li><li>7) data station</li></ol>  |                  |

## Reagents

- a) Methane sulphonic acid stock (2.0 M): Weigh 96.1 g methane sulphonic acid and dilute to 500 mL with deionized water.
- b) Eluent (0.02 M): dilute 10.0 mL of 2.0 M methane sulphonic acid stock to 1L. Filter through a 0.45 µm nylon membrane filter.
- c) Regenerent solution: deionized water.
- d) Ammonium standard 1000 mg/L: Dissolve 2.965 g predried ammonium chloride (analytical grade) in 1 L deionized water. 1mL= 1mg NH<sub>4</sub>.
- e) Calcium standard 1000 mg/L: Dissolve 2.497 g predried calcium carbonate (analytical grade) in 1 L of 400 mN hydrochloric acid.
- f) Magnesium standard 1000 mg/L: Dissolve 4.952 g predried magnesium sulphate (analytical grade) in 1 L of 400 mN hydrochloric acid.
- g) Potassium standard 1000 mg/L: Dissolve 1.907 g predried potassium chloride (analytical grade) in 1 L deionized water.
- h) Sodium standard 1000 mg/L: Dissolve 2.542 g predried sodium chloride (analytical grade or better) in 1 L deionized water.

(Note: New standards should always be checked against old stock standards. A log of these comparison results should be maintained).

## Procedure

- a) Allow all samples and standards to reach laboratory temperature before analysis.
- b) Establish a constant background conductivity using the following instrument conditions:

|                          |  |
|--------------------------|--|
| Eluent:                  | 0.020 M methane sulphonic acid   |
| Regenerant:              | Deionized water  |
| Separator:               | 4x50 Cation Precolumn (Guard)<br>Dionex IONPac-CS12<br>4X250 Cation Separator Column<br>Dionex IONPac-CS12 |
| Suppressor:              | Cation Self Regenerating Suppressor<br>Dionex CSRS-1   |
| Eluent Flow Rate:        | 1.0 mL/min   |
| Operating Pressure:      | 900 psi  |
| Regenerent Flow rate:    | 10 mL/min  |
| Regenerent Current:      | 200 mA   |
| Background Conductivity: | 0.5 - 2 µS   |
| Injection Volume:        | 25 µL  |

- c) Run a blank and at least a four point calibration curve of composite standards for each detector range. The calibration curve should include at least one calibration point for each decade of the concentration range. Calibration should be run daily when the analysis is run.
- d) Run samples through the chromatograph with standards after every five samples.

## Calculations

Calibration curves are programmed into the data station to be read directly off the chromatogram in terms of peak heights.

**Precision** In a laboratory study, authentic samples gave the following coefficients of variations (C.V.):

| <u>Cation</u>   | <u>Standard (mg/L)</u> | <u>C.V. (%)</u> | <u>Standard (mg/L)</u> | <u>C.V. (%)</u> |
|-----------------|------------------------|-----------------|------------------------|-----------------|
| Na              | 0.08                   | 3.7             | 0.16                   | 3.5             |
| NH <sub>4</sub> | 0.20                   | 1.3             | 0.40                   | 2.0             |
| K               | 0.20                   | 1.8             | 0.40                   | 2.8             |
| Mg              | 0.10                   | 2.5             | 0.20                   | 2.7             |
| Ca              | 0.20                   | 2.8             | 0.40                   | 1.5             |

- Quality Control**
- Record the old and new standard concentrations, along with preparation dates, in a QC record sheet. New standards should be within 5% of old standards, unless previous information suggest old standards have deteriorated. Record this information on QC record sheet as a comment.
  - Record and plot the mid-range check standard run between every fifth sample. Maintain this record in such a manner to allow comparison between runs. If limiting the ions to record, do at least Ca and K. When sufficient data is recorded, determine control limits. For the interim, control limits of  $\pm 10\%$  should be used.

**Note:** This is not an independent reference standard. This check is to monitor within run drift.

- Confirm all standards with an alternate salt.

- References**
- Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992.
  - Dionex Corporation, Basic Ion Chromatography, 1228 Titan Way, Sunnyvale, CA. 94088-3603, U.S.A.
  - Dionex Corporation, Self-Regenerating Controller Users Guide, Document No.034720, 1228 Titan Way, Sunnyvale, CA. 94088-3603, U.S.A. October 1992.
  - Dionex Corporation, Installation Instructions and Troubleshooting Guide for the Cation Self-Regenerating Suppressor-1 (4mm), Document No. 034651, 1228 Titan Way, Sunnyvale, CA. 94088-3603, U.S.A. June 1993.
  - Dionex Corporation, Installation Instructions and Troubleshooting Guide for the IONPAC CS12 Analytical Column, Document No.034657, 1228 Titan Way, Sunnyvale, CA. 94088-3603, U.S.A. March 1992.

- Revision History**
- April 1, 1996: Original draft.
- October 29, 1996: Procedure vetted by private sector laboratories. Note regarding alternative methods added.
- July 13, 1997: Minor editing; SEAM code replaced with EMS code.
- January 9, 1998: EMS codes confirmed; Ca MDL updated.
- December 31, 2000: Minor editing; Supplement #2 merged into main Lab Manual. Reference to out-of-print manual deleted.

**Note 1:** While anions and cations are usually reported for water samples on an elemental basis, for air samples, the convention is to report on an ion weight basis. Thus, ammonia is reported as mg/L as NH<sub>4</sub> and nitrate is reported as mg/L as NO<sub>3</sub>.

**Note 2: Note that the listed anions and cations may alternatively be analyzed according to any relevant procedure specified in this edition of the BC Environmental Laboratory Manual.**

## **Total Particulate - PM10 - HiVol**

|   |  |
|---|--|
| <b>Parameter</b>                        | Particulate < 10µm (PM10)  |
| <b>Analytical Method</b>                | Part. HiVol Teflon   |
| <b>EMS Code</b>                         | <b>PM10 5305</b>   |
| <b>Introduction</b>                     | A measured volume of ambient air is drawn through an inlet that passes only particles less than 10 µm. The particulate which is collected on a 0.3µm Teflon coated borosilicate glass fibre filter constitutes PM10 particulate.   |
| <b>Method Summary</b>                   | PM10 is the designation for particulate matter in the atmosphere that has an aerodynamic diameter of 10 micrometers (µm) or less. A high volume (HV) PM10 sampler draws a known volume of ambient air at a constant flow rate through a size selective inlet and through one or more filters. Particles in the PM10 size range are then collected on the filter(s) during the specified 24 hour sampling period. Each sample filter is weighed before and after sampling to determine the net weight (mass) gain of the collected PM10 sample.   |
| <b>MDL</b>                              | 2 µg/m <sup>3</sup>  |
| <b>Matrix</b>                           | Ambient Air Particulate  |
| <b>Interferences and Precautions</b>    | Damage to filters (holes), misalignment or leaking gaskets in filter assembly can result in loss of particulate.   |
| <b>Sample Handling and Preservation</b> | <p>Filters are shipped flat in white 10" x 12" envelopes with the opening on the 12" axis. The envelope and filter are both stamped with a unique identifying number. A kraft paper wrapper folded in three on the long axis is also shipped. Filters should NOT be folded before sampling. The shipping envelopes are stamped "DO NOT BEND PRIOR TO USE".</p> <p>The sampling surface of the filter appears like soft blotting paper. The non-sampling surface has a sheen and appears to be a woven fabric.</p> <p>For return to the laboratory, filters should be gently folded once along the long axis, with the particulate surface inward. The filter should be placed inside the brown paper wrapper and re-inserted in the same envelope in which it was shipped.</p> <p>If unable to return filters for analysis within 10 days of sampling, store exposed filters at 4°C or less. Return filters for reweighing within 30 days of sampling.</p> |
| <b>Stability</b>                        | Most samples are stable for long periods of time.  |
| <b>Apparatus</b>                        | <ol style="list-style-type: none"><li>a) Controlled environment room: temperature 20°C ± 3°C, humidity 30-40% ± 5%(24 hour average).</li><li>b) Analytical balance, 5 decimal place.</li></ol>   |
| <b>Reagents</b>                         | <ol style="list-style-type: none"><li>a) Filters: Pallflex TX40HI20WW EMFAB, 8" x 10" (20.3 cm x 25.4 cm), or equivalent.</li></ol>  |

## Procedure

- a) Inspect filters for pinholes, tears, lumps, or creases using light box. Any filters with these defects should not be used. Remove any fibres from edge of filter. Do not use any filters that have begun to de-laminate.
- b) Gently stamp filters and envelopes with an identification number taking care to keep the number stamp on the outer edge of the filter, not in the sampling area. Stamp impression should be on the glossy under surface of the filter.
- c) Equilibrate filters in controlled environment for 72 hours. Note: Teflon coated filters take longer to equilibrate than normal glass fibre filters which can be equilibrated in 24 hours.
- d) Pre-weigh the filters, and record in log. Filters may be rolled loosely for weighing if desired.
- e) Ship the filters flat in envelopes to the field.
- f) On return of filters from field, equilibrate for 72 hours. If necessary, gently remove any insects embedded in the filters with Teflon tipped tweezers. If more than 6 insects are found discard the filter. Recover any dislodged material from the filter using a soft camel hairbrush to sweep out envelope. This constitutes part of the sample.

Note any irregularities in the filters currently. If the following irregularities are found, reject the filter.

- 1) Hole or tear in filter except if on fold.
- 2) Sample area misaligned such that sample has been lost (filter misaligned, FMA).
- 3) Leakage of particulate at margins (gasket leak, margin not clear, MNC).
- 4) Filter sampled wrong side up.
- 5) Sampling time less than 18 hours or greater than 30 hours. Enter a comment in the report indicating 'time range failure' (TRF). If filters are explicitly marked "SPECIAL STUDY" other time ranges are acceptable.

If the following irregularities are found, they should be noted on the report but the analysis completed:

- 1) Marks on surface (MOS) of the filter after sampling.
- 2) Filter misaligned (FMA) so no margin visible.
- 3) Sampling surface against envelope, wrapper or time chart.

Record all of the above comments in comment section of the report.

- g) Weigh the filters to the nearest 1 mg after equilibration. Record the weight.
- h) Archive the filters for a period of 2 years.

## Calculation

PM10 Particulate in  $\mu\text{g}/\text{m}^3$ =

$$\frac{(\text{final weight}) - (\text{initial weight}) \times \text{Conversion factor}}{\text{time of exposure, hr}}$$

where conversion factor =  $1000 \times 35320 / (40 \times 60)$

note: 1000 is  $\mu\text{g}/\text{mg}$   
35320 is  $\text{cu ft}/\text{m}^3$  and  $\text{mg}/\text{g}$   
40 is standard flow rate in  $\text{cu ft}/\text{min}$  and 60 is  $\text{min}/\text{hr}$



**Precision**

The standard deviation on duplicate weighings of 8" x 10" (20.3 x 25.4cm) Teflon filters returned from the field after sampling is 1 mg.

**Quality Control**

- a) Laboratory Equipment:
- 1) Balance:
    - i) Initial: 3 to 5 weights in the range of the filter weights should weigh to  $\pm 0.0005$  g of nominal weights.
    - ii) On-going: a standard weight should be weighed daily and every two hours when the balance is in use. Record weights, date, time, and operators initials. Weights should be  $\pm 0.0005$  g of nominal weights. Failure requires re-calibration.
    - iii) Annual calibration and certification of balance by a certified tester.
  - 2) Constant humidity:
    - i) A reading with a wet/dry bulb sling psychrometer to be taken and recorded every 6 months. Reading to be  $\pm 6\%$  of desired reading.
    - ii) On-going humidity should be  $<40\%$  and not vary by more than  $\pm 5\%$ . Record humidity daily. Design humidity is 35%.
  - 3) Temperature should be kept between 15 and 30°C, and should not vary more than  $\pm 3^\circ\text{C}$ . Target temperature is 20°C.
- b) Assessment of data accuracy
- 1) Field duplicates: co-located samplers should give results  $\pm 15\%$ .
  - 2) Lab duplicates: prior to shipping to field, randomly select and re-weigh 4 in every set of 50 un-exposed filters. Record initial weight, re-weight, date and time of each, and initial the record. The re-weigh should be done between 3 and 24 hours after the initial weighing. Re-weigh the entire batch if any re-weighs differ by more than  $\pm 5$  mg (0.005 g) from the original weight. Plot an x-bar R chart of data as a control chart. Interim warning limits and control limits  $\pm 3.0$  mg and  $\pm 4.5$  mg. Out of control points indicate a need to re-calibrate the balance, improve operation procedure, or failure to control humidity and temperature.
  - 3) Trip duplicates: For every batch of 50 (unexposed) filters, 4 filters, chosen at random, are sent to the field as trip blanks. On return, these unexposed filters are conditioned and reweighed. The re-weigh should be done between 3 and 48 hours after the initial weighing. Re-weigh the entire batch if any re-weighs differ by more than  $\pm 5$  mg (0.005 g) from the original weight. Plot an x-bar R chart of data as a control chart. Interim warning limits and control limits  $\pm 3.3$  mg and  $\pm 5.0$  mg. Out of control points, in absence of out of control points in b. above indicate a lack of proper impaction of particulate in field, a failure to properly handle filters in field or laboratory causing a loosening of particulate, or a need to improve operation procedure.

Samples which fail this test should be recorded as "FAILED DUPLICATE WEIGHT TEST".

**References**

- a) Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Specific Methods, EPA/600/R-94/038b, April 1994, Section 2.11.0 (January 1990).

**Revision History**

April 1, 1996: Initial draft.

October 29, 1996: Procedure vetted by private sector laboratories.

January 12, 1998: EMS code confirmed; out-of-print reference deleted.

December 31, 2000: Minor editing; Supplement #2 merged with main Lab Manual. At request of E. Tradewell, note added regarding storage and return of exposed filters.

November 4, 2002: Conditioning criteria (humidity) specs updated.

## Total Particulate – PM10/PM02 - 47 mm - HiVol

|   |   |                                      |
|---|---|--------------------------------------|
| <b>Parameter and EMS Codes</b>          | Total Particulate (PM10)<br>Total Particulate (PM02)  | <b>PM10 5306</b><br><b>PM02 5306</b> |
| <b>Analytical Method</b>                | 47mm HiVol Teflon filter  |                                      |
| <b>Introduction</b>                     | A measured volume of air is drawn through a 47 mm filter using a Partisol Model 2000 air sampler.   |                                      |
| <b>Method Summary</b>                   | Air particulate is trapped on a pre-weighed Teflon filter. The weight change after sampling is used to calculate the particulate in $\mu\text{g}/\text{m}^3$ .  |                                      |
| <b>MDL</b>                              | A detection limit of $6 \mu\text{g}/\text{m}^3$ is based on duplicate weighing of triplicates weighings of exposed filters (July - August 1996) returned from the field. This was revised in June 2000 to $2\mu\text{g}/\text{m}^3 \pm 6$ .   |                                      |
| <b>Matrix</b>                           | Ambient Air Particulate   |                                      |
| <b>Interferences and Precautions</b>    | Damage to the filter such as cracks or pinholes that allow particulate to escape during sampling may reduce the reported values. Failure to protect sampling surface during shipment may cause loss of particulate.   |                                      |
| <b>Sample Handling and Preservation</b> | Use non-serrated forceps to handle filters. Store and transport filters in cassettes housed in petri dishes. On initial use and after each return from field use, filter cassette holders should be rinsed in deionized water, soaked for at least 1 hr in clean dilute FL70 detergent solution, rinsed with deionized water at least 8 times, and air dried in a dust free environment.  |                                      |
| <b>Apparatus</b>                        | <ol style="list-style-type: none"><li>a) Pallflex TX40 HI20-WW 47mm filters</li><li>b) Cassette filter holder (Partisol series 2000, part #59-002388)</li><li>c) Balance, with resolution of 0.01 mg</li><li>d) Non-serrated forceps</li></ol>  |                                      |
| <b>Procedure</b>                        | <ol style="list-style-type: none"><li>a) Inspect each filter visually for integrity and apply the criteria given in Procedure paragraph 6, of Total Particulate - PM10 - HiVol (EMS code PM10 5305).</li><li>b) Equilibrate the 47 mm filters before use as follows:<ol style="list-style-type: none"><li>1) Label and number both covers of each petri dish.</li><li>2) Place the petri dish cover under the bottom half of the dish.</li><li>3) Place each inspected filter into a separate dish.</li><li>4) Record the filter number, relative humidity, temperature, date and time at the beginning of equilibration.</li><li>5) Equilibrate each filter for at least 24 hours (Teflon filters usually require 72 hours to equilibrate) at a constant humidity 30- 40% <math>\pm</math> 5%, and constant temperature of <math>20^\circ\text{C} \pm 2^\circ\text{C}</math>. The PM02 filters should be equilibrated at a humidity of 30 - 40 % <math>\pm</math> 5% and constant temperature <math>20^\circ\text{C} \pm 2^\circ\text{C}</math>.</li></ol></li></ol> |                                      |

- c) Weigh each filter three times, and record its mass in grams. The average of these three weights is the initial weight.
- d) Ship the filters to the field in petri dishes.
- e) On return of filters from the field, equilibrate for 72 hours and weigh each filter three times, and record its mass in grams. The average of these three weights is the final weight. PM02 filters should be re-weighted within ten days after end of sampling period. If unable to process within this time period store at 4°C or less and re-weigh within thirty days of sampling.

**Calculation**

Particulate in  $\mu\text{g}/\text{m}^3 =$   

$$\frac{1,000,000 \times (\text{average 3 final weights,g}) - (\text{average 3 initial weights,g})}{\text{time of exposure in hours}}$$

where: 1,000,000 is  $\mu\text{g}/\text{g}$  and flow rate is  $1 \text{ m}^3/\text{hr}$

**Precision**

Standard deviation on duplicate weighings of 47 mm Partisol filters returned from the field after sampling is  $2.3 \mu\text{g}/\text{m}^3$  for results in range 11 to  $66 \mu\text{g}/\text{m}^3$ . Estimated coefficient of variation is 9%.

**Quality Control**

- a) Balance Weights: record weight of a 1, 2, and 5 g nominal weight Class S weight, initially and every two hours during weighing periods. Limits for acceptance of weights should conform to balance manufacturer's specifications.
- b) Prior to shipping filters to field repeat the weighing process for 4 in 50 or 4 in a weighing set (whichever is smaller). Average of triplicate weights initial and repeat weighing must agree to within 1 mg.
- c) After return of filters from the field, repeat the weighing process for 4 in 50 or 4 in a set. Average of triplicate weights initial and repeat must agree to within 1 mg.

**Reference**

- a) Quality Assurance Handbook for Air Pollution Measurement Systems Volume II: Ambient Air Specific Methods, PA/600/R-94/038b, April 1994, Addendum 2.11.
- b) Operating Manual, Partisol 2000 Air Sampler, p.3-1 to 3-9, Rupprecht and Patachnick, Albany, New York, December 1993, version 1.00.

**Revision History**

- April 30, 1996: Initial draft.
- October 29, 1996: Procedure vetted by private sector laboratories.
- January 12, 1998: EMS codes confirmed.
- June 24, 1998: PM02 procedures revised.
- December 31, 2000: Minor editing; Supplement #2 merged with main Lab Manual.
- November 4, 2002: Conditioning criteria (temp. & humidity) specs updated.

## Total Particulate - PM02 - HiVol

|   |  |
|---|--|
| <b>Parameter</b>                        | PM 2.5µm HiVol (PM02)  |
| <b>Analytical Method</b>                | Tot. Part. HiVol-Teflon (8 x 10 filter)  |
| <b>EMS Code</b>                         | <b>PMO2 5305</b>   |
| <b>Introduction</b>                     | A measured volume of ambient air is drawn through an inlet that passes only particles less than 2.5 µm. The particulate which is collected on a 0.3 micron Teflon coated borosilicate glass fibre filter constitutes PM02 particulate.   |
| <b>Method Summary</b>                   | PM-2.5 is the designation for particulate matter in the atmosphere that has an aerodynamic diameter of 2.5 micrometers (µm) or less. A high volume (HV) PM 2.5 sampler draws a known volume of ambient air at a constant flow rate through a size selective inlet and through one or more filters. Particles in the PM 2.5 size range are then collected on the filter(s) during the specified 24-hour sampling period. Each sample filter is weighed before and after sampling to determine the net weight (mass) gain of the collected PM02 sample.  |
| <b>MDL</b>                              | 2 µg/m <sup>3</sup>  |
| <b>Matrix</b>                           | Ambient Air Particulate  |
| <b>Interferences and Precautions</b>    | Damage to filters (holes), misalignment or leaking gaskets in filter assembly can result in loss of particulate.   |
| <b>Sample Handling and Preservation</b> | <p>Filters are shipped flat in white 10" x 12" envelopes with the opening on the 12" axis. The envelope and filter are both stamped with a unique identifying number. A kraft paper wrapper folded in three on the long axis is also shipped. Filters should NOT be folded before sampling. The shipping envelopes are stamped "DO NOT BEND PRIOR TO USE".</p> <p>The sampling surface of the filter appears like soft blotting paper. The non-sampling surface has a sheen and appears to be a woven fabric.</p> <p>For return to the laboratory, filters should be gently folded once along the long axis, with the particulate surface inward. The filter should be placed inside the brown paper wrapper and re-inserted in the same envelope in which it was shipped.</p> |
| <b>Stability</b>                        | Conditioned filters shipped from Laboratory should be used within thirty days of preparation date. Filters should be weighted with ten days of sampling date. If unable to process with ten days of sampling, store at 4 °C or less and reweight within thirty days of sampling.   |
| <b>Apparatus</b>                        | a) Controlled environment room: temperature 20 °C ± 2 °C. Humidity (30 – 40)% ± 5 (24 hour average).   |
| <b>Principle or Procedure:</b>          |  |
| <b>Procedure</b>                        | See Total Particulate - PM10 - HiVol. 24-hour  |

**Revision History**

March 20, 1995: Initial draft.

October 29, 1996: Procedure vetted by private sector laboratories.

January 12, 1998: EMS codes confirmed; E. Tradewell confirmed filter size.

June 24, 1998: Updated using new EPA protocols.

December 31, 2000: Minor editing; Supplement #2 merged with main Lab Manual.

## **Total Particulate - Teflon - HiVol**

|   |  |
|---|--|
| <b>Parameter</b>                        | Particulate: Total   |
| <b>Analytical Method</b>                | Tot. Part. HiVol Teflon (8 x 10 filter)  |
| <b>EMS Code</b>                         | <b>TP-T 5305</b>   |
| <b>Introduction</b>                     | A measured volume of ambient air is drawn through a high volume sampler and is collected on a 0.3µm Teflon coated borosilicate glass fibre filter. The collected material constitutes total particulate.   |
| <b>Method Summary</b>                   | A high volume (HV) sampler draws a known volume of ambient air at a constant flow rate through one or more filters. Particles are then collected on the filter(s) during the specified 24 hour sampling period. Each sample filter is weighed before and after sampling to determine the net weight (mass) gain of the collected total particulate sample.   |
| <b>MDL</b>                              | 2.0 µg/m <sup>3</sup>  |
| <b>Matrix</b>                           | Ambient Air Particulate  |
| <b>Interferences and Precautions</b>    | Damage to filters (holes), misalignment or leaking gaskets in filter assembly can result in loss of particulate.   |
| <b>Sample Handling and Preservation</b> | <p>Filters are shipped flat in white 10" x 12" envelopes with the opening on the 12" axis. The envelope and filter are both stamped with a unique identifying number. A kraft paper wrapper folded in three on the long axis is also shipped. Filters should NOT be folded before sampling. The shipping envelopes are stamped "DO NOT BEND PRIOR TO USE".</p> <p>The sampling surface of the filter appears like soft blotting paper. The non-sampling surface has a sheen and appears to be a woven fabric.</p> <p>For return to the laboratory, filters should be gently folded once along the long axis, with the particulate surface inward. The filter should be placed inside the brown paper wrapper and re-inserted in the same envelope it was shipped in.</p> |
| <b>Stability</b>                        | Most samples are stable for long periods of time.  |
| <b>Principle or Procedure</b>           | See Total Particulate - PM10 - HiVol   |
| <b>Revision History</b>                 | April 11, 1995: Initial Draft.<br>October 29, 1996: Procedure vetted by private sector laboratories.<br>January 12, 1998: EMS codes confirmed; E. Tradewell confirmed filter size.<br>December 31, 2000: Minor editing; Supplement #2 merged with main Lab Manual.   |

## **Total Particulate - HiVol - Metals - ICP**

|   |  |
|---|--|
| <b>Parameters</b>                       | The HiVol metals package now includes a total of 25 metals. See table on following page for EMS codes and for detection limits.  |
| <b>Analytical Method</b>                | Strong Acid Digestion; ICP Analysis  |
| <b>EMS Code</b>                         | See following page.  |
| <b>Introduction</b>                     | Either nitric /perchloric acid digestion or aqua regia digestion is used to bring the metals into solution. The metal content is then determined by ICP analysis.  |
| <b>Method Summary</b>                   | Following acid digestion, aqueous solutions of samples are converted to aerosols in the nebulizer of the ICP and transported to a high temperature plasma (6000 to 8000°K). This excitation source produces atomic and ionic emission spectra at wavelengths specific to the elements of interest which can be determined either simultaneously or sequentially. |
| <b>MDL</b>                              | The following MDL concentrations are extrapolated from aqueous solutions at the normal operating conditions. For instrument and method MDL values see Section C - Metals.  |
| <b>Matrix</b>                           | Ambient Air Particulates   |
| <b>Interferences and Precautions</b>    | The normal field exposure limit is 24 hours. In order to achieve better detection limits longer exposure times may be used. The laboratory requisition should indicate special test, exposure time, so lab staff will accept this data. For further discussion, see elsewhere in this manual.  |
| <b>Sample Handling and Preservation</b> | Do not touch the sampling surface or use talced gloves when handling filters, as this may cause Zn contamination. Unused portions of filters are archived in paper envelopes.  |
| <b>Stability</b>                        | Samples are stable.  |
| <b>Apparatus</b>                        | a) Filter cutter, 4.6 cm diameter, stainless steel   |
| <b>Reagents</b>                         | a) Nitric Acid, Concentrated, analytical<br>b) Perchloric acid, 70%, analytical  |



**Table of EMS Codes and Recommended Detection Limits for HiVol metals package**

| Element            |                 | EMS Code<br>(nitric/perchloric<br>acid digestion) | EMS Code<br>(aqua regia<br>digestion) | MDL                      |
|--------------------|-----------------|---|---------------------------------------|--------------------------|
| Silver - Total     | Intermediate    | AG-T 5038   | AG-T 6038                             | 0.003 mg/L               |
|                    | Loading (24 hr) | AG-T 5312   | AG-T 6040                             | 0.002 ug/m <sup>3</sup>  |
| Arsenic - Total    | Intermediate    | AS-T 5038   | AS-T 6038                             | 0.2 mg/L                 |
|                    | Loading (24 hr) | AS-T-5312   | AS-T 6040                             | 0.1 ug/m <sup>3</sup>    |
| Boron - Total      | Intermediate    | B--T 5038   | B--T 6038                             | 3.0 mg/L                 |
|                    | Loading (24 hr) | B--T 5312   | B--T 6040                             | 2.0 ug/m <sup>3</sup>    |
| Beryllium - Total  | Intermediate    | BE-T 5038   | BE-T 6038                             | 0.0002 mg/L              |
|                    | Loading (24 hr) | BE-T 5312   | BE-T 6040                             | 0.0001 ug/m <sup>3</sup> |
| Bismuth - Total    | Intermediate    | BI-T 5038   | BI-T 6038                             | 0.024 mg/L               |
|                    | Loading (24 hr) | BI-T 5312   | BI-T 6040                             | 0.01 ug/m <sup>3</sup>   |
| Cadmium - Total    | Intermediate    | CD-T 5038   | CD-T 6038                             | 0.06 mg/L                |
|                    | Loading (24 hr) | CD-T 5312   | CD-T 6040                             | 0.03 ug/m <sup>3</sup>   |
| Cobalt - Total     | Intermediate    | CO-T 5038   | CO-T 6038                             | 0.003 mg/L               |
|                    | Loading (24 hr) | CO-T 5312   | CO-T 6040                             | 0.002 ug/m <sup>3</sup>  |
| Chromium - Total   | Intermediate    | CR-T 5038   | CR-T 6038                             | 0.02 mg/L                |
|                    | Loading (24 hr) | CR-T 5312   | CR-T 6040                             | 0.01 ug/m <sup>3</sup>   |
| Copper - Total     | Intermediate    | CU-T 5038   | CU-T 6038                             | 0.6 mg/L                 |
|                    | Loading (24 hr) | CU-T 5312   | CU-T 6040                             | 0.4 ug/m <sup>3</sup>    |
| Manganese - Total  | Intermediate    | MN-T 5038   | MN-T 6038                             | 0.01mg/L                 |
|                    | Loading (24 hr) | MN-T 5312   | MN-T 6040                             | 0.008 ug/m <sup>3</sup>  |
| Molybdenum - Total | Intermediate    | MO-T 5038   | MO-T 6038                             | 0.004 mg/L               |
|                    | Loading (24 hr) | MO-T 5312   | MO-T 6040                             | 0.002 ug/m <sup>3</sup>  |
| Nickel - Total     | Intermediate    | NI-T 5038   | NI-T 6038                             | 0.02 mg/L                |
|                    | Loading (24 hr) | NI-T 5312   | NI-T 6040                             | 0.01 ug/m <sup>3</sup>   |
| Phosphorus - Total | Intermediate    | P--T 5038   | P--T 6038                             | 0.04 mg/L                |
|                    | Loading (24 hr) | P--T 5312   | P--T 6040                             | 0.02 ug/m <sup>3</sup>   |
| Lead - Total       | Intermediate    | PB-T 5038   | PB-T 6038                             | 0.5 mg/L                 |
|                    | Loading (24 hr) | PB-T 5312   | PB-T 6040                             | 0.3 ug/m <sup>3</sup>    |
| Antimony - Total   | Intermediate    | SB-T 5038   | SB-T 6038                             | 0.14 mg/L                |
|                    | Loading (24 hr) | SB-T 5312   | SB-T 6040                             | 0.09 ug/m <sup>3</sup>   |
| Selenium - Total   | Intermediate    | SE-T 5038   | SE-T 6038                             | 0.02 mg/L                |
|                    | Loading (24 hr) | SE-T 5312   | SE-T 6040                             | 0.01 ug/m <sup>3</sup>   |
| Silicon - Total    | Intermediate    | SI-T 5038   | SI-T 6038                             | 0.11 mg/L                |
|                    | Loading (24 hr) | SI-T 5312   | SI-T 6040                             | 0.07 ug/m <sup>3</sup>   |
| Tin - Total        | Intermediate    | SN-T 5038   | SN-T 6038                             | 0.03 mg/L                |
|                    | Loading (24 hr) | SN-T 5312   | SN-T 6040                             | 0.02 ug/m <sup>3</sup>   |
| Strontium - Total  | Intermediate    | SR-T 5038   | SR-T 6038                             | 0.17 mg/L                |
|                    | Loading (24 hr) | SR-T 5312   | SR-T 6040                             | 0.1 ug/m <sup>3</sup>    |
| Tellurium - Total  | Intermediate    | TE-T 5038   | TE-T 6038                             | 0.02 mg/L                |
|                    | Loading (24 hr) | TE-T 5312   | TE-T 6040                             | 0.01 ug/m <sup>3</sup>   |
| Titanium - Total   | Intermediate    | TI-T 5038   | TI-T 6038                             | 0.07 mg/L                |
|                    | Loading (24 hr) | TI-T 5312   | TI-T 6040                             | 0.04 ug/m <sup>3</sup>   |
| Thallium - Total   | Intermediate    | TL-T 5038   | TL-T 6038                             | 0.03 mg/L                |
|                    | Loading (24 hr) | TL-T 5312   | TL-T 6040                             | 0.02 ug/m <sup>3</sup>   |
| Vanadium - Total   | Intermediate    | V--T 5038   | V--T 6038                             | 0.005 mg/L               |
|                    | Loading (24 hr) | V--T 5312   | V--T 6040                             | 0.003 ug/m <sup>3</sup>  |
| Zinc - Total       | Intermediate    | ZN-T 5038   | ZN-T 6038                             | 0.17 mg/L                |
|                    | Loading (24 hr) | ZN-T 5312   | ZN-T 6040                             | 0.1 ug/m <sup>3</sup>    |
| Zirconium - Total  | Intermediate    | ZR-T 5038   | ZR-T 6038                             | 0.006mg/L                |
|                    | Loading (24 hr) | ZR-T 5312   | ZR-T 6040                             | 0.004 ug/m <sup>3</sup>  |

**Procedure**

- a) Use the filter cutter to remove 2 discs from the HiVol filter, two blank portions from an unexposed filter should be analyzed separately.
- b) Add the filter discs to 75 mL calibrated digestion tubes.
- c) Add two mL HNO<sub>3</sub> and heat cautiously to oxidize any organic matter; do not take to dryness.
- d) Cool, then add 3.75 mL HClO<sub>4</sub>, heat until dense white fumes are present.
- e) Cool and make up to 75 mL with deionized water, final matrix = 5% HClO<sub>4</sub>.
- f) Filter through Whatman #41 filter paper and collect the filtrate in a 250 mL polyethylene bottle.
- g) Analyze for As, Cd, Cu, Pb, Zn by ICP by procedures given in Section – C.

**Calculation:**

From the results obtained in mg/L from the ICP analysis, select the calculation method appropriate to the reporting requirements.

- a) Total µg on digested portion of filter:

$$\mu\text{g} = \mu\text{g/mL} \times 75 \text{ mL}$$

- b) Total µg on filter:

$$\mu\text{g} = \frac{\text{mg}}{\text{L}} \times 0.075 \text{ L} \times \frac{0.043 \text{ m}^2}{0.003322 \text{ m}^2} \times \frac{1000 \mu\text{g}}{\text{mg}}$$

- c) Total µg/m<sup>3</sup> based on flow rate of the sampler and exposure time of the filter:

$$\mu\text{g/m}^3 = \frac{\text{mg}}{\text{L}} \times 0.075 \text{ L} \times \frac{0.043 \text{ m}^2}{0.003322 \text{ m}^2} \times \frac{1 \text{ min}}{1.1355 \text{ m}^3} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1}{\# \text{ hrs}} \times \frac{1000 \mu\text{g}}{\text{mg}}$$

$$\text{or: } \mu\text{g/m}^3 = \text{mg/L} \times \frac{14.249}{\# \text{ hours}}$$

where: 0.075 L = volume of digestate  
 0.043m<sup>2</sup> = total area of filter exposed  
 0.003322m<sup>2</sup> = area of filter analyzed (2 discs 4.6 cm diameter)  
 1.1355 m<sup>3</sup>/min = flow rate  
 # hours = number of hours filter exposed

**Accuracy**

The recovery of Cd, Pb, and Zn from Standard reference filters was 102%, 99%, and 103%, respectively with coefficient of variation of 4, 12 and 2%. The concentration ranges were 1 to 10, 7 to 300 and 10 to 100 µg/filter for Cd, Pb, and Zn.

**Quality Control**

Digest two filter blanks with each batch of 35 or fewer filters, plus two sample filters in duplicate for each batch. Blank results should be less than twice the MDL, otherwise the digestion must be repeated. Duplicate filter digests should agree within ±30%. Blanks and duplicates should be recorded in a database. When sufficient data is available, a duplicate control chart should be constructed for each metal.

**References**

None listed.

**Revision History**

April 1, 1996: Initial draft.

October 29, 1996: Procedure vetted by private sector laboratories; and at their request, a note was added regarding substitution of aqua regia digestion for perchloric acid digestion procedure.

January 12, 1998: EMS codes added and confirmed; minor editing.

March 19, 1998: Table reformatted for clarity.

December 31, 2000: Minor editing; Supplement #2 merged with main Lab Manual. Reference to the 1994 Lab Manual deleted. Preference for use of aqua regia digestion noted.

**Note: Aqua regia digestion is preferred over the nitric/perchloric acid digestion procedure. Note that these different procedures have been assigned different EMS codes.**

## Total Particulate – HiVol - Anions - Ion Chromatography

|                                      |  |                              |                  |
|--------------------------------------|--|------------------------------|------------------|
| <b>Parameter</b>                     | Nitrate-Soluble<br>Sulphate-Soluble<br>Chloride-Soluble  |                              |                  |
| <b>Analytical Method</b>             | Water Extraction; Ion Chromatography - Anion   |                              |                  |
| <b>EMS Code</b>                      |  | <u>Intermediate</u>          | <u>Loading</u>   |
|                                      | Nitrate-Soluble  | <b>NO3- 5068</b>             | <b>NO3- 5022</b> |
|                                      | Sulphate-Soluble   | <b>SO4- 5068</b>             | <b>SO4- 5022</b> |
|                                      | Chloride-Soluble   | <b>CL-S 5068</b>             | <b>CL-S 5022</b> |
| <b>Units</b>                         | a) Intermediate results:   | mg/L                         |                  |
|                                      | b) Loading results:  | µg/m <sup>3</sup>            |                  |
| <b>Introduction</b>                  | Ambient air is sampled on a HiVol air filters (Teflon) using the procedure entitled "Total Particulate - Teflon - HiVol".  |                              |                  |
| <b>Method Summary</b>                | Discs cut from the HiVol filter are extracted with deionized water and the resulting anions are separated and measured using an ion chromatograph yielding intermediate results with units of mg/L. (See Anions – Ion Chromatography – Precipitation, methods NO3- 5068, SO4- 5068, and Cl-S 5068.) Values are then connected to units of µg/m <sup>3</sup> .  |                              |                  |
| <b>MDL</b>                           | <u>Intermediate</u>  |                              |                  |
|                                      | Nitrate-Soluble  | 0.01 mg/L as NO <sub>3</sub> |                  |
|                                      | Sulphate-Soluble   | 0.01 mg/L as SO <sub>4</sub> |                  |
|                                      | Chloride-Soluble   | 0.01 mg/L                    |                  |
| <b>Matrix</b>                        | Ambient Air Particulates   |                              |                  |
| <b>Interferences and Precautions</b> | Interferences can be caused by substances with retention times similar to those of the ion of interest. Large amounts of an anion can interfere with peak resolution of an adjacent anion. Note that unlike water samples, Nitrate is reported on an ion weight basis, i.e., as mg NO <sub>3</sub> /L and µg NO <sub>3</sub> /m <sup>3</sup> .   |                              |                  |
| <b>Principle or Procedure:</b>       |  |                              |                  |
| <b>Apparatus</b>                     | <ul style="list-style-type: none"> <li>a) Filter cutter, 4.6 cm diameter</li> <li>b) Oscillating hot plate</li> <li>c) An ion chromatography system consisting of: <ul style="list-style-type: none"> <li>1) selectable eluent supply</li> <li>2) high pressure, pulseless pump</li> <li>3) sample injection port and sample loop</li> <li>4) anion guard and separator columns</li> <li>5) anion micro membrane suppressor</li> <li>6) conductivity detector</li> <li>7) data station</li> <li>8) auto sampler</li> </ul> </li> </ul> |                              |                  |

## Reagents

- a) Concentrated Stock Eluent: Dissolve 15.12 g sodium bicarbonate ( $\text{NaHCO}_3$ ) and 18.02 g sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) with deionized water into a 1.000 L flask. Dilute to volume and store in a 1 liter poly bottle.
- b) Working Eluent Solution: Dilute 10.0 mL of concentrated stock eluent to 1.000 L in a volumetric flask. ( $1.8 \text{ mM NaHCO}_3 / 1.7 \text{ mM Na}_2\text{CO}_3$ ) Filter before use.
- c) Regenerent Solutions: 0.025 N Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) - Dilute 26.8 mL concentrated sulphuric acid to one liter to prepare a 1.00 N  $\text{H}_2\text{SO}_4$  solution. Dilute 25.0 mL of this solution to one liter.
- d) Stock Chloride Standard Solution: Dry 2 to 3 g of sodium chloride ( $\text{NaCl}$ ) at  $140^\circ\text{C}$  for 2 hours and cool in a desiccator. Dissolve 1.648 g  $\text{NaCl}$  in deionized water and dilute to 1.0 liter ( $1.00 \text{ mL} = 1.00 \text{ mg Cl}$ ). Store in a poly bottle under refrigeration.
- e) Stock Nitrate Standard Solution: Dissolve 1.630 g anhydrous potassium nitrate ( $\text{KNO}_3$ ) in deionized water and dilute to 1.0 liter ( $1.00 \text{ mL} = 1.00 \text{ mg NO}_3$ ). Store in a poly bottle under refrigeration.
- f) Stock Sulphate Standard Solution: Dissolve 1.479 g anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) in deionized water and dilute to 1.0 liter ( $1.00 \text{ mL} = 1.00 \text{ mg SO}_4$ ). Store in a poly bottle under refrigeration.

## Procedure

- a) Use a filter cutter to remove 3 discs from the hi vol (Teflon) filters.
- b) Add the exposed filter discs to a 200 mL tall plastic beaker.
- c) Add 50 mL deionized water.
- d) Extract at room temperature for 2 hours, with swirling, using the oscillating hot plate.
- e) Filter using Whatman No. 40 filter paper and collect the filtrate into a 100 mL flask.
- f) Quantitatively transfer the extract to a 100 mL volumetric flask and dilute to volume with deionized water.

Determine the anion concentrations according to the procedures for an anion scan given below:

- 1) Allow all samples and standards to reach laboratory temperatures before analysis.
- 2) Establish a constant background conductivity using the following instrument conditions:

Eluent: .0018 M NaHCO<sub>3</sub> / 0.0017 M Na<sub>2</sub>CO<sub>3</sub>  
 Separator: 4 x 50 Anion Precolumn (Guard)  
 Dionex IONPac®-AG4-SC  
 4 x 250 Anion Separator Column  
 Dionex IONPac®-AS4-SC  
 Suppressor: Anion Micro Membrane Suppressor  
 Dionex AMMS-1  
 Eluent Flow: 2.0 mL/min.  
 Operating Pressure: 900 psi  
 Regenerent: 0.025 N H<sub>2</sub>SO<sub>4</sub>  
 Regenerent Flow: 2.0 - 3.0 mL/min  
 Backgrd. Conduct: 12 - 16 µS  
 Injection Volume: 25 µL

- 3) Pipette 5.0 mL of each sample or standard solution into a 5 mL autosampler vial (Dionex Polyvial™), then add 50 µL of concentrated stock eluent. Cap vial with a 0.22 µm filter cap and shake. Load into the autosampler.
- 4) Run a blank and at least a four-point calibration curve of composite standards for each detector range. The calibration curve should include at least one calibration point for each decade of the concentration range. Calibration should be run daily when the analysis is run.
- 5) Run samples through the chromatograph with standards after every five samples.

## Calculations

Calibration curves are programmed into the data station to be read directly off the chromatogram in terms of peak heights and in units of mg/L of anions in the filtrate. Subtract blanks before calculations.

- a) To convert the results of anions in the filtrate to air sampled.

$$\mu\text{g}/\text{m}^3 = \frac{\text{mg}}{\text{L}} \times 0.100 \text{ L} \times \frac{0.043 \text{ m}^2}{0.003322 \text{ m}^2} \times \frac{1 \text{ min}}{1.1355 \text{ m}^3} \times \frac{1 \text{ hr}}{60 \text{ Min}} \times \frac{1}{\# \text{ hrs}} \times \frac{1000 \mu\text{g}}{\text{mg}}$$

where: 0.100 L = volume of filtrate  
 0.043 m<sup>2</sup> = total area of filter exposed  
 0.003322 m<sup>2</sup> = area of filter analyzed ( 2 discs 4.6 cm diameter )  
 1.1355 m<sup>3</sup>/min = flow rate  
 # hrs = number of hours filter exposed.

$$\text{Simplified: } \mu\text{g}/\text{m}^3 \text{ anion X} = \text{mg}/\text{L} \times \frac{18.999 \text{ anion}}{\# \text{ hrs}}$$

- b) To convert the results of anions in filtrate to High Vol filters:

$$\text{mg anion X} = \text{CV},$$

where: C = mg/L anion X in the filtrate  
 V = 0.100 L of filtrate.

## Precision

RSD = 1.18% at 31.0 mg NO<sub>3</sub>/L (water)  
 RSD = 1.49% at 98.5 mg SO<sub>4</sub>/L (water)  
 RSD = 2.29 % at 10.0 mg Cl/L (water)

|                         |  |
|-------------------------|--|
| <b>Accuracy</b>         | 100.7% at 31.0 mg NO <sub>3</sub> /L (water)<br>104% at 98.5 mg SO <sub>4</sub> /L (water)<br>98.2% at 10.0 mg Cl/L (water)  |
| <b>Quality Control</b>  | Digest two filter blanks or reagent blanks with each batch of 35 or less filters, and two sample filters in duplicate for each batch. The filter blanks may be high; therefore, data should be blank subtracted. Duplicate filter digests should agree within ± 30%.   |
| <b>References</b>       | a) J.P. Smith, D. Grodjean and J.N. Pitts, J. Air Pollut. Contr. Assoc. 28;930 (1978).   |
| <b>Revision History</b> | <p>April 30, 1996: Initial Draft.</p> <p>October 29, 1996: Procedure vetted by private sector laboratories.</p> <p>July 14, 1997: Minor editing; MDL code for µg/m<sup>3</sup>; SEAM code replaced by EMS code; Intermediate EMS codes added.</p> <p>January 12, 1998: EMS codes confirmed.</p> <p>December 31, 2000: Minor editing; Supplement #2 merged into main Lab Manual. Units added. Reference to out-of-print manual deleted.</p> |

**Note 1: While anions and cations are usually reported for water samples on an elemental basis, for air samples, the convention is to report on an ion weight basis. Thus, ammonia is reported as mg/L and µg/m<sup>3</sup>/d as NH<sub>4</sub> and nitrate is reported as mg/L and µg/m<sup>3</sup> as NO<sub>3</sub>.**

**Note 2: Note that the listed anions and cations may alternatively be analyzed according to any relevant procedure specified in this edition of the BC Environmental Laboratory Manual.**

## Total Particulate - HiVol - Sodium - Ion Chromatography

|                                      |   |
|--------------------------------------|---|
| <b>Parameter</b>                     | Sodium - Soluble  |
| <b>Analytical Method</b>             | Ion Chromatography – HiVol extrn  |
| <b>EMS Code</b>                      | a) Intermediate results <b>NA-S 5318</b><br>b) Loading results <b>NA-S 5018</b>   |
| <b>Introduction</b>                  | Ambient air is sampled on a HiVol air filters (Teflon) using the procedure entitled “Total Particulate - HiVol - Teflon”  |
| <b>Method Summary</b>                | Discs cut from the HiVol filter are extracted with deionized water and the soluble sodium is determined on an ion chromatograph. The sodium is separated from other ions through a cation ‘guard’ and cation ‘separator’ column with a methane sulphonic acid eluent. A self regenerating membrane suppressor is attached to the end of the column to neutralize the acid before detection. |
| <b>MDL</b>                           | 0.01 mg/L Na (intermediate result)  |
| <b>Units</b>                         | a) Intermediate result: mg/L<br>b) Loading: $\mu\text{g}/\text{m}^3$  |
| <b>Matrix</b>                        | Ambient Air Particulates  |
| <b>Interferences and Precautions</b> | Interferences can be caused by substances with retention times similar to those of the ion of interest.   |
| <b>Principle or Procedure:</b>       |   |
| <b>Apparatus</b>                     | a) Filter cutter, 4.6 cm diameter<br>b) Oscillating hot plate<br>c) An ion chromatograph consisting of:<br>1) selectable eluent supply<br>2) high pressure, pulseless pump<br>3) chromatography module<br>4) cation guard and separator columns<br>5) cation membrane suppressor<br>6) conductivity detector<br>7) data station   |
| <b>Reagents</b>                      | a) Methane sulphonic acid stock (2.0 M): Weigh 96.1 g methane sulphonic acid and dilute to 500 mL with deionized water.<br>b) Eluent (0.02 M): dilute 10.0 mL of 2.0 methane sulphonic acid stock to 1L. Filter through a 0.45 $\mu\text{m}$ nylon membrane filter.<br>c) Sodium standard 1000 mg/L: Dissolve 2.542 g predried sodium chloride (Analar) in 1 L deionized water.             |
| <b>Procedure</b>                     | a) Use the filter cutter to remove 3 discs from the hi vol (Teflon) filters. Carry two blanks through all steps of the procedure.   |



- b) Add the exposed filter discs to a 200 mL tall plastic beaker.
- c) Add 50 mL deionized water and let stand.
- d) Filter using Whatman No. 40 filter paper, quantitatively transfer to a 100 mL volumetric flask and dilute to volume with deionized water, and collect the filtrate.
- e) Allow all samples and standards to reach laboratory temperature before analysis.
- f) Establish a constant background conductivity using the following instrument conditions:

|                          |  |
|--------------------------|--|
| Eluent:                  | 0.020 M methane sulphonic acid   |
| Regenerant:              | Deionized water  |
| Separator:               | 4x50 Cation Precolumn (Guard)<br>Dionex IonPac CG12<br>4X200 Cation Separator Column<br>Dionex IonPac CS12 |
| Suppressor:              | Cation Self Regenerating Suppressor<br>Dionex CSRS-1   |
| Eluent Flow Rate:        | 1.0 mL/min   |
| Operating Pressure:      | 900 psi  |
| Regenerant Flow rate:    | 10 mL/min  |
| Regenerant Current:      | 200 mA   |
| Background Conductivity: | 2-6 µS   |
| Injection Volume:        | 25 µL  |

- g) Load extract into auto-sampler.
- h) Run a blank and a four point calibration curve of standard for each detector range.
- i) After thirty samples, rerun a new calibration curve.

**Calculations**

A calibration curve is normally programmed into the data station to be read directly off the chromatogram in terms of peak heights and in units of mg/L of sodium in the filtrate. Subtract blanks before calculations.

- a) To convert the results of sodium in the filtrate to air sampled:

$$\mu\text{g}/\text{m}^3 = \frac{\text{mg}}{\text{L}} \times 0.100 \text{ L} \times \frac{0.043 \text{ m}^2}{0.003322 \text{ m}^2} \times \frac{1 \text{ min}}{1.1355 \text{ m}^3} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1}{\# \text{ hrs}} \times \frac{1000 \mu\text{g}}{\text{mg}}$$

where:

0.100 = volume of filtrate

0.043 m<sup>2</sup> = total area of filter exposed

0.003322 m<sup>2</sup> = area of filter analyzed (2 discs 4.6 cm in diameter)

1.1355 m<sup>3</sup> = flow rate

# hrs = number of hours filter exposed

Simplified:  $\mu\text{g}/\text{m}^3 \text{ Na} = \text{mg}/\text{L} \times \frac{18.999 \text{ Na}}{\# \text{ hrs}}$

b) To convert the results of sodium filtrate to High Vol. filters:

$$\text{mg Na} = CV$$

where:

C = mg/L Na in the filtrate

V = 0.100 L of filtrate

**Precision**

In the ministry's contract laboratory, authentic samples gave the following coefficients of variations (C.V.) 3.7 % at 0.8 mg/L and 3.5% at 0.16 mg/L.

**Quality Control**

Digest two filter blanks or reagent blanks with each batch of 35 or fewer filters, and two sample filters in duplicate for each batch. The filter blanks may be high; therefore data should be blank subtracted.

**References**

- a) Dionex Corporation. Basic Ion Chromatography, 1228 Titan Way, Sunnyvale, CA. 94088-3603, U.S.A.
- b) Dionex Corporation. Self-Regenerating Controller Users Guide, Document No.034720, 1228 Titan Way, Sunnyvale, CA. 94088-3603, U.S.A. October 1992.
- c) Dionex Corporation. Installation Instructions and Troubleshooting Guide for the Cation Self-Regenerating Suppressor-1 (4mm), Document No. 034651, 1228 Titan Way, Sunnyvale, CA. 94088-3603, U.S.A. June 1993.
- d) Dionex Corporation. Installation Instructions and Troubleshooting Guide for the IONPAC CS12 Analytical Column, Document No.034657, 1228 Titan Way, Sunnyvale, CA. 94088-3603, U.S.A. March 1992.
- e) J.P. Smith, D. Grosjean and J.N. Pitts, J. Air Pollut. Contr. Assoc. 28;930 (1978).

**Revision History**

- April 1, 1996: Initial draft.
- October 29, 1996: Procedure vetted by private sector laboratories. Note regarding alternative methods added.
- January 12, 1998: EMS codes added; minor editing.
- December 31, 2000: Minor editing; Supplement #2 merged into main Lab Manual. Erroneous EMS code (for loading) corrected.

**Note: Note that the sodium may alternatively be initially analyzed according to any relevant procedure specified in this edition of the BC Environmental Laboratory Manual.**

## Sulfation Index

|   |  |
|---|--|
| <b>Parameter</b>                        | Sulfation Index  |
| <b>Analytical Method</b>                | Turbidimetric Analysis: Intermediate Result<br>Turbidimetric Analysis: Loading Result  |
| <b>EMS Code</b>                         | a) Intermediate results <b>SUFI 5000</b><br>b) Loading results <b>SUFI 5001</b>  |
| <b>Introduction</b>                     | A lead oxide plate is exposed to ambient air for a period of 30 days. During this time sulfur dioxide and sulfur trioxide in the air are collected by lead oxide as the result of both oxidation and absorption processes and converted to lead sulfate.   |
| <b>Method Summary</b>                   | The lead oxide plates undergo extractions and the sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined using a spectrophotometer and compared to a curve prepared from standard sulfate solutions.   |
| <b>MDL</b>                              | 0.02 mg SO <sub>3</sub> /plate or 0.5 mg/L SO <sub>3</sub>   |
| <b>Units</b>                            | Intermediate result: mg/L as SO <sub>3</sub><br>Loading result: mg/dm <sup>2</sup> /d  |
| <b>Matrix</b>                           | Lead oxide paste   |
| <b>Interferences and Precautions</b>    | Care must be taken to ensure that the plates are prepared in a uniform manner and that the paste will adhere to the bottom of the plate.   |
| <b>Sample Handling and Preservation</b> | Plates should be handled with care to avoid dislodging the dried absorbent paste.  |
| <b>Principle or Procedure:</b>          |  |
| <b>Apparatus</b>                        | a) Test tubes, 23 x 200 mm<br>b) Vortex mixer<br>c) UV/visible double beam spectrophotometer<br>d) Spectrophotometric cells, 5 cm, glass or quartz   |
| <b>Reagents</b>                         | a) Sulfation Plates:<br>1) Add 500 mL 10% ethanol and 5.0 g glass fibre filters to a Waring blender.<br>2) Blend for 1 hour and then add 2.5 g gum tragacanth.<br>3) Blend for a further 10 minutes and then add 100 g Lead oxide (PbO <sub>2</sub> ).<br>4) Blend for 10 minutes and then adjust the blending speed so that it is just sufficient to maintain a mixing action.<br>5) Add 5.0 mL of the prepared suspension to each 48 mm plastic petri dish - approximately 75 plates may be prepared.<br>6) Dry overnight at 60°C.<br>7) Add a drop of chloroform to the centre of the plate and apply pressure till dry, to provide adhesion of the material to the petri dish. |

- 8) Place covers on the petri dishes.
- b) Sodium phosphate buffer (1000 mg/L with respect to phosphate): dissolve 4.0g Na<sub>3</sub>PO<sub>4</sub> · 12 H<sub>2</sub>O in deionized water and dilute to one litre.
- c) Acid reagent: to 100 mL of glacial acetic acid add 30 mL concentrated HCl. Dilute to 200 mL with deionized water.
- d) Barium chloride crystal, reagent grade.
- e) Stock sulfur solution (100 mg/L S): dissolve 0.5499 g K<sub>2</sub>SO<sub>4</sub> in deionized water and dilute to one litre.

### Procedure

Note: carry a blank through all steps of the procedure.

- a) Quantitatively transfer the exposed lead oxide plate to a 250 mL beaker.
- b) Add 50 mL buffer solution.
- c) Allow to extract overnight and then heat to boiling temperature and hold for 2 minutes.
- d) Cool. Filter through Whatman # 40 filter paper and collect the filtrate.
- e) Transfer to a 100 mL volumetric flask and dilute to volume with deionized water.
- f) Prepare a series of standards (1.0, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0, 12.0 mg/L S) by pipetting 1, 2, 3, 4, 6, 8, 10, 12 mL of stock solution into 100 mL volumetric flasks and diluting to volume. Also prepare a reagent blank.
- g) Pipette 25.0 mL sample, standard and blanks into 24 x 200 mm test tubes.
- h) Add 2.0 mL acid reagent.
- i) Mix on a Vortex mixer.
- j) Add 0.5 g Barium Chloride crystals.
- k) Cover the tubes with Parafilm®.
- l) Mix on Vortex mixer to dissolve the barium chloride.
- m) Allow to stand for 30 minutes and then invert 6 times. Immediately read the absorbance of the solutions at 420 nm using 5 cm cells.

### Calculation

Prepare a calibration curve from the readings of the standard solutions. Determine the concentration of sulfur in the samples by comparing the "sample - blank" reading with the calibration curve.

$$\text{mg SO}_3 = 2.5 \text{ CVF}$$

where: C = mg/L Sulphur in extract  
 V = litres extract as diluted  
 F = reactivity factor for lead oxide

### Precision

A study of replicate plates exposed to ambient air for intervals of 14 to 21 days gave a relative standard deviation of 5.2 %.

### Quality Control

Carry a reagent blank and an unexposed plate through all steps of the procedure.

### References

- a) N. A. Huey, J. Air Poll. Contr. Assoc. 8:610 (1968).

b) A. J. Lynch, N. R. McQuaker, and M. Gurney. Environ. Sci. and Technol. 12;169 (1978).

**Revision History**

April 1, 1996: Initial draft.

October 29, 1996: Procedure vetted by private sector laboratories.

January 13, 1998: Minor editing and EMS codes confirmed.

February 16, 1998: Revision of EMS codes to eliminate redundant code for intermediate results; MDLs updated.

December 31, 2000: Minor editing; Supplement #2 merged into main Lab Manual.

## Fluoridation Index

|  |   |
|--|---|
| <b>Parameter</b>                         | Fluoridation Index  |
| <b>Analytical Method</b>                 | Specific Ion Electrode (Intermediate results)<br>Specific Ion Electrode (Loading results)   |
| <b>EMS Code</b>                          | a) Intermediate results <b>FLRI 5003</b><br>b) Loading results <b>FLRI 5004</b>   |
| <b>Introduction</b>                      | A calcium oxide plate is exposed to ambient air for a period of 30 days. During this time fluoride in the ambient air is collected as calcium fluoride.   |
| <b>Method Summary</b>                    | The plates undergo an extraction and the fluoride which is isolated is determined using the selective ion electrode procedure.  |
| <b>MDL</b>                               | Intermediate results: 0.1 mg/L F<br>Loading results: 0.05 µg/dm <sup>2</sup> /d   |
| <b>Matrix</b>                            | Calcium oxide paste   |
| <b>Interferences and Precautions</b>     | The plate extract may suppress the response of the ion selective electrode, to correct for this, results are calculated by 3 point standard addition method.  |
| <b>Sample Handling and Preservation</b>  | Plates should be handled with care to avoid dislodging the dried absorbent paste.   |
| <b>Stability</b>                         | Expected to be stable.  |
| <b>Precision</b>                         | A study of replicate plates exposed to ambient air for intervals of 14 to 21 days gave a relative standard deviation of 5.9%.   |
| <b>Principle or Procedure: Apparatus</b> | Expanded scale digital ion analyzer fitted with a double junction reference electrode and a fluoride selective ion electrode.   |
| <b>Reagents</b>                          | a) Fluoridation Plates:<br>1) Add 500 mL deionized water and 5.0 g glass fibre filters to a Waring blender.<br>2) Blend for 1 hour and then add 50 g of calcium oxide.<br>3) Blend for a further 10 minutes and then adjust the blending speed so it is just sufficient to maintain mixing action.<br>4) Add 3.5 mL of the prepared suspension to a 48 mm plastic petri dish. Approximately 100 plates may be prepared.<br>5) Dry overnight at room temperature.<br>6) Add a drop of chloroform to the centre of each plate and apply pressure until dry, to provide adhesion of the material to the plate.<br>7) Place the covers on the petri dishes.<br>8) Retain at least four plates from each batch to be used as blanks.<br>b) Hydrochloric acid, concentrated.<br>c) Hydrochloric acid, 6 N: Dilute 500 mL of concentrated HCl to 1 L with deionized water. |

- d) Sodium hydroxide 6 N: Dissolve 240 g NaOH in deionized water and dilute to 1 L with deionized water.
- e) Total ionic strength adjustment buffer (TISAB): Dissolve 116 g of sodium chloride in approximately 1 L of deionized water. Add 114 mL of glacial acetic acid and 50 mL of CDTA stock solution. Adjust the pH to 5.8 by adding 10 N sodium hydroxide. Adjust to volume with deionized water, in a 2 L volumetric flask.
- f) CDTA Stock Solution: dissolve 36 g of CDTA (1,2 cyclohexylenediamine tetra acetic acid ) in 200 mL of 1 N NaOH.
- g) Fluoride solution I (1000 mg/L F): dissolve 2.210 g of anhydrous NaF in deionized water and dilute to 1 L.
- h) Fluoride solution II (50 mg/L): dilute 50 mL fluoride solution I to 1000 mL with deionized water.
- i) Stabilization solution: dissolve 0.5 g gum arabic in 100 mL 1 + 1 glacial acetic acid, and filter. Keep refrigerated.

**Procedure**

- a) Quantitatively transfer the exposed Calcium oxide plate to a 150 mL polyethylene beaker.
- b) Use deionized water to adjust the final volume to about 40 mL and then add 1.0 mL concentrated HCl. Also prepare at least two blank unexposed plates in the same manner as the sample.
- c) Allow to extract overnight.
- d) Use 6 N HCl or 6 N NaOH as required to adjust the pH to slightly acidic. Adjust volume to 50 mL.
- e) Pipette two aliquots of sample and spike with 0.5 mL and 1.0 mL respectively with fluoride solution II. (0.5 mg/L and 1.0 mg/L).
- f) Add TISAB in 1:1 ratio with sample.
- g) Analyze the samples and the above spiked samples using a fluoride selective ion electrode.
- h) Calculate the result from the spike additions and the raw fluoride results. Results should be blank corrected.

**Quality Control**

Carry at least two blank unexposed plates and a reagent blank through all steps of the procedure.

**References**

- a) A.J. Lynch, N.R. McQuaker and M. Gurney, Environ. Sci. Technol. 12;169 (1978).

**Revision History**

- April 1, 1996: Initial Draft.
- October 29, 1996: Procedure vetted by private sector laboratories.
- January 13, 1998: Minor editing; EMS codes verified.
- March 20, 1998: Revision of EMS code to eliminate redundant variable for intermediate results.
- December 31, 2000: Minor editing; Supplement #2 merged with main Lab Manual.

## FLUORIDATION PLATES

Extracted  
by: \_\_\_\_\_

100mL of samples  
(includes 50 mL TISAB)

Extraction  
Date: \_\_\_\_\_

| Sample Number   | Raw Result | 0.5 mg/L Spike Result | 1.0 mg/L Spike Result | Days of Sampling | Average Percent Recovery | Concentration Standard Additions   | Blank correction mg/L | Final Result, from ug           |
|---|------------|-----------------------|-----------------------|------------------|--------------------------|------------------------------------|-----------------------|---------------------------------|
|   |            |                       |                       |                  |                          |                                    |                       | unit correct:                   |
| Blank A   | 0.217      | 0.594                 | 1                     |                  |                          | 0.282                              | average               | mg/l<br>x1000<br>ug/mg<br>x0.05 |
| spike recovery  |            | 75%                   | 78%                   |                  | 77%                      |                                    | 0.329                 | gives ug per plate.             |
| Blank B   | 0.291      | 0.645                 | 1.13                  |                  | Avg. blank               | 0.376                              |                       |                                 |
| spike recovery  |            | 71%                   | 84%                   |                  | 77%                      |                                    |                       |                                 |
|   |            |                       |                       |                  |                          |                                    |                       |                                 |
| sample #26672   | 0.656      | 1.14                  | 1.7                   |                  |                          | 0.652                              | 0.323                 | 16.14                           |
| spike recovery  |            | 97%                   | 104%                  |                  | 101%                     |                                    |                       |                                 |
| sample #28210   | 0.403      | 0.872                 | 1.44                  |                  |                          | 0.408                              | 0.079                 | 3.94                            |
| spike recovery  |            | 94%                   | 104%                  |                  | 99%                      |                                    |                       |                                 |
|   |            |                       |                       |                  |                          |                                    |                       |                                 |
|   |            |                       |                       |                  | <b>units:</b>            | mg/L (except where show otherwise) |                       |                                 |
| Corrections for days of sampling not shown since data not available |            |                       |                       |                  |                          |                                    |                       |                                 |