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Section 7 Water-soluble ion filter extraction:

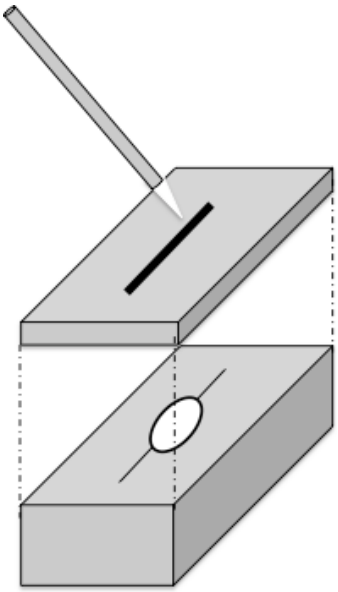
General summary: Teflon and Nuclepore filters are cut in half with a ceramic blade. One half is destined for ion chromatography (IC) analysis (section 7), the other destined for inductively coupled plasma mass spectrometry (ICP-MS, section 8).

We outline the steps necessary to obtain anion and cation data via IC from Teflon and Nuclepore filters. Filters are cut in half with a ceramic knife. The filter is then spiked with 120 μL of IPA before 2.9 mL of Milli-Q water are added. Filter/water are sonicated together for 30 min. Extractions are filtered through a 0.45 μm filter before being sampled (separately) via anion/cation IC columns along with reference ion standards.

IC analysis

Up until now analysis of filters has been non-destructive (e.g. BC and weighing of absolute filter mass). Both IC and ICP-MS analysis are destructive hence the following procedures most be followed with the utmost care!

Step 1: Cutting 25 mm filters in half



- Filter cutting is a standard practice to obtain different data from each half
- We have a custom filter cutter. It is presently being stored in the sexton analytical chemistry lab (in 'tools' drawer).
- To use, place the Teflon filter in the center of the cutting board and place cover (with narrow slit) on top. Use the ceramic knife to cut the filter in half
- When cutting Nuclepore filters, place a blue separator pad underneath the filter (NB: separator pads come with pre-packaged SPI-brand nuclepore).

Caution: Clean the knife-edge and all surfaces touching the filter between each cut with methanol and KimWipe.

Step 2: Separation of filter halves:

Dividing filters in half for analytical purposes has been reported in previous studies (Zhang et al., 2013).

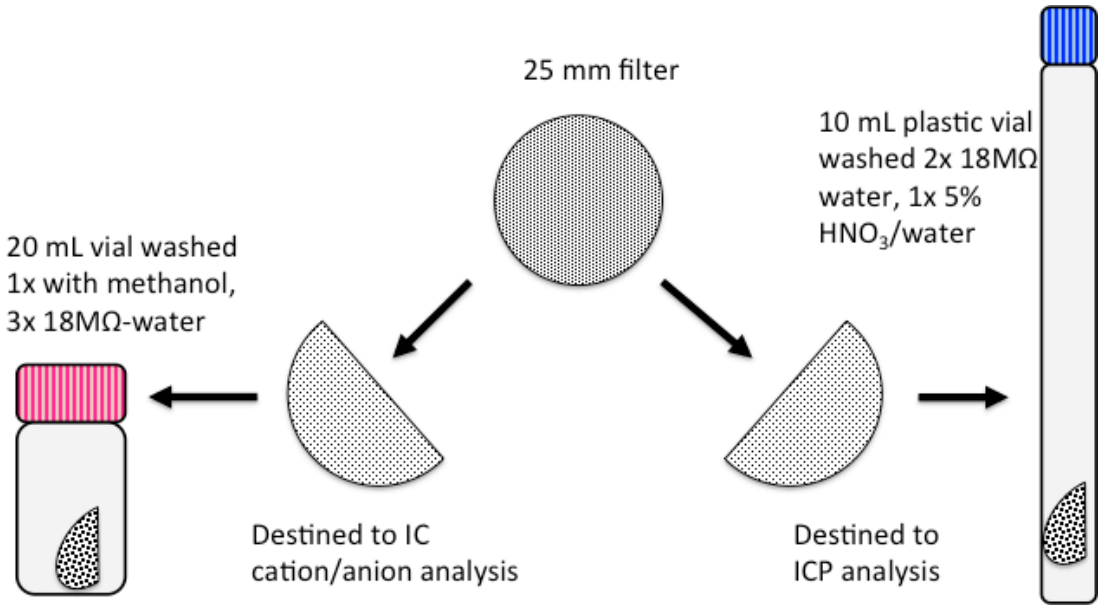


Figure 1: Division of filter halves destined for trace metal (ICP) and trace ion analysis. Pink-capped vials are Simport-brand polypropylene containers (cat. No. M959-20FMA). Larger 40 mL vials (cat. No. M959-40FMA) are used for 37 mm filters. 10 mL vials come from Sexton Water lab (near ICP-MS) itself.
Cutting the filter should be done simultaneous to labeling of pink and blue-capped vials. Vials should be cleaned and dried the day before.

Step 3: Logging completion stages of IC and ICP results

Since IC and ICP results are multi-staged (prepping, extracting, analyzing, and receiving final results), it is important to keep track how far along each sample has been processed. We record the stages of data processing in an IC/ICP logbook located in the Sexton lab. The appearance is as follows:

The **small**-sized stickers are obtained from petri dishes (in which filters are stored). These stickers are transferred to log book once an initial extraction has been made (at least one of IC or ICP). The date of any given step is written *after completion of that step*. Legend for the columns:

Site ID: ____CHTS_____ Year:___2014_____

Sticker	IC						ICP-MS			
	Extraction		Submitted		Received		Extraction			
	Date	Vol,ml	Anion	Cation	Anion	Cation	Date	Vol,ml	Sub'd	Rec'd
1										
13048-CHTS-8N	June 4	6	June 10	June 12	June 15	June 20	June 4	6	June 10	June 18
13049-CHTS-1T	June 4	6	June 10	June 12	June 15	June 20	June 4	6	June 10	June 18
13050-CHTS-2T	June 4	6	June 10	June 12	June 15	June 20	June 4	6	June 10	June 18
13051-CHTS-3T	June 4	6	June 10	June 12	June 15	June 20	June 4	6	June 10	June 18
13052-CHTS-4T	July 5	6	July 6	Aug 11	July 10	Aug 15	July 5	6	July 6	July 16
13053-CHTS-5T	July 5	6	July 6	Aug 11	July 10	Aug 15	July 5	6	July 6	July 16
13054-CHTS-6T	July 5	6	July 6	Aug 11	July 10	Aug 15	July 5	6	July 6	July 16
13055-CHTS-7T	July 5	6	July 6	Aug 11	July 10	Aug 15	July 5	6	July 6	July 16
10										

- **Extraction:** date and volume of IC/ICP filter extraction/storage. Samples at this stage are in a state ready for measurement by IC or ICP instruments. We use 3 mL of liquid extract for half a filter so we write 6 mL, referring to what volume would be for the whole filter.

- **Submitted:** date IC anion/cation aliquot is physically handed over to person in charge of IC or ICP analysis. For IC, this means transferring 0.5 mL of sampler to IC vial (properly labeled). For ICP, submitted means filter half is boiled in >3 mL of 5% HNO_3 for two hours (remaining volume is then made up to 3.0 mL mark).

- **Received** means data has been received electronically as an excel spreadsheet (both IC and ICP are received in this manner)

- **Vol** means the extraction volume. Note that as of June 5th 2014 onwards filters are first cut in half with ceramic blade and cut halves are divided into above IC/ICP halves. Before this date filters were extracted first in IPA/water, then in acid. Hence for new samples the 'extraction volume' should always means the volume one must multiply IC/ICP analysis to obtain absolute mass on the **entire** undivided filter. If 0.5 filters is dissolved in 3 mL of water, to recreate absolute ion mass you would multiply concentration results by 3 mL/0.5 = 6 mL.

Water-soluble (inorganic) ion analysis via ion chromatography (filter half #1):

After samples have been divided, one half is destined for IC analysis, the other for ICP-MS. The procedures below are for extraction and analysis of the water-soluble ion half of cut filter.

- Place the half of Teflon or Nuclepore filter at the bottom of the 20 mL pink-capped vial. The vial should also be appropriately labeled (e.g. filter 13026-CHTS-2N in the shorthand would be CHTS-26, etc.).
- Ensure filter is "dirty-side up", and that vials are clean (triply washed).
- Add 120 µL of HPLC-grade isopropyl alcohol (IPA) *directly onto filter* half. IPA should absorb into Teflon filter (less so for Nuclepore).
- The extract is then sonnicated for 20 minutes.
- Take a cleaned 6 mL syringe and suck up the entire 3 mL extract. Place a 0.45 micron filter head on syringe and push, slowly, the liquid to a brown 8 mL amber vial labeled [4-letter code]_sample#, e.g. "CHTS_27"
- Filter extracts are stored in lab fridge, grouped in bags of 16 extracts per bag (one cartridge).

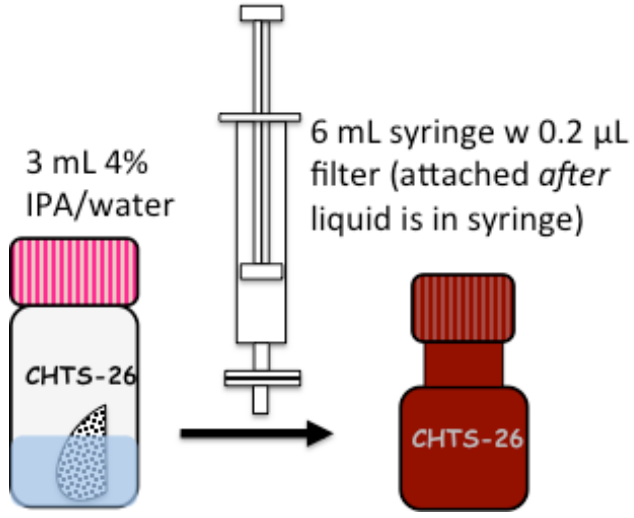


Figure 2: transfer of liquid extract from 20 mL pink vials to 8 mL amber vials. Amber vials are washed once with methanol, 3 times with water before use. Amber vials are from Fisher Scientific ¼ Oz (VCAT N2004-9025). Syringe is from Fisher Scientific (VCAT S7510-5/ Cat. No. 03-377-22). Syringe filters from Fisher Scientific (VCAT F2513-10/ Cat. No. 03-397-24).

Anion Filter Spike Test

Filters were spiked with known amounts of anions to determine the efficacy of extracting water-soluble compounds. We added a known amount of standard directly onto filters then let them dry overnight. Extractions were performed by adding IPA and water to filters, the sonicating solution as in field extractions. Many recoveries were > 100%,possibly due to measurement error with pipette tip or from standard solutions. The tabled values indicate that concentrations below 0.1 μg/mL become unreliable.

Table 1: Percent recovery for seven anions at nine concentrations compared with expected concentrations

Nitrate conc* [μg/mL]	Fluoride	Chloride	Nitrite	Bromide	Nitrate	Phosphate	Sulfate
0.05	237%	151%	101%	106%	112%	166%	213%
0.1	152%	122%	69%	103%	138%	113%	117%
0.25	108%	129%	69%	101%	110%	148%	109%
0.5	97%	113%	77%	94%	97%	90%	96%
0.75	102%	117%	89%	105%	104%	105%	115%
1.0	101%	112%	92%	104%	114%	105%	108%
2.0	95%	106%	92%	99%	102%	96%	102%
3.0	99%	110%	99%	104%	107%	100%	105%
6.0	98%	106%	101%	103%	107%	99%	105%

*Concentrations of F, Cl, NO_2, Br, NO_3, PO_4, and SO_4 relative to NO_3 are 0.2, 0.3, 1.0. 1.0. 1.0, 1.5 and 1.5, respectively.

IC Filter extract auto-sample preparation (anion and cation)

There are several critical steps in operating the ion chromatography (IC) systems located in room N310 (Chem Eng, Sexton). There are two IC systems in the sexton lab: Dionex ICS 1100 with AS-DV autosampler (anions) and ICS 1000 with AS40 autosampler (cations). Historically both have been used for cations and anions.

- Cation analysis scans for six ions: lithium (Li^+), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}).
- Anion analysis scans for seven ions: Fluoride (F^-), Chloride (Cl^-), Nitrite (NO_2^-), Bromide (Br^-), Nitrate (NO_3^-), Phosphate (HPO_4^{2-}) and Sulfate (SO_4^{2-}).
- The IC instruments are Dionex ICS-1000 (anions or cations) and Dionex ICS-1100 (anions or cations). Anions and cations were separated using an IonPac AS9-HC and CS-12 analytical and guard column, respectively. Anion and cation suppressors are AERS 500 4mm and CSRS Ultra II 4mm, respectively.

Saving/retrieving raw cation/anion data:

Anions: For Dell Optiplex 9010 computer, files are saved in

ChromeleonLocal/Instrument Data/ICS_1600/Data/SPARTAN/ [Site_name&Code]/[date]

Cations: For APC XS 1300 computer, filter are saved in

ROB_LAB_PRINTER_1/2014/SPARTAN_Cations/[Site_name&Code]/[date]

File naming system follows the form [date run]_[4-letter abbrev.]_[cartridge #]

Preparing samples: Transfer via disposable pipette tip a 0.5 mL aliquot of the water extract into labeled PolyVials (Thermo Scientific #079797) from amber vials. Write in, under "IC submitted" logbook column, the date submitted for analysis.

Calculating IC ion masses

IC results are reported as the peak area in micro Siemens (μS) versus time (minutes). Hence peak areas A_i are in units $[A_i] = \mu S*min$. To convert peak area to mass, we require standards and known liquid volume extraction. New standards are prepared weekly; preparation is described in next section.

All ions peak areas are inspected by hand before converted to concentrations values via calibration curves specific to that ion run. All non-zero ion concentrations are quantified. Negative concentrations are non-existent by definition since peaks are referenced to baseline. The extraction volume is combined with concentrations of calibration reference peaks in chromeleon software. Output is an excel spreadsheet with all extract masses.

Preparing IC standards for quantitative anion and cation analysis (sexton campus)

Preparing standards and eluent: Graydon S, Crystal W, Codey B. or a trained student prepares the IC standards for the week. New standards are prepared at once per week. The matrix of standard ions expires a year from purchase, hence standards are replaced annually.

Anion column: AS23 standard bore (4 × 250 mm) Dionex

Cation column: CS12A (5 μm 3 x 150 mm) Dionex P/N 057185, serial no. 001704

Anion standards: (Dionex Seven Anion Standard, 50 mL Prod.no. 056933)

[F^- = 20 mg/L, Cl^- = 30 mg/L, NO_2^- = 100 mg/L, Br^- = 100 mg/L, NO_3^- = 100 mg/L, PO_4^- = 150 mg/L, SO_4^- = 150 mg/L]

Cation standards: (Dionex Six Cation-II Standard, 50 mL Prod.no. 046070)

[Li^+ = 50 mg/L, Na^+ = 200 mg/L, NH_4^+ = 250 mg/L, K^+ = 500 mg/L, Mg^{2+} = 250 mg/L, Ca^{2+} = 500 mg/L]

Standards are made in the following tabulated sequence. Use 1-10 mL or 0.1-1 mL Eppendorf Pipettes for liquid transfers into volumetric flasks. All volumetric flasks are saved in a plastic bag. Each flask is labeled for its intended concentration. Wash standard flasks at the beginning of every month.

Dilute original standard matrix 100-fold to make "STD 1.0" (wrt Bromide/Nitrate/Nitrite). That is, say, add 100 μl of standard solution into a 10 mL vol. flask and fill with Milli-Q water. Other standards (STD 0.25, etc) are a fraction of this concentration. Best practice is to start with highest standard (either 2.0 or 3.0) and dilute others by varying degrees.

Table 1: Anion standard list. NB Nitrite is the reference anion. Nitrite = 100 mg/L initial concentration.

Standard label	Reference ion Concentration	Method of preparation*
STD 2.0	2.0 mg/L	500 μL anion sol^n in 25 mL flask
STD 1.5	1.5 mg/L	375 μL anion sol^n in 25 mL flask
STD 1.0	1.0 mg/L	16.67 mL of STD 1.5 in 25 mL flask
STD 0.75	0.75 mg/L	18.75 mL of STD 1.0 in 25 mL flask
STD 0.5	0.5 mg/L	16.67 mL of STD 0.75 in 25 mL flask
STD 0.25	0.25 mg/L	12.50 mL of STD 0.5 in 25 mL flask
STD 0.1	0.1 mg/L	4.00 mL of STD 0.25 in **10 mL** flask
STD 0.05	0.05 mg/L	5.00 mL of STD 0.1 in **10 mL** flask

*Fill each flask to mark with Milli-Q water before transferring solution to next standard

Table 2: Cation Standard list. Ammonium is the reference cation. Ammonium (NH_4) = 250 mg/L initial concentration.

Standard label	Reference ion Concentration	Method of preparation*
STD 2.0	2.0 mg/L	200 μL cation sol^n in 25 mL flask
STD 1.5	1.5 mg/L	7.5 mL of STD 2 in **10 mL** flask
STD 1.0	1.0 mg/L	12.5 mL of STD 2 in 25 mL flask
STD 0.75	0.75 mg/L	18.75 mL of STD 1.0 in 25 mL flask
STD 0.5	0.5 mg/L	16.67 mL of STD 0.75 in 25 mL flask
STD 0.25	0.25 mg/L	12.50 mL of STD 0.5 in 25 mL flask
STD 0.1	0.1 mg/L	4.00 mL of STD 0.25 in **10 mL** flask
STD 0.05	0.05 mg/L	5.00 mL of STD 0.1 in **10 mL** flask

*Fill each flask to mark with Milli-Q water before transferring solution to next standard

Running Cation and Anion IC: Eluent

Eluent is what carries samples from auto sample tray to detector, separates samples while passing through column, and rinses out instrument in between runs. Hence is it **very** important no changes be made to its concentration. Preparation must be performed precisely and accurately.

Anion Eluent: (for use in AS-23 column; AERS 500 4mm suppressor: NEW instrument)

To make 0.25 mM sodium carbonate stock solution, dissolve 26.50 g Na_2CO_3 powder in 1L flask with Milli-Q water. To make 0.25 stock solution of $NaHCO_3$, dissolve 21.00 g $NaHCO_3$ powder in 1L flask with Milli-Q water.

To make anion eluent solution (of 4.5 mM sodium carbonate + 0.8 mM sodium bicarbonate).

a) Add 36 mL of 0.25 mM sodium carbonate solution in 2L volumetric flask
b) Add 6.4 mL of 0.25 mM sodium bicarbonate solution in *same* 2L volumetric flask
c) Fill to 2L mark with Milli-Q water.

Pour eluent into plastic container labeled "ELUENT" and attach top cap/hose. NB: Use 1-10 mL Eppendorf Pipettes for liquid transfers.

Cation Eluent: (for AS-23 column, 4mm AERS suppressor: OLD instrument)

NB: Use 1-10 mL Eppendorf Pipettes for liquid transfers

To make 20 mM MSA (methanesulfonic acid):

a) Add 1.30 mL of pure MSA (Fluka; >99% pure; code: 64280-500mL-F) in 1 L volumetric flask
b) Fill flask to mark with Milli-Q water

Running IC:

Crystal, Graydon, Codey, or co-op student start the IC run for anions and/or cations, and check on its completion the next day.

-For anions (new system) it is important to ensure 5ml water vials are topped up before leaving overnight since vials #45 and 46 seem to get skipped by sampling program.

-For cations (old system) water peaks will show evidence of calcium. There is likely some contamination within the IC system causing carry-over. Presently we are running 2 water vials between each sample AND between each sample.

REFERENCES:

Zhang, R., Jing, J., Tao, J., Hsu, S.-C., Wang, G., Cao, J., … Shen, Z. (2013). Chemical characterization and source apportionment of $PM_{2.5}$ in Beijing: seasonal perspective. *Atmospheric Chemistry and Physics*, *13*(14), 7053–7074. doi:10.5194/acp-13-7053-2013