Section 8 ICP-MS Chemical filter extraction, analysis:

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 trace metal information via ICP from Teflon and Nuclepore filters. Filter halves are combined with 3mL of 7% HNO_3/water in pre-washed vials. The acid/filter combination is boiled at 100 °C for 2 hours. Filters are then discarded, vials with acid/metals are submitted, and trace metals (25 total) are quantized.

Filter cutting

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

- 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.
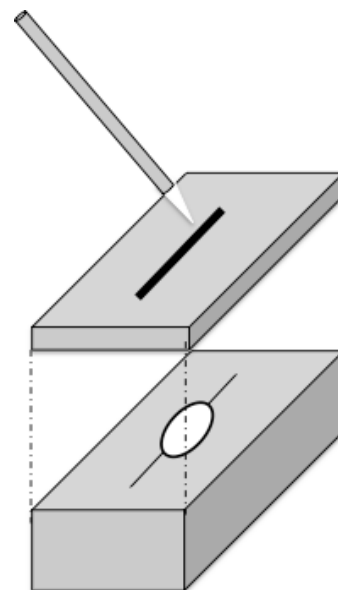
Step 2: Separation of filter halves:

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

25 mm filter

10 mL plastic vial washed 2x 18MΩ water, 1x 5% HNO_3/water

20 mL vial washed 1x with methanol, 3x 18MΩ-water

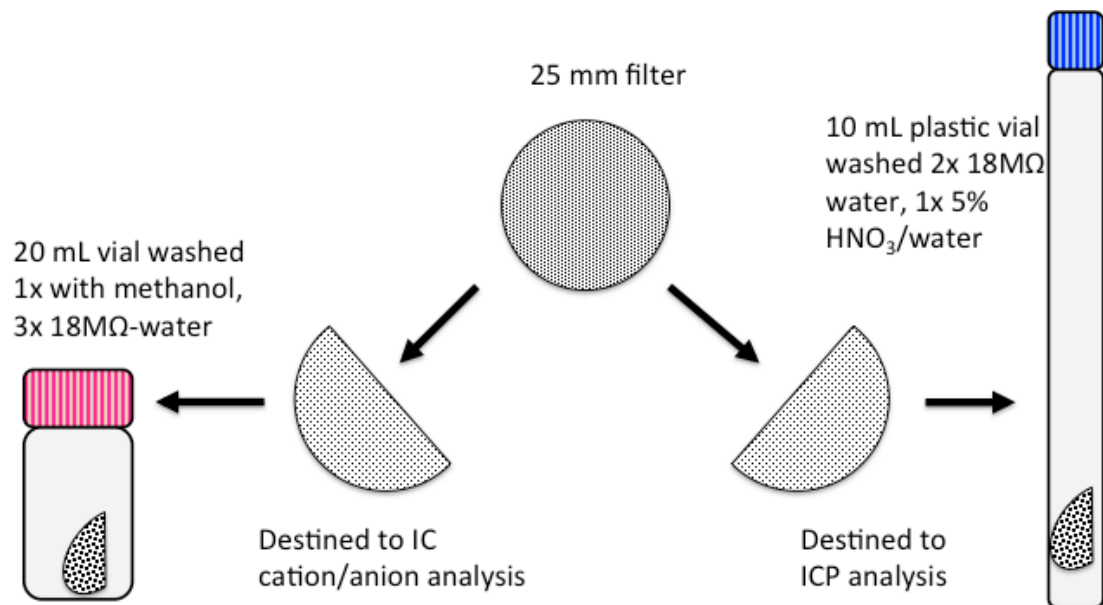Destined to IC cation/anion analysis

Destined to ICP analysis

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. Pink capped vial (destened for IC) or blue capped vial (destined for ICP-MS). Samplme is n a state ready for submission. We use 3 mL of liquid extract for half a filter, hence 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.

Filter extraction for ICP-MS (filter half #2)

Place cut filter half (Nuclepore or Teflon) directly into a prewashed (twice water, once with 10% nitric acid left to stand overnight) 10 mL ICP sample vials using methanol-wiped tweezers. Vials and caps are obtained as needed from Water Trace Analysis Lab near the ICP-MS instrument. (NB: We do not acidify filters in pink polypropylene vials as these vessels permanently absorb nitric acid, which leeches out in later analyses; this was in fact confirmed in tests).

Next, add 2.8 mL of water and 0.2 mL of concentrated trace metal grade nitric acid (6.7%) [Note we did not combine with HCl or HF]. We find that Teflon filters tend to float above the liquid, so Teflon filters must be 'folded' to squeeze vial walls before they submerge.

Once all filters are placed in **labeled** 10 mL plastic vials, place these vials pairwise in plastic containers used for the heating block (also located in Water trace analysis lab). The heating block has enough room to hold 48 samples total (24 blocks). Add enough water to bathe the acid water within the vials. Heat the vials for two hours with cap on (placed loosely to allow vapor to escape) in fume hood at 97°C (EPA, 2007).
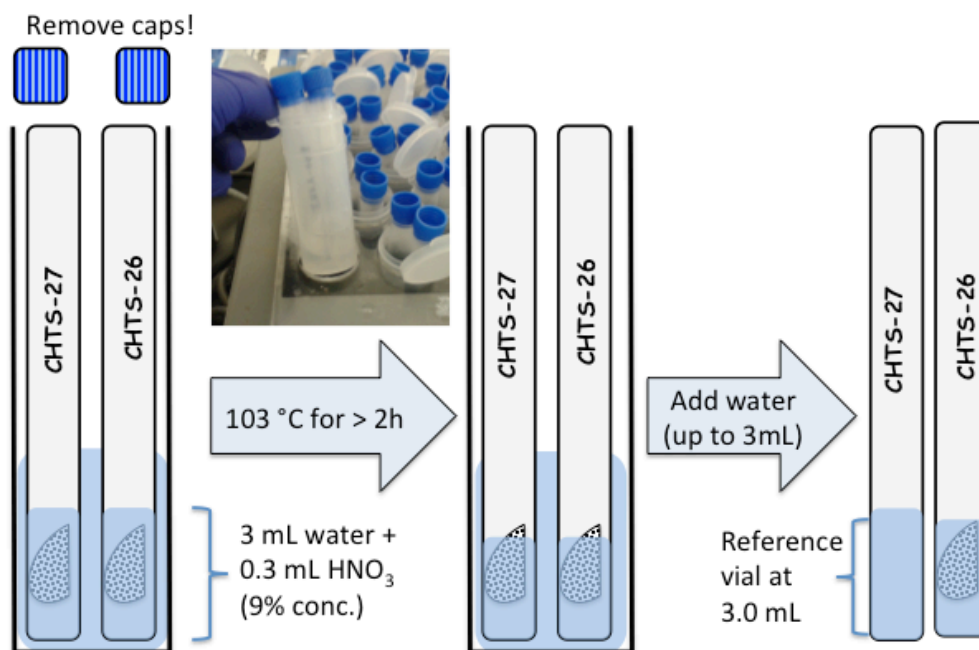
Once liquid boils off below 3 mL, remove filters using a clean pair of tweezers (preferably nylon). When all filters are discarded, fill a 10 mL sample vials to 3 mL as a reference, then compare vials side by side and fill sampled vials in 100 uL aliquots up to reference mark. Once all vials are filled to mark, submit for ICP analysis.

The ICP-MS we use is a Thermo Scientific X-Series 2. Water lab will scan for 25 elements: Li, Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sb, Ba, Ce, Pb, U. Note

that Silicon is **not** among standards. Although Si standards exist in lab, they require a separate analysis, and we have been told the ICP does not always show linear (stable?) calibration plots. After submitting a few samples for Si we have found high background levels, indicating both from our samples' point of view and the instrument the ICP we are using is not well suited for Si quantization. We caution that nitric acid *may* contain traces of Al. Since vials were prewashed with acid, Al results may be affected.

ICP Detection limits

Once ICP results have been received, they are compared with known detection limits (DL). These limits are (in ng/mL):

Element	Detection Limit (ppb or ng/mL)	Extraction efficiency (5% HNO$_3$)	Element	Detection Limit (ppb or ng/mL)	Extraction efficiency (5% HNO$_3$)
7Li	0.4	78%	59Co	0.4	80%
23Na	10	334%	60Ni	0.4	80%
24Mg	10	117%	65Cu	0.7	79%
27Al	4	132%	66Zn	0.6	90%
31P	10	556%	75As	0.4	62%
39K	10	269%	82Se	1	62%
44Ca	10	401%	107Ag	0.4	71%
47Ti	0.5	82%	111Cd	0.4	76%
51V	0.4	78%	121Sb	2	62%
52Cr	0.4	81%	137Ba	0.5	86%
55Mn	0.8	81%	140Ce	0.4	79%
56Fe	7	110%	208Pb	0.4	80%

We determined extraction efficiency by placing a droplet of trace element reference water on a Teflon filter and allowed to dry overnight. The filter was then treated as a field-sampled ICP extraction. The results indicate that Na, P, K, and Ca were much too high. Al, Fe, and Mg were also high, but realistic. All other compounds were underestimated.

There are instances when ICP elemental concentrations are reported as negative values. It is common that metals are below the minimum concentration detection limit. ICP calibrations curves must span a much wider range of concentrations than IC (three orders of magnitude vs one), hence many elements fall well below the minimum values of calibration curve. When the concentration of a given element falls below the DL and/or zero, the concentration is then reported as such to avoid bias.

REFERENCES:

EPA. (2007). *Standard Operating Procedure for Trace Metal Analysis of Ambient Air Particulate Samples using ICP-MS. SOP MLD 061.*

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