

Trace Element Analysis Core

Lab methods

General

All prices are based on analysis of up to 10 elements of interest to the investigator. More analytes can be included in the run after discussion with TEA Lab staff. Typically we do not analyse for major elements (Na, mg, Ca, K,) but these can be included if they are trace constituents of the matrix. Similarly we do not analyse samples with ppm levels of trace elements, unless dilute substantially before analysis. Mercury can be included as an analyte in a regular analytical run, however, low level Hg analysis usually requires cold vapor generation which is run separately to the other elements and requires an additional analysis charge.

Specific Analyses

Trace metals in solution

Samples are supplied as solutions and are analysed for trace element concentrations with our Agilent 7500cx ICP-MS. Most analytes are analyzed in collision mode (employing He) except Cd (both mode), Hg and Pb (no gas mode). Selenium and Fe are analysed in collision mode with H₂. The sample stream is 'T-ed' in with an (multi) internal standard solution prior to the sample introduction system. All analyte counts are ratioed to an appropriate internal standard. A 6 – 7 point external calibration curve from NIST Traceable primary multi-element standard solutions is run for each batch. Typically the concentration range spans 0.01 – 50 µg/L. Calibrations are checked with a second source calibration standard which is also run every 10 samples as a continuing check. We typically recalibrate every 20 – 30 samples during analysis of a large sample batch. A standard reference material (A NIST or CRC-CNRC water sample) is run every 20 samples. SEAWATER samples or BIOLOGICAL buffer samples CANNOT be run undiluted because of high total dissolved salts; please inform us if your samples have high TDS.

Trace Metals in solids

Solids require acid digestion prior to analysis. Solid samples should be dried and homogenized prior to being submitted for analysis.

Closed vessel (microwave digestion under pressure)

For biological samples we use a MARS5 EXPRESS system (CEM, Mathews, NC). Approximately 100 mg is weighed into a digestion vessel, smaller sample masses can be submitted if necessary. Two ml of optima HNO₃ is added and the vessel is capped and placed in the digestion rack. The 40 place rack can accommodate 34 samples with 2 blanks, 2 SRMS and 2 duplicates for QC purposes. The lab has a range of certified quality control materials suitable for biological and environmental sample types. The vessels

are heated to 180°C in 10 minutes and held at that temperature for a further 10 minutes. After the samples have cooled they are brought up to approximately 15 ml volume with DI water. Sample masses and final digestate volume can be scaled up or down depending on the situation. Digested samples are usually diluted a further 10- 100 times with DI prior to analysis. Lesser dilutions and/or method of standard additions can be used if there is significant matrix effects during the analysis. Once in solution, the samples are analysed as described above in the trace metals in solution section.

Open Vessel (microwave digestion at atmospheric pressure)

Some low biomass, not fatty, biological tissues will digest readily at 105-110°C. Many procedures for sediment digests are not total digestions and can also be conducted by this method. In an 'open vessel' digest a weighed sample is placed in either a 15 ml or 50 ml centrifuge tube and an appropriate volume of optima (or trace metal grade for soils and sediments) HNO₃ is added. Low biomass organic samples or toenail analysis is performed in the 15 ml centrifuge tubes with addition of 0.5 mls HNO₃. For sediment/soils 0.25-0.5 g sediment are weighed into 50 ml tubes and 5 mls trace metal grade HNO₃ is added. The tubes are loaded into a microwave rack and heated to 105-110°C with a ramp of 15 mins and a hold time of 45 mins. Temperature is monitored in one tube using the MARS5 express fiber optic temperature sensor. After the vessels have cooled they are made up to volume with DI water and a final weight is recorded. After any necessary further dilutions they are analysed as described above in the trace metals in solution section. The benefits of this method are increased throughput and reduced costs; 120 15ml tubes can be processed at one time (108 samples and 12 QCs) and fifty 50 ml samples. We use this method routinely for toenail digestions, cell pellet digests and sediment/soil extractions.

Arsenic speciation in solutions

Arsenic speciation in solutions is conducted by ion chromatography coupled to ICP-MS. We employ an Agilent LC 1120 interfaced with our Agilent 7500c ICP-MS. For well water/drinking water etc. we analyse for As(III) and As(V) using a Hamilton PRP100X column with a 20 mM phosphate eluant. For urine samples we utilize the same column but also include arsenobetaine, monomethyl arsenic acid, and dimethylarsenic acid. Alternatively, we use a Dionex AS16 column with a 50 mM tetramethylammonium hydroxide (TMAOH) gradient method. Both columns give similar retention orders for these As species.

Arsenic speciation in solids

Arsenic speciation in solids requires extraction of the arsenic species into a solution. Typically we use 50:50 methanol:water with sonication for extraction of biological tissues. However, extraction efficiency varies markedly and is affected by the form of As in the solid and the solid matrix. It is advisable to determine total As and soluble As as well as the sum of the recovered As species. Other

extracting solutions may be employed (eg. trifluoroacetic acid, TMAOH). Please discuss options with the TEA lab director (bpj@dartmouth.edu) . Once in solution, As speciation is conducted as described above. A Dionex As7 column with a HNO₃ gradient may also be used. This column has different exchange characteristics than the two aforementioned ion exchange columns, resulting in a different retention order for the arsenic compounds and allowing tentative identification of arsenosugars based on literature reports.

Mercury Speciation

We use ethylation with NaBH₄ to convert methylHg and inorganic Hg to the volatile ethylated derivatives. These volatile species are then purged with an inert gas (ultra pure He) and trapped on Tenax traps. The Tenax traps are then thermally desorbed and the ethylated Hg species are carried in a He gas stream onto a packed gas chromatography column heated isothermally at 90 ° C. The effluent flow from the column is directed to an ICP-MS, which serves as an element specific detector to generate chromatograms for ¹⁹⁹Hg, ²⁰¹Hg, and ²⁰²Hg. We use isotope dilution for quantification so all samples are spiked prior to analysis with an appropriate amount of enriched ¹⁹⁹Hg²⁺ and CH₃ ²⁰¹Hg⁺. For water samples we require >50 mls. Biological tissues are extracted in KOH/methanol or 4M HNO₃. We require > 10 mg of biological samples. More in depth descriptions of our Hg speciation methods are published in:

Jackson, B., V Taylor, R.A. Baker, E. Miller. 2009. Low level mercury speciation in freshwaters by isotope dilution GC-ICP-MS. *Environ. Sci. Technol.* 43, 2463–2469

Taylor, V.F., B.P. Jackson, C.Y. Chen, 2008. Mercury speciation and total trace element determination of low-biomass biological samples. *Anal. Bioanal. Chem.* 392:1283–1290.

Method Development

We have experience in hyphenated techniques for speciation analysis and laser ablation ICP-MS for 2D mapping of biological or geological thin sections. Much of this work requires some tinkering to arrive at suitable analytical conditions, or requires extensive data processing after the analysis. We welcome enquiries for research in spatial distribution and/or metal speciation in biological and environmental samples.