

Standard Operation Procedure

Analysis of Major, Minor and Trace Elements in Soil and Sediment Samples with ICP-OES and ICP-MS

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1. Application

This method covers the digestion of soil and sediment samples for the analysis of *leachable* components (major, minor, and trace elements or total minerals, heavy metals, and micro-nutrients) by ICP-OES (TJA Iris Advanced ICP-OES) and ICP-MS (VG PlasmaQuad PQ2 Turbo Plus ICP-MS).

- 1.1 Soil and sediment samples contain major (Si, Al, Fe, Ti, Mn, Ca, Mg and Na), minor, and trace components. Alternatively, soil and sediment samples contain fraction one or structural components which are held within aluminum-silicate minerals and fraction two components which are held in soil and sediment by other mechanisms (precipitated, replaced, absorbed, complexed, exchanged, etc).
- 1.2 If a soil/sediment sample is totally dissolved, such as with a mixture of hydrofluoric acid (HF) and other acids, the measured components include both fraction one and fraction two components and the measured concentrations are “total

concentrations” of a sample. These concentrations are comparable to the concentrations obtained by other methods such as XRF methods and NAA methods.

- 1.3 The exclusive analysis of fraction two components has more applications than the analysis of total concentrations in agricultural or environmental areas, since fraction one components are “inert” while fraction two components are “active” and “available” in agricultural or environmental processes.
 - 1.3.1 Fraction two components are supposed to be “all-leached” out by treating samples with concentrated acids (except HF acid) at a high temperature and the measured concentrations are “total leachable concentrations.” These leachable concentrations are often referred as “total concentrations” or “total minerals,” although these “total concentrations” are conceptually not true total concentrations at all.

1.3.2 The total leachable concentrations are not directly comparable to XRF or NAA results, since the XRF or NAA concentrations are true total concentrations. However, this is highly element-dependent and may be sample-dependent. For example, the leachable concentration of silicon is far less than the total concentration of silicon, but the leachable concentration of mercury is usually close to (>95%) the total concentration of mercury in samples.

1.4 The total (leachable) components seem simple and well defined conceptually but the analysis of these leachable components is actually defined operationally. The measured results could be widely variable if a given sample is processed (leached) with different procedures or conditions. The results of leachable concentrations in soil or sediment samples should be interpreted carefully, keeping these considerations in mind.

1.5 There are unlimited versions of procedures available in literature for the process of soil and sediment samples, considering the numerous combinations of sample weight, acid type, acid amount, acid concentration, digestion time duration, digestion temperature, digestion pressure, and equipments. Since the measured results could be variable if a given sample is processed with different/alternative procedures or conditions, *a procedure without alternative steps* is preferred, developed, and used at this laboratory to achieve the greatest consistency in analyzing

different types of samples and/or samples at different times. In general, results obtained by a consistent method are comparable mutually.

2. Summary of method

2.1 A dried and ground sample (0.5 gram) and 5 mL of concentrated nitric acid are added into a 50-mL Folin digestion tube. The mixture is heated at 120-130 °C for 14-16 hours and then is treated with hydrogen peroxide. After digestion, the sample is diluted to 50 mL. This solution is further 1:1 diluted for the analysis of major and minor components by ICP-OES and further 1:9 diluted for the analysis of minor and trace components by ICP-MS.

2.2 After solid samples are converted into solutions samples, the procedures of “Elemental analysis of solution samples with ICP-OES” and “Elemental analysis of solution samples with ICP-MS” are followed.

3. Safety

All chemicals should be considered as potential health hazard. All relevant laboratory safety procedures are followed.

4. Interference

4.1 This method covers the analysis of over 30 elements by ICP-OES and ICP-MS. Even a general discussion of interferences is lengthy but not necessarily relevant to a specific element/isotope. The analysis of

metals and non-metals by ICP-OES and ICP-MS has been established and there is an enormous amount of literature available relevant to this subject. Reading the published articles is recommended.

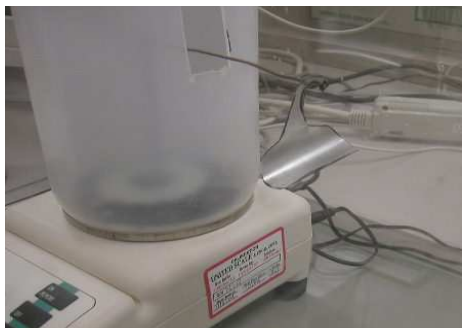
- 4.2 In this method, the solution for ICP-OES analysis contains < 500 ppm of dissolved solid and the solution for ICP-MS analysis contains <100 ppm of dissolved solid. The major components are Fe, Al, K, Ca, Mg and Mn. These components either do not pose significant interferences with other elements/isotopes or the potential interferences are well understood and controlled. Significant interferences in general are not expected, although some specific element/isotope may be interfered.

5. Sample collection, preservation and handling

A representative sample of soil/sediment is dried and ground. A five-gram vial or equivalent is used to hold a sub sample for airtight storage.

6. Apparatus and device

- 6.1 Analytical balance (accurate to 1 milligram with a custom-made weighing pan for easier sample handling). The balance is interfaced to a computer via an RS-232 cable.



- 6.2 Borosilicate digestion tubes or equivalent (25 mm o.d. × 200 mm length) with graduations of 12.5, 25, 35 and 50 mL (e.g. KIMAX Borosilicate 47125-50 for use in Folin-Wu non-protein nitrogen determinations). The tubes are cleaned by soaking in 10% nitric acid bath overnight and rinsed with de-ionized water several times. The cleaned tubes are placed in tube racks upside down and let air-dried.
- 6.3 Insulated aluminum block with holes drilled to it to accommodate the Folin-Wu digestion tubes. Half of the tube (about 100 mm) is still exposed to air. The aluminum block is stacked on the top of a hot plate (e.g. Lindberg/Blue Hot Plate, Model: HP 53014C).



- 6.4 Ten-mL universal pipette for dispensing concentrated nitric acid (e.g. Fisher Cat #136-8720).

- 6.5 ICP-OES: TJA Iris Advantage ICP-OES.
- 6.6 Eight-mL polystyrene test tubes (13 mm × 100 mm. e.g. Cat #2110 by Perfector Scientific) for the ICP-OES autosampler are used “as is.”
- 6.7 ICP-MS: VG PlasmaQuad PQ2 Turbo Plus ICP-MS (quadrupole ICP-MS).
- 6.8 Fourteen-mL polystyrene test tubes (17 mm × 100 mm. e.g. Falcon plastic tubes, Cat #14-959-8 by Fisher Scientific) for the ICP-MS autosampler are cleaned by soaking in 10% nitric acid overnight and rinsed with de-ionized water for several times. The tubes are air-dried before use.

7. Reagents

- 7.1 Concentrated nitric acid (> 68%) (e.g. TraceMetal grade. Fisher A509-212).
- 7.2 Hydrogen peroxide (>30%) (e.g. Certified A.C.S. grade. Fisher H325-500). Note: hydrogen peroxide is usually preserved with tin (Sn).
- 7.3 Single-element and multi-element primary standard solutions.

8. Pre-digestion

- 8.1 Dry samples at 60 °C for two days. Large stones/rocks or plant materials are removed. Grind the samples (Calcareous samples may be ground to very fine powders). Small-size samples are wrapped in

plastic film and broken or ground to avoid contamination of normal grounding. Extremely small size samples are used “as-is.” Store in a five-gram vial or other appropriate container for airtight storage. Note: Samples may be dried at 60 °C or at 110 °C. The water content could be different.

- 8.2 Weigh 0.50±0.01 g of the sample (unknown samples, in-house quality control sample, and/or NIST SRMs) into 50-mL cleaned and air-dried digestion tubes (Finely ground calcareous sample powders: 0.25 gram, sandy samples: 1.00 gram). Make one to three digestion blanks.
- 8.3 Spike 0.04 mL of 10,000 ppm of Y (yttrium) as an IRS (internal reference standard) for the analysis by ICP-OES. Spike 0.2 mL of 10 ppm of Rh (rhodium) as an internal standard for the analysis by ICP-MS.
- 8.4 Carefully add drops of 20–30% (v/v) nitric acid to moisten the samples. This is especially important for calcareous samples to prevent them from foaming over.
- 8.5 After the samples have been moistened with the diluted nitric acid, add 5 mL of concentrated nitric acid. Soak at room temperature for 2-3 hours.

Note: A digestion with perchloric acid should be avoided for safety concerns. Samples digested with HClO₄ are not good for the analysis of V, Cr, As, ⁷⁷Se, Rb and

several other isotopes using quadrupole ICP-MS.

9. Hot plate digestion

9.1 Place all of the digestion tubes in a block heater. Cover the tubes with plastic film to retard water evaporation. Contamination from the plastic film is not considered. Alternatively, use small glass funnels.

9.2 Set the block heater at 130°C (Block Heater Lindberg Blue: t = 115°C at mark 2.5, t = 130°C at mark 3.0, t = >170°C at mark 7). Turn the power on.

Note: Samples should not be charred during digestion. If charred, add nitric acid to re-dissolve. However, this could cause higher blank concentrations for several elements.

9.3 The temperature will ramp up to 120-130°C after 1.5 hours. Keep heating at 120-130°C for 14-16 hours.

9.4 Remove film cover and properly dispose it. Take the tubes off the block heater. Let cool for several minutes (This is very important).

9.5 Add 30% hydrogen peroxide at a ratio of 1 mL per sample. Place all of the tubes back onto the block heater. Heat for 20-30 minutes.

Note: Samples digested with H₂O₂ are not good for Sn analysis if the hydrogen peroxide is preserved with tin.

9.6 Take the tubes off the block heater and let them cool. Add hydrogen peroxide (as indicated in step 9.5 above) and digest for another 20-30 minutes.

9.7 Take all of the tubes off the block heater. Add water to the 50 mL mark. Let sit for 30 minutes or more.

9.8 Mix the samples. Leave overnight to let particles settle down. After this digestion (1st dilution), nominal dilution factor = (50 mL/0.5 gram) = 100. Y = 8 ppm. Rh = 40 ppb.

Note: A typical digestion time table at SPAL – start heating in the afternoon (3 pm), heat overnight with plastic film cover, take the cover off in the early morning (7 am) the next day, and add hydrogen peroxide afterwards.

Note: Samples may not be heated above 130-140°C. Localized overheating may cause a sample to boil over and be lost.

Note: Soil/sediment samples may contain MnO₂. Hydrogen peroxide reacts with MnO₂ quickly. Hydrogen peroxide also reacts with some other components quickly in a hot nitric acid medium. Therefore, add hydrogen peroxide only after the sample tubes have been cooled.

Note: After a soil sample is digested with concentrated acid (without HF) at a high temperature, the majority of the sample remains as a solid and 5-10% of the sample is leached into solution (this ratio

is much higher for calcareous soil samples). If a sample is digested at a dilution factor (DF) of 100 (e.g. 0.5 gram of soil sample is digested and diluted to 50 mL) the solution does not contain 1% of the total dissolved solid (TDS) but contains <0.1% of the TDS. This kind of solution can generally be directly introduced to ICP-OES or ICP-MS. However, most components may still be significantly higher than “optimum” concentration ranges. In SPAL, the solution is analyzed by ICP-OES with a further 1:1 dilution for major and most minor elements. With the SPAL’s specific model of the ICP-MS instrument (VG PlasmaQuad PQ2 Turbo Plus ICP-MS), this kind of solution is analyzed with a further 1:9 dilution for minor and trace elements. One may argue that why not to use less amount of soil at the start so that the second dilution or any further dilution is avoided. Firstly, as it is pointed out in section 1 (Application), any “alternative” steps should be avoided as much as possible in order to achieve a consistent analysis. The leaching efficiency would be different if the acid to soil ratio is changed. Secondly, larger-size sample is more “representative” than smaller-size sample for samples such as soil or sediment which is usually fairly “inhomogeneous.” Thirdly, the size of half a gram of sample is widely used in other procedures. The size of a sample of course can be changed if the consistency is not an issue in some special projects.

10. Measurement by ICP-OES

10.1. Sample preparation for ICP-OES

10.1.1 Set 8-mL autosampler tubes in ICP-OES sample racks.

10.1.2 Add 3 mL of sample solution and 3 mL of 2% nitric acid to the 8-mL autosampler tube. Mix. After this 2nd dilution (for ICP-OES), nominal dilution factor = $(6 \text{ mL}/3 \text{ mL}) \times (50 \text{ mL}/0.5 \text{ gram}) = 200$. Y = 4 ppm.

Note: It might be labor intensive if a lot of samples need to be diluted before analysis. In-line dilution might an option. In SPAL, digested solutions are poured to the 8-mL autosampler tubes. The volume is adjusted to 3 mL by inserting a tubing into the autosampler tube to a prefixed depth and sucking any extra solution out (The tubing is connected to a vacuum device). Dispense 3 mL of 2% nitric acid to the autosampler tubes by using a re-pipette. Cover a rack of samples with plastic film and the whole rack of samples are mixed by pushing the film tightly against the tubes and using up-side down actions.

Note: Since an internal reference standard is used, the volume inaccuracy during dilution is irrelevant. A sample solution may be analyzed with other dilution ratios (i.e. 2:8, or 5:5 dilutions). During the data processing in later stage, the dilution factor is always 100, whether the dilution is 1:5, 2:3, or 4:1 (See Appendix 1 in “Elemental analysis of solution samples with ICP-OES”).

10.2. Measurement by ICP-OES

10.2.1 A detailed procedure is given in “Elemental analysis of solution samples with ICP-OES.”

10.2.2 Digestion blanks are also measured with other samples.

10.3. Reporting after ICP-OES

10.3.1 The details are given in “Elemental analysis of solution samples with ICP-OES.”

10.3.2 After the concentration of Y is normalized to 8 ppm, the dilution factor is 100 either for the digested solution (1st dilution, actual DF = 100, Y = 8 ppm) or for the further diluted solution (2nd dilution, actual DF = 200, Y = 4 ppm), if accurately 0.5 gram of soil is spiked with 0.04 mL of 10,000 ppm of yttrium as the internal reference standard.

11. Measurement by ICP-MS

11.1 Sample preparation for ICP-MS

11.1.1 Add sample solutions (1 mL) to the 14-mL Falcon tubes containing 9 mL of 2% nitric acid. Mix well. After this dilution (2nd for ICP-MS), total dilution factor = $(10 \text{ mL}/1 \text{ mL}) \times (50 \text{ mL}/0.5 \text{ gram}) = 1,000$. Rh = 4 ppb.

11.1.2 Depending on sample matrix and analyte concentration, the sample may be diluted in other ratios.

11.2 Measurement by ICP-MS

11.2.1 A detailed procedure is given in “Elemental analysis of solution samples with ICP-MS.”

11.2.2 Digest blanks are also measured with other samples.

11.2.3 In the menu, select “soil” and edit it if needed.

Note: The analysis by ICP-MS is flexible and is easily expanded to other elements. In combination with the working standard, both of the working standard and the acquisition menu can be changed accordingly for additional elements.

11.3 Data processing

11.3.1 The details are given in “Elemental analysis of solution samples with ICP-MS.”

11.3.2 The overall DF is 1,000, after this procedure is followed exactly. Otherwise, adjust the DF accordingly.

Scenario 1: 10 mg/kg (10 ppm or 10,000 ppb) of element X in 0.5 gram of solid sample with 0.2 mL of 10 ppm Rh is digested and diluted to 50 mL (1st DF = 100). This 1st solution (X = 100 ppb, and Rh = 40 ppb) is further diluted by 1:9 (2nd DF = 10) to contain 10 ppb of X and 4 ppb of Rh in a 2nd solution (overall DF = 1000). This 2nd solution is measured against a standard containing 1 ppb of X and 4 ppb of Rh and the measured result is 10 ppb. After applying the overall dilution factor of 1000, the concentration of X in the solid material is $10 \text{ ppb} \times \text{DF } 1000 = 10,000 \text{ ppb} = 10 \text{ ppm}$.

Scenario 2: Element X in the 2nd solution (X = 10 ppb and Rh = 4 ppb) is still much higher than the standard (X = 1 ppb and Rh = 4

ppb). This 2nd solution is diluted by 5 times (3rd DF = 5, total DF = $100 \times 10 \times 5 = 5000$) to contain 2 ppb of X and 0.8 ppb of Rh and this 3rd solution is measured. There are two ways to process here. Option 1: ignore the third dilution factor. The signal ratio of 3rd solution (2 ppb X/0.8 ppb Rh) is compared to the signal ratio of standard (1 ppb X/4 ppb Rh) and the concentration in the 3rd solution is calculated to be 10 ppb of X per 4 ppb of Rh. After applying the dilution factor, X in the solid sample is $10 \text{ ppb} \times 1000 = 10 \text{ ppm}$. Option 2: At step 13.2, set the IRS concentration to be 0.8 ppb Rh for this specific sample (3rd solution), X in this 3rd solution will be calculated to be 2 ppb against a standard of 1 ppb X with 4 ppb Rh. Now the total DF is 5000 and X in the solid sample is $2 \text{ ppb} \times 5000 = 10 \text{ ppm}$.

12. Quality assurance (QA) and quality control (QC)

ICP-OES and ICP-MS, either combined or used alone, have broad applications in unlimited situations. A general discussion about QA/QC practice is not specific to a particular application, yet detailed discussions about various applications become too lengthy and are beyond the scope of this procedure. Some basics are given in “Elemental analysis of solution samples with ICP-OES” and “Elemental analysis of solution samples with ICP-MS.”

– End –