

ICP-OES analysis

**Deliverable 3.3, SOPs for all Physicochemical Methods,
Annex I, page 120.**

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TRACE ELEMENT ANALYSIS IN COLLOIDAL SILICA BY ICP-OES				

1 SUMMARY

The sample is digested by acid and/or diluted, and is thereafter analyzed for trace elements by inductively coupled plasma optical emission spectroscopy (ICP-OES). The analyzed elements are: Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, SO₄, Sn, Sr, Ti, V, Zn och Zr. For the analysis of boron, the sample is prepared and analyzed according to instruction SI055.

2 GENERAL INFORMATION

The analysis of colloidal silica by ICP-OES usually requires the pre-removal of silica from the sample, using digestion in a mixture of hydrofluoric acid and perchloric acid. The digestion is performed at 200°C in an open platinum bowl. The silica is thereby converted to silicon tetrafluoride which is evaporized from the sample. The remaining dry sample is thereafter dissolved in 1% HNO₃ and analyzed by ICP-OES. Samples which may contain organic material must be digested without perchloric acid (see section 7.1.3).

Small losses of some analyte elements, especially B and Zr, have been observed after the digestion of colloidal silica by hydrofluoric and perchloric acid. In samples with high concentrations of Al, Fe, K, Mg, S, Ti and Zr, these elements are therefore analyzed after 1:50 dilution by 1% HNO₃, without acid digestion. B is analyzed according to instruction SI055.

The ICP-OES instrument ICAP 6500 (ThermoFisher) or ICAP 7400 (ThermoFisher) are used. The method was developed in 2011 and the report limits were thereafter determined [Ref 11.2].

The analysis of Ag requires a separate calibration standard.

A copy of this instruction can be found in folder ICP/AAS Nr.7

3 HAZARDS AND SAFETY

Training, and reading instruction SHM003 is required prior to handling hydrofluoric acid and perchloric acid.

All handling of hydrofluoric acid and perchloric acid must be performed in a fume hood equipped with scrubber.

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Perchloric acid (HClO₄), is explosive in contact with organic material. Samples containing organic material must therefore be digested without HClO₄ (section 7.1.3).

Hydrofluoric acid (HF) is highly corrosive and extremely toxic.

Safety goggles, visor, plastic apron and HF-resistant gloves must be used while handling HF.

At least one more person must be present in the same room while handling HF and/or HClO₄.

4 QUALITY ASSURANCE OF ANALYTICAL METHOD

The control sample QP SOL ICP is analyzed weekly.

5 APPARATUS

- 5.1 ICP instrument, ICAP 7400 or ICAP 6500 Duo
- 5.2 Auto-burette for internal standard (Y)
- 5.3 Platinum bowls, 80 ml
- 5.4 Disposable plastic tubes, 12 ml
- 5.5 Fume hood equipped with scrubber
- 5.6 Hot plate

6 CHEMICALS

- 6.1 Hydrofluoric acid, HF, 48 %, trace analysis
- 6.2 Perchlorid acid, HClO₄, 70 %, trace analysis
- 6.3 Hydrochlorid acid, HCl, 37 %, trace analysis
- 6.4 Nitric acid, HNO₃, 65 %, trace analysis
- 6.5 Yttrium solution (internal standard), 10 mg/l
- 6.6 Calibration standards, prepared according to instruction FU385

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7 PROCEDURE

7.1 Sample preparation

7.1.1 Samples digested by HF+HClO₄

Weigh the sample in a platinum bowl, using four digits precision. Make two replicates for each sample. The sample weight should be adjusted to the concentration of SiO₂.

Weigh ~3,0 g of samples containing ≤ 30% SiO₂

Weigh ~2,0 g of samples containing 31-50 % SiO₂

Weigh ~1,0 g of samples containing > 50% SiO₂

Turn on the hot plate and allow it to warm up.

Add 2,5 ml HClO₄ and 5 ml HF.

Evaporate the sample to dryness on the hot plate (200 °C).

Dissolve the remaining dry sample in 100 µl HNO₃ and ~5 ml ultrapure water. The dissolution may require some warming.

Transfer the sample to a 12 ml plastic vial with 1 ml Yttrium solution (10 mg/l) and adjust the volume to 10 ml by ultrapure water.

7.1.2 Samples analyzed directly after dilution

Weigh ~0,2 g sample with a precision of four digits. Make two replicates for each sample. Add ~2 ml ultrapure water, 1 ml Yttrium solution (10 mg/l) and 100 µl HNO₃. Adjust the volume to 10 ml with ultrapure water.

7.1.3 Samples containing organic matter

Weigh the sample according to section 7.1.1.

Turn on the hot plate and allow it to warm up.

Add 2,5 ml HNO₃ (conc.) and 5 ml HF.

Evaporate the sample to dryness on the hot plate (200 °C).

Dissolve the remaining dry sample in 100 µl HNO₃ and ~5 ml ultrapure water. The dissolution may require some warming.

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Transfer the sample to a plastic vial with 1 ml Yttrium solution (10 mg/l) and adjust the volume to 10 ml by ultrapure water.

- 7.1.4 Samples containing high concentrations of Al (e.g. Levasil CAT80 F).

Weigh ~1,2 g of sample. Make two replicates for each sample. Digest the sample as described in 7.1.1., but use a larger volume of HNO₃ (0,5 ml HNO₃ and 5 ml ultrapure water) to dissolve the dry residue, and heat the solution for a few minutes to completely dissolve the sample. Transfer the sample to a plastic vial with 1ml Yttrium solution (10 mg/l) and adjust the volume to 10 ml with ultrapure water.

- 7.1.5 Acidic colloidal silica with low (5%) SiO₂ concentration
Register the sample under test plan ICP Sol 5%. Store samples in refrigerator to avoid coagulation.

Weigh ~18g of sample with a precision of four digits. Make two replicates for each sample.

Digest and prepare the sample as described in section 7.1.1.

- 7.2 Analysis

Analyze the samples on ICP-OES (ICAP 6500 or ICAP7400) using the method SOL. For the analysis of K in samples with high concentrations of Na, the digested sample must be diluted to reach a Na-concentration of ≤50 mg/kg in the diluted sample.

Ag is analyzed by the method SOLAg, using calibration standards containing Ag.

The line wavelenghts and detector alignment used in the SOL-method are summarized in the table below.

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Element (ICP)	Wavelength (nm)	Detector alignment
Al	396,152	Radial
Ag	328,068	Axial
Ba	455,403	Radial
Ca	315,887	Axial
Cd	226,502	Axial
Co	238,892	Axial
Cr	267,716	Axial
Cu	224,700	Axial
Fe	259,940	Radial
K	766,490	Axial/Radial
Mg	280,270	Radial
Mn	257,610	Axial
Mo	202,030	Axial
Na	589,592	Radial
Ni	231,604	Axial
Pb	220,353	Axial
SO ₄	182,034	Axial
Sn	189,989	Axial
Sr	421,552	Radial
Ti	337,280	Axial
V	290,882	Axial

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Element (ICP)	Wavelength (nm)	Detector alignment
Zn	213,856	Axial
Zr	339,198	Axial

8 CALCULATING AND REPORTING

8.1 Reporting

Concentrations are reported in mg/kg unit, rounded off to two significant figures.

The difference between the two replicates should be $\leq 10\%$ of the average concentration, but a larger difference can be accepted if the concentration is near the report limit.

Report limits when 2 g sample is weighed are presented in the table below. For samples with $>50\%$ SiO_2 the report limits must be adjusted to account for the dilution factor.

Element (ICP)	mg/kg
Al	1
Ag	1
Ba	0,1
Ca	1
Cd	0,01
Co	0,01
Cr	0,03
Cu	0,01
Fe	0,05

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Element (ICP)	mg/kg
K	0,4
Mg	0,1
Mn	0,01
Mo	0,05
Na	1
Ni	0,01
Pb	0,05
S	0,1
SO ₄	0,6
Sr	0,03
Sn	0,05
Ti	0,03
V	0,04
Zn	0,01
Zr	0,5

9 WASTE DISPOSAL

Samples and calibration standards can be discarded in the sink.

10 ADDITIONAL INSTRUCTIONS

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11 REFERENCES

- 11.1 The method was developed at the CA laboratory at Nouryon in Bohus, as described in report RD2005215;CA05-51.
- 11.2 Report CA2011-030
- 11.3 Instruction FU385