

## Quick Routine Acid Digestion of Iron and Copper Ores for ICP-OES or ICP-MS Analysis

Relevant for: Iron and copper ore mines, refineries and their (contract) laboratories

High temperature acid digestion with Multiwave 5000 in Rotor 20SVT50 can replace classical fusion/dissolution techniques. It provides liquid samples fit for element determination by ICP optical and mass spectroscopy as used in iron and copper prospecting, mining and ore refining. The advantages are robustness, higher digestion speed, fast and reproducible results.



### 1 Introduction

In the mining industry there is a large demand for fast routine digestions for elemental analysis:

- in **prospecting** for new mining projects or in developing and maintaining existing mines, large numbers of mineral samples have to be analyzed quickly. These samples consist of ore and dead rock of varying ratio and are analyzed for geochemical lead elements to give the information to find or follow the geological formations that allow the most profitable mining operation.
- In **process control**, when the refining process needs to be closely controlled. A lot of different types of process samples have to be analyzed with short turnaround time to allow swift reaction to keep the process under optimum conditions. For refining the analytical task is more specific: yield of process steps, quality of separation steps with the smallest possible amount of energy or reagent input.

In the past, fusion methods for the digestion of minerals and specific acid dissolution methods in combination with specialized photometric and electrochemical methods were used in large scale routine laboratories. With the widespread use of ICP optical or mass spectrometry modern high-

temperature acid digestion becomes more and more attractive:

- No additional dissolved solids from fusion reagents. This reduces burden on the ICP sample introduction system and torch.
- Avoiding solid reagents reduces the risk of contamination.
- Swift streamlined digestion process in closed vessel.

The method described in the following suits for the samples studied and will be a good starting point for samples with different composition that may require some modifications e.g. of the acid mixture.

### 2 Instrumentation, Samples

Multiwave 5000 with Rotor 20SVT50 was used for acid digestion.



Fig. 1: Multiwave 5000 and Rotor 20SVT50

ICP-OES analysis was done on a SPECTRO ARCOS 2 in radial view mode, with a Scott glass spray chamber.

## 2.1 Reference Materials and Samples

Sample Name	Sample Type
<b>NCS DC 11006a</b>	<b>SRM Fe Ore, China</b>
<b>Samples from Cu ore refining</b>	
Con B III	Purified Cu ore (high Si)
1st Clnr Tail I	Waste from Cu ore purification
Con III	Purified Cu ore
Con A IV	Purified Cu ore
Con A III	Purified Cu ore
Con A II	Purified Cu ore
Con I	Purified Cu ore
<b>Fe ore samples, Al rich</b>	
Samarco 1, 2	Enriched, purified Fe-ore pellets
RE8104 – RE8110	Fe ore

The samples of type “purified Cu ore” are samples from different points of the refinement process.

The iron ore samples with relatively high Al content are from different places in an iron mine.

## 3 Experimental

### 3.1 Preparing the Acid Digestion

100 mg of samples were directly weighed into the digestion vessel on an analytical balance with a resolution of 0.1 mg.

**Aqua regia** was prepared freshly per vessel by dispensing 6 mL HCl and 2 mL HNO<sub>3</sub>.

The “**4-acid mixture**” was prepared by directly dispensing into the digestion vessels:

2 mL HNO<sub>3</sub> (65%, p.a.),

6 mL HCl (32%, p.a.),

1 mL HBF<sub>4</sub> (40%, synthesis grade), and

1 mL HClO<sub>4</sub> (72%, p.a.)

**Note 1:** HBF<sub>4</sub> provides just the amount of fluoride ions required to dissolve silicates out of a boric acid complex. No more complexation with boric acid is necessary. HBF<sub>4</sub> also is not rated “toxic” as HF itself. If it is not available as “analysis grade”, make sure that your source meets your purity requirements.

**Note 2:** Digesting inorganic material with addition of 1 mL of HClO<sub>4</sub> in closed vessel can be considered harmless, as this 1 mL high-boiling acid will certainly stay inside the closed vessel.

Directly after weighing in the samples the vessels were closed and inserted into the rotor.

### 3.2 Acid Digestion

The temperature program used was a 15 min ramp to a temperature of 230 °C, which was held for 25 min.

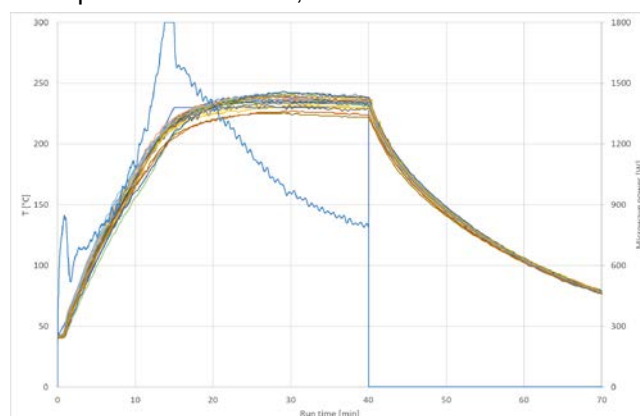


Fig. 2: Power (blue) and temperature curves for a full 20 position Rotor 20SVT50

After cooling the vessels were opened carefully under the fume hood, the digested solutions were poured into 50 mL PP sample tubes and filled up to 50 mL with DI water.

### 3.3 ICP-OES Measurement

Shortly before ICP-OES measurement 0.5 mL of that sample were mixed with 100 µL of a 100 ppm Sc as internal standard and 100 µL of a 10 g/L LiCl solution as ionization buffer and filled to 10 mL volume.

Calibration was done with a set of multielement standards of 1, 2, 5, 10, and 20 mg/L plus additional standards for Fe and Cu with 50 and 100 mg/L. For elements with a concentration below 5 mg/L in the sample a second reprocessing was done with exclusion of the standards above 5 mg/L, so the high standards wouldn't influence the calibration in the lower range too much.

The overall dilution factor was 10.000-fold, so 1 ppm in solution was about 1% in solid.

Element	Al		Ca		Mg		Fe		Pb		Zn		Mn		As		Ba	
$\lambda$ [nm]	396.152		396.847		279.553		194.699		220.353		213.856		257.611		189.759		455.404	
cert-% w/w	0.78	0.7%	0.73	1.2%	0.40	0.6%	54.74	0.1%	0.18	0.00%	0.30	0.01%	1.01	0.02%	0.22	0.00%	0.97	
Avg-% w/w	0.76	2.3%	0.79	6.4%	0.40	0.8%	61.52	3.0%	0.15	0.8%	0.28	0.7%	1.00	4.3%	0.22	0.8%	1.04	2.5%
Recovery%	<b>97.0</b>		<b>108.6</b>		<b>100.7</b>		<b>112.4</b>		<b>80.2</b>		<b>93.4</b>		<b>98.3</b>		<b>103.3</b>		<b>107.6</b>	
Run 1	0.79	1.0%	0.86	7.7%	0.40	0.7%	63.31	1.6%	0.14	0.7%	0.28	0.4%	0.97	0.4%	0.23	0.3%	1.05	1.8%
Run 2	0.78	3.6%	0.75	2.4%	0.40	0.8%	60.31	3.2%	0.14	1.1%	0.28	1.2%	0.99	1.2%	0.22	1.1%	1.03	3.5%
Run 3	0.79	1.5%	0.77	2.1%	0.40	1.0%	60.93	1.8%	0.15	0.8%	0.28	0.0%	1.02	0.0%	0.22	0.6%	1.05	2.5%
LOD [mg/L]	0.033		0.0007		0.0003		1.8		0.035		0.0008		n.a.		0.0046		0.0017	

Table 1: Results for the iron ore certified reference material NCS DC11006a after 4-acid digestion. The CRM was digested 3 times with 3 sample replicates in each run. For each element the left column is the concentration value in the ore in % w/w, the right column gives the RSD in %. The line with the recoveries shows very good agreement with the certified values. Also the repeatability within and between runs is excellent.

## 4 Results

The digestions were performed with a 4-acid mixture and with aqua regia for comparison. In general, aqua regia left, as could be expected, more of the sample undigested, while the fluoride from the fluoroboric acid ( $\text{HBF}_4$ ) succeeded to digest the silicates in most cases.

In Table 1 the results are given for repeated 4-acid digestion of the iron ore certified reference material NCS DC11006a. In Fig. 3 it can be seen that the 4-acid-mix can digest this sample completely.

In each of the 3 runs 3 CRM replicates were digested to establish the reproducibility in one run and within different runs. The repeatability between runs can be seen in the table, the replicates within a run showed a similar reproducibility.

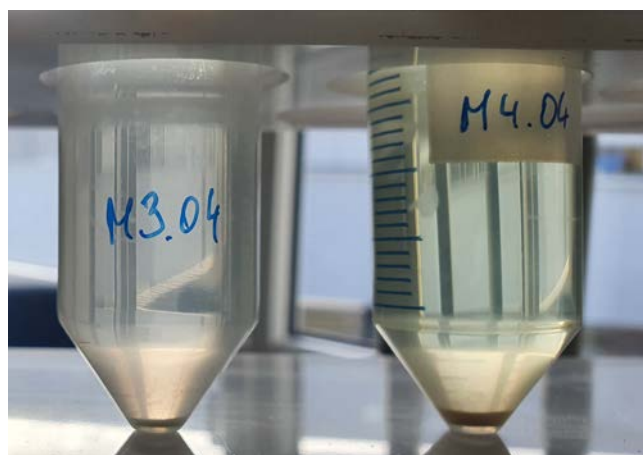


Fig. 4: Digestion of iron ore (RE8104): 4-acid-mix (left) can reduce the grey residue to a minimum as compared to aqua regia (right).

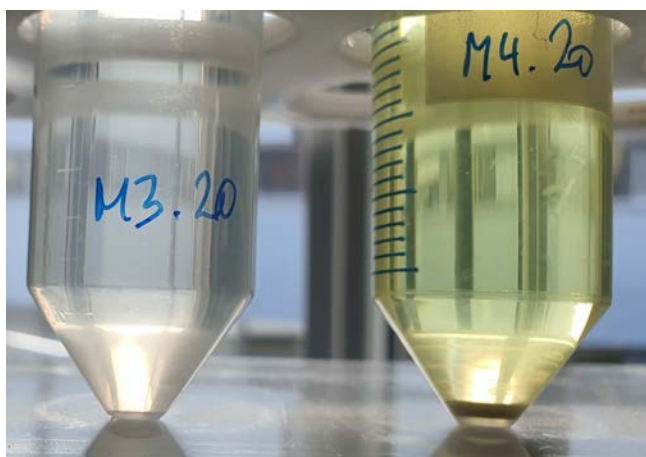


Fig. 3: Digestion of CRM NCS DC 11006a iron ore. 4-acid-mix (left) dissolves the sample completely, while aqua regia leaves a small grey residue

For the iron ore samples no certified reference values are available. Attempts to establish peroxide fusion with ICP-MS analysis and XRF as independent methods to provide reference values were unsuccessful due to big variations between methods.

Table 2 presents data for the 4-acid digestion of iron ore and copper process samples. The wide range of concentrations from middle ppm up to high percent made it necessary to work with different calibrations for elements with low and high concentrations. This was done by excluding the highest standards (> 10 mg/L) from re-processing, so the re-processed data was used for all values up to 5 mg/L. Taking the dilution factor into account, this corresponds to 5% w/w.

Aqua regia digestions of iron ores show incomplete recovery of several elements. For iron concentrates (Samarco 1 & 2), and the concentrates from copper processing the aqua regia digestions may be a valid alternative, because they show satisfactory recoveries.

In Fig. 5 it can be seen that the 4-acid-mix can digest all samples completely. Aqua regia digests the iron concentrates completely and some of the copper concentrates, while the samples that contain more of the original ore minerals leave more residues.



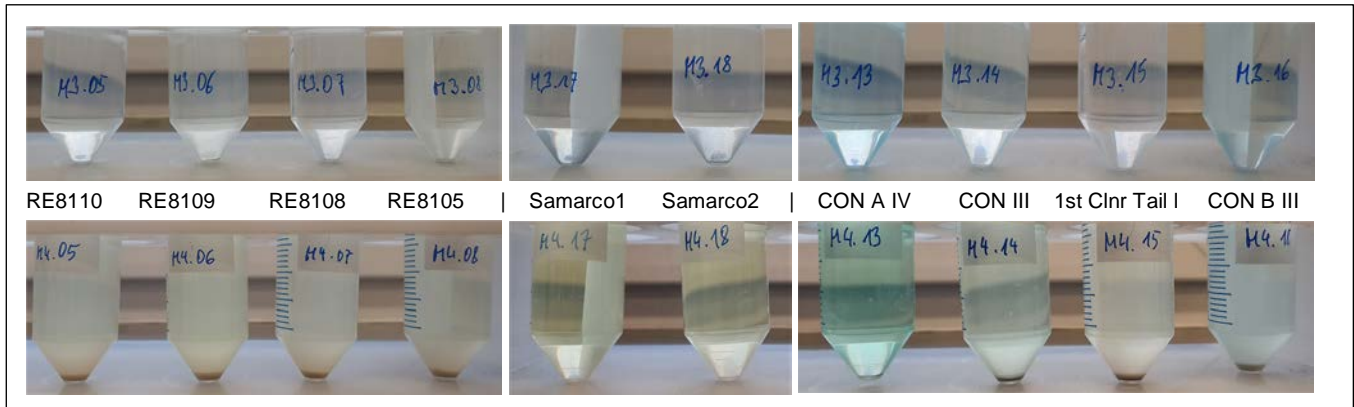


Fig. 5: Upper row 4-acid-mix, lower row aqua regia. Left picture shows that iron oxides dissolve completely with 4-acid-mix. Middle pics: Samarco concentrates dissolve completely. Right pics: Cu processing samples dissolve completely in 4-acid mix.

	Al	Ca	Fe	Cu	Ni	Mg
<b>Copper ore Processing</b>						
Con B III	2.43	0.67	14.09	35.44	0.080	7.32
1st Clnr Tail I	8.87	2.46	24.73	0.26	0.100	10.91
Con III	4.22	0.87	18.75	29.38	0.074	7.96
<b>Con A IV</b>	1.22	0.30	18.91	67.97	<b>0.040</b>	1.08
Con A III	0.85	0.27	17.23	67.23	0.012	1.02
Con A II rosa	0.71	0.21	17.27	71.52	0.009	0.74
Con A II groß	2.08	0.46	19.20	59.70	0.052	2.00
<b>Con I</b>	2.41	0.61	16.52	38.26	<b>0.052</b>	2.53
<b>Iron Ores</b>						
<b>RE8104</b>	7.24	0.85	41.79	1.12	<b>0.148</b>	5.63
RE8105	7.31	0.49	25.03	1.03	0.099	7.86
<b>RE8106</b>	5.76	1.75	17.87	0.48	<	8.00
RE8108	8.62	0.71	32.33	0.95	0.114	10.00
RE8109	7.82	1.19	31.04	0.78	0.106	8.56
RE8110	8.95	0.94	31.37	0.73	0.141	8.96
Samarco 1	0.40	1.1	73.99	<	<	0.091
Samarco 2	1.02	0.37	82.5	<	<	<

Table 2: Results in weight-% for the iron and copper ore samples for 4-acid-mix digestion.

## 5 Summary

Classical methods for element determination of major to minor levels are **XRF**, or **fusion** with inorganic salts, prior to acid dissolution for ICP-OES.

XRF requires a large calibration with very similar reference samples with respect to physical parameters like particle size or sample thickness. Fusion reagents add large amounts of dissolved solids into the liquid analytical sample for ICP-OES, adding to the complexity of the spectra. Classical photometric, gravimetric, and electrochemical methods are more and more replaced by ICP spectroscopy, although the precision is worse for major components like Fe or Cu.

Acid digestion, however, is very well suited as sample preparation for these techniques, because it bears no

risk of contamination by the use of solid inorganic reagents and only uses clean acids instead.

We could show that high-temperature acid digestion with **Multiwave 5000** and **Rotor 20SVT50** can provide stable and complete digestions within only **40 minutes for 20 samples**.

Digesting an iron ore standard reference material, we also could show the good precision (recovery) and the good reproducibility between replicates in one run and within different runs. This is important for rapid and reliable screening of large numbers of prospecting samples.

It must be considered, however, that all methods for analysis of minerals have their specific challenges and interferences, so careful method calibration and validation is necessary, especially, when ICP is used for determination of major components.

The method described in this application report was used to digest ore samples from a screening or prospecting activity and other samples that come from process control.

For the **screening purpose** hydrofluoric acid will be necessary due to silicate content in prospecting samples. However, by changing from hydrofluoric acid (HF) to fluoroboric acid (HBF<sub>4</sub>) we could eliminate the necessity for an additional complexation run with saturated boric acid afterwards and in the same instance change from a dangerously toxic to a less dangerous reagent.

For **process control** samples the acid mixture can be further adapted to the composition of the sample, which in some cases will allow to omit the hydrofluoric acid or to further optimize the digestion time.

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