

Acid Digestion of Chromium Ores for Analysis with ICP

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

Acid digestion of chromium ores for determination of the metal content with ICP-OES or -MS is demanding due to the stability of the generic chromite. Multiwave 5000 with Rotor 20SVT enables this difficult task with the convenience and safety of the SmartVent technology.



Wavelength dispersive **XRF** was performed on Axios Malvern Panalytical with matrix matched calibration (GeoMUL1).

ICP-MS analysis was done on an Agilent 7500 cx with the use of Ge, In, and Re as internal standards.

Acid digestion was performed with **Multiwave 5000** with Rotor 20SVT50, allowing a digestion temperature up to 250°C with the acid mixture used.

1 Introduction

In the mining industry there is a large demand for fast routine 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 find or follow the geological formations that allow the most profitable mining operation.

While classical techniques for analysis involve fusion, for example with sodium peroxide (Na_2O_2) as a flux, acid digestion is rather difficult, due to the stability of the generic chromite mineral. Weathering processes, which may have been different for chromium ores from different mines strongly influence the stability of the chromite.

The method described in the following suits for the samples studied. However, depending on the source of the samples their composition may vary and require some modifications e.g. to the acid mixture. In any case, it may be used as a starting point.

2 Instrumentation, Samples

Fusion and dissolution were done with a Claisse LeNEO (Malvern Panalytical).



Fig. 1: Rotor 20SVT50 and Multiwave 5000

2.1 Reference Materials and Samples

Sample Name	Sample Type
NCS DC 72303	Chromite CRM, China
SARM 131	Chrome ore CRM, South Africa
SARM 146	Chrome ore with 100% chromite, CRM, South Africa
IGS 30	Chrome ore, Philippines, British Geological Survey
KZ01 – KZ05	Samples from Cr-mine in Kazakhstan

Table 1: Certified reference materials and genuine samples used.

2.2 Reagents

For acid digestion the following acids were used in two different mixtures.

Reagent	Quality & Concentration
HClO ₄	72 %, analytical grade
HF	42 %, synthesis grade
H ₃ PO ₄	85 %, analytical grade
H ₂ SO ₄	96 %, analytical grade

Table 2: Acids used in this study

For fusion of the ore samples Na₂O₂ powder, analytical grade, was used.

3 Experimental

3.1 Reference Determinations

To establish reference values for unknown chromite samples, fusion decomposition was used to provide samples for WD-XRF and for ICP-MS determination.

For **WD-XRF** determination, the sample was heated at 1000 °C for 4 hours, then newly ground and 1.5 g thoroughly mixed with 12 g of 'Claisse LiT/LiM/LiBr 49.75/49.75/0.50% flux' in platinum crucibles following the "General Oxide Program" of the LeNEO fluxer at 1050 °C.

The WD-XRF measurements were made using a matrix matched calibration with geological reference materials (mainly GeoPT samples from IAG) as calibrants, which were prepared in the same way as the samples.

For **ICP-MS** measurements, 200 mg sample was mixed with 3 g of Na₂O₂ p.A. in a zirconium crucible for fusion at 700 °C. The fusion cake was dissolved in 10 ml HCl conc and diluted with 15 ml HCl 3 mol/l. After complete reaction the solution was filled up to the mark in a 250 ml volumetric flask and was ready for further dilution for the ICP-MS measurement.

3.2 Acid Digestion

About 100 mg of sample was directly weighed into the digestion vessel on an analytical balance.

To allow for differences in the geological origin of the samples, two acid mixtures were used in comparison

μ~3: 3 mL H₃PO₄, 2 mL HClO₄, 2 mL H₂SO₄

μ~4: 3 mL H₃PO₄, 2 mL HClO₄, 2 mL HBF₄

Both mixtures contain enough phosphoric acid as a high-boiling acid to allow a digestion temperature of 250°C.

Note 1: HBF₄ 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. HBF₄ also is not rated "toxic" like HF. 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 to 2 ml of HClO₄ in closed vessels can be considered harmless, as this high-boiling acid will certainly stay inside the vessel and also no reactive organic matter is expected in ore samples.

Directly after adding the acid mixture the vessels were closed and inserted into the rotor.

The **temperature program** used was a 20 min ramp to a target temperature of 250 °C, which was held for 60 min.

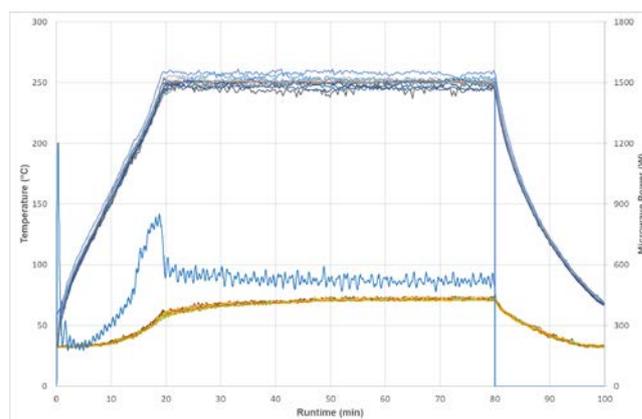


Fig. 2: Typical temperature and power curves for a partially loaded Rotor 20SVT50

After cooling, the vessels were opened under the fume hood, the digested solution was poured into autosampler vials, the digestion vessel rinsed with deionized water and the rinsing liquid added to the sample solution.

Shortly before measurement with ICP-MS the internal standard solution was added and filled to the final volume.

% w/w	Al ₂ O ₃					Cr ₂ O ₃					Fe ₂ O ₃					MgO					MnO					
	Ref.	μ~3	Rec.	μ~4	Rec.	Ref.	μ~3	Rec.	μ~4	Rec.	Ref.	μ~3	Rec.	μ~4	Rec.	Ref.	μ~3	Rec.	μ~4	Rec.	Ref.	Fusion	μ~3	Rec.	μ~4	Rec.
NCS DC 72303	12.1	13.9	115	14.4	119	49.4	48.2	98	50.1	101	16.4	16.5	101	16.7	102	15.7	15.2	97	16.7	106	0.28	0.28	0.29	104	0.29	104
SARM 131	14.6	14.3	98	17.2	118	41.8	36.4	87	43.6	104	30.7	26.5	86	31.4	102	9.2	9.0	99	10.4	114	2.08	0.26	0.25	96	0.26	100
SARM 146	14.5	12.6	86	16.3	112	46.9	36.4	78	47.1	100	25.6	21.9	86	28.2	110	10.6	9.4	88	11.2	105	0.22	0.23	0.20	87	0.22	100
IGS 30	29.1	24.8	85	30.8	106	35.0	28.3	81	35.8	102	16.0	13.0	81	15.7	98	16.6	15.2	92	17.7	106	n.a.	0.12	0.12	100	0.14	117

Table 3: Results for the chromium ore CRMs after digestion with 2 different acid mixtures: μ~3 ... Microwave digestion & ICP-MS, μ~4 ... Microwave digestion & ICP-MS, Ref. ... Certified Reference value, Rec. ... Recovery. The reference values for MnO of SARM 131 are doubtful and were complemented by values obtained by Na₂O₂-fusion with ICP-MS determination. IGS 30 had no value for MnO.

4 Results

A number of certified reference materials (see Table 1) is available and was used to develop and test the acid digestion method. In the past different acid mixtures were used and it turned out that samples from different geographical origins have slightly different requirements. "Weathered" chromite samples, like ones from South African mines, are somewhat easier to digest, they also do not require the use of HF or HBF₄ for a clear solution. Most of the certified reference materials come from that region, too. Results of the analysis are shown in Table 3 and show good recoveries. In general, the recoveries for the acid mixture with HBF₄ is somewhat higher. However, samples from Kazakhstan required the use of fluoride to dissolve the silica content.

The effective digestion temperature in a vessel is also very important. In experiments with a temperature of 220 – 230 °C the oxidation of the chromite did not reach the orange chromate oxidation state and a lot of dark, undissolved residue was observed (Fig. 3). Most likely the residue consisted of undigested chromite. In the cooler vessels the recoveries of several elements (Cr, Fe) were significantly lower.

For samples from a Kazakh origin (KZ1 – KZ5) XRF analysis values were used for comparison, because

for the above-mentioned CRMs values from XRF proved to be closest to the certified values. Especially for refractory elements like Cr and Mg peroxide fusion with ICP-MS analysis shows somewhat lower results. Agreement for samples was good, as can be seen in Table 3.



Fig. 3: Samples KZ03 (2 vessels from left) and KZ04 (2 vessels from right) with acid mix μ~4 digested at different temperatures. Both greenish solutions with heavy grey residue to the left and right reached only 230°C, while the clear, orange solutions in the middle reached a digestion temperature of 250°C.

Table 4: Results (in % w/w) and Recoveries (in % relative to the reference value). Samples in columns headed with "μ~3" or "μ~4" were digested with the respective acid mixture, while the "Rec."-columns show the recovery compared to the XRF analysis value for that element.

% w/w	Al ₂ O ₃					Cr ₂ O ₃					Fe ₂ O ₃					MgO				
	XRF	μ~3	Rec.	μ~4	Rec.	XRF	μ~3	Rec.	μ~4	Rec.	XRF	μ~3	Rec.	μ~4	Rec.	XRF	μ~3	Rec.	μ~4	Rec.
KZ1	1.40	1.09	78	1.03	74	3.5	3.4	97	4.3	121	7.37	7.4	100	7.28	99	39.0	40.48	104	39.53	101
KZ2	1.89	2.27	120	1.69	89	10.7	10.1	95	10.4	97	8.43	7.92	94	7.87	93	35.7	36.85	103	33.45	94
KZ3	3.46	3.93	114	3.67	106	21.4	20.5	96	20.7	97	9.65	9.59	99	8.81	91	31.2	32.73	105	28.84	92
KZ4	4.06	4.76	117	4.41	109	25.7	23.8	93	25.5	99	10.21	10.13	99	9.69	95	29.0	30.65	106	30.54	105
KZ5	5.23	5.72	109	5.12	98	32.8	30.2	92	32.1	98	11.08	10.34	93	11.05	100	26.0	27.25	105	26.61	102

5 Summary

For the challenging chromium ore analysis, classical methods like XRF and fusion with inorganic salts are widely used as sample preparation for classical photometric, gravimetric, and electrochemical methods.

Nowadays, ICP-OES and ICP-MS are more and more used, due to their higher potential for sample throughput. Acid digestion is very well suited as quick and reliable sample preparation for these techniques. Speed is an important argument and we could show that high-temperature acid digestion with **Multiwave 5000** and **Rotor 20SVT50** can provide stable and complete digestions within only 80 minutes.

In addition, it reduces the risk of contamination from solid inorganic reagents as it only uses clean acids in small amounts.

The method described in this report was used to digest chromium ore samples that come most likely from a screening or prospecting activity.

For the **screening** purpose hydrofluoric acid will be necessary for the large majority of prospecting sites due to silicate minerals in the samples. However, by changing from hydrofluoric acid (HF) to fluoroboric acid (HBF₄) no complexation run with boric acid was necessary. In addition the toxic hydrofluoric acid could be replaced by the less dangerous reagent tetrafluoroboric acid.

For **process control** samples the acid mixture can be further adapted to the known composition of the sample, thus allowing to further reduce the time to provide the results.

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