

S determination in copper concentrates and other sulfides

Suitable analyzers

- ELEMENTRAC CS-d

Used accessories

- ceramic crucibles (90149)
- copper accelerator (90240)
- ceramic boats (90160)
- suitable calibration material

Description of the challenge

Samples with a high sulfur content (e.g. ores) could either be analysed with an induction furnace or with a resistance furnace. Typical samples with high sulfur contents which could be analyzed with both types of furnaces are e.g. limestone, ZnS and ores (see application note 1028; 1035; 1045; 1061; 1062; 1064). On the one hand the induction furnace has an advantage regarding the analysis time, because it can measure the samples a little bit faster (max 70-80 seconds) than a resistance furnace (max 300 seconds). On the other hand a resistance furnace can process in general higher sample amounts (e.g. 350 mg and more) in comparison to an induction furnace (e.g. 150 mg). Higher sample weights are easier to handle and in general can cause an improved repeatability of the sulfur measurement. When the applied temperature in the resistance furnace is too low the danger of minor sulfur determination increases because not all of the present sulfur is oxidized.

Due to the higher temperature an induction furnace is suitable to oxidize all of the enclosed sulfur fractions, but minder determination of sulfur could occur when a significant amount of copper is present. Copper inside a sample can form copper sulfide during combustion which is not detected via the IR cells (ASTM 1941-10; Note 7). This application note compares the two combustion techniques for typical samples and the measured sulfur content.

To reduce sputtering and forming of copper sulfide in the induction furnace the new ramping function & intelligent lance management of the ELEMENTS software is used:



Fig 1: crucible with copper concentrate and copper accelerator (measured with ramping)



Fig 2: crucible with copper concentrate and copper accelerator (standard application)

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Application settings for the induction furnace:

I) General & Furnace

Sample type:	Advanced
Standby Flow:	180 l/h
Furnace purge through:	detector cells
Purge time:	2 sec
Purge flow:	180 l/h
Lance purging:	on
Purging while closing:	off

Stabilizing

Lance valve:	off
Stabilize baseline:	off
Setting time:	25 sec

II) Analysis

Flow:	180 l/h	Ramping:	on
Holding time:	180 sec	Start voltage:	10 %
Chamber only:	20 sec	Voltage:	90 %
Lance and chamber:	20 sec	Ramping time:	10 sec
Drift compensation:	off		

Channel	Min time [sec]	Max time [sec]	Integration delay [sec]	Comparator level [mV]	Comparator peak [%]
High S	45	200	7	10	0.5

III) Postwaiting

Postwaiting time:	10 sec
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Application settings for the resistance furnace:

I) General & Furnace

Resistance furnace flow:	Enable
Temperature:	1450 °C
Temperature tolerance:	20 °C

Stabilizing

Stabilize baseline:	on
Stability:	0.01 V
Minimum time:	20 sec
Maximum time:	60 sec

II) Analysis

Flow:	180 l/h
Drift compensation:	off

Channel	Min time [sec]	Max time [sec]	Integration delay [sec]	Comparator level [mV]	Comparator peak [%]
High S	60	300	5	10	1

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Sample preparation

Make sure that the sample is disintegrated to a suitable sample size and is free from contaminations. Please dry the sample until mass constancy at 105°C. Pre heat the ceramic crucibles at least for 1h at 1000°C. Let the crucibles cool down in a desiccator. For the ceramic boats (90160) a preheating could improve the repeatability of measurements.

Preparation of analyzer and its calibration

Prepare the ELEMENTRAC CS-d (e.g. exchange anhydron, sodium hydroxide, catalyst if necessary and clean dust trap and check the combustion tube of the resistance furnace). Calibrate the analyzer with several weights of ZnS (e.g. ELTRA 91900-2001). For the resistance furnace use sample weights from 100 – 700 mg, for the induction furnace from 60 – 200 mg.

Preparation of the induction furnace

- Run three warm up samples (e.g. steel samples (92400-3050) with a minimum weight of 500 mg and 1.7 g tungsten as accelerator

- Calibrate the analyzer with suitable calibration material (e.g. ZnS from ELTRA 91900-2001)

- (1) Weigh in approx. 60 – 200 mg of the sample into the ceramic crucible
- (2) Add 2 scoops of copper accelerator (approx. 2g)
- (3) Place the crucible on the pedestal (use tongs!) and start analysis

Repeat steps (1)-(3) at least five times with different sample weights and use the linear regression function in the Elements software for calibration

-> **Now start with the actual analysis.**

Preparation of the resistance furnace

- Run three warm up samples (e.g. coal samples (92511-3080) with a minimum weight of 350 mg

- Calibrate the analyzer with suitable calibration material (e.g. ZnS from ELTRA 91900-2001)

- (1) Weigh in approx. 100 – 700 mg of the sample into the ceramic boat and introduce it into the furnace

After finishing of the analysis remove the combustion boat and run another sample. Repeat step (1) at least five time with different sample weights and use the linear regression function in the Elements software for calibration

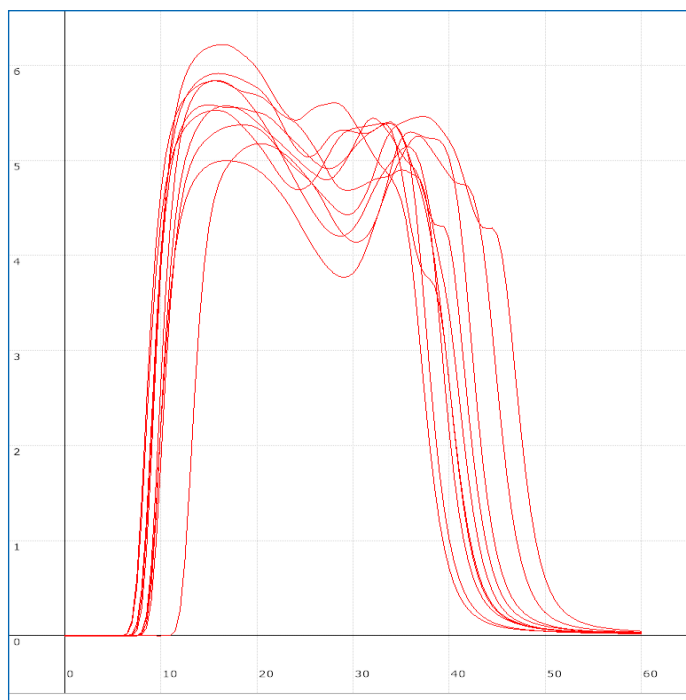
-> **Now start with the actual analysis.**

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Typical results with the resistance furnace

NCSDC 28058 copper concentrate ⁽¹⁾	
Weight (mg)	Sulfur (%)
305.8	22.63
295.3	22.69
304.6	22.62
297.3	22.60
303.0	22.42
304.6	22.59
294.7	22.49
297.3	22.54
301.8	22.49
303.2	22.58
Average	
	22.57
Deviation / Relative deviation	
	0.08 (0.4%)



⁽¹⁾ certified values: S: 22.87 % ± 0.4
 Certified according other method (combustion & titrimetric determination of sulfur & gravimetric precipitation as BaSO₄)

Crosscheck of the application with other substances

To check this application settings other substances have been analyzed additionally:

Substance	Normal S concentration	No of analysis	Typical sample weight	Measured S content	Verification
ZnS Alfa Aesar LOT: T27E034	32.9	10	350 mg	32.8 ± 0.09	Ok
MoS ₂ Alfa Aesar LOT: R31D042	40.05	10	300 mg	29.75 ± 2.51	Too low

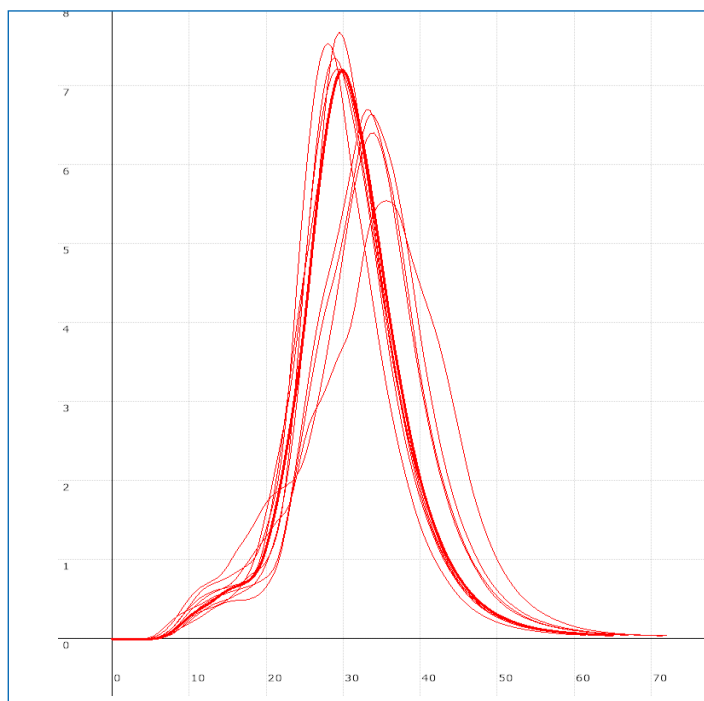
Conclusion: sulfur measurement with the resistance furnace

The chosen application settings are suitable for a reliable measurement of copper concentrates and ZnS. Other ores with a high sulfur content may also be analyzed with these settings (see other ELTRA application notes). Obviously the applied temperature is not sufficient to release all the sulfur from the molybdenum sulfide. The measured sulfur content of MoS₂ is too low and it will be measured again with the induction furnace of the ELEMENTRAC CS-d (see next pages):

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Typical results with the induction furnace	
NCSDC 28058 copper concentrate ⁽¹⁾	
Weight (mg)	Sulfur (%)
151.8	23.67
152.7	23.81
154.1	23.80
150.5	23.48
151.5	23.53
149.3	23.63
152.9	23.43
153.2	23.85
154.2	23.63
149.4	23.91
Average	
	23.67
Deviation / Relative deviation	
	0.16 (0.7%)



⁽¹⁾ certified values: S: 22.87 %+- 0.4
 Certified according other method (combustion & titrimetric determination of sulfur & gravimetric precipitation as BaSO₄)

Crosscheck of the application with other substances

To check this application settings other substances have been analyzed additionally:

Substance	Nominal S concentration	No of analysis	Typical sample weight	Measured S content	Verification
ZnS Alfa Aesar LOT: T27E034	32.9	10	110 mg	32.9 ±0.16	Ok
MoS ₂ Alfa Aesar LOT.R31D042	40.05	10	80 mg	39.9 ±0.33	OK

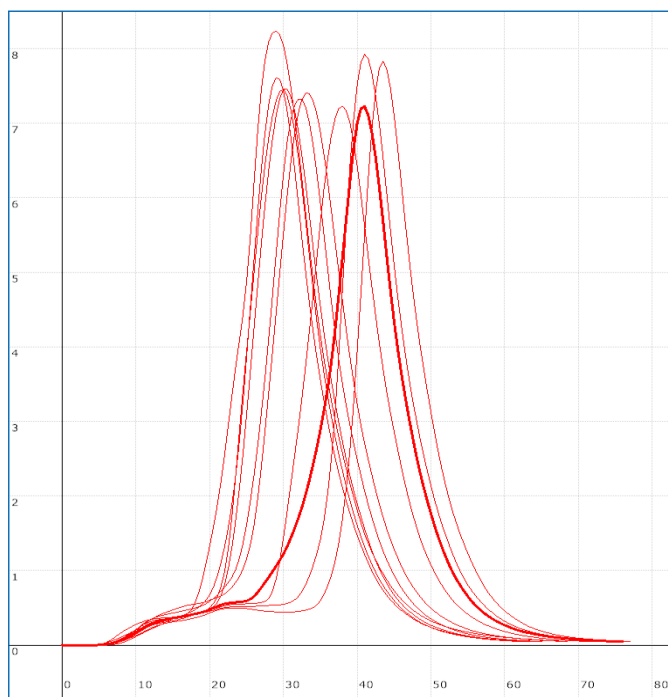
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Results of MoS₂ with the induction furnace in detail:

Sample: MoS₂ (Alfa Aesar; Lot R31D042)⁽²⁾

Weight (mg)	Sulfur (%)
99.1	39.75
78.9	39.79
81.9	40.27
85.2	40.16
79.2	40.26
80.9	40.17
80.9	39.98
83.0	39.49
79.4	39.29
80.9	39.81
Average	
	39.90
Deviation / Relative deviation	
	0.33 (0.8%)



⁽²⁾ calculated, nominal value: S. 40.05 %

Conclusion: sulfur measurement with the ELEMENTRAC CS-d induction furnace

With the applied settings the sulfur analysis of copper concentrates, ZnS and MoS₂ is safe, repeatable and reliable with the induction furnace. The measured sulfur content of the copper concentrate show a slightly higher sulfur value in comparison to the certified value and the resistance furnace measurements. The correct measurement of MoS₂ and ZnS in the induction furnace could indicate that the induction furnace measurement is more reliable due to the higher temperature. Unfortunately the certification does not mention the applied combustion temperature.

Summary

The ELEMENTRAC CS-d is the ideal analyzer for sulfur analysis in samples with a high sulfur content. The resistance furnace assures a best possible precision in sulfur measurement due to the analysis of high sample weights. The induction furnace can provide a higher temperature and assures the complete oxidation of all sulfur species of a sample.

The new ELEMENTS software with its intelligent lance management and ramping function is able to overcome known problems with the sulfur analysis of copper containing samples. The smooth combustion in the induction furnace reduces forming of dust and allows a reliable sulfur measurement.