ANALYSIS OF BASE METAL SULFIDES USING XRF AND FUSION

Introduction

Sulfide ores are important sources for several elements, such as Cu, Zn, Pb, Ni, Co, Mo, Bi, Sb, Cd, Ag, Au, Se, Te. To obtain maximum yields from a deposit, it is crucial to know the concentrations of the valuable elements in ores and concentrates at various stages of the mining process.

Wet-chemical methods have always been the reference techniques for analysis of these materials. For routine analysis, however, other methods are often preferred. X-ray fluorescence (XRF) is advantageous as it does not require sample digestion, which saves time and avoids the use of hazardous chemicals and generation of waste.

Previously, accurate and repeatable XRF sample preparation and analysis of metal sulfides was challenging. The concentration ranges involved made it difficult to obtain suitable reference materials, making calibration difficult and costly. The strongly varying mineralogy of the materials requires sample preparation by fusion for best accuracy. Additionally, accurate calibration materials are needed. Also, due to the high sulfide and metal content, retention of all elements during sample fusion, while preventing damage to expensive platinum ware, is challenging.

The universal need of mining industries for quick, reproducible and accurate sulfide analysis prompted Malvern Panalytical to develop the analytical solution described here. This method is revolutionary as it alleviates the difficulties traditionally encountered in XRF analysis of base metal sulfides and greatly simplifies the entire analytical process.

The method includes synthetic calibration standards, covering 21 elements in concentration ranges typically encountered in base metal sulfide ores and concentrates. If needed, addition of elements and/or extension of concentration ranges is straightforward.

The solution includes a ready-to-use flux and fusion method that ensures complete oxidation and retention of all elements, including sulfur, in the fused bead. The preparation method is designed for electric fusion systems like TheOx and Eagon 2 while the analytical program can be deployed on Zetium or Axios spectrometers. If desired, the method is fully automatable.

Zetium wavelength dispersive XRF spectrometer

The combination of Zetium with Malvern Panalytical fusion systems like TheOx, Eagon and LeNeo offers an excellent combination for elemental analysis of a wide range of materials. The electrical fusion systems provide outstanding temperature control, resulting in unrivalled reproducibility of the sample preparation process.

In addition, the wavelength dispersive XRF analyzer with integrated sample handler and software has unmatched stability, even in harsh environments common to mining and minerals processing.

Lastly, the advanced algorithms incorporated in the SuperQ analytical software easily deal with challenging analytical requirements, while the intuitive user interface makes accurate routine analysis easy to perform.

Adding value in process control of sulfides and oxides:

- Complete sample analysis: covering over 20 elements in one analysis, essential for grinding and flotation process optimization

- Accuracy: the same or better than required by the classical methods referred to in applicable norms

- Speed: sample preparation and analysis in less than 45 minutes, covering all elements while classical methods require more time just for determination of one element only

- Simplicity: a complete method not requiring highly qualified personnel, in contrast to AA, ICP and wet-chemical techniques

Sample preparation and measurement details

The dedicated sample preparation approach, including a special flux with integrated oxidizers, is demonstrated for the fusion of copper sulfide-based materials. Although copper ores and concentrates were chosen as the example in this study, this method is also applicable to base metals such as Ni, Mo and Zn. The method ensures that all chemical compounds present in the sample are oxidized and retained within the bead.

All specimens mentioned in this study were prepared with TheOx fusion system where up to six beads can be prepared simultaneously in one fusion cycle. This fusion cycle, 'from cold to cold', including oxidation stage, takes about 45 minutes. The method is also available for LeNeo and Eagon 2 fusion systems.

A dedicated application for copper sulfide-based materials was set up on a Zetium WDXRF spectrometer equipped with a 4 kW Rh- anode X-ray tube. The measurement program includes analysis of 21 essential elements and takes less than 10 minutes, allowing the analysis of about 50 specimens within an 8-hour working shift. The number of analytes and the measurement time can be increased or decreased depending on specific needs.

Calibration

A set of synthetic calibration standards for copper ores and concentrates was used for calibration. This set consists of 11 standards prepared in duplicates and covers more than 20 major and minor chemical elements critical for copper ores and concentrates. Examples of calibration plots obtained are given below.

Calibration was performed using SuperQ software, which employs powerful matrix correction algorithms and handles losses and gains on ignition in a robust manner, which is essential for the correct analysis of these types of materials.

The graphs below show the resulting calibrations obtained for Cu and S. Note that each marker consists of 4 separate data points, obtained by measuring 4 different beads. This demonstrates the excellent precision of the method.

Calibration for Cu

Calibration for S
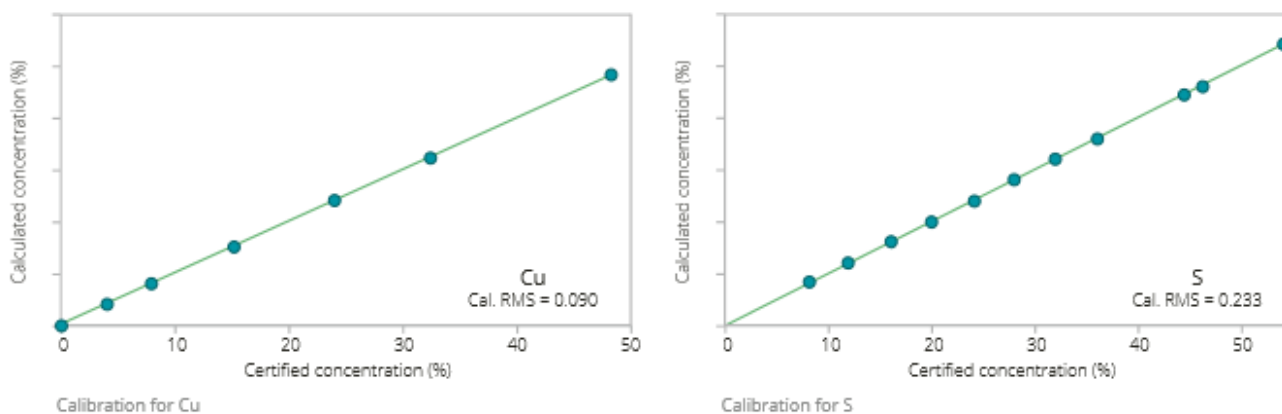
Accuracy

The accuracy of the method was validated by using five different Certified Reference Materials (CRMs). Four replicated beads were prepared for each of the CRMs using the employed method and analyzed using the synthetic calibrations. The results of Cu are given in Table 1. The results of other elements are given in Tables 2 and 3. Note that the tables list up to three types of analyses:

- Classic methods: titrimetric (incl. iodometric) and/or electrogravimetric and/or gravimetric methods

- Instrumental methods: AAS and/or ICP-OES and/or ICP-MS and/or XRF

- Combustion method

In addition to the certified values, standard deviations are listed as given in the certificates of the CRMs. The result obtained by the method described here was calculated as an average of 4 individual results obtained on different bead specimens and accompanied with its standard deviation. Actual absolute difference between certified value and calculated average is also shown in the tables next to allowed difference in accordance with ISO Guide 33 regarding accuracy assessment.

Precision

One bead of CRM OREAS 991 was measured 11 times to demonstrate the 'repeatability' of the instrument and the 'reproducibility' of the method. Subsequently 11 beads were prepared from the same CRM and each bead was measured once. The results are listed in Table 4 and demonstrate the excellent precisions of the instrument and the sample preparation.

Table 1. Results of copper for various CRMs

Cu analysis (%)	CCU-1e		OREAS 99	OREAS 99B			OREAS 991	OREAS 992
Type of analysis	Classic	Instrumental	Classic	Classic (Umpire labs)	Instrumental (4 acids)	Classic & instrumental (aqua regia)	Classic	Classic
Certified value	23.07	22.88	25.89	28.90	28.90	28.74	20.66	43.90
Standard deviation of certified value (1σ)	0.11	0.51	0.10	0.10	0.68	0.78	0.05	0.18
Calculated average of 4 MP beads	23.06		25.96	28.70			20.79	44.06
Standard deviation of 4 MP beads (1σ)	0.14		0.14	0.07			0.06	0.13
Difference MP vs. certified	**0.01**	**0.18**	**0.07**	**0.20**	**0.20**	**0.04**	**0.13**	**0.16**
Allowed difference*	**0.27**	**1.03**	**0.25**	**0.26**	**1.37**	**1.7**	**0.18**	**0.41**

* The allowed difference (statistical insignificance of a difference between certified and calculated value) is calculated in accordance with ISO 10469:2006 (electrogravimetric hydroxide separation) regarding trueness assessment

Table 2. Results of additional elements in CRM CCU-1e

CRM CCU-1e	Ca (%)	Co (%)	Fe (%)	Pb (%)	S (%)	S (%)	Zn (%)	As (%)
Type of analysis					different	combustion		
Certified value	0.129	0.0301	30.7	0.703	35.28	35.52	3.02	0.101
Standard deviation of certified value (1σ)	0.012	0.0014	1.4	0.031	0.47	0.31	0.1	0.014
Calculated average of 4 MP beads	0.138	0.0306	31.14	0.714	34.85		2.96	0.126
Standard deviation of 4 beads (1σ)	0.006	0.0007	0.15	0.012	0.30	0.30	0.004	0.001
Difference MP vs. certified	**0.009**	**0.0005**	**0.44**	**0.011**	**0.43**	**0.67**	**0.06**	**0.025**
Allowed difference*	**0.025**	**0.0029**	**2.80**	**0.063**	**0.99**	**0.69**	**0.20**	**0.028**

* The allowed difference was calculated in accordance with ISO Guide 33 regarding accuracy assessment

Table 3. Results of additional elements in CRMs OREAS 99b and 992

	OREAS 99b									OREAS 992	
	Fe (%)		Pb (%)		S (%)			Zn (%)		S (%)	Ni (%)
Type of analysis	Instrumental (4 acids)	Instrumental (aqua regia)	Instrumental (4 acids)	Instrumental (aqua regia)	Combustion	Instrumental (4 acids)	Instrumental (aqua regia)	Instrumental (4 acids)	Instrumental (aqua regia)	Combustion & acid gravim	
Certified value	30.18	31.08	0.0619	0.0625	31.60	30.80	29.9	0.22	0.216	36.97	1.5**
Standard deviation of certified value (1σ)	2.01	0.95	0.0023	0.0083	0.70	0.50	2.20	0.014	0.024	0.557	n/a
Calculated average of 4 MP beads	30.59		0.0627		31.60			0.215		36.85	1.60
Standard deviation of 4 beads (1σ)	0.05		0.0027		0.10			0.001		0.185	0.004
Difference MP vs. certified	**0.41**	**0.49**	**0.0008**	**0.0002**	**0**	**0.80**	**1.70**	**0.005**	**0.001**	**0.12**	**0.10**
Allowed difference*	**4.02**	**1.90**	**0.0053**	**0.0168**	**1.40**	**1.00**	**4.40**	**0.028**	**0.048**	**1.13**	**n/a**

* The allowed difference was calculated in accordance with ISO Guide 33 regarding accuracy assessment.

Table 4. Instrument and sample preparation precision determined using OREAS 991

	Cu (%)	Zb (%)	Pb (%)	S (%)	Fe (%)	As (%)	Mg (%)	Al (%)	Si (%)	Ca (%)
One bead measured 11 times (XRF instrument precision)										
Average	20.26	0.027	0.0158	28.08	25.90	0.0193	0.486	1.89	6.45	1.09
Standard deviation	0.025	0.0009	0.0013	0.036	0.024	0.0008	0.0047	0.0056	0.014	0.005
Relative standard deviation (rel. %)	0.12	3.3	8.4	0.13	0.09	4.1	0.97	0.3	0.22	0.4
	Cu (%)	Zb (%)	Pb (%)	S (%)	Fe (%)	As (%)	Mg (%)	Al (%)	Si (%)	Ca (%)
11 different beads measured 1 time each (method precision: instrument & sample preparation)										
Average	20.69	0.028	0.0131	28.11	25.95	0.0190	0.476	1.93	6.46	1.10
Standard deviation	0.079	0.0011	0.0018	0.08	0.079	0.0013	0.0105	0.026	0.018	0.004
Relative standard deviation (rel. %)	0.38	3.8	14	0.30	0.30	6.8	2.2	1.4	0.28	0.4

Zetium configuration

Tube settings

Tube settings	
Tube anode material	Rh
Maximum voltage (kV):	60
Maximum current (mA):	160
Maximum power (W):	4000*
Tube window material	Be

Filters

Position	Filtermaterial
1	None
2	Brass (440 µm)
3	Al (750 µm)
4	Al (200 µm)

Crystals

Position	Crystal	2d (nm)
1	PX10	0.4027
2	Ge 111-C	0.6532
3	PE 002-C	0.8749
4	PX1	5.086
5	Lif 220	0.2848

Collimators

Position	Collimator
1	150 µm
2	550 µm

Collimator masks

Position	Diameter (mm)
1	37
2	30
3	27
4	6
5	10
6	20

Detectors

No.	Detector	Quality	Saturation (kcps)	Detector window
1	Flow	40	2500	0.6 µm high transmission for B
2	Xe sealed	48	1000	
3	Hiper Scint.	150	3500	
4	Duplex	50	3000	

Conclusion

Malvern Panalytical's solution for the elemental analysis of copper ores and concentrates provides fast, ready-to-use multi-element analysis of base metal ores and concentrates. This method ensures the high-precision, high-accuracy analysis required for efficient process control.

The solution consists of:

- Calibration standards

- Dedicated fusion recipe and flux

- Complete method setup

- Results validation

The method adds significant value over the classical chemical methods as referenced in norms while providing results with the same or better quality.

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