Challenge
Routine method for Cu determination in geological labs

Solution
Flame AAS routine on novAA 800 F with automatic standard preparation and over-range dilution

Copper Quantification in Geological Samples by Flame-AAS

Introduction

The demand for copper especially by the electronic industry has constantly increased over the last decades, and it is expected that 20 million tons of copper ore will be dug up annually by 2020. There are applications of copper in wiring and cables, in circuit boards and electronic assemblies that are driving this development; and so the grade of copper impacts on the price to be achieved by mining companies and smelters.

Flame atomic absorption spectrometry (AAS) is a simple, robust and cost-effective method used by many mining companies and smelters to quantify copper – in ores and pre-concentrated metallic form – over a wide concentration range from medium ppm (mg/kg) to high percentage (wt%) values. In contrast, impurity control of high-purity copper e.g., for antimony, bismuth, phosphorous, and tin is typically done by ICP-techniques that are true multi-element techniques with significantly higher sensitivity; hence, covering the ppb (µg/kg) to ppm (mg/kg) range.

This application note describes a straightforward method using the flame AAS novAA 800 F for copper quantification in geological and metallic samples. For high ease of use, the instrument was equipped with an autosampler (AS-FD) capable of both, (i) calibration standard preparation and (ii) automatic over-range dilution for highly concentrated samples. Analytical quality parameters incl. RSD values and spike recovery rates were obtained, and method robustness was further tested using an industry-specific certified reference material (CCU-1c).

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Materials and Methods

Samples and reagents

- Grinded copper ore
- Copper ore reference material (CCU-1c)
- HCl (32%, p.a. Roth)
- HNO_3 (65%, p.a. Roth)
- Certified standard solutions (1000 mg/L Cu Sigma Aldrich)

Sample preparation

About 0.1 g of the copper ore reference material (CCU-1c) and grinded copper ore were both dissolved in 20 mL of aqua regia on a hotplate heated to 50 degrees Celsius, and the clear solution was filled up to 100 mL with deionized water to give a solution with a nominal concentration of 1 g/L.

Aqua regia was used due to significant Al_2O_3 content in the reference material, so that incomplete digestion and wrong results were avoided. That is, for copper ores without alumina or silica contents as well as for metallic copper, dissolution in nitric acid is sufficient/recommended.

One aliquot of the grinded ore sample was manually diluted by factor 500 and submitted to analysis, while for a second aliquot of the grinded ore sample and the dissolved reference material the automatic dilution functionality of the AS-FD was used instead (dilution factor 500).

Calibration

All calibration standards and QC samples were prepared automatically by the AS-FD autosampler from a 10 mg/L copper stock solution, which was prior made from commercially available 1000 mg/L copper standard (Sigma Aldrich) in 0.6% nitric acid. Table 1 shows the concentrations of the calibration solutions used.

Table 1: Concentration of calibration standards

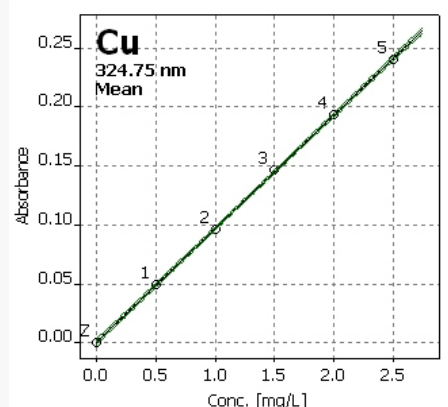| Standard	Concentration [mg/L] Cu
Cal. 0	0
Cal. 1	0.5
Cal. 2	1.0
Cal. 3	1.5
Cal. 4	2.0
Cal. 5	2.5

Figure 1: Calibration curve, Linear, R_2(adj.) = 0.9998

Instrument settings

A novAA 800 F equipped with a 50 mm burner head and an injection switch SFS 6.0 – for introduction of small sample volumes and a continuous rinsing of the system – was used, alongside an AS-FD autosampler with integrated over-range dilution. Please note that the autosampler was also used for automatic preparation of calibration standards.

Table 2: Instrument settings

Parameter	Specification
Temperature	20 °C (room temperature)
Burner width	50 mm
Fuel type	C_2H_2/air
Fuel gas flow	40 L/h
Burner angle	0°
Autosampler	AS-FD
Injection switch	SFS 6.0

Method parameters

Table 3: Method parameters

Element	Wavelength [nm]	Split [nm]	Lamp current [mA]	Burner-high [mm]
Cu	324.75	1.2	2.0	7

Results and Discussion

The copper content in the grinded ore sample was measured twice; first a manually diluted aliquot, and then another sample aliquot that was automatically diluted by the AS-FD autosampler. For both sample aliquots consistent results were obtained (Table 4).

So, geological routine labs with copper ore samples of varying and/or unknown copper concentrations can improve ease of use and productivity significantly using the autosampler (without sacrificing precision). The recorded quality parameters RSD and spike recovery rate for a QC sample showed values about 1% and 101%, respectively.

The results collected for the copper ore reference material show good agreement with certified values (Table 5), which further highlights the robustness of this flame AAS method.

Table 4: Results for grinded copper ore sample

Sample	Element	DF[1]	Concentration [g/L]	RSD [%]	QC spike concentration [mg/L]	QC spike recovery [%]
Grinded copper ore	Cu	500[2] (manual)	2.08 ± 0.02	1.2	1.0	101
	Cu	500[3] (automatic)	2.08 ± 0.02	1.7	-	-

1 ... dilution factor

2 ... manual dilution by hand (0.1 mL in 50 mL)

3 ... automatic dilution by AS-FD autosampler (50 µL in 25 mL)

Table 5: Results for copper ore reference material (CCU-1c)

Sample	Element	DF[1]	Concentration [mg/kg]	RSD [%]	Certified concentration [mg/kg]
CCU-1c	Cu	500[2] (automatic)	255.0 ± 0.3	0.2	256.2

1 ... dilution factor

2 ... automatic dilution by AS-FD autosampler (50 µL in 25 mL)

Summary

The novAA 800 F for flame AAS allows fast and precise analysis of copper contents in ore samples after a simple hot plate digestion in nitric acid or aqua regia.

When the AS-FD autosampler was used alongside, both user-friendliness and productivity were significantly increased, since the autosampler offers (i) automatic over-range dilution of samples with unknown and varying copper concentrations and (ii) automatic preparation of calibration standards.

Figure 2: novAA 800 F