



# Determination of fluorine in copper concentrate via high-resolution graphite furnace molecular absorption spectrometry and direct solid sample analysis – Comparison of three target molecules



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## ABSTRACT

The chemical composition of complex inorganic materials, such as copper concentrate, may influence the economics of their further processing because most smelters, and particularly the producers of high-purity electrolyte copper, have strict limitations for the permissible concentration of impurities. These components might be harmful to the quality of the products, impair the production process and be hazardous to the environment. The goal of the present work is the development of a method for the determination of fluorine in copper concentrate using high-resolution graphite furnace molecular absorption spectrometry and direct solid sample analysis. The molecular absorption of the diatomic molecule CaF was measured at 606.440 nm. The molecule CaF was generated by the addition of 200 µg Ca as the molecule-forming reagent; the optimized pyrolysis and vaporization temperatures were 900 °C and 2400 °C, respectively. The characteristic mass and limit of detection were 0.5 ng and 3 ng, respectively. Calibration curves were established using aqueous standard solutions containing the major components Cu, Fe, S and the minor component Ag in optimized concentrations. The accuracy of the method was verified using certified reference materials. Fourteen copper concentrate samples from Chile and Australia were analyzed to confirm the applicability of the method to real samples; the concentration of fluorine ranged from 34 to 5676 mg kg<sup>-1</sup>. The samples were also analyzed independently at Analytik Jena by different operators, using the same equipment, but different target molecules, InF and GaF, and different operating conditions; but with a few exceptions, the results agreed quite well. The results obtained at Analytik Jena using the GaF molecule and our results obtained with CaF, with one exception, were also in agreement with the values informed by the supplier of the samples, which were obtained using ion selective electrode potentiometry after alkaline fusion. A comparison will also be made for the three target molecules and the three independently developed methods for the determination of fluorine, although all three methods used direct solid sample analysis.

## 1. Introduction

Copper concentrate is the first product of the copper production line and is usually produced by a smelting process, which can be undertaken in a variety of furnaces. The product of this smelting stage is a mixture of roughly equal parts of copper, iron and sulfur that contains around 30% copper. Besides these major components, copper concentrate also contains gold and silver as well as arsenic, bismuth,

lead, selenium, tellurium, tungsten, and even halogens, such as fluorine. The purpose of the smelting stage is to eliminate as much of the unwanted iron, sulfur and gangue materials (such as silica, magnesia, alumina and limestone) as possible, while minimizing the loss of copper [1]. The composition of complex inorganic materials, such as copper concentrate, influences the economics of their further processing because most smelters have strict limitations on the permissible concentrations of impurities. Most copper concentrate is

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sold directly to smelters and refineries. These intermediaries process it into refined copper. The price paid for copper concentrate depends in part on the concentration of impurities, and fluorine is among the most important ones [2,3].

Fluorine is an undesirable element in copper concentrate due to the formation of a corrosive acid brine mixture of hydrofluoric acid and sulfuric acid. This contamination requires the application of fluorine removal processes, which increases smelter costs. The corrosive acid brine may also cause accelerated corrosion of equipment in the acid plant [4]. In addition to the problems caused in refineries, fluorine also plays an important role as an air pollutant due to its high phytotoxic potential. An excess of fluorine in vegetation can cause leaf damage, affect plant growth and result in public health problems [5].

Fluorine is frequently determined using techniques such as ion chromatography (IC) [7], ion selective electrodes (ISE) [8], X-ray fluorescence spectrometry (XRF) [9], gas chromatography (GC) [10], in addition to classical techniques such as gravimetric and titrimetric determination. Nevertheless, each of them has its limitations or disadvantages, such as interferences, time consumption, poor precision and selectivity, or high cost, and most of them require an extensive sample preparation before the actual determination. Inductively coupled plasma mass spectrometry (ICP-MS) cannot be used for the direct determination of fluorine because of its extremely high ionization energy of 17.42 eV, which cannot be reached in an argon plasma. It can also not be determined by ICP optical emission spectrometry (ICP OES), as all the emission lines of fluorine are too far in the vacuum UV to be detected by an optical spectrometer.

Atomic absorption spectrometry (AAS) has become an established analytical technique for quantitative determination of trace metals and metalloids in complex matrices. However, AAS cannot access the vacuum-UV region of the spectrum either, where the halogens and other non-metals have their absorption lines. Nevertheless, this obstacle was overcome in recent years due to the availability of instrumentation for high-resolution continuum source atomic absorption spectrometry (HR-CS AAS). This equipment can equally be used for molecular absorption spectrometry (MAS) using the electron excitation spectra of suitable diatomic molecules. These spectra exhibit a pronounced rotational fine structure [11] and can be found in the UV and visible range of the electromagnetic spectrum, the same range where most of the atomic absorption lines are located.

HR MAS was applied with good results for the determination of the halogens and sulfur in a wide variety of samples [11–13]. In order to obtain the best sensitivity using HR MAS for the determination of non-metals, it is necessary to optimize conditions to promote formation of the target diatomic molecule. It is desirable to choose a molecule with bond strength greater than 400 kJ mol<sup>-1</sup> to ensure its stability at elevated temperatures and to reduce the risk for competitive reactions [11]. The literature reports the determination of fluorine via the rotational molecular absorption lines of different diatomic molecules with this characteristic. Strontium mono-fluoride (SrF) was evaluated for fluorine in water samples [14]; gallium mono-fluoride (GaF) for drinking water [15], toothpaste [16] and organic compounds [17]; aluminum mono-fluoride (AlF) for toothpaste [18] and etching solutions of the photovoltaic industry [19]. Calcium mono-fluoride (CaF) is the molecule most studied, with application in tea [20], milk [21], plant material [22], niobium oxide [23], coal [24], wine [25], baby food [26], flour [27] and eye shadows [28]. The use of calcium as molecule-forming reagent for fluorine determination is of advantage, because it also acts as a chemical modifier and provides lower sensitivity, which is of advantage when no real trace concentrations have to be determined. In addition, the molecular absorption bands of CaF are in the visible range of the spectrum, where only very few atoms have absorption lines, and scattering of radiation at volatilized particles is much less pronounced than in the far UV, so that the risk for spectral interference is minimal [23].

The vaporization in a graphite furnace (HR GF MAS) allows the

direct analysis of solid samples, which is characterized by higher sensitivity, lower limits of detection, and essentially no reagents are required, which means there is no hazardous waste. Nevertheless, inorganic matrices, such as copper concentrate are known to be difficult to volatilize in the pyrolysis stage, and the great amount of matrix vaporized together with the analyte increases the background signal. To overcome this problem, the samples are generally submitted to a digestion process before being analyzed. The most widely used method to get geological and inorganic materials into solution is digestion with strong acids. However, such a digestion increases the risk of contamination and/or analyte losses, particularly in the case of the halogens, uses hazardous reagents and inevitably dilutes the sample [29]. Because of the high volatility of the halogens in strongly acidic medium, alkaline fusions are frequently used to bring samples into solution for their determination [30]; however, such fusions introduce an additional, much undesired matrix that would further complicate the later determination of trace elements, such as fluorine.

In order to avoid the need for acid digestion, the characteristic of calcium to act as chemical modifier promises to help reduce effects of the inorganic matrix when direct solid sample analysis is used, as seen in the literature [22,24,28]. The goal of this work was the development of a method for the determination of fluorine via the CaF molecule in copper concentrate using HR GF MAS and direct solid sample analysis. The results were compared with those obtained with two similar methods that were developed independently at Analytik Jena by different personnel and using different target molecules, InF and GaF. The results were also compared with the values informed by the supplier of the samples, which were obtained by ISE potentiometry after alkaline fusion.

## 2. Experimental

### 2.1. Instrumentation

A high-resolution continuum source atomic absorption spectrometer Model contrAA 600 (Analytik Jena, Jena, Germany) was used for all measurements throughout this work. This instrument is equipped with a transversely heated graphite tube atomizer. The primary radiation source is a xenon short-arc lamp with a nominal power of 300 W, operating in a hot-spot mode, which emits a spectral continuum between 190 and 900 nm. The high-resolution double monochromator with a linear charge-coupled device (CCD) array detector with 588 pixels has a spectral resolution of about 1.5 pm per pixel at 200 nm and about 4.5 pm per pixel at 600 nm.

Transversely heated and pyrolytically coated solid sampling (SS) graphite tubes (Analytik Jena, Part No. 407-A81.303) and SS graphite platforms (Analytik Jena, Part No. 407-152.023) were used for all measurements. An M2P microbalance (Sartorius, Göttingen, Germany) was used for weighing the samples directly onto the SS platforms. A pre-adjusted pair of tweezers, which is part of the SSA 6 manual solid sampling accessory (Analytik Jena), was used to transfer the SS platforms to the atomizer. An automatic introduction accessory for solid samples, Model SSA600L (Analytik Jena), which also makes possible to automatically add modifier solutions etc. on top of the solid samples, was used in the experiments carried out at Analytik Jena. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as the purge gas with a flow rate of 2.0 L min<sup>-1</sup> during all stages, except during vaporization, where the internal gas flow was stopped.

The molecular absorption of fluorine has been measured via the CaF molecule, monitoring only the center pixel (CP) at 606.440 nm for lower fluorine concentrations up to about 1000 mg kg<sup>-1</sup>, and the less sensitive line at 606.033 nm was used for higher fluorine concentrations. The determination via InF has been carried out at the 234.718-nm line using three pixels for evaluation, and the determination via GaF at two different wavelengths, depending on the fluorine concentration in the sample. Low concentrations up to about 200 mg kg<sup>-1</sup>

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