

OP-04

EXTRACTION AND ETAAS DETERMINATION OF TRACE ELEMENTS IN MINERALS

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Abstract

Determination of trace elements in minerals is important to determine the purity of minerals, to determine the presence of very rare but important elements in the minerals, which could be extracted and used, to obtain data which give very important information on the geology of the mines and mineral localities. In this work a review of trace elements determination in minerals by electrothermal atomic absorption spectrometry (ETAAS) with previous extraction separation is given.

Introduction

The knowledge of the kind and amount of trace elements incorporated in the structure of a natural mineral could help to answer on many questions about mineral deposit formation, its physical and chemical properties, crystalline deformations, etc. Because trace elements present in the natural structure basically change the primary physical and chemical characteristics of the minerals, they may limit its application for many useful purposes. Therefore, development of appropriate methods for determination of trace elements in mineral matrices has a great importance. Electrothermal atomic absorption spectrometry (ETAAS) is one of the most frequently used methods for determination of trace elements in mineral samples¹. However, very often, some additional operations in the preparation of mineral samples are necessary because of matrix interferences. In order to avoid these interferences and because of the very low concentration of trace elements in the samples investigated, it is necessary to separate and concentrate those elements from the samples. Liquid-liquid is the most present methods for trace elements separation and concentration. In this work a review of the application of extraction for trace elements separation and concentration and their determination in minerals by ETAAS is given.

Matrix Interferences

Matrix interferences are very often the most serious problem in ETAAS determination of trace elements in minerals. Matrix elements as a main constituent of the minerals have very high concentrations in the solutions after dissolution of the mineral samples. In some cases, depending on the matrix and matrix interferences it is possible to determine trace elements in minerals directly from the solution. Thus, a direct determination in silicate minerals is suggested for the determination of Pb, Co and Be, Au, Pb^{2,3}. Direct determination is applied also for iron matrix [4] or sulfide minerals⁴⁻⁶. Direct determination of trace elements was performed also using direct introducing of solid mineral samples into a graphite furnace, for silicate samples^{7,8} or other type of minerals⁹⁻¹¹.

In most case interferences from the matrix, especially from the matrix elements, which are constitutive elements of the minerals, are very high and direct determination of trace elements is not possible. Thus, the main macroelements of minerals which were the subject of our investigation are sulfides of arsenic (realgar and orpiment), arsenic and thallium (lorandite), antimony (stibnite) iron (marcasite, pyrite), lead (galena), zinc (sphalerite), as well as carbonates (dolomite, calcite, aragonite). The investigations showed that in the case of gold determination in arsenic, antimony, iron, and thallium sulfide minerals or in dolomite, the absorbance of gold decreased¹². Also, in the case of the determination of silver we found that the interfering elements (especially when they are present in high concentration) tend to decrease the absorbance of silver¹³. It was also found¹⁴ that thallium, arsenic, iron and calcium interfere on the determination of lead by decreasing the Pb absorbance.

The interferences of thallium, arsenic, antimony, iron, lead and zinc as matrix elements on copper determination were also studied¹⁵. The results show the same effect. In some cases spectral interference from iron was found (in the presence of high amounts) in the determination of gold¹² or thallium¹⁶ which is solved by previous precipitation of iron¹² or by mathematical correction¹⁶. It should be noted that the results showed that background absorption was present and that the use of background correction was necessary.

In cases when matrix interferences do not give an opportunity for direct determination of trace elements, matrix modification or separation of investigated elements is necessary. Thus, in the case of the determination of nickel and cobalt in silicate minerals, NH₄F was added as a matrix modifier¹⁷; am-

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monium hydrogen phosphate was added in the determination of silver in different geological materials¹⁸ or ascorbic acid in molybdenum determination¹⁹ or in silicates²⁰. In the case of relatively high concentration of thallium in some sulfide and carbonate mineral samples modification with sulfuric acid is satisfactory to eliminate matrix interferences⁴, but in cases of trace concentration it is necessary to use another matrix modifiers²¹ or even to separate thallium from the matrix¹⁶.

Nickel is used as matrix modifier in many publications for trace elements ETAAS determination of Ga and In²² in different geochemical materials, Sb or Se in silicate and sulfide materials²³. In some cases for trace element determination in mineral samples the application of different matrix modifiers is also suggested²³⁻²⁵.

Separation and Concentration

In most cases, the elimination of a matrix, and the concentration of trace elements from minerals is performed by different methods. Thus, there are a few papers dealing with concentrations of some trace elements by ion exchange separation, such as determination of some rare elements in silicate minerals²⁶ or Au, Ag and Cd²⁷ on Dowex ion-exchange resin column or on some other column for the determination of different trace elements [28-30].

However, the most present methods for trace elements separation and concentration were performed by extraction of their metal complexes into organic solvent. There are cases of direct extraction of chloride, bromide or iodide complexes of trace elements into some organic solvent, as for Ti^{2,4,31,32}, Te^{33,34}, Au^{3,12,35,36}, Pt³⁷, Pd³, As^{37,38}, Sb³⁹ or Se³⁹.

There are different methods for trace elements separation and concentration from mineral matrix followed by ETAAS determination, applying extraction of complexes with some organic ligands into different organic solvent: TOMA in xylene⁴⁰, di-2-ethylthiophosphoric acid in toluene⁴¹, *N*-benzoyl-*N*-phenylhydroxylamine in toluene⁴², trioctylmethylammonium in MIBK⁴³, petroleum sulfides in toluene^{44,45}, bis(2-ethylhexyl) dithiophosphate/*p*-octylamine in toluene⁴⁶ or in cyclohexane⁴⁷, isoamyl acetate¹⁶, trioctylphosphine oxide in MIBK⁴⁷, different dithiocarbamates in toluene²¹, in methylisobutyl ketone (MIBK)^{15,48-51}, in CCl₄^{14,15,48,49} or in CHCl₃^{15,51}, diphenyl thiocarbamate in MIBK, butyl acetate or toluene¹³, dibutyl sulfide in toluene⁵².

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