cadmium coflotations performed separately by each collector were established. The results of ETAAS analyses are compared with those obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

**USING OF CHEMICAL MODIFIERS IN ETAAS DETERMINATION OF SELENIUM IN COPPER CONCENTRATE**

Bora Ristova¹, Trajče Stafilov², Dragan Mihajlović³

¹ Mines and Flotation of Copper “Bučim”, Radoviš, Macedonia
² Institute of Chemistry, Faculty of Science, Sts., Cyril and Methodius University, POB 162, 1000 Skopje, Macedonia; e-mail: trajcest@iunona.pmf.ukim.edu.mk
³ RZ Technical Control, 1000 Skopje, Macedonia

**Key words: copper concentrate, selenium, determination, matrix modifiers, ETAAS**

Using of different chemical modifiers in the determination of some elements in copper concentrates by ETAAS has been proposed. Different ammonium salts (ammonium molibdate, ammonium vanadate, ammonium nitrate, ammonium sulfate and ammonium dichromate), Ba(OH)₂, H₃BO₃, and V₂O₅, compared with Ni(NO₃)₂ as a classical modifier for thermal stabilization of selenium were investigated. It was found that ammonium dichromate give the best results as a modifier. In presence of ammonium dichromate, pyrolysis temperature was extended up to 1100 °C. In the atomization stage, a constant absorbance was obtained between 1900 and 2300 °C. After preliminary investigation, the method for determination of selenium in copper ores and concentrates was developed. Limit of detection of 1 ng/mL Se was achieved, without preconcentration of Se or separation of sample matrix.

**DETERMINATION OF SOME TRACE ELEMENTS IN MARCASITE AND PYRITE BY ATOMIC ABSORPTION SPECTROMETRY**

Trajče Stafilov¹, Dragica Zendelovska²

¹ Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, P.O. Box 162, 91001 Skopje, Macedonia; e-mail: trajcest@iunona.pmf.ukim.edu.mk
² Institute of Preclinical and Clinical Pharmacology with Toxicology, Faculty of Medicine, Sts. Cyril and Methodius University, 50 Divizija, 1000 Skopje, Macedonia

**Key words: Trace elements, determination, marcasite, pyrite, AAS**

A method for the determination of chromium, cobalt, lead and nickel in marcasite and pyrite (FeS₂) by Zeeman electrothermal atomic absorption spectrometry (ETAAS) was purposed. Interferences were investigated by measuring the absorbance of investigated elements in series of samples with varying mass ratios of investigated elements and iron as potential interfering element. It was found that iron tends to decrease absorbance of Co, Cr, and Pb and increase the absorbance of Ni in their ETASS determination. Therefore, to avoid the interference of iron, a method for extraction of iron and determination of investigated elements in inorganic phase was
Iron was extracted by isoamyl acetate in hydrochloride solution. Optimization of extraction procedure was performed. It was found that quantitative extraction of iron was obtained when the concentration of HCl is over 7 mol/l. It was also found that the recovery of iron depends on the mass of iron and it was determined that a mass of up to 0.5 g of iron mineral is a maximal mass of mineral sample.

Optimal instrumental parameters used for these determinations are: temperature and time for drying 120 °C, 30 s, for pyrolysis 300 °C for Pb, 750 °C for Co, 800 °C for Ni and 1000 °C for Cr, with 3 s, for atomizing 2100 °C for Pb, 2300 °C for Co, 2400 °C for Ni and 2500 °C for Cr and for cleaning temperature of 2500 °C, with 3 s.

The procedure was verified by the method of standard additions. The results of Pb, Co, Cr and Ni determination and the recovery show that satisfactory results were obtained (from 96.2 to 102.5 %). The determination of these elements was also performed for iron ore reference samples.

Investigated mineral samples originate from Alšar (marcasite) and Bučim (pyrite) mines from the Republic of Macedonia. It was found that the detection limits of the method are 10 ng/g for Ni and Cr and 30 ng/g for Pb and Co, determined by Zeeman ETAAS. Relative standard deviations range from 0.55 to 2 %.

INFLUENCE OF TEMPERATURE AND MOBILE PHASE COMPOSITION ON RETENTION PROPERTIES OF THE MACROLIDE ANTIBIOTICS CLARITHROMYCIN AND ROXITHROMYCIN IN REVERSED-PHASE LIQUID CHROMATOGRAPHY

A.Pappa-Louisi, P.Agrafiotou, G.Zissopoulou, P.Liatsi

Laboratory of Physical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece; apappa@chem.auth.gr

Key words: clarithromycin, roxithromycin, HPLC retention.

The reversed-phase (RP) chromatographic behaviour of the macrolide antibiotics clarithromycin and roxithromycin was extensively studied as a function of mobile phase composition and column temperature. Experimental retention data sets of these drugs obtained on two octadecyl silica based columns in buffered mobile phases of pH 7.0 modified with one, two or three of the following organic solvents: methanol, acetonitrile and isopropanol were fitted through adequate equations describing the retention of a solute with the organic modifier content in the mobile phase. The physical meaning of the fitted parameters was discussed besides the dependence of these equation coefficients on the type of organic modifier(s) and composition of mobile phase. The van't Hoff plots (plots of the natural logarithms of the capacity factors of solutes against the inverse of absolute column temperature) for probe macrolides in different binary, ternary and quaternary eluent systems showed good linearity over the range of temperature from 25 to 70° C. However, the sorption enthalpies of these solutes calculated from the slopes of the corresponding regression lines were exothermic (i.e. negative) in all mobile phases, except for the case where acetonitrile or mixture of acetonitrile- isopropanol (6/1, v/v) were used as organic modifiers. The results of our study provide a satisfactory thermodynamic explanation for the retention processes of these macrolides in RP-HPLC and give additional information on the selection of optimal separation conditions for the determination of clarithromycin in human plasma using roxithromycin as an internal standard and vice versa.