

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

BORA RISTOVA¹, TRAJČE STAFILOV² AND 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

Abstract

Using of different chemical modifiers in the determination of some elements in copper concentrates by ETAAS has been proposed. Different ammonium salts (ammonium molybdate, ammonium vanadate, ammonium nitrate, ammonium sulfate and ammonium dichromate), $\text{Ba}(\text{OH})_2$, H_3BO_3 , and V_2O_5 , compared with $\text{Ni}(\text{NO}_3)_2$ 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.

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

1. Introduction

The high volatility of selenium, low wavelength (196 nm) of his resonance line, and presence in anionic form are some of basic problems in electrothermal atomic absorption (ETAAS) determination of this element. For the elimination of matrix interference in charring stage, different modifiers were proposed: $\text{Ni}(\text{NO}_3)_2$ [1], Pd [2], Pd + ascorbic acid [3], Ni + $\text{Mg}(\text{NO}_3)_2$ [4] etc. Our investigation shown that ammonium dichromate can be used as a successfully chemical modifier in ETAAS determination of selenium in many types of matrix.

2. Experimental

Instrumental

All measurements were performed on Varian SpectrAA 640Z AAS with Zeeman background correction. The optimal instrumental conditions estimated as optimal are given in Table 1.

Procedure

Five grams of copper concentrate were taken into a beaker of 400 ml and 45 ml concentrated HCl and 15 ml concentrated HNO_3 were added. This solution was heated 30-40 min on a hot plate. Then, 25 ml redistilled water were added and the solution was heated for another 15 min. The solution was cooled and filtered off. The filtrate was collected in a volumetric flask of 100 ml, and filled with redistilled water. From this solution the determination of the investigated elements by AAS was performed.

Table 1. Optimal instrumental parameters for selenium determination by ETAAS

Wavelength	327.4 nm
Spectral width slit	0.5 nm
Calibration mode	Peak height
Lamp current	4 mA
Background correction	Zeeman
DRY: Temperature	90 °C
Time	20 s
Ramp time	2 s
CHARRING: Temperature	1100 °C
Time	20 s
Ramp time	1 s
ATOMIZING: Temperature	2300 °C
Time	3 s
Ramp time	0 s
GAS	Argon

3. Results and Discussion

The high volatility, low wavelength (196 nm) of its resonant line, and its presence in anionic form are some of the basic problems in Se determination by ETAAS. Due to the volatility of selenium compounds and for the elimination of matrix interference in the pyrolysis stage, satisfactory chemical modifiers must be used which prevent their loss during the pyrolysis stage. On the other hand, the value of the bond energy of Se-O in SeO_2 is high, which requires a relative high temperature of atomization (2600 °C).

Several chemical modifiers for thermal stabilization of selenium were investigated: BaO as a modifier with base characteristics (added in graphite tube in form of saturated solution of $\text{Ba}(\text{OH})_2$), B_2O_3 as a relative neutral matrix (added in form of H_3BO_3), and V_2O_5 as a modifier with acid characteristics (added in form of ammonium vanadate). The solutions of the modifiers were injected into graphite atomizer before solution of analyte (H_3BO_3), immediately after injection of analyte aliquot ($(\text{NH}_4)_2\text{VO}_4$), and after evaporation of the sample solution by heating of tube ($\text{Ba}(\text{OH})_2$).

Those interferences were corrected by using of several chemical modifiers for thermal stabilization of Se: different ammonium salts (molybdate, vanadate, nitrate, sulfate and dichromate), $\text{Ba}(\text{OH})_2$, H_3BO_3 , and V_2O_5 , compared with $\text{Ni}(\text{NO}_3)_2$ as a classical modifier for Se. 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 (Fig. 1). In the atomization stage, a constant absorbance was obtained between 1900 and 2300 °C (Fig. 2). Different temperature gradients in pyrolysis and atomization stages were applied.

After preliminary investigation, the method for determination of selenium in copper ores and concentrates was developed. Limit of detection of 1 ng/ml e was achieved, without any preconcentration of Se or separation of sample matrix.

The methods were checked by the standard addition method and by comparison of the results obtained by this method and by spectrographic analysis and by their application to referent standard samples.

4. Conclusion

A method has been developed for determination of selenium in copper ores and concentrates by Zeeman ETAAS. Several chemical modifiers were used for a prevention of the volatilization of selenium: boric acid, ammonium molybdate, ammonium vanadate, ammonium nitrate and ammonium dichromate. The best results were obtained using ammonium dichromate as a modifier. Charring temperature was extended up to 1200 °C. In the atomization stage, a constant absorbance was obtained between 1900 and 2300 °C. Agreement of the results, obtained by proposed method and ICP spectrometry, suggest that suggested ETAAS method is reliable.

References

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