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Determination of Hg from Cu concentrates by X-ray fluorescence through preconcentration on polyurethane foam

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Abstract

A methodology was developed for the separation and determination of microamounts of mercury from copper concentrate samples by wavelength dispersive X-ray fluorescence (WDXRF) after solid-phase extraction of mercury from iodide medium using polyurethane foam (PUF). The best sorption conditions for the Hg–KI–PUF system were settled using X-ray fluorescence technique after collection of ground PUF on a filter paper by vacuum filtration and direct measurement of the intensity signal of the sorbed mercury on PUF. The main parameters of sorption such as iodide concentration, pH, shaking time and sample dilution effect were studied. The system shows rapid kinetic sorption and maximum X-ray intensity signal was achieved after shaking for 2 min a 0.01 mol l^{-1} iodide solution containing microamounts of mercury in the pH range from 1.0 to 9.0. Effective sorption up to a volume of 0.9 l allows preconcentration of mercury. A linear fit up to 50 μg mercury was obtained by the plot of the initial mercury mass in the bulk solution (0.5 l) vs. its respective XRF intensity signal measurement on ground PUF after the sorption process. The calibration sensitivity, quantification and detection limits found were 9.09 CPS μg^{-1}, 9.0 and 2.7 μg, respectively. The sorption of many elements was also evaluated under the best conditions. High concentrations of Cu(II) and Fe(III) interfere seriously. Mercury-selective separation could be achieved using citrate or EDTA as masking agent; no interference due to copper matrix samples was observed in citrate medium. This methodology was evaluated by recovery for mercury determination in copper concentrate ore samples supplied by a mining industry and copper sulfate salts; the results were between 98% and 106%.
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1. Introduction

Mercury environmental pollution derives from a wide variety of sources such as its mining, the smelting of mercury-bearing ores, coal and oil combustion and others, besides its usage in many industrial products. With the aim to reduce the discharge and disposal of mercury-containing products, it is recovered from materials as electronic devices, dental amalgams, batteries, thermometers and mainly from the spent catalyst used in the production of chlorine and caustic soda. Nearly all mercury mined today is extracted from cinnabar (HgS) ores; nonferrous metal ores as cooper, gold, lead and zinc often contain trace amounts of mercury that is emitted to the atmosphere during smelting of the concentrate mineral with generation of enriched mercury fly ash, dust and slag [1–3].

Among the instrumental techniques used for mercury determination, the cold vapor atomic absorption spectrometry (CVAAS) is the most widely used one, but it is not free from interferences. Chemical interferences due to elements present in the sample, particularly those that undergo a reduction to metals and form amalgams, constitutes the most serious one. Therefore, samples containing large amount of copper besides having higher consumption of reagent reductor can introduce serious error in CVAAS analyses of mercury [4] and need special treatment. Welz and Schubert-Jacobs [5] have applied a 5 mol l^{-1} HCl solution with Fe(III) addition to eliminate the effects of Cu, Ni and Ag, while Szmyd and Baranowska [4] have used a solution of 1,10-phenanthroline and thiosemicarbazide in 1.5% HCl solution as a masking agent. Sometimes, a special

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sample treatment associated with separation or preconcentration procedures before measurement of mercury contents can be applied.

Solid phase extraction (SPE) is an effective process usually adopted for metal separation in analytical chemistry methodologies. A number of solid sorbent systems for off-line preconcentration of mercury such as activated carbon [2], inorganic metal oxides [6], and solid supports holding special reagents [7–10] have been known.

Recently, the sorption of mercury from thiocyanate solution by polyurethane foam (PUF) was thermodynamically evaluated by using ^{203}Hg radiotracer and the maximum sorption of mercury was achieved in 1.0 mol l^{-1} thiocyanate solution at pH 1.0. Cations as Zn(II), Cu(II), Fe(III), Mn(II), Co(II) and Sr(II), as well as some electrolytes as chloride, fluoride, acetate, molybdate, EDTA and thiosulfate, were responsible for a decrease on the sorption percent of Hg–SCN complex [1]. Polyurethane foam (PUF) has also been used as a solid sorbent in separation and preconcentration procedures for the determination of metal elements by X-ray fluorescence techniques [11–15]. Peräniemi and Ahlgrén [16] have also reported a preconcentration methodology combined with X-ray fluorescence for the determination of arsenic, selenium and mercury in aqueous solution using zirconium-loaded activated charcoal as adsorbent.

This paper shows a selective and simple procedure to separate mercury from solutions of low iodide concentration using PUF as a solid sorbent. The methodology was evaluated for trace mercury determination in copper concentrate samples through measurements of mercury direct into PUF by wavelength dispersive X-ray fluorescence (WDXRF).

2. Experimental

2.1. Reagents

Double-distilled water was used to prepare the solutions and all reagents were of analytical grade, unless otherwise specified.

An open-cell, polyether-type commercial polyurethane foam (PUF), Scotch-Brite™ (3 M), was ground in a blender with double-distilled water, squeezed between nylon disks, dried in a stove at 80 °C and stored in a polypropylene flask.

Mercury solutions used were prepared from dilutions of a standard stock mercury solution (MERCK) of 1.0 g l^{-1} in 0.1 mol l^{-1} nitric acid.

2.2. Instrumentation

A Rigaku, model B3, wavelength dispersive X-ray fluorescence spectrometer with a silver anode X-ray tube operated at 40 kV and 30 mA, a LiF analyzer crystal, and a NaI–Tl scintillation detector, was used to measure the intensity fluorescence signal of mercury L_α line (2θ=35.92) after a 40-s counting time.

An Analyser 300 pH meter was used for pH values measurements.

A VKS-100 Mechanical Shaker operated at 100 cpm was used for shaking the system by batch process.

2.3. General procedure

The experiments were carried out in a batch process at ambient temperature (25±2 °C). An aliquot of the mercury stock solution containing up to 50 μg were transferred to an Erlenmeyer stoppered flask of 50 ml. The volume was set to 25 ml with double-distilled water after addition of 4.15×10^{-2} g of KI salt to make a 0.01 mol l^{-1} solution. Afterward, a 100-mg portion of ground PUF was added, the Erlenmeyer was stoppered and the system mechanically shaken for 10 min. The PUF was then filtered by means of a Millipore® vacuum system using a rapid filtration disk paper to obtain a homogeneous PUF tablet of 2.0-cm diameter. The tablet was dried by squeezing under vacuum, covered with a Mylar® film and placed to the XRF spectrometer to measure the characteristic intensity of the mercury sorbed on PUF.

3. Results and discussion

3.1. Effect of pH and shaking time

The influence of the solution pH and shaking time on mercury sorption were studied in distinct experiments. Mercury (25 ml, 2 μg ml^{-1}) in 0.01 mol l^{-1} KI solutions were extracted by PUF as described in "General procedure". The pH was adjusted from 1.0 to 9.0 by proper addition of hydrochloric acid or sodium hydroxide solution. The shaking time was varied from 2 to 60 min. After the process of mercury sorption, the samples were placed to the spectrometer and the characteristic intensity of Hg was measured. The system Hg–KI–PUF has pointed out a very rapid kinetic sorption behavior with a linear and constant intensity signal of mercury within the whole pH and time range investigated. As the results have shown no dependence on pH and time, a pH value of 5.0 and a shaking time of 10 min were chosen to be used in the experiments.

3.2. Effect of iodide concentration

To find the best iodide concentration required for maximum sorption of mercury, 50 μg of mercury in 25 ml potassium iodide solution in the concentration range from 10^{-7} to 5×10^{-2} mol l^{-1} were tested following the method described in "General procedure". The effect of iodide concentration on mercury sorption is shown in Fig. 1. The sorption efficiency increases with iodide concentration increase and reaches a constant signal value over 5.0×10^{-3}

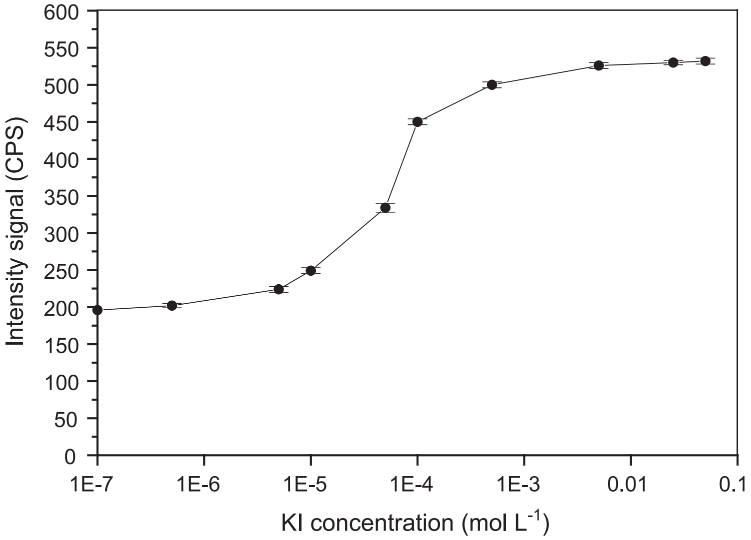

Fig. 1. Effect of KI concentration on mercury sorption by PUF (100 mg PUF; 50 μg Hg; 25 ml; 10 min).

mol l^{-1}, when the system exhibits the highest and almost constant sorption. The stepwise intermediate complexes of mercury iodide species are $[Hg(I)]^+$, $[Hg(I)_2]$, $[Hg(I)_3]^-$ and $[Hg(I)_4]^{2-}$. On the basis of their stability constants of, respectively, $10^{12.87}$, $10^{23.82}$, $10^{27.60}$ and $10^{29.83}$ [17] and the percentage of the species present in solution as a function of KI concentration, the neutral HgI_2 species is probably responsible for the sorption of mercury on PUF from very low iodide concentrations up to 1.0×10^{-5} mol l^{-1}. From a KI concentration range from 1.0×10^{-5} to 5.0×10^{-3} mol l^{-1}, an increase in mercury sorption was achieved. This behavior may be due to a more favorable kind of sorption related to increasing of ionic species in solution such as $[Hg(I)_3]^-$ (30%) and $[Hg(I)_4]^{2-}$ (70%) at 5.0×10^{-3} mol l^{-1}. According to the cation chelation sorption mechanism [18], these species form ionic pair with K^+ positive sites in the foam. This mechanism states that the polyethylene oxide portion of the foam can assume a helical structure with inwardly directed oxygen atoms defining cavities where the complexation of simple cations such as K^+ occurs. The complex anions as $[Hg(I)_3]^-$ and $[Hg(I)_4]^{2-}$ are retained as counter ions to the cations captured in the cavities. The shape of the curve presented in Fig. 1 characterizes a typical mixed sorption mechanism where has occurred a translation from species more weakly sorbed into another one with higher sorption affinity. A potassium iodide concentration above 5.0×10^{-3} mol l^{-1} was established as optimum for mercury sorption on PUF.

3.3. Effect of foreign ions

The effect of foreign ions on the Hg–KI–PUF system was examined under the best extraction conditions by XRF measurements of the mercury intensity signal on PUF after the sorption process. The results show that the presence of 8 mg sodium, potassium, calcium, magnesium, aluminum, chloride, sulfate, citrate and EDTA did not interfere on mercury sorption (25 ml, 0.32 μg ml^{-1} Hg, 0.025 mol l^{-1} KI). Interferences were found in the presence of 8 mg iron or copper, respectively, as iodide in acidic medium, reduces iron(III) to iron(II) and copper(II) to copper(I) (CuI precipitation), with iodine formation. To eliminate the copper and iron interferences, sodium citrate was tested as a masking agent. Fig. 2 shows the sorption behavior of the system in a higher concentration range of sodium citrate. The results present a small increase on the mercury intensity signal until 0.1 mol l^{-1} citrate concentration, decreasing slightly afterward, to a linear and constant signal up to 0.5 mol l^{-1} citrate concentration. The same experiments were carried out for copper and iron in a 0.5 mol l^{-1} citrate medium and no interference for the both elements was observed. Also, no interference was obtained on the intensity signal of mercury (8 μg) in the presence of each 8 mg of Zn(II), Fe(III), Cd(II), Mo(VI), Pb(II), As(III), Bi(III), In(III), Cu(II) and Al(III) using 0.5 mol l^{-1} sodium citrate as masking agent. A decrease of around 30% in the mercury intensity signal was obtained when a 0.1 mol l^{-1} EDTA solution was used as masking agent at the same conditions, probably due to the competition between iodide and EDTA mercury complexes. The selectivity achieved for the Hg–KI–PUF system using citrate medium leads up to apply the methodology to determine trace mercury in copper concentrate samples.

3.4. Effect of sample dilution

To verify the effect of the sample volume on the sorption of 50 μg mercury from 0.025 mol l^{-1} iodide solutions, the sample volume was ranged from 25 to 900 ml for a shaking time of 1 h, following the “General procedure”. The results show a slight but steady decrease in the intensity signal of the mercury sorbed on PUF with increasing dilution volume. This effect is probably due to the mass/volume ratio

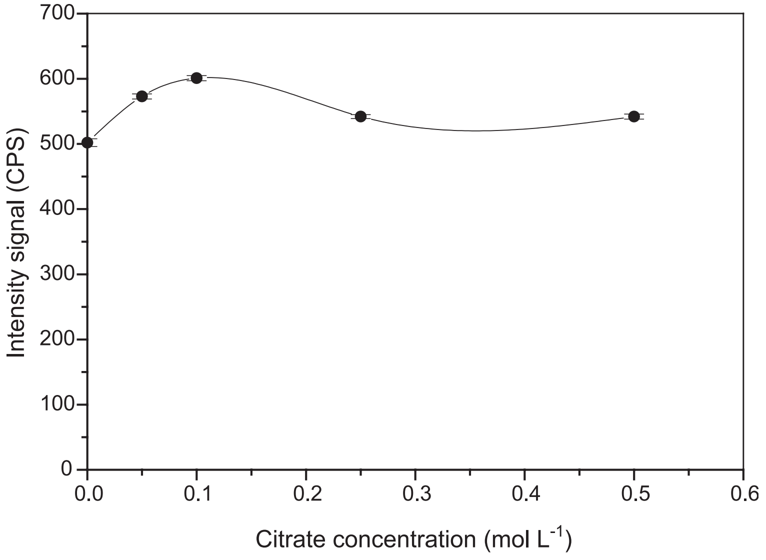

Fig. 2. Effect of citrate concentration on mercury sorption by PUF (100 mg PUF; 50 μg Hg; 0.025 mol l^{-1} KI; 25 ml, 10 min).

dependence on time attainment of the sorption equilibrium of the mercury species on PUF as a result of the decrease of the mercury concentration in the bulk solution with time and the reduction of the number of the effective shocks between the remained mercury species in solution and the sorbent. However, the rapid kinetic and high-affinity sorption between the mercury iodide species and PUF still allows an almost quantitative sorption of mercury for the whole volume range studied as can be seen in Fig. 3. Therefore, the proposed procedure using the KI–PUF system permits an effective sorption of mercury up to 900-ml sample volumes with preconcentration factors around 36-fold and can be applied for further mercury determination in sample solutions at ppb levels by WDXRF spectrometry.

3.5. Analytical characteristics of the Hg–KI–PUF–WDXRF system

To assess the behavior of the studied system, the parameters of mercury sorption into PUF were set and the mercury amount in 500 ml samples (0.5 mol l^{-1} sodium citrate) was varied from 10 to 50 μg. A linear fit up to 50 μg mercury was obtained by the plot of the initial mercury mass in the bulk solution vs. its respective X-ray fluorescence intensity signal (I) on ground PUF after the sorption process. The linear calibration curve fitted is expressed as: I (CPS)=9.09 [Hg μg]−0.18 (R^2=0.9985), where the slope corresponds to the calibration sensitivity in CPS μg^{-1}; no meaningful change in the slope was verified when mercury was measured in high concentration of copper sulfate solution using

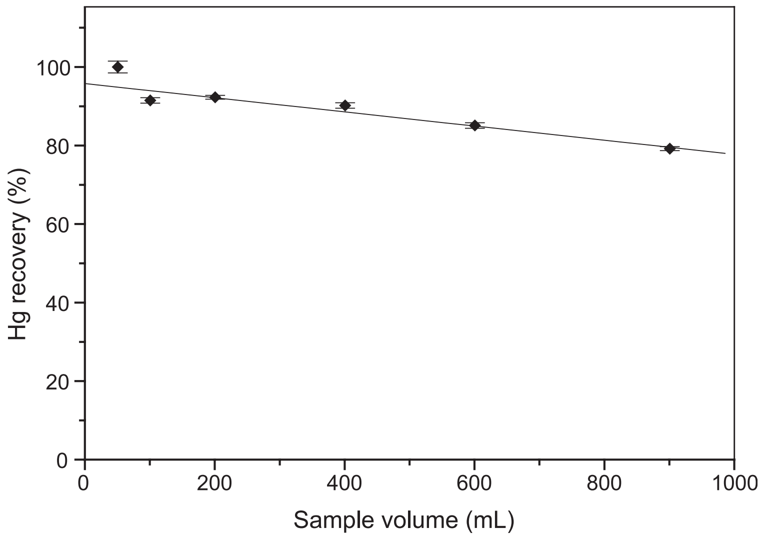

Fig. 3. Effect of sample volume on mercury sorption by PUF (100 mg PUF; 50 μg Hg; 0.025 mol l^{-1} KI; 60 min).

Table 1
Determination of mercury in copper concentrate ores and copper sulfate salts by the KI–PUF–WDXRF system

Copper concentrate ores and sulfate salts	Hg added (μg)	Hg found (μg)	Recovery (%)
C17–22[a]	0.00	26.4	101.6
	25.0	52.2	
C9–43	0.00	3.63	98.3
	10.0	13.4	
C2–163	0.00	4.63	98.4
	10.0	14.4	
$CuSO_4$ commercial	5.00	5.30	106.0
$CuSO_4$ p.a.	5.00	5.15	103.0
$CuSO_4$ commercial	25.0	25.1	100.5
$CuSO_4$ p.a.	25.0	25.1	100.5

[a] Copper concentrate mass=0.5000 g.

the same calibration conditions. The detection limit (3σ) and quantification limit (10σ) found were of 2.7 and 9.0 μg, respectively, where (σ) is the standard deviation of the mean intensity signal measurements of 10 PUF blank samples at mercury Lα analytical line for a counting time of 40 s.

3.6. Application

The performance of the system Hg–KI–PUF–XRF for separation and determination of mercury from copper matrix samples were evaluated by addition and recovery of known amounts of mercury to copper concentrate ores and sulfate salt samples. The ore sample (up to 1.0000 g) in 100-ml PTFE flasks were wetted with water and succeeded by 2 ml bromine addition. After 2 min, a 10 ml sulfuric and nitric acid aqueous solution was added (0.5 H_2SO_4:6.5 HNO_3:3 H_2O v/v). The system was warmed almost to dryness, cooled at ambient temperature and diluted up to 500 ml. Adjustments of pH, 0.5 mol l^{-1} sodium citrate and 0.025 mol l^{-1} potassium iodide concentration were done by addition of NaOH (tablet) and proper amounts of the solid KI salt, respectively, and then proceeded as in the “General procedure”.

The results in Table 1 show that mercury at trace level amount can be determined in copper concentrate samples with recoveries between 98% and 106% for the whole procedure.

4. Conclusion

The sorption of the system Hg–KI on PUF shows rapid kinetic and no influence of pH in the range from 1.0 to 9.0 allowing effective sorption of mercury into PUF from samples solutions up to 900 ml with low iodide concentrations. These advantages permit preconcentrate and determine mercury at ppb level in aqueous solution. The direct determination of Hg on PUF by WDXRF is linear up to a mercury amount of 50 μg when a 0.5-l sample volume was used, with a detection and quantification limit of 2.7 μg or 5.4×10^{-3} mg l^{-1} and 9.0 μg, respectively. This performance is better to that reported by Peräniemi and Ahlgrén [16] in relation to mercury preconcentration and determination using zirconium-loaded activated charcoal as adsorbent and EDXRF where a detection limit of 5.8×10^{-2} mg l^{-1} was achieved. The methodology is highly selective for mercury since citrate or EDTA can be used as masking agent for Cu and Fe interferences and no meaningful change in the slope of the calibration curve was observed. These system features have enabled the successful determination of trace amount of mercury in copper concentrate ores and copper sulfate salts with recoveries between 98% and 106%.

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