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AAS determination of trace elements in high-purity gold after matrix separation by solvent extraction

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Summary. A method is described for the determination of 20 trace elements in gold of a qualification of about 4 – 5 N. The matrix is separated by solvent extraction into methylethylketone/chloroform and the trace elements are determined in the aqueous phase by AAS (flame or graphite furnace). The procedure is optimized as to minimize the number of contamination sources.

Introduction

The use of high-purity gold in microelectronics has prompted the interest towards trace analysis in this metal during the last decades [1 – 10]. The application of AAS methods to this analysis required the use of several approaches for eliminating or reducing the matrix interferences – standard addition [1], buffering [2] or matrix separation [3].

Gold separation by solvent extraction is a well-known technique employing mainly oxygen- or sulphur-containing organic solvents [3, 11 – 13].

The extraction system methylethylketone/chloroform ($MEK/CHCl_3$) has been applied to the separation of microquantities of gold from accompanying macrocomponents in iron pyrites, copper and lead concentrates [13].

The purpose of the present work was to study the possibilities of this extraction system for the separation of the gold matrix with a view to the subsequent AAS determination of the microtrace content.

Experimental

Reagents. Nitric acid and hydrochloric acid "SUPRAPUR" from Merck. Methylethylketone and chloroform were used after distillation. The standard solutions of the elements were prepared from Merck titrisols with concentrations 1 mg/ml. Redistilled water from a quartz still was employed.

Apparatus. The atomic absorption spectrometer PU SP192 equipped with a fast graphics registration device was used for the measurements in an air-acetylene flame at the most sensitive lines of the elements. µl volumes of the solutions were introduced by pulse aspiration (dipping method).

The atomic absorption spectrometer PE 400 with deuterium background correction and graphite furnace HGA 76B was used for the electrothermal AAS measurements. As, Sb, Sn, Bi, Se and Te were determined on a ZrC-coated platform in a pyrolytically coated graphite tube using $PdCl_2$ (1 mg/ml) as a modifier. Ash – 1300° C, atomization – 2400° C, max. power, gas stop. Pt, V and Al were determined in a pyrolytically coated graphite tube without a modifier. Ash – 1200° C (Pt), 1400° C (Al), 1600° C (V), atomization – 2650° C for the three elements, max. power, gas stop.

Sample dissolution and extraction were performed in PTFE centrifugal tubes (NALGENE) of 50 ml volume. Other reaction vessels needed were of quartz or polypropylene. A box with clean air supply was used.

Procedure. Place 0.5 g of the gold sample into a PTFE centrifugal tube (NALGENE) with a volume of 50 ml. Etch with nitric acid (1 + 1), wash with water and dissolve with 2 ml of *aqua regia* using an IR heater. Evaporate the solution to a wet residue and dissolve it in 3 ml of 1 mol/l hydrochloric acid (flame AAS) or in 3 ml of 1 mol/l nitric acid (graphite furnace AAS). Extract the solution with 25 ml of (1 + 1) $MEK/CHCl_3$ mixture in the tube for 10 min. After centrifugation transfer the upper (aqueous) layer into another tube by means of an automatic pipette, add another 5 ml of the extractant and shake for another 10 min. Centrifugate and transfer the aqueous phase into a polypropylene tube of 3 ml volume and subject to analysis. Calibrate towards aqueous standard solutions prepared in the corresponding acid presaturated with the extractant. Run a blank sample through the whole procedure.

Results and discussion

Upon dissolution of gold with *aqua regia*, the complex ion $[AuCl_4]^-$ is obtained, which is very stable ($\log K' = 29.6$) [14]. The value of the stability constant reveals that even with a minimal concentration of chloride ions, the equilibrium should be practically shifted towards the formation of this complex.

It has been found [15] that gold(III) extraction from hydrochloric acid solutions with saturated aliphatic ketones, e.g. methylethylketone, takes place by the hydrate-solvate mechanism both in the presence and absence of an inert solvent, the composition of the extracted complex being:

$$H_3O^+[H_2O]_m[MEK]_n[AuCl_4]^-.$$

The inert solvent, chloroform in this case, causes an enhancement in selectivity of the extraction system towards gold [13] due to the decreased active concentration of ketone.

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Table 1. Extraction of 0.5 g of gold with (1 + 1) MEK/$CHCl_3$ from hydrochloric acid medium

Molarity HCl[a]	0.5		1.0			
$V_{aq}:V_{org}$	1:2	1:4	1:2	1:4	1:4 1:2	1:8 1:2
Concentration of Au(III) in the aq. phase after extr., %	8	7	4	0.5	0.2	$<10^{-4}$

[a] The acidity of the aqueous phase decreases after the first extraction step (from 1 mol/l to approx. 0.6 mol/l HCl), but no correction of acidity is required

Table 2. Recovery of trace elements in the aqueous phase after the separation of 0.50 g of gold by solvent extraction. N = 14, RSD is between 2 and 10%

1 mol/l HCl, Flame AAS			1 mol/l HNO_3, ETAAS		
Element	added µg	found µg	Element	added µg	found µg
Cu	0.5	0.48	Bi	0.2	0.20
Zn	0.5	0.52	Sb	0.2	0.20
Cd	0.5	0.50	Te	0.2	0.19
Co	0.5	0.45	Se	0.2	0.19
Mn	0.5	0.48	As	0.2	0.20
Fe	1.0	1.10	Pt	0.2	0.19
Pb	1.0	1.10	Sn	0.2	0.20
Ni	1.0	1.10	V	0.2	0.20
Pd	1.0	0.95			
Cr	1.0	0.95			
Rh	1.0	1.05			
Ag	0.5	0.16			
Bi	20.0	20.1			
Sb	20.0	20.2			
Te	20.0	19.5			
Se	20.0	19.5			
As	20.0	20.5			
Pt	20.0	19.8			
Sn	20.0	20.1			
V	20.0	20.0			
Tl	20.0	9.3			

Table 3. Content of trace elements in pure gold, N = 3

Flame AAS		ETAAS		Comparative method [17][a]	
Element	$\bar{x}$, %	Element	$\bar{x}$, %	Element	$\bar{x}$, %
Cu	0.5×10^{-4}	As	2.4×10^{-5}	As	2.1×10^{-5}
Fe	0.6×10^{-4}	Sb	1.2×10^{-5}	Sb	1.0×10^{-5}
Pb	1.2×10^{-4}	Sn	0.5×10^{-5}	Sn	0.7×10^{-5}
Ni	0.6×10^{-4}				
Co	$<1.0\times10^{-5}$	Bi	6.0×10^{-6}		
Mn	$<1.0\times10^{-5}$	Al	6.0×10^{-4}	Cu	0.6×10^{-4}
Cd	1.0×10^{-5}	Se	$<1.0\times10^{-6}$	Fe	0.6×10^{-4}
Cr	0.5×10^{-4}	Te	$<1.0\times10^{-6}$	Pb	1.0×10^{-4}
Pd	1.0×10^{-4}	V	$<1.0\times10^{-6}$	Ni	0.7×10^{-4}
Rh	0.5×10^{-4}	Pt	$<1.0\times10^{-6}$	Co	1.5×10^{-6}
Zn	0.5×10^{-4}			Mn	1.9×10^{-6}

[a] Matrix separation by reduction with hydrazine and subsequent ETAAS determination of the trace elements

Experiments were performed for optimizing the conditions for the separation of the matrix gold by solvent extraction into (1 + 1) MEK/$CHCl_3$ from hydrochloric acid medium. The results are presented in Table 1. Since hydrochloric acid is not suitable for the graphite furnace AAS determination of some trace elements, e.g. As, Sb, Sn [16], the extraction of the gold(III) chlorocomplex was attempted from 1 mol/l nitric acid as well. It was found that the concentration of Au(III) in the aqueous phase after a double extraction with MEK/$CHCl_3$ (1 + 1) from 1 mol/l nitric acid at $V_{aq}:V_{org} = 1:8$ and 1:2, respectively, decreases by more than 4 orders of magnitude. The recovery of µg amounts of trace elements in the aqueous phase after the extraction separation of the matrix was determined. The results are presented in Table 2. It can be seen that the majority of trace elements quantitatively remain in the aqueous solution. Only Ag and Tl are partly coextracted with gold.

As a result of the performed studies the above method was worked out for the determination of 20 trace elements in pure gold.

A pure gold sample was analysed by this procedure. As a comparative method, that described in [17] was used, consisting of matrix separation with hydrazine and graphite furnace AAS determination of the trace elements remaining in solution. The results are presented in Table 3.

It may be concluded that matrix separation by solvent extraction with MEK/$CHCl_3$ combined with subsequent flame or graphite furnace AAS determination, permits to determine 20 trace elements in gold with qualification between 4 and 5 N.

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