DETERMINATION OF PRECIOUS AND RARE METALS IN MINERALS CONCENTRATES AND TAILINGS, USING k_0 BASED INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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Abstract

Under the frame of CRP "Validation of nuclear techniques for analysis of precious and rare metals in mineral concentrates", in order to improve the utilization of nuclear analytical techniques in terms of high accuracy and precision for the analysis of precious and rare metals in mineral concentrates, It was carried out the project "Determination of precious and rare metals in minerals concentrates and tailings, using k_0 based instrumental neutron activation analysis" Au, Ag, were analysed in copper concentrates, Re in molybdenum concentrates and In and Ga in tails of zinc concentrates. To this effect, two in house secondary reference materials, i.e. a copper concentrate for the determination of precious metals at the trace levels and heavy mineral concentrate for the determination of lanthanides and actinides at minor trace levels, the CRP prepared and distributed among 8 participants of different countries.
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1. Objectives

Program Objectives
To implement analytical techniques optimizing the process control of metallurgical plants participate in the QA-QC program of this CRP.

Research Objectives
Development and improve of Neutron Activation technique k_0 method in determinations of: Rhenium in Molybdenum concentrates; Gold and Silver in Copper concentrated and Gallium and Indium in residue of Zinc electrolytic refining.

2. Experimental methods

Sampling
Mining companies prepared all samples in good analytical conditions.

Development Methods

At first, different samples and matrixes matter of our investigation were analysed, in order to find optimums work conditions of measurement, so as sample quantity, geometrical effects, irradiation time, decay time, death time, measurement time, detection limit, gamma-ray self attenuation, spectral interference and others[1]. Then, it was got some internal control standard to study which would be the results about precision and accuracy, this standards were analysed by the following methods: **Au, Ag by Gr-AAS; Re by ICP; In by AAS**. It is necessary mention that it was impossible to find a laboratory when to analyse Gallium for any method.

3. Results

Research objectives
Rhenium in Mo concentrated was determined by ^{188}Re: 155 keV was obtained a CV of 6% and quantification limit of 40 ppm.

Silver in copper concentrated. The level of autocoincidence for ^{110m}Ag: 657, 884 keV are similar, was chosen the peak 884 keV that has a variation coefficient of 6% and a quantification limit of 5 ppm.

Gold in copper concentrated was analysed by ^{118}Au: 411.8 keV, obtaining a CV of 26 %, this variation is due to the low concentration, since the limit of quantification is 0.1 ppm. It did not see neutron self-absorption because there were not elements with absorption cross section high such as ^{197}Au and ^{59}Co.

Indium in tails of zinc concentrated was determined by ^{116m}In: 417,1097,1293 keV, using all this energy like an internal quality control, the coefficient of variation is 6 % and quantification limit is 10 ppm.

Gallium in tails of zinc concentrates was analysed by ^{72}Ga. 834 keV.

Table 1. Neutron Activation Analysis Results in comparison with reference material.

Sample	*Au*	*Ag*	*Re*	*In*	*Ga*
Reference Material	0.20 ± 0.07	122 ± 3	604 ± 4	725 ± 32	
Copper Concentrate	0.19 ± 0.05 n = 22	111 ± 7 n = 20			
Molybdenum Concentrate			606 ± 28 n = 19		
Tail				732 ± 25 n=18	147 ± 7 n=13

Programme Objectives (Participate in the QA-QC program of this CRP) Analysis of two reference materials: CCu-1c: for intercomparison results among other countries [2].

Analysis of IGS-36 monazite reference material. They had been carried out under conditions and parameters obtained in this work.

In agree of our work conditions and maintaining a dead time bellow 5%, and based on sodium standard behaviour were established the following operational conditions:

Table 2. Operational conditions of work.

Element	*Geometry*	*T.irrad.*	*T.decaim.*	*T.cont.*
	(cm)	*(s)*		*(s)*
Ce	*5,5*	*120*	*20d*	*8000*
Dy	*12,5*	*5*	*3h*	*1500*
Eu	*12,5*	*5*	*3h*	*1500*
La	*5,5*	*120*	*20d*	*8000*
Nd	*12,5*	*120*	*10d*	*8000*
Tb	*5,5*	*120*	*20d*	*8000*
Ta	*5,5*	*120*	*20d*	*8000*
Th	*5,5*	*120*	*20d*	*8000*
Sm	*12,5*	*5*	*3h*	*1500*
U	*12,5*	*120*	*10d*	*8000*
Yb	*12,5*	*120*	*10d*	*8000*

Correction factors [3].

Neutron self-shielding. It was used the calculus by numerical approximations given by Dwork and Hofmann.

Gamma ray self attenuation. It was carried out by relation of gamma transmitted photons and incidents using a collimated source of ^{152}Eu placed in perpendicular way to the sample, evaluating a range of energy between 122 keV to 1405 keV, extrapolating the values found to the peaks of the radionuclids of our interest [4].

Uranium fission products. It was used the Erdtman formula assuming a *f=30* determining the level of interference in La and Ce, and obtaining the following results:

Sample	La (%)	Ce (%)
IGS-36	0.06	0.39
RRDCM.475	0.11	0.68
RRDCF.476	0.09	0.57

4. Results discussion

It is shown in the below table that the relative difference in percentage of the obtained concentrations in relation to the reference value depend on the standard used under the same operational conditions.

Std. Na	**Std. Au**	**Std. Used**	
Ce	9.0	-3.8	Au
Dy	-5.6	8.4	Au
Eu	- 23.9	-23.4	Au/Na
La	-21.4	-9.8	Au
Nd	-9.9	-10.6	Au/Na
Tb	-22.3	-31.1	Na
Th	-2.1	-13.0	Na
Sm	-12.7	-3.5	Au
U	17.6	48.6	Na
Yb	37.9	41.6	Au/Na

These differences can be explained by the level of uncertainty that produce to use different values of Q in k_0 formula. Is for that reason, it has not an accuracy value of the coincidence correction factor mainly for the ^{24}Na:1368 keV, ^{140}La:487 keV and ^{160}Tb:879 keV in a geometry of 5.5 cm producing an increase of the concentrations values obtained using the gold standard.

5. Quality Assurance

Validation of NAA-k_0 has been carried out by analysis of two standard reference materials: NIST 1633ª Coal fly ash and NIST 2704 Buffalo River Sediment. There was used Heydorn chart for precision in nuclear techniques and Shewart for accuracy [5].

Under the research contract, IAEA sent us two Copper Concentrates and two Thailand Monazite samples to participate in intercomparison results.

Procedures were written of the methods developed.

6. Conclusion

Neutron Activation Analysis k_0 method is a good method for trace concentrations in mineral concentrates so is observed in gold and silver determinations.

According to obtained results in the Heydorn and Shewart test it was found that Au, In, Re, Ag and Ga presents a good precision with the time and an acceptable accuracy in concordance with detection limit and range of concentration.

K_0 method in analysis of rare elements is an alternative acceptable in comparison with radiochemical method and related techniques.

The level of error in determination of Eu, Tb and Yb in Monazite samples was verified that is high.

It should be good an enlargement of this program for validation of the methods developed in REE analysis for the complexity that has the method and the importance of the elements in the industry.

7. References

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