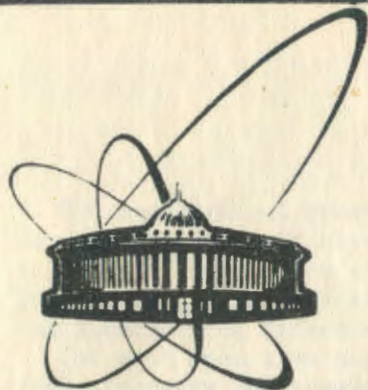


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T. V. Shishkina, S. N. Dmitriev , S. V. Shishkin

DETERMINATION OF GOLD IN NATURAL WATERS
BY NEUTRON ACTIVATION - γ -SPECTROMETRY
AFTER PRECONCENTRATION
WITH TRIBUTYL PHOSPHATE
AS SOLID EXTRACTANT

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Hydrogeochemical prospecting for new deposits of gold by determining the gold content of natural waters is very promising, as is shown by some authors^{/1-4/}. The main obstacle for a wide use of such a prospecting is the absence of suitable methods of determination of gold in natural waters.

The most sensitive methods for gold are neutron activation- γ -spectrometry and atomic absorption spectrometry. Because gold concentration in natural waters is extremely small (in the nanogram per litre range), preconcentration is always necessary.

The fact that in natural waters gold may exist in various species makes it necessary to turn all possible species into one chemical form before preconcentration. For this purpose, the original water samples or the evaporation residues were treated by acids^{/5-9/}. Methods of gold preconcentration from natural waters, such as solvent extraction^{/5-11/}, sorption^{/12-15/}, coprecipitation^{/16-17/}, are used often and successfully. Activated charcoal is often chosen because of the possibility of accomplishing the procedure under the field conditions^{/12-14/}.

However, the reported results of investigations of gold sorption from natural waters by activated charcoal are at variance with each other. Hamilton et al.^{/12/} found that activated charcoal adsorbs the ionic and colloidal species of gold completely at $\text{pH} \leq 5$ (recovery $\geq 95\%$). Gold recovery was decreased with increasing pH (e.g., it was $\approx 85\%$ at pH 6.5), so that the original water samples need to be acidified.

Plyusnin et al.^{/13/} showed that complete recovery of gold is achieved only after addition to the original sample of natural water of 25 ml of aqua regia per litre. According to the results of Khamidova et al.^{/14/}, activated charcoal adsorbs all gold only within a little interval of pH 3-5. The disagreement of the above mentioned results with each other is probably due to the different compositions of the water samples.

The necessity of the preliminary acidification of water is one of the most critical stages of this method, because the explorer should convey perceptible amounts of acids to the sites of sampling for performing sorption under the field conditions. Furthermore, addition of relatively large quantities of acids to water samples, which may contain as little

as 1 ng l^{-1} gold, inevitably leads to contamination problems and high blanks.

More reliable data must be obtained if natural water samples are evaporated and then the solid residue is treated. In this case the methods for the determination of gold in rocks and other solid samples can be directly used in the analysis of waters. However, the samples must be evaporated in laboratory. Each of them weighs not less than 500 g. Therefore it is difficult to transport a large number of samples. Gold can also be adsorbed irreversibly on the walls of containers.

It is necessary to develop a method for the determination of gold in natural waters which can be used on the site of sampling. The method must concentrate gold irrespectively of the natural water composition and be most suitable to practice under the field conditions. The present work deals with the preconcentration of gold from natural waters with tributyl phosphate as a solid extractant.

EXPERIMENTAL

Apparatus and Reagents

A solid extractant containing about 45% of tributyl phosphate - SE(TBP) was used. The content of gold in original SE(TBP) was less than 0.04 ng g^{-1} . All solutions of gold were prepared by dissolving gold metal (99.99%) in a minimum amount of aqua regia, diluting to 200 mg per litre with 2 M HCl preliminarily saturated by chlorine. ^{195}Au was used as a tracer. Spiked concentrates were counted in a sodium iodide detector. Medical activated charcoal "Carbolen" was used. All acids were analytical grade.

Preparation of "Equilibrated" Gold Solutions

An aliquot of gold solution containing ^{195}Au tracer was added to 1-l sample of river water (to give a final concentration of $1 \mu\text{g l}^{-1}$ gold). The water was stored to equilibrate with the gold for 20 days before use.

Preparation of Standard Concentrates

Standard concentrates were prepared simultaneously with "equilibrated" gold solutions. The same aliquot of gold solution containing ^{195}Au tracer as that for "equilibrated" solu-

tion was added to 5 g of powdered solid extractant and the mixture was well shaken and dried.

Preparation of a Chlorine Saturated Solid Extractant

Powder of a solid extractant (particle size < 150 mesh) was placed in a glass column. Gaseous chlorine was passed through a layer of SE(TBP) until it got yellow as a whole. SE(TBP) absorbed about 10%-wt of chlorine. A chlorine saturated SE(TBP) was kept in closed polyethylene containers. Experiments with the spiked ^{195}Au river water showed that sorption properties of SE(TBP) remained the same at least during one year.

Procedures

Preconcentration with Activated Charcoal

25 ml of aqua regia and then 250 mg of activated charcoal were added to a 1-l water sample. The mixture was shaken for 30 min. The suspension was filtered. The filter disk with the activated charcoal residue was dried.

Instrumental Neutron Activation

Samples were packed into aluminium foil and then into aluminium containers. These containers were irradiated for 20 min in the WWR-CM reactor on a thermal-neutron flux of $10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$.

Activity Measurements

The samples were subjected to γ -spectrometry four days after irradiation with a lithium-drifted germanium detector having a resolution of 4.5 keV for the 1332-keV peak of ^{60}Co and coupled to a 4096-channel analyser NOKIA LP-4900. The gold was determined according to the 412 keV peak of ^{198}Au . The detection limit (L_D) was calculated from 18 , i.e.

$$L_D = \frac{(2.71 + 4.65 I_B^{-1/2}) C}{I_N},$$

where I_B is the count rate of the background; I_N is the net count rate; C is the calibration factor.

RESULTS AND DISCUSSION

The authors^{'19'} showed that the solid extractant containing about 45% TBP is very efficient and suitable for concentrating gold from hydrochloric acidic solutions. In these solutions gold exists as a chloro complex. However, in natural waters gold is contained in various species: colloidal gold, humate, and fulvate complexes, and various inorganic complexes^{'12'}. Commercially available SE(TBP) is not a universal extractant for all species of gold. It can be used for concentrating gold from natural waters if first all species of it will turn into well extractable species. Plyusnin et al.^{'13'} added aqua regia to turn all species into the chloro complex, but under the field conditions this procedure is extremely awkward. In the present work we propose to use the chlorine saturated solid extractant for simultaneously oxidizing the gold, forming a chloro complex, and for extracting it.

The efficiency of the solid extractant for concentrating gold from natural waters was tested. A total of 20 samples of "equilibrated" gold solution were prepared as stated above. Preconcentration with the solid extractant was carried out after 20 days. 5 g of the chlorine saturated solid extractant was added to a sample of "equilibrated" gold solution. The mixture was shaken for 10 min. The necessary shaking time was found in preliminary experiments. After filtering and drying the samples of the solid extractant they were counted by a sodium iodide detector. Results of counting were compared with those for the standard concentrates prepared simultaneously with "equilibrated" gold solutions from aliquots of a gold solution containing ^{195}Au tracer. It was found that more than $98 \pm 2\%$ of gold was adsorbed on SE(TBP).

Results of experiments with "equilibrated" gold solutions were tested with samples of original natural waters. We investigated various types of natural waters: surface fresh and mineral waters containing very low levels of gold and waters with a high gold content which were associated with deposits of gold.

Immediately after sampling 5 g of a chlorine saturated solid extractant was added to the 1-l water sample. The mixture was shaken for 10 min. The suspension was filtered. The solid extractant residue was transported to a stationary laboratory, washed with distilled water, dried, and ashed at a temperature of 400°C . Preliminary experiments with spiked ^{195}Au concentrates have shown that losses of gold at ashing are negligible. Ashing of gold concentrates was used to de-

crease weight (final weight about 1.5 g). The residues were analysed by neutron activation- γ -spectrometry. The results are given in the Table.

Table. Results of determinations of gold content in some natural waters using extraction with SE(TBP) and sorption on activated charcoal

Place of sampling	Content of gold (ng l ⁻¹)	
	SE(TBP)	activated charcoal
water from gallery connected with deposit stream No.1	11.5	9.5
stream No.2	12.2	13.5
stream No.3	9.0	6.2
Kingarga River	24.5	17.5
Eho-Ugun River	3.4	3.5
mineral water (Arshan)	3.5	3.5
mineral water (Nilova Pustin)	3.8	3.0
	2.8	3.2

The efficiency of the proposed method was confirmed by the simultaneous use of the activated charcoal preconcentration technique^{/13/}. Activated charcoal was analysed by neutron activation - γ -spectrometry. The results of analysis of all concentrates are shown in the Table, and are means of triplicate samples. Comparison of the results allows one to conclude that using the chlorine saturated solid extractant containing about 45% TBP for the concentration of gold from natural waters is very efficient.

In preliminary experiments we studied the possibility of back-extraction of gold from SE(TBP) by solutions which some workers^{/20-23/} proposed for desorption and back-extraction of gold from various sorbents and extractants. It was stated that the acidic solution of thiourea was the most efficient back-extractant. We found that in the recommended conditions of experiments^{/23/} gold was removed from SE(TBP) to 88%.

In the present work the back-extraction of gold by various solutions of thiourea was investigated in detail. It was found that the presence of acid did not influence the recovery

ry of gold. Therefore a further investigation was carried out with neutral solutions of thiourea. The optimum conditions of back-extraction were found under recovery of gold from powder of SE(TBP) preliminarily saturated by gold containing ^{195}Au tracer. It was found that gold was removed completely if the content of thiourea in the solution was $>0.005\text{ M}$. Back-extraction was most efficient at a high temperature (about 100°C). The necessary time for the process was not more than 5 min. Thus the recovery of gold with hot neutral 0.025 M solutions of thiourea (10 ml per 1 g SE(TBP)) is recommended.

Concentrates from natural waters (SE(TBP)) were treated by those solutions. The suspension was filtered and washed off with hot distilled water. The filter liquor was evaporated at about 90°C in a polyethylene container with a disk of filter paper. The sizes of the paper disks corresponded to those of the container bottom. Gold was retained completely on the paper which was analysed by neutron activation- γ -spectrometry. The detection limit for back-extracted concentrate measurements was 0.2 ng , being the same for ashed residue measurements. However, the filter paper weight (0.1 g) was smaller than that of the ashed residue, that permits the simultaneous irradiation of a larger number of samples. This method was tested on known auriferous deposits and gave good results^{4/}.

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