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USE OF MOLYBDENUM AS TRACER

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The co-precipitation of tungsten and molybdenum by α-benzoinoxime has been studied. Comparison of relative yields for both elements is made. Results showed coincidence and let conclude that molybdenum can be used as tracer to calculate sample to standard relative yield for tungsten. Analyses of water samples for tungsten were made and results were also presented.

Introduction

Neutron activation analysis has been extensively applied for tungsten determination in several materials. Despite its high sensitivity, when analysis of very small contents is intended, radiochemical separation is frequently needed.

Among published methods, use of steps of precipitation by α-benzoinoxime has been reported for isolation of tungsten.[1,2] Conversion of the precipitate to trioxide is necessary for chemical yield determinations. Considering the fact that molybdenum is precipitated under similar conditions than tungsten, we have explored the feasibility of using tungsten and molybdenum co-precipitation by α-benzoinoxime both as a separation technique and as an indirect method for yield calculation of tungsten through molybdenum. Application to tungsten analysis in water samples is also presented.

Experimental

Development of the method

Experiments were made following the technique described by HILLEBRAND and LUNDELL.[3] Precipitations by α-benzoinoxime were performed in inactive samples to which 450 μg and 70 μg of irradiated molybdenum and tungsten had been previously added to serve as carriers and tracers simultaneously. Determinations of absolute yield (Table 1) showed that the procedure was not quantitative, probably due to the fact that carrier masses were very small, however, addition of larger quantities would not be advisable because of the large volume of the precipitate. At that stage, the question to be answered was whether the yield for tungsten was the same to the one of molybdenum. To search that two runs of four experiments of precipitation were made under similar conditions. Activity ratios for molybdenum and tungsten were calculated with respect to a sample arbitrarily taken as standard (Tables 2 and 3). Maximum disparity between results was 3%, which might be considered small, if statistical errors associated to the measurements were taken into account. Therefore molybdenum could be used as tracer for tungsten yield calculations.

Table 1
Determination of absolute yield for molybdenum

Sample, No.	Yield, %
1	89 ± 1
2	84 ± 1
3	88 ± 1
4	84 ± 1

Peak measured: 140.4 keV from ^{99m}Tc

Table 2
Comparison of activity ratios for molybdenum and tungsten.
Run No. 1-sample: Sarandi stream

Ratio	Molybdenum*	Tungsten**
2/1	0.948 ± 0.004	0.97 ± 0.01
3/1	0.910 ± 0.004	0.912 ± 0.009
4/1	0.745 ± 0.004	0.731 ± 0.008

*Calculated by measuring the 140.4 keV peak from ^{99m}Tc.
**Mean value of yields calculated by measurement of 134.2 keV; 479.5 keV and 685.7 keV peaks from ^{187}W.

Table 3
Comparison of activity ratios for molybdenum and tungsten.
Run No. 2-sample: Santo Domingo stream

Ratio	Molybdenum*	Tungsten**
2/1	1.012 ± 0.006	0.990 ± 0.008
3/1	1.034 ± 0.006	1.024 ± 0.008
4/1	1.020 ± 0.006	0.990 ± 0.007

*Calculated by measuring the 140.4 keV peak from ^{99m}Tc.

**Mean value of yields calculated by measurement of 134.2 keV; 479.5 keV; 551.5 keV; 618.2 keV and 685.7 keV peaks from ^{187}W.

Determination of tungsten in water samples

Water samples were analyzed for tungsten as part of a work related to the search of an activable tracer to be used in contamination studies in the River Plata in Argentine. Sources were: River Plata, 5,000 m off the shore and four tributary streams. Equal volumes were collected during one day at 30 min intervals and then mixed to form a pool from which samples were taken. Sediments were removed by filtration and afterwards the samples were stored at low temperatures in order to avoid the decomposition of organic matter. Previous determinations of molybdenum showed that its natural contents in these samples were sufficiently high thus it was unnecessary to add an additional quantity of it. Two 50 ml aliquots were taken for analysis, one for making the standard by addition of a known volume of a solution prepared from Spec-Pure elemental tungsten (Johnson, Matthey and Co, London). Both sample and standard were treated in similar way. Aliquots were heated until dryness and part of the residues was sealed in quartz ampoules for irradiation. As neither molybdenum nor tungsten were lost, not even partially, during the evaporation, measurement of molybdenum activity could serve for ascertaining the sample to standard relative yield of the operation.

Irradiations were carried out in the RA–3 reactor at a thermal flux of about $2 \cdot 10^{13}$ n $\cdot$ cm^{-2} $\cdot$ sec^{-1} during 8 hrs. Irradiated samples were dissolved after 24 hrs and molybdenum and tungsten carriers were added. Tungsten was separated following the technique mentioned before. A 40 cm^3 Ge(Li) detector coupled to a 4096 multichannel analyzer was used for measurements. Measured gamma-spectra showed peaks of ^{82}Br besides the expected ones of ^{99}Mo and ^{187}W, so that a step of bromine elimination had to be made before precipitation. After dissolution in

10 ml of water, 1 ml of HBr, 3 ml of fuming H_2SO_4, 5 ml of fuming HNO_3 and 10 ml of H_2O_2 were added. The solution was heated until half of the initial volume was evaporated; fuming HNO_3 and H_2O_2 were added again and heating went on until dryness. This procedure was twice repeated. Losses of molybdenum or tungsten did not occurr following this method.[4]

The finally adopted technique was: (a) dissolution of the sample; (b) bromine removal; (c) redissolution and addition of carriers and (d) precipitation.

Calculations

Peak areas were calculated using COVELL's method. Concentration of tungsten in the samples was found out using the simple formula:

$$C = 20 \frac{A_W(S)}{A_W(Std)\dfrac{A_{M_o}(S)}{A_{M_o}(Std)} - A_W(S)} \; m_W, \; \mu g/l$$

where A_W, A_{Mo} – tungsten and molybdenum activities (including decay corrections

S – sample;

Std – standard;

m_W – tungsten mass added in the standard, μg.

Results and discussion

Results are shown in Table 4. Sub-microgram levels of tungsten were determined with good precision.

The co-precipitation of tungsten with molybdenum by α-benzoinoxime can be used succesfully for radiochemical separation of tungsten, with the additional ad-

Table 4

Results for tungsten analysis from water samples

Sample	Concentration, μg/l
River Plata	0.53 ± 0.04
Los Plátanos stream	0.96 ± 0.05
Gimenez stream	0.74 ± 0.06
Sarandí stream	0.42 ± 0.01
Santo Domingo stream	0.91 ± 0.04

vantage of the possibility of using molybdenum as tracer for yield calculations. This method can be extended still if chemical steps other than precipitation are performed provided that yields for both elements are not altered.

*

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