INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS FOR DETERMINING Mo IN URANIUM CONTAINING MATERIALS

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A purely instrumental method for the deter-
mination of Mo in uranium containing mate-
rials is presented. The precision and accuracy
were verified by the analysis of several Stan-
dard Reference Materials with different pro-
portions of Mo and U. Detection limits varied
from 0.8 to 1.3 µg/g for Mo. The method can
be applied to determine Mo in the studies of
agricultural zone characterization.

INTRODUCTION

Molybdenum plays an active role in soils, where it is
involved in both nitrate reduction and nitrogen fixation.
It is an essential trace element for plants, and its level
depends on soil contents and soil conditions[1].

The elemental concentration variability, in time and
in space, in the agricultural zone is a serious difficul-
ty in the study of interrelation of inorganic elements
in soil-plant systems[2]. Thus the analysis of a large num-

ber of samples is necessary to evaluate the distribution
of one element in an agricultural field and to have repre-
sentative results of the whole. In this case, the choice
of analytical techniques which allow a non-destructive,
accurate, fast analysis with a minimum pretreatment is
important.

Although neutron activation analysis with a separa-
tion and preconcentration step (RNAA), has successfully
been used to determine Mo in several kinds of materials
with high accuracy even at very low concentrations[3-5],
these procedures require the use of specific reagents,
an effort to dissolve samples, and are more expensive
and less available.

In this paper, the interference of ^{235}U fission in Mo
determination, using instrumental neutron activation ana-
lysis (INAA) is measured. Although the sensitivity of
a purely instrumental method for Mo is lower than for
RNAA, its main advantage is faster practical determination
with lower cost and good accuracy. The possibility of re-
ducing the analysis time is interesting when it is neces-
sary to analyze a large number of samples.

The precision and accuracy of the INAA were verified
by means of several Standard Reference Materials with
different proportions of Mo and U.

FORMULATION

The determination of molybdenum by INAA using a nuclear
reactor is based on the γ-spectrometric measurement of
^{99}Mo produced by the reaction $^{98}Mo(n,\gamma)^{99}Mo$. However,
^{99}Mo is a uranium fission product and could interfere in
molybdenum determination by INAA if uranium is present.

The specific counting (measured in counts per gram of the element under the experimental conditions) is denoted by letter S followed by the symbols of the target element and the element formed . Thus, for example, S_{MoMo} means the specific counting of molybdenum-produced by (n,γ) reaction and S_{UMo} means the specific counting of ^{99}Mo formed from uranium fission. The activity measured is denoted by letter C followed by the symbol of the nuclide measured.

The equation for the activity of ^{99}Mo formed in the irradiation of a sample with uranium contents is given by

$$C99_{Mo} = [S_{MoMo} \cdot m_{Mo} + S_{UMo} \cdot m_{U}]$$

or

$$m_{Mo} = \frac{C99_{Mo}}{S_{MoMo}} - \frac{S_{UMo}}{S_{MoMo}} \cdot m_{U} \qquad (1)$$

where: m_{Mo} and m_{U} are the masses of molybdenum and uranium, respectively.

The errors in the specific counting values for standards are smaller than measured for samples once the error in countings of pure element standards can be controlled. However, the total errors in m_{Mo} determination are larger than those associated with statistical counting, due to the need of subtraction of uranium contribution.

EXPERIMENTAL

Preparation of samples and standards

Approximately 100 mg of standard reference materials IAEA-Soil-7, NRCC-PACS-1 Marine Sediment, IAEA-S-1 Lake Sediment, ICHTJ-CTA-FFA-1 Coal Fly Ash were weighed into

polyethylene bags, previously washed with nitric acid (1:5) and several times with distilled water followed by drying.

Mo and U standards were prepared by pipetting aliquots (25-100 µl) of standard solutions obtained from their high purity compounds (Johnson Matthey Chemicals, Ltd. and ESPI), onto filter paper (Whatman n° 42) followed by drying under an IR lamp. Standards were then folded and placed in polyethylene bags.

Irradiation and counting

All irradiations were carried out in the IEA-R1 reactor at a thermal neutron flux of 1.84×10^{12} $ncm^{-2}s^{-1}$.

Countings were performed with a high resolution solid state ORTEC POP TOP Ge detector, model 20190P, with a resolution of 1.80 keV for the 1332 keV peak of ^{60}Co. The detector was connected to an ACE card, model 916A MCB, 8192-channel analyzer. Peak search and area evaluation were done by the Program VISPECT in TURBO BASIC language.

Calibration curve

To plot the calibration curve standards of Mo and U with different masses (0.41, 0.82, 1.24, 2.81 and 4.14) were irradiated, in aluminium tube, for 8 h, cooled for 4 d. After opening, each standard was transferred to a planchet for counting.

The specific countings (S_{MoMo} and S_{UMo}) were measured in order to obtain a calibration curve.

Reference material analysis

In the analysis of reference materials, four samples, one standard of Mo (2.81 µg) and one standard of U (2.81

µg) wrapped together in an Al foil were irradiated in an aluminium tube for 8 h. For counting each sample or standard was transferred to the appropriate planchet. The molybdenum was measured after at least 36 h to allow the establishment of ^{99}Mo-^{99m}Tc equilibrium. Molybdenum was determined via the 140 keV peak of ^{99}Mo-^{99m}Tc and uranium via the 228 or 278 keV peak of ^{239}Np. For each irradiation the contributions of uranium to ^{99}Mo production and molybdenum contents were determined by Eq. (1). All the counts were corrected for cooling time and extrapolated to the end of irradiation to be applied in Eq. (1).

RESULTS AND DISCUSSION

Sensitivity

The sensitivity (expressed here as specific counting) was considered as the slope of calibration curve, in the same conditions used for standard reference material analysis, applying the least-squares method.

Mo sensitivity (when the target element is molybdenum) –

S_{MoMo} = (0.66±0.06) counts/µg Mo,
correlation coefficient, r = 0.98496.

Mo sensitivity (when the target element is uranium) –

S_{UMo} = (1.14±0.01) counts/µg U,
correlation coefficient, r = 0.99982.

From the values of sensitivities the importance of correcting for the interference of the uranium fission reaction in the determination of Mo was verified.

TABLE 1

Results for Standard Reference Materials and the corresponding LD for molybdenum (all values in µg/g)

Sample/split	U	Mo	LD_{Mo}
IAEA-Soil-7			
1	2.8	2.0	0.78
2	2.2	2.5	
3	2.2	2.9	
4	2.1	2.2	
Mean±SD	(2.3±0.3)	(2.4±0.4)	
certified value[7]	(2.6±5) (c)	2.5 (r)	
NRCC-PACS-1 Marine Sediment			
1	2.9	10.3	1.3
2	3.1	10.7	
3	3.4	11.6	
4	4.2	14.6	
5	4.5	11.3	
Mean±SD	(3.6±0.7)	(11.7±1.7)	
certified value[7]		(12.3±0.9) (c)	
IAEA-SL-1 Lake Sediment			
1	3.9	1.6	0.93
2	4.2	2.2	
3	2.9	1.3	
4	3.1	0.8	
Mean±SD	(3.5±0.6)	(1.5±0.6)	
certified value[7]	(4.02±0.3) (c)	1.3 (r)	
ICHTJ-CTA-FFA-1 Coal Fly Ash			
1	15.9	19.1	1.1
2	16.1	15.7	
3	14.1	14.5	
Mean±SD	(15.4±1.1) (c)	(16.4±2.4)	
certified value[7]	(15.1±0.8)	17 (r)	

(c) Certified value.
(r) Reference value.

Accuracy and precision

The accuracy and precision of the method were verified by analyzing five standard reference materials (SRM). Table 1 shows the results obtained for the uranium and

molybdenum contents and the corresponding limits of de-
tection (LD) for molybdenum. According to the literature[6],
the limits of detection were calculated as 3 times the
standard deviation of the background on which the photo-
peak is situated.

The decay times varied from 6 to 12 d, depending on
the level of sample activity.

The determination of sensitivities for each irradiation
run, as was practised in this work, was required to achieve
the highest accuracy of molybdenum determination.

The agreement between the values obtained and litera-
ture values supports the accuracy of the INAA procedure
developed here. However, in the case of samples of higher
uranium contents, Mo results not entirely satisfactory
could be expected.

This method can be applied to determine Mo in geolog-
ical materials, at ppm level, for example in the studies
of agricultural zone characterization.

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