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URANIUM DIOXIDE BY X-RAY FLUORESCENCE
SPECTROMETRY**

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DETERMINATION OF TRACE METALS IN NUCLEAR-GRADE URANIUM DIOXIDE BY X-RAY FLUORESCENCE SPECTROMETRY

Vera Lucia Ribeiro Salvador and Kengo Imakuma*

ABSTRACT

A method is described for the simultaneous determination of low concentrations of Ca, Cr, Cu, Fe, Mn and Ni in nuclear-grade uranium dioxide by X-ray fluorescence spectrometry, without the use of chemical treatment. The lower limits of detection range from $2 \mu\text{g g}^{-1}$ for nickel and manganese to $5 \mu\text{g g}^{-1}$ for copper. Samples are prepared in the form of double-layer pellets with boric acid as a binding agent. Standards are prepared in a U_3O_8 matrix, which is more chemically stable than UO_2 and has similar matrix behaviour. The correlation coefficients for calibration curves are better than 0.999. Errors range from 2.4% for chromium to 6.8% for nickel.

DETERMINAÇÃO DE ELEMENTOS TRAÇOS EM DIÓXIDO DE URÂNIO DE GRAU NUCLEAR POR FLUORESCÊNCIA DE RAIOS-X

RESUMO

Descreve-se um método para a determinação simultânea de baixos teores de Ca, Cr, Cu, Fe, Mn e Ni em dióxido de urânio de grau nuclear pela técnica de fluorescência de raios-X, sem a utilização de tratamento químico.

Obteve-se um limite mínimo de detecção entre $2 \mu\text{g g}^{-1}$ para o níquel e manganês e $5 \mu\text{g g}^{-1}$ para o cobre.

As amostras foram preparadas na forma de pastilha prensada de dupla camada, utilizando-se ácido bórico como aglutinante.

Os padrões foram preparados em matriz de U_3O_8 , por ser mais estável quimicamente que a matriz de UO_2 , e apresentar comportamento matricial muito semelhante.

Os coeficientes de correlação das curvas de calibração foram melhores que 0.999.

A faixa de erro nas determinações foi de 2,4% para o cromo a 6,8% para o níquel.

INTRODUÇÃO

Many thermonuclear reactors utilize uranium dioxide as fuel, which must have a high grade of purity in order to guarantee safe operation. Several techniques have been developed for the determination of trace elements in nuclear materials. Trace concentrations are usually determined by neutron activation, optical emission spectrometry, atomic absorption spectrometry and spark-source mass spectrometry. These techniques are very sensitive but can show some limitations depending on the elements to be determined.

In this work, X-ray fluorescence spectrometry was investigated for the determination of some impurities in nuclear fuel, namely Ca, Cr, Cu, Fe, Mn and Ni. The concentration range studied was 0.001 - 0.015% [1].

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EXPERIMENTAL

Preparation of Standards and Sample

Standards were prepared by adding known amounts of Ca, Cr, Cu, Fe, Mn and Ni to 1.0 g of Specpure U_3O_8 and adding boric acid to give a total mass of 2.0 g. These mixtures were ground in a mortar and pressed at 1.6 ton cm^{-2} for 1 min into a circular mold (40-mm diameter) to form a double-layer pellet. Samples were mixed with boric acid in a 1:1 ratio and pressed into pellets as described for standards.

A commercial standard disk of aluminium metal was prepared for detection of fluctuations of X-ray intensities.

Study of Characteristic First-order Reflection $K\alpha$ line

The high mass-absorption coefficient of uranium in the matrix causes a considerable absorption effect on the characteristic lines of the elements of interest. An approximately constant amount of uranium was utilized in the standards and samples in order to compensate for this effect.

The $K\alpha$ lines of the elements, detected with a tungsten target tube, LiF (200) analyzer crystal, and scintillation counter, are shown in Figure 1. The positions of lines and possible interferences from other elements were examined for each spectrum.

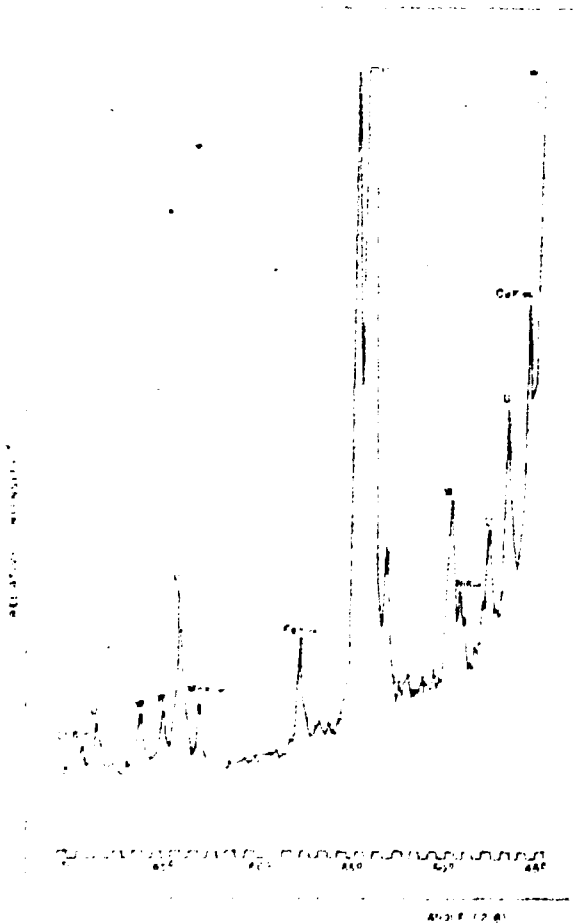


Figure 1 - The $K\alpha$ spectra of Cr, Mn, Fe, Ni and Cu, and the L spectrum of uranium recorded with a LiF (200) analyzer, scintillation counter and tungsten X-ray tube.

Instrumentation

The commercial, semi-automatic X-ray spectrometer used was coupled with a stabilized 3-kW generator. A tungsten target X-ray tube was used for Cr, Cu, Fe, Mn and Ni; a chromium tube and a flow proportional counter were used for calcium. The analyzer crystal was LiF (200) for all elements except calcium for which a EDDT(020) crystal was used. Tube voltages and currents were 50 kV and 50 mA, respectively, for all elements except calcium, for which the current was 35 mA.

A six-position specimen chamber permitted sequential measurements of fluorescence intensities of six pellets. For each set of measurements, the spectrometer was loaded with five standards or samples; the remaining position was occupied permanently by the aluminium standard.

The Siemens relations [6] for several pairs of currents and voltage, i.e., $(I_b)^2/I_f$ = the minimum value, and the Diaz-Guerra relation [3], i.e., $[(I_f + I_b)^2 - (I_b)^2]$ = the maximum value, were used, where I_b is the background intensity and I_f is the net fluorescent intensity. For these conditions, the sensitivities and lower limits of detection are expected to be maximal and minimal, respectively. Conditions established in this manner are summarized in Table I.

RESULTS AND DISCUSSION

Calibration Graphs

The standards were processed in triplicate and, for each standard, the average net intensity was plotted vs. concentration (Figure 2). Background intensity was subtracted from each sample spectrum and the fluctuation of the counts was corrected, when necessary, by means of a standard pellet. Least-squares statistics for the calibration graphs are listed in Table II.

Table I

Optimized Conditions for the Proposed Method

Characteristic line ($n = 1$)	Ca K_{α}	Cr K_{α}	Cu K_{α}	Fe K_{α}	Mn K_{α}	Ni K_{α}	
Wavelength (Å)	3.360	2.291	1.542	1.937	2.103	1.659	
Beam angle	Line	44.85°	69.33°	45.03°	57.53°	63.00°	48.68°
	Background	43.45°	66.99°	44.70°	57.00°	62.65°	48.30°
		45.32°	69.86°	45.50°	58.06°	63.40°	49.06°
Fixed time (s)	100	200	100	100	400	100	
Collector (cm)	450	150	150	150	150	150	
Tube height analyzer	Base	0.80	0.55	0.65	0.60	0.60	0.65
	line (V)						
	Channel window (V)	0.85	0.85	1.05	0.95	0.95	0.90

The error caused by the use of a U_3O_8 matrix instead of UO_2 was neglected because the absorption coefficients of U_3O_8 and UO_2 , for the wavelengths considered, are nearly the same [6].

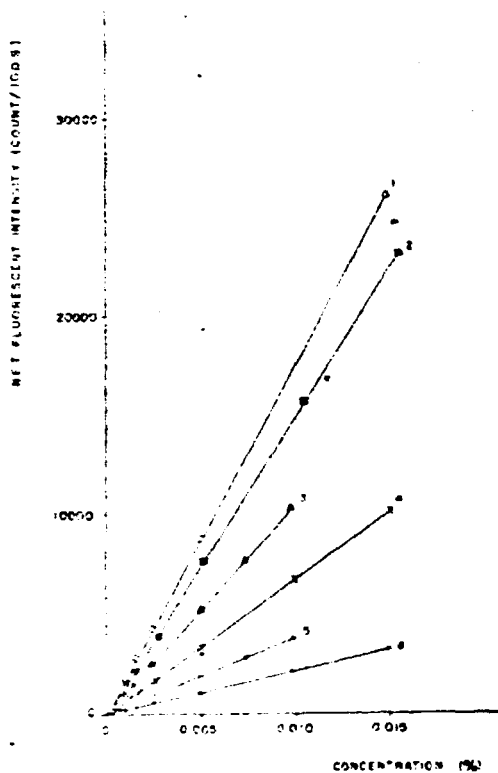


Figure 2 — Calibration graphs: (1) Calcium; (2) nickel; (3) copper; (4) iron; (5) manganese; (6) chromium.

Table II

Least-squares Statistic for Calibration Graphs

Element	Intercept (a)	Slope (b)	Standard errors			Correlation coefficient
			s_{xy}	s_b	s_b	
Ca	-66	174	137	85	1	0.9999
Cr	76	41.2	75	46	0.6	0.9996
Cu	-65	105	159	112	2	0.9993
Fe	27	67.7	65	40	0.5	0.9998
Mn	-76	152	125	87	2	0.9998
Ni	37	149	109	67	0.8	0.9999

Imprecision, Inaccuracy, Sensitivity and Lower Limit of Detection

The imprecision and inaccuracy of the methods were tested on samples containing 1.0 g of standard n° 95-2 U_3O_8 from New Brunswick Laboratory. The results, based on a minimum of five replicates for each sample, are listed in Table III. The values obtained for imprecision and inaccuracy are less than 5% for all elements except copper and nickel. The larger errors for these two elements are probably caused by interfering lines from other elements.

The sensitivities and estimated detection limits (3σ criterion) are given in Table IV.

Table III
Imprecision and Inaccuracy for the Method

Element	Cr	Cu	Fe	Mn	Ni
Nominal concentration ($\mu\text{g g}^{-1}$)	42	21	220	22	44
Concentration found ($\mu\text{g g}^{-1}$)	41 \pm 2	22 \pm 2	218 \pm 6	22 \pm 6	47 \pm 2
Imprecision (%)	4.9	9.1	2.8	4.5	4.3
Inaccuracy (%)	2.4	4.8	4.5	0.0	6.8

Table IV
Sensitivity and Lower Limit of Detection

Element	Sensitivity (10^3 counts $\text{s}^{-1}/\%$)	Lower limit of detection ($\mu\text{g g}^{-1}$)
Ca	17.0	4
Cr	2.2	4
Cu	10.1	5
Fe	6.9	3
Mn	3.7	2
Ni	15.0	2

The use of double-layer pressed pellets has contributed to improve detection limits, because of the low degree of dilution. When fused pellets are used, the detection limits for calcium, copper and iron are usually about $400\text{--}500\ \mu\text{g g}^{-1}$ [2]. The imprecision and inaccuracy of the method are similar to those achieved with emission spectrometry [4].

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