

Voltammetric determination of uranium in rocks, soils and sediment by using the catalytic nitrate reduction

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(Received November 20, 1996)

The differential pulse voltammetry with a hanging drop mercury electrode using catalytic reduction was used to determine uranium at trace level in rocks, soils and sediments. Some the instrumental parameters were established at optimal conditions. A softer digestion than the normal high pressure method was applied to dissolve the samples. A liquid liquid extraction procedure was used to separate the uranium from matrices. The precision and accuracy of method were evaluated, using certified Soil-7, 312 and 314 samples from IAEA which uranium concentrations lie from 2 to 60 $\mu\text{g/g}$. The results are in good agreement with those obtained from other techniques and reference materials.

Introduction

Previous experiments have shown the feasibility of uranium determination by catalytic nitrate reaction using chronocoulometry¹ and differential pulse polarography.² It was also seen that the substitution of dropping mercury electrode for hanging drop mercury electrode offers similar or better results.¹

In the present work we have proposed an alternative method for uranium at trace level determination using the catalytic nitrate wave and differential pulse voltammetry, with a hanging drop mercury electrode.

The main experimental parameters as modulation amplitude, electrolyte composition, scan rate, electrode area and others were examined to obtain a better signal to noise ratio and an experimental calibration curve with high sensitivity. The established method was evaluated, considering precision and accuracy by comparison with some results of other techniques and with reference materials from International Atomic Energy Agency (IAEA).

Experimental

Apparatus and reagents

A voltammetric analyzer Methrom 646 and a VA 647 stand for electrochemical analysis in differential pulse voltammetry mode were used. The electrolysis assembly was a three electrode system: a hanging mercury drop (HMDE) with 0.6 mm² area, a silver/silver chloride reference electrode and a Pt wire as auxiliary electrode. All voltammetric measurements were obtained at room temperature.

All chemicals were of analytical grade without previous purification, with exception of the uranium standard solution. It was prepared from NBA 950a U₃O₈ dissolved

in 0.5M nitric acid (Suprapur, Merck). The water in all solutions was prepared by a Millipore-Q system.

The support electrolyte was prepared in the voltammetric cell by adding 50 μl 86% formic acid to 20 ml solution 10 mM lithium nitrate. The final concentration of formic acid was 55 mM, (pH 2.5).

Evaluation of instrumental parameters

The best set of instrumental and analytical parameters determined by using a standard solution with $3.8 \cdot 10^{-7}\text{M}$ of uranium. The measurements were repeated many times daily during at least 60 days to assure the minimum interference of temperature's fluctuation, current transients and others. Modulation amplitude of 150 mV, scan rate of 5.0 mV/s, initial potential of -0.75 V and peak current of -1.0 V were established as the best conditions to obtain greater signal/noise ratio. The peak current was determined by twenty measurements and showed as result the value $1033 \pm 11 \text{ mV} \times \text{Ag/AgCl}$.

The influence of numerous ions in the catalytic uranyl/nitrate reaction has been described in many papers in literature.⁴⁻⁶ It was also verified in previous paper¹ that a liquid-liquid extraction is an accepted and recommended practice to separate uranium from the matrix.

Detection limit and standard deviation

A calibration curve was obtained with standard solution from $5 \cdot 10^{-8}$ to $6 \cdot 10^{-7}$ M of uranium, always with subtraction of blank (electrolyte support, in this case). The slope of the linear curve was $1.34 \cdot 10^{-9} \text{ M}/\mu\text{A}$. Six simulate samples with $4.3 \cdot 10^{-7}$ M of uranium were analyzed and the result $[(3.9 \pm 0.1) \cdot 10^{-7} \text{ M}]$ showed $\pm 2.7\%$ of precision and -8.6% of bias. The detection limit ($3.8 \cdot 10^{-9} \text{ M}$) was determined as three times the standard deviation of the blank.

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Table 1. Comparison of uranium concentrations determined by different techniques

Technique sample	RM material IAEA, ^a µg/g	INAA, ^b µg/g	CCCD, ^c µg/g	DPV, ^d (this work) µg/g
MU19A	–	5.9	5.5 ± 0.1	6.0 ± 0.2
MU19B	–	23.9	33.3 ± 0.2	30.0 ± 40.4
BJ2	–	4.4	3.4 ± 0.6	3.6 ± 0.6
Soil-7	2.6	–	–	3.2 ± 0.6
312	16.5	–	–	17.1 ± 0.8
314	56.8	–	–	58.8 ± 1.4

^aReference material from the International Atomic Energy Agency.

^bInstrumental neutron activation analysis.⁷

^cChronocoulometric catalytic determination.⁸

^dDifferential pulse voltammetry.

Mineralization of the sample

The sample dissolution was done by an industrial process of mineralization.³ An aliquot of the previously homogenized dry sample was weighed (0.5 g) and transferred to a PTFE beaker. 0.5 ml concentrated sulfuric acid was added and the beaker was heated (100 °C) during 6 hours. Then, it was heated for acid evaporation to completeness. Three ml concentrated nitric acid and 3 ml 40% hydrofluoric acid were added to the sample and the beaker was heated again till all the acids have been evaporated. This procedure was repeated twice yet. Hydrofluoric acid was eliminated by successive additions of portions of nitric acid and complete evaporation. The residue was finally dissolved in 6M nitric acid and uranium was separated by liquid liquid extraction as described in the literature.⁸

Voltammetric determination

Aliquots of the liquid liquid extraction product were added to the electrochemical cell with 20 ml of electrolyte and the voltammogram was obtained from -0.75 to -1.2 V × Ag/AgCl by differential pulse voltammetry (modulation pulse = 150 mV and scan rate = 5.0 mV/s). The determination of uranium was performed by the standard addition method considering always the blank solution.

Results and discussion

The differential pulse voltammetric method for uranium using the catalytic uranyl/nitrate reaction was applied to reference materials and other samples that have been analyzed by chronocoulometry and instrumental neutron activation analysis.¹ Although it was necessary to use a time consuming separation procedure, the proposed method is eminently suitable for the determination of ultra trace quantities of uranium.

The results from this work and those from chronocoulometric catalytic determination (CCCD) and instrumental neutron activation analysis (INAA) are presented in Table 1. Considering the reference materials, the mean relative errors for three measurements were +23.1%, +3.6% and +3.5% to samples Soil-7, 312 and 314, respectively. These values are consistent taking into account the confidence limits of RM samples. The differences (+5.3%, -6.3% and +7.7% to medium values of MU19A, MU19B and BJ2, with respect to CCD and INAA) are also acceptable inasmuch as the uranium concentration is low.

The dissolution procedure used evinced good performance and it is recommended as an alternative method to pressure PTFE bombs. It is a quite rapid experiment and it requests less reagent than the conventional method. For more refractory samples more investigations are necessary.

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The authors thank Professor Dr. Ivano G. R. GUTZ for helpful suggestions, FAPESP and CAPES.

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