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CONTROLLED-POTENTIAL-COULOMETRIC DETERMINATION OF URANIUM AT A PLATINUM ELECTRODE

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ABSTRACT

A controlled-potential-coulometric method has been developed for determining uranium at a solid electrode which features high specificity and a precision of 0.1% relative standard deviation at the 5 mg uranium level. Uranium and added iron, necessary for the electrolytic oxidation of uranium, are reduced to U(IV) and Fe(II) with excess Cr(II). At a sequence of controlled potentials, the excess Cr(II) is oxidized to Cr(III), Fe(II) and U(IV) are oxidized to Fe(III) and U(VI), then the Fe(III) is reduced to Fe(II). The difference in the measured number of coulombs for the oxidation of Fe(II) and U(IV) and for the reduction of Fe(III) to Fe(II) is proportional to the quantity of uranium.

INTRODUCTION

The current need for a controlled potential coulometric method for uranium is its use in an automated analyzer already constructed for plutonium determination (ref. 1). Initial objectives were high specificity, precision of 0.1% relative standard deviation at low-milligram uranium level and use of solid electrode with long-term stability. A mercury pool electrode is used almost exclusively for uranium because it provides adequate hydrogen overvoltage for reduction of U(VI) without reduction of hydrogen ion. No system with the desired features employing solid electrode has been described. Carbonaceous electrodes of glassy carbon, boron carbide and graphite have not provided reproducible surfaces necessary for precise measurements. Reticulated vitreous carbon (RVC), a honey-comb material with large surface area, had large, variable background currents and a limited cathodic range in acidic media (ref. 2). In a method developed by Davies et al. (ref. 3), Bi(III) and high chloride concentration provided the necessary overvoltage for hydrogen at platinum electrode. During our investigation, measurement of low milligram amounts of uranium was not sufficiently reliable (ref. 2). Phillips and Crossley (ref 4) determined uranium at a solid electrode by reducing uranium with electrogenerated hydrogen. Removal of adsorbed hydrogen was slow and affected electrode stability. Because uranium is difficult to reduce electrolytically without hydrogen interference, a chemical reductant was sought. Cr(II) was selected because its potential is sufficiently low to reduce uranium and it is readily oxidized electrolytically without significant oxidation of U(IV).

In the method developed here, uranium and added iron are reduced with excess Cr(II). At a sequence of controlled potentials at a platinum electrode, the excess Cr(II) is oxidized to Cr(III), Fe(II) and U(IV) are oxidized to Fe(III) and U(VI), and Fe(III) is reduced to Fe(II). The difference in the measured number of coulombs for the oxidation of Fe(II) and U(IV) and for the reduction of Fe(III) to Fe(II) is proportional to the quantity of uranium. Added iron is necessary for the oxidation of uranium.

EXPERIMENTAL

Apparatus

The apparatus is centered about a Princeton Applied Research 173D potentiostat-galvanostat and a 179D digital coulometer. A strip chart recorder and a digital multimeter complete the system.

The electrolysis cell has been described in detail previously (ref. 5). The working electrode is a strip of platinum gauze formed into a cylinder, the platinum counter electrode and the saturated calomel reference electrode, isolated from the cell solution by separate compartments, are connected to the cell solution by porous Vycor disks. The counter electrode is located in the center of tne cell to provide a uniform potential gradient. The reference electrode is located adjacent to the working electrode for best control. Stirring is provided by a glass paddle driven by a 1800 rpm synchronous motor.

Reagents

Deionized water and AR grade chemicals were used for all reagents.

Selection of Chemical Method

Sulfuric acid was selected as electrolyte. Because of its high boiling point, interfering volatile ions can be removed by fuming. Uranium determinations were independent of sulfuric acid concentration over the range of 0.5 to 2 M. To minimize the effect of acidity of a sample, 0.5 M H_2SO_4 was selected as electrolyte for the method.

Added iron was necessary for the oxidation of U(IV). For iron to uranium ratios of < 1, electrolyses times were very long. At molar ratios of 1 to 1 or greater, oxidation times were < 20 min.

A potentiometric titration of uranium and iron with Cr(II) to a -0.25 V endpoint assured quantitative reduction of uranium and iron but avoided addition of large excess of reductant. All potentials are vs saturated calomel electrode.

Electrolysis potentials for the method were established using the following conditions: 0.02 mmol (5 mg) uranium, 0.03 mmol Fe(III), 10 ml 0.5 M H_2SO_4,.

nitrogen sweep during electrolysis and titration with Cr(II) to a -0.25 V endpoint. A potential of 0.25 V was selected for the first oxidation; at this potential 99.99% of Cr(II) is oxidized to Cr(III) without oxidizing the U(IV) and Fe(II). At the second oxidation potential of 0.52 V, 99.95% of U(IV) is oxidized to U(VI). The Fe(III) is reduced to Fe(II) at a potential of 0.25 V. All electrolyses are continued to a 50 μA current endpoint.

RESULTS AND DISCUSSION

Diverse Ion Effects

The results of detailed investigation of the effect of 45 metal cations are presented in Table 1. Interference is defined as a change significant at the 95% confidence level relative to uranium alone. The level of uranium used for each test was 0.02 mmol (5 mg). The initial molar ratio tested was 1:1. If a result was significantly different, lower ratios were tested. Not all the elements in the alkali and alkaline earth groups were tested. The results of representative members are considered to apply to all members of the group. Most elements normally found in nuclear fuel cycle materials do not interfere. Several elements, osmium, selenium, and ruthenium did not interfere in the uranium determination but impaired electrode response so that sufficiently low current could not be attained in subsequent analyses. Bismuth, gold, iridium, molybdenum, rhenium and tellurium interfered even at 1:100 molar ratio.

TABLE I

TOLERANCE LEVEL OF METAL CATIONS

Mole Ratio With Respect to U	Cations
1:1	Al, As, B, Be, Ca, Cd, Ce, Cr, Co, Fe, Ga, Hf, In, La, Mn, Na, Nb, Ni, Os, Pb, Pu, Th, Tl, Zn, Zr
1:10	Sb, Se, Sn, Rh, Ta
1:100	Cu, Hg, Pd, Pt, Ru, W, V

Au, Bi, Ir, Mo, Re, Te interfered at 1:100

To ensure applicability of the method for determining uranium in uranium-plutonium mixtures the tolerance for plutonium was investigated in greater detail. There was no significant difference in results for five measurements of equal ratios of uranium and plutonium relative to five measurements of uranium alone.

Nonmetallic ions are yet to be studied. It is expected that many potentially interfering nonmetallic anions can be effectively removed by fuming with sulfuric acid.

Treatment to Restore Effective Electrode Behavior

The platinum-gauze working electrode was stable during the six months of method development. During the study of interfering ions, however, several elements impaired electrode response so that reaction endpoint of 50 µA could not be attained. The cleaning procedure to restore effective electrode behavior is as follows: after rinsing electrode in deionized water, immerse in concentrated nitric acid for 5 min, rinse with water and immerse for 1 h in 0.5 M H_2SO_4. A more severe cleaning was necessary after electrolysis of gold, iridium and rhenium: electrode was rinsed in water, immersed in aqua regia for 45 s, rinsed in water and immersed in 0.5 M H_2SO_4 for 1 h.

Measurement Precision

Within day precision was < 0.1% relative standard deviation at the 5 mg uranium level. The relative standard deviation for 32 analyses measured over a 2-week period was 0.17%. Even during investigation of diverse ion effects covering a 3-week period the precision of uranium standard determinations remained 0.17%.

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