NARROW SPAN COULOMATIC ANALYSIS OF NEPTUNIUM

P.K. Kalsi, L.R. Sawant, R.C. Sharma*, S. Vaidyanathan

Fuel Chemistry Division,
Bhabha Atomic Research Centre,
Bombay - 400 085, India

*Radiochemistry Division,
Bhabha Atomic Research Centre,
Bombay - 400 085, India

Received 27 December 1993
Accepted 12 January 1994

A narrow span (E'±0.1 V) controlled potential coulometric method has been developed for the determination of neptunium in 1M H2SO4 with a RSD of 0.2%. The main advantage of this method over the existing coulometric methods is that it can tolerate up to a 5-fold excess of plutonium. The method involves carrying out the electrolysis to about 97% and calculating by an iterative computation the formal electrode potential in situ, which is used to calculate the total amount present in the sample. The method consists in oxidation of all the neptunium to Np (VI) by Ce(IV), destruction of excess Ce(IV) and reduction of Np(VI) to Np(V) by NaNO2, destruction of excess nitrite by sulfamic acid followed by coulometric titration of Np(V) to Np(VI).

INTRODUCTION

Coulometric determination of neptunium is an established method. R.W. Stromatt1 reported a primary coulometric method in 1N H2SO4 with an RSD of 0.05% at
1 mg level of neptunium, wherein it was mentioned that a 4.7-fold excess of plutonium may cause a bias of 1% in the neptunium determination. Kasar et al. reported a secondary coulometric method in 1M H₂SO₄ with a precision of ±0.25% at 2-5 mg level of neptunium. In an earlier paper we reported a narrow span coulometric method (E_o' ±0.1 V) for the determination of metal ions in aqueous solutions, which form reversible couples. This method minimizes interference from ions having formal potentials (E_o') close to the ion of interest and also saves about 70% in analysis time without any loss of precision and accuracy. The applicability of this method was demonstrated for the determination of iron. However, the determination of plutonium gave 2% lower values, which was attributed to a slight deviation in the experimental coulogram from the theoretical one. The present paper describes the successful application of this method for the determination of neptunium which can also tolerate up to a 5-fold, excess of plutonium.

EXPERIMENTAL

Apparatus

Potentiostat (Model-273, EG & G PARC) and 5 1/2 digit multimeters of Solartron were used to record solution potentials (E) and readout voltages (RO). A specially fabricated electrolytic cell shown in Fig. 1 was used.

Chemicals

All the chemicals used were of AR or GR grade. Solutions were prepared as given in Ref. (2).