DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY FOR DETERMINATION OF SOME HEAVY METALS IN URANIUM

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ABSTRACT

The direct determination of some metals impurity in uranium by using differential pulse anodic stripping voltammetry (DPASV) method at a hanging mercury drop electrode and in a carbonate buffer media was developed. It was found that the carbonate buffer show the strongest affinity for uranium and gives the best separation between the DPASV peaks of heavy metals impurities. The carbonate concentration markedly affects the oxidation and reduction the major and the minor constituents of the uranium samples. In 0.1 M carbonate buffer solution pH 10, copper, bismuth, thalium, lead, cadmium, zinc, could be determined without the removal of the uranium matrix. Recovery and relative standard deviation (RSD) of this method was in the range of 174% - 85.2% for recovery and 36.8% - 1.2% for RSD. The larger error of analytical result was obtained for Zn at low concentration. In general, the analytic results error and RSD decreased with increasing metals concentration.

Keywords: *heavy metal determination, differential pulse anodic stripping voltammetry, uranium*

INTRODUCTION

The need for a simple, reliable and accurate analytical procedure for the determination of heavy metals in uranium is most pronounced in the area of nuclear fuel technology. It is well known that in trace metal analysis the analytical results mainly depend on errors introduced in the sample pretreatment steps (the dissolution, pre concentration and separation of interfering component). It is therefore desirable that the number of analytical steps be kept to a minimum or, if possible, avoided altogether.

Direct determination of metals impurities in uranium by using atomic absorption spectrometry (AAS) was impossible without preliminary separation. Chemical interferences in the presence of uranium matrix and/or the spectrum of the uranium are the most common problems encountered in using AAS for direct determination of trace amount of metals in uranium.

Electrochemical techniques play an important role in establishing the valency state in the determination of metals. Stripping voltammetry has been widely used for trace metals in several materials determination since this method usually does not require the pre-concentration and the separation step prior to the determination [1-5]. Ligia et all [2] have used stripping voltammetry in the analysis of trace metals in marine water sample. Rohonozaman [3] has determined trace metals in agriculture soils by using voltammetric technique. Locately et all [4] have determined trace of metals in cooper alloy using voltammetric method. Saryati et all [5] have validated voltammetric method to trace metal in biological sample determination. Oxidation-reduction potentials for Cu(II)-Cu(O), Pb(II)-Pb(O), Cd(II)-Cd(O) and Zn(II) - Zn(O) are more negative than those for U(VI)–U(V) and U(VI)–U(IV) in the media without any strongly complex forming agent. It means that U(VI) is more easily reduced than most heavy metals impurities ordinarily present in uranium. Therefore, the direct determination of heavy metals in uranium by anodic stripping voltammetry (ASV) would seem to be impossible without the removal of uranium matrix.

In the solution containing the complex forming agent, the oxidation-reduction potentials for ions shift to more negative direction depending on the stability of the complex ions. Boris [6] has shown that in acidic solution media pH 1.1 peak potential of U(VI) was -0.1 V , but in alkaline carbonate buffer solution media pH 10 peak potential of U(VI) was -1.26 V. The formation of stable complex between U(VI) and carbonate ions markedly affects the reduction of U(VI), so that the peak potential was shift about 1 V more negative direction, while the carbonate complex of Cu(II), Pb(II), Cd(II) and Zn(II) are not so stable in comparison with U(VI)-carbonate complex. The carbonate media is, therefore, considered to promising for the determination of Cu, Cd, Pb, Zn, Bi, Tl in uranium materials, by using ASV without the uranium disturbance.

In this paper, an evaluation of the differential pulse anodic stripping voltammetry (DPASV) method in the determination of trace amount of some metals in uranium, based on the complex formation of U(VI) with carbonate, will be reported.

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EXPERIMENTAL SECTION

Material

The standard solution of metals (Cu, Bi, Pb, Cd, Zn, Tl and Bi) 1 g/100 mL Titrisol, uranyl nitrate, sodium carbonate, sodium hydrogen carbonate used in this experiment were analytical grade from Merck. Where are the uranium standard material is supplied by JAERI (JAERI U 1-3 and JAERI U II, with specification as at Table 1) was used to validate the DPASV method.

A pH 10 carbonate buffer solutions was prepared by mixing equal volumes of sodium hydrogen carbonate and sodium carbonate solutions of equal concentrations. This buffer solution was electrolytic purification by using a large mercury electrode.

Instruments

The voltammograms were recorded on EG&G PAR model 384B polarographic analyzer. The working electrode was an EG&G PAR model 303A static mercury drop electrode and hanging mercury drop electrode (HMDE) was employed. Ag/AgCl (saturated KCl) and platinum wire are used as reference and auxiliary electrode, respectively. An XY recorder for Houston Instrument was used. In differential–pulse mode of operation (DPP), the voltammogram were recorded at a slow scan rate (0.25 – 2.0 mVs^{-1}), pulse height 20 mV and frequency 100 hz with a medium drop size. Metals determined by anodic differential-pulse stripping voltametry (DPSV) were pre-concentrated for 2 min at -1.20 V. Dissolved oxygen was removed by purging with nitrogen gas.

Procedure

Preparation of samples

The sample of uranium was dissolved in concentrated nitric acid solution and evaporated up to dryness. The residue was dissolved by the addition of a few milliliter of carbonate buffer, transferred in to 10 ml calibrated flask and diluted to the mark with carbonate buffer. An aliquot of the sample solution was transferred into the voltammetric cell and the heavy metal content was determined by standard addition procedure.

RESULT AND DISCUSSION

According to Boris [5] and Kolthoff [6] the electrode reaction of hexavalent uranium in carbonate media was an irreversible process to gain with one electron,

$$UO_2^{2+} \leftrightarrow UO_2^{+} \text{ or } U(VI) \leftrightarrow U(V)$$

Cyclic voltammogram of U(VI) from this experiment show that U(VI) give a reduction peak at -1.27 V and an oxidation peak at -0.55 V in the carbonate buffer solutions (Fig 1). According to William [8], because of the large separation of two peaks, this electrode reaction becomes irreversible. The reduction peak potential shifts to more positive direction and peak height decrease, with increasing concentration of total carbonate. This means that reduction reaction of U(VI) was affected by the carbonate concentration Hypothetical reaction of V(VI) in carbonate buffer have been proposed by Boris [6], that the over-all process involving the reduction of UO_2^{2+} or UO_2OH^+ as reactive species is preseded by the dissociation of the carbonate complex. The rate determining is the formation of UO_2^{2+} or UO_2OH^+ followed by complex formation of $UO_2(CO_3)_3^{5-}$

$$UO_2(CO_3)_3^{4-} \leftrightarrow UO_2^{2+} + 3\,CO_3^{2-}$$
$$OH^- \updownarrow + e^- \leftrightarrow UO_2\,(CO_3)_3^{5}$$
$$UO_2OH + 3\,CO_3^{2-}$$

The behaviour of some metals in the carbonate-hydrogen carbonate buffer has been studied. The results presented in Fig 2. show the dependence of peak potentials on the concentration of carbonate, which was varied in range 0.1 – 0.5 M. The peak potentials of all metals which has been studied were

Table 1. Specification of uranium standard:

	JAERI U - 1.3	JAERI U -II
Al	16 (µg/g)	-
Cd	0,53 (µg/g)	-
Co	2,6 (µg/g)	8 (µg/g)
Cr	13 (µg/g)	-
Cu	5,3 (µg/g)	13 (µg/g)
Fe	43 (µg/g)	-
Mn	6.8 (µg/g)	9 (µg/g)
Mo	7.1 (µg/g)	16 (µg/g)
Ni	26 (µg/g)	64 (µg/g)
P	45 (µg/g)	60 (µg/g)
Pb	-	2 (µg/g)
Si	28 (µg/g)	29 (µg/g)

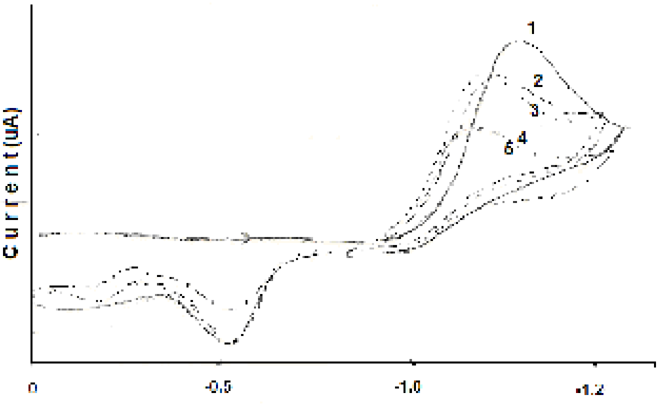

Figure 1. Cyclic voltammogram of UO_2^{2+} in carbonate buffer pH 10 in the variation of carbonate concentration. (0.1M $^{(1),}$ 0.2 M $^{(2),}$ 0.3 M$^{(3),}$ 0.4 M$^{(4)}$ and 0,5 M$^{(5)}$)

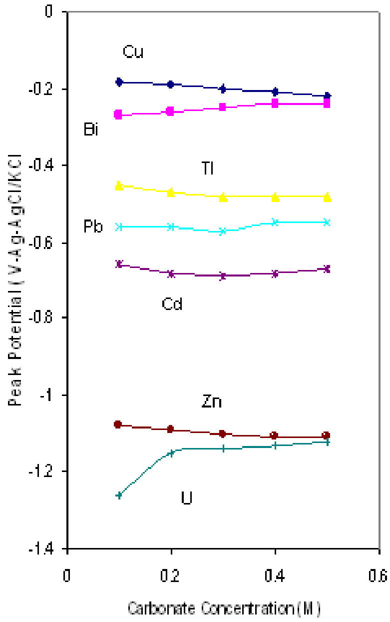

Figure 2. Dependence of DPASV peak of metals on the concentration of carbonate

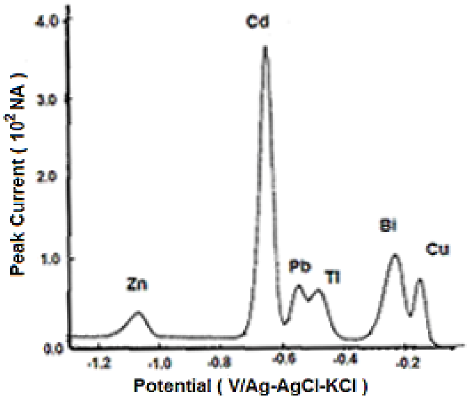

Figure 3. Defferential pulse anodic stripping voltammetry of metals in the carbonate buffer solutions pH 10. Zn = 20 ng/mL, Cd = 10 ng/mL, Pb = 10 ng/mL, Tl = 10 ng/mL, Bi = 100 ng/mL, Cu = 5 ng/mL.

more positive than U peak potential. This is a proof that stability of carbonate – metals impurity is much lower than that of carbonate- uranium complex. At carbonate concentration 0.1 M the peak of every metals were separated about 0.1 V and especially for U peak, was separated from Zn peak about 0.18 V in the negative direction. Consequently, for analytical applications it is important that the concentration of carbonate is kept at 0.1 M, this concentration is sufficient to ensure a successful formation of UO_2^{2+} complex and to give a satisfactory buffer capacity and conductivity to the medium. It is important to note that the carbonate buffer in some instances contains significant amounts of impurities, especially zinc and lead. By electrolytic purification using large mercury electrode, the impurities could be successfully removed.

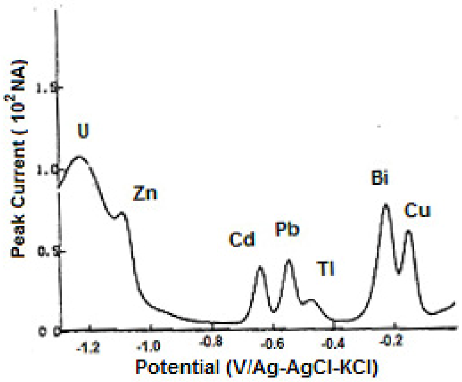

Figure 4. Defferential pulse anodic stripping voltammetry of metals in the carbonate buffer solutions pH 10 in the present of 0.001 g uranyl nitrate per 10 mL solution. Zn = 10 ng/mL, Cd = 2 ng/mL, Pb = 4 ng/mL, Tl = 4 ng/mL, Bi = 10 ng/mL, Cu = 2 ng/mL.

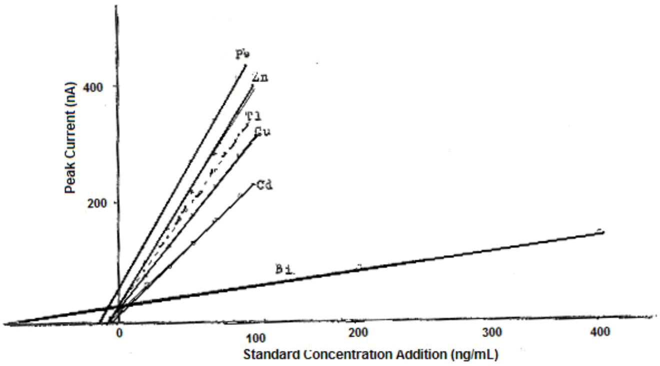

Figure 5. Additions standard curve for concentration determination of Zn, Cd, Pb, Tl, Bi and Cu in uranium samples

Under this condition, the simultaneous determination of metals in uranium by using DPASV method can be done with potential deposition at -1.2 V. The relationship between peak height and concentration of metals was linear over a range of 0.05 µg/mL to 0.55 µg/mL for Cu, Cd, Pb, Tl and Zn and 0.5 µg/mL to 7.5 µg/mL for Bi. The detection limit for a particular metal in the absence of uranium, calculated using statistic method based on the standard curve, are 1.5 ng/mL for Zn, Cd, Pb , Cu and Tl , 40,1 ng/mL for Bi. This metals limit of detection in carbonate buffer pH 10 was higher than limit of detection metals in citrate buffer pH 4.5, about 0.7 µg/mL [5].

Figure 3, shows the non ideal peak potential separation for Pb - Tl and Bi – Cu, which could cause some difficulty in analysis. However, by experience with the arrangement of the applications of scanning rate, pulse height and frequency these two peaks can be separated. Especially for Cu and Bi simultaneous determination is important at very low scanning rate, about 0.25 mV s^{-1}. By this experimental condition, there are ≤ 4% error in the simultaneous determination of Zn, Cd, Pb, Tl, Cu and Bi in the simulation of metal solu-

Table 2. Concentration of Cu, Cd and Pb in uranium standard determination result, in 5 time repetitions.

Sample standard	Concentration (μg/g)		
	Cu(II)	Pb(II)	Cd(II)
JAERI U - 1.3	5.50 ± 0.450	-	0.55 ± 0.041
JAERI U -II	12,5 ± 1,17	2.0 ± 0.15	-

Table 3. Concentration of Zn, Cd, Pb, Tl, Cu and Bi in uranyl nitrate, in 5 time repetitions.

Sample	Concentration (μg/gL)					
	Zn	Cd	Pb	Tl	Bi	Cu
I	n.d	nd	23.5±2.4	nd	nd	16.5±9.1
II	34.8±12,8	20.5±2.4	44.4±4.4	22.6±3.9	nd	31.1±5.9
III	120.6±16.6	96.6±6.6	121.4±7.9	105.6±4.9	954.5±108.3	117.5±1.4
IV	522.5±53.3	491.8±28.1	524.3±30.3	495.5±39.7	5107.2±506.2	523.9±52.3

Note: I = uranyl nitrat without any metal additions
II = I with 20 μg/mL of Zn, Cd, Pb, Tl , Cu and 200 μg/mL Bi per gram of uranyl nitrate.
III = I with 100 μg/mL of Zn, Cd, Pb, Tl, Cu and 1000 μg/mL Bi per gram of uranyl nitrate
IV = I with 500μg/mL of Zn, Cd, Pb, Tl , Cu and 5000 μg/mL Bi per gram of uranyl nitrate
nd = un detected

tions, with 5 ng/mL for Zn, Cd, Pb, Tl, Cu and 50 ng/mL for Bi concentration.

Uranium, affects on the shape of Zn peak, but does not affect the other peak (Fig.4), because the Zn peak is close to the U peak. Nevertheless a good linearity of standard addition curve for all metals can be obtained (Fig. 5), so that for some metals in uranium determination can be done by using standard addition method.

All samples in Table 2 and 3 were determined by following the procedure out lined in the Experimental section. The same amount of acid as used for sample dissolution was taken as a blank and treated by the same procedure as the samples. The result in Table 2 and 3 have been corrected for the blank values. JAERI U I-3 and JAERI II are standard sample that used to validate the DPASV method. There are only Cu, Cd and Pb that can be taken for analysis from those standard samples. For all metals impurity analysis an uranyl nitrate with addition amount of metals was used as sample.

Recovery and relative standard deviation (RSD) of this method was presented in Table 4. are in the range of 174% - 85.2% for recovery and 36.8% - 1.2% for RSD. The larger recovery and RSD, that means a large error in analytical result, was obtained for Zn at lower concentration, because of the Zn peak potential effect (Fg.4). In general, the analytic result error decreases with increasing metals concentration.

CONCLUSION

The carbonate buffer show the strongest affinity for electrode reaction of U(VI) and gives the best separation between the DPASV peaks of heavy metals impurities. The carbonate concentration markedly affects the oxidation and reduction the major and the minor constituents of the uranium samples. In 0.1 M carbonate buffer solution pH 10, copper, bismuth, thalium, lead, cadmium, zinc, could be determined without the removal of the uranium matrix.

Recovery and relative standard deviation (RSD) of this DPASV method was in the range of 174% - 85.2% for recovery and 36.8% - 1.2% for RSD. The larger error of analytical result was obtained for Zn at low concentration. In general, the analytic results error decreased with increasing metals concentration.

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