Voltammetry of calcon in the presence of hafnium ions

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A method for the determination of hafnium by cyclic voltammetry was described. The method is based on the formation of hafnium electroactive complex with calcon (1-(2-hydroxy-1-naphtylazo)-1-naphtol-4-sulfonic acid). The optimum analytical conditions are the following: acetic buffer solution (pH 2.4), scan rate, 0.5 Vs^{-1}. The reduction peak of the complex was proportional to the Hf(IV) concentration in the range $1.8 \cdot 10^{-7}$ to $8.0 \cdot 10^{-6}$ mol L^{-1}. The detection limit of Hf(IV) concentration is $1.99 \cdot 10^{-7}$ mol L^{-1}. The influence of foreign ions on the Hf(IV) determination was studied. It was established, that some metals like cadmium and titanium could be determined with hafnium simultaneously. The proposed method was tested on model solutions and used in the determination of hafnium in terbium base alloy.

Keywords: *hafnium · calcon · cyclic voltammetry*

Hafnium is one of the metals, which have great importance for development of various areas of medicine. Hafnium is used for making plates for bone connection in orthopedic surgery. The quality of these materials essentially depends on the nature and content of components. Such materials are inert and contain low quantity of hafnium, which is capable to penetrate into tissue of human. The analysis of the objects containing such low quality of Hf(IV) is complicated in the analytical chemistry. Therefore, it makes determination of Hf(IV) very important. Not many reagents are known for hafnium determination. The complex of hafnium with 4-(2-pyridylazo)resorcinol [1], biacetylmonoxime nicotinylhydrazone [2] and 3-hydroxychromone [3] have been proposed for spectrophotometric determination of hafnium. However, some of these methods have low sensitivity (detection limit is 10^{-5}–10^{-6} mol L^{-1}) and low selectivity. Voltammetric methods are competitive among the methods for hafnium content control enabling increase of sensitivity and selectivity. The direct voltammetric determination of Hf(IV) is practically impossible, what is connected with the state its ions in the aqueous solution and strong hydrolytic properties. Only the polarographic determination of hafnium with 4-(2-pyridylazo)resorcinol and 4-(2-pyridylazo)-2-naphtol [4] are known (detection limit is 10^{-5} mol L^{-1}). Previously we have shown that sensitive and relative selective determinations of hafnium can be carried out by cyclic voltammetry using the calconcarboxylic acid [5]. The related compound calcon (1-(2-hydroxy-1-naphtylazo)-1-naphthol-4-sulfonic acid) also forms complex with numerous metals and was used early for spectrophotometric determination of Cu(II) [6], Fe(II) [7] and voltam-

metric determination of Mo(VI) [8], Zn(II) [9], Co(II) [10-12], Ni(II) [10,11] and Zr(IV) [13].
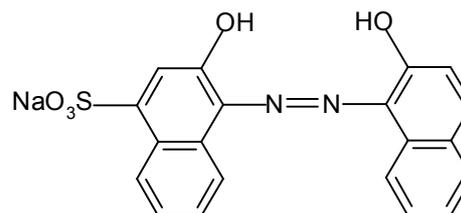
In the present paper, we show that calcon can also be used for voltammetric determination of hafnium.

Experimental

Apparatus

All voltammetric curves were obtained on digital voltammetric equipment which combines a personal computer with a dropping mercury working electrode (DME), a saturated calomel reference electrode and a platinum-wire counter electrode. The pH-meter model MV 870 DIGITAL-pH-MESSGERÄT was used for the pH measurements.

Reagents

All reagents were of analytical grade and the solutions were prepared with bi-distilled water.

A stock standard solution of $1 \cdot 10^{-2}$ mol L^{-1} Hf(IV) was prepared by dissolving 0.1855 g hafnium sulphate in 50

ml volumetric flask with 2 mol L^{-1} H$_2$SO$_4$. The solution was standardized titrimetrically with EDTA.

Stock standard solution of 1·10^{-3} mol L^{-1} calcon was prepared by dissolving a precise amount of dye in aqueous-ethanol solution (10 vol. %).

The necessary stabilization of pH was achieved by HCl+NH$_4$Cl and acetic buffer solutions.

Procedure

A 10.0 ml volume of solution containing Hf(IV) 4·10^{-6} mol L^{-1}, calcon 4·10^{-5} mol L^{-1} and acetic buffer solution (pH 2.4) was transferred into a voltammetric cell. Dissolved oxygen was removed from the solution by argon purging. The voltammogram was recorded by applying a linear scan (0.5 V s^{-1}) in the range of 0.0 to -1.3 V. The peak of the complex was observed at -0.39 V (Fig.1).

Procedure for terbium-base alloy

Weigh a 0.0876 g sample was dissolved in 3 ml concentrated hydrochloric acid and 1 ml concentrated nitric acid with heating. The solution was evaporated to solid residue. After addition of 2 ml of concentrated sulfuric acid it was evaporated again to appearance of fume. Cool the solution and transferred to the 50 ml standard flask; dilute the solution to the mark with 2 mol L^{-1} H$_2$SO$_4$. Transfer an aliquot of 0.1 ml into a 25 ml flask and analysis as already described.

Results and Discussion
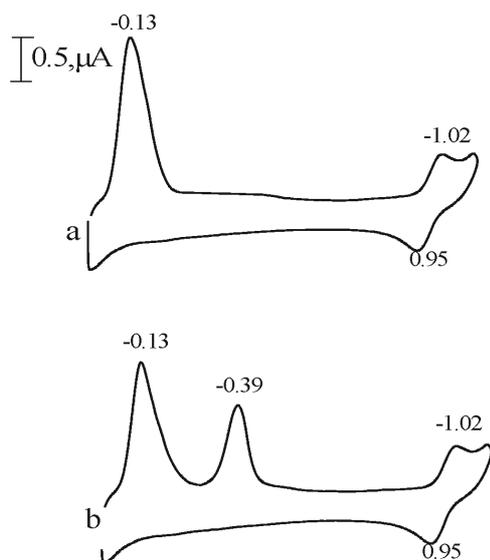
Voltammetric measurements

Calcon (Calc) is reduced on DME in within a wide range of pH. Two peaks are observed down to pH 4.5 but below pH 4.5 there are three peaks [14]. The cyclic voltammogram of the calcon at the pH 2.4 is shown in Fig. 1a. As shown in this figure the reduction peaks of calcon are at -0.13 V and -1.02 V. No peak was found on the voltammograms in the solutions containing acetic buffer solution and 4·10^{-6} mol L^{-1} Hf(IV).

When Hf(IV) is added to calcon on the voltammogram a new peak appears at -0.39 V (Fig. 1b). It has more negative potential than the reduction peak of the calcon. This peak has the form of isosceles triangle. The current of the calcon reduction peak decreases, and that of the new peak increases with increasing of Hf(IV) concentration. It testifies that the new peak is caused by the reduction of hafnium complex. The absence of anodic peaks on the voltammograms testifies that the reduction peak of the complex is an irreversible process.

Effect of pH

The influence of pH on voltammetric characteristics of Hf(IV) complex with calcon was studied in the pH range 0.7–6.5 (Fig. 2). Potential of the new peak is negative with an increase of pH showing that the hydrogen ions act as reactants in the reduction process.

It was established that the stable and maximum current was in the range pH 2.2–2.6. When the pH was below 2.2, the peak current increased and when the pH value was more than 2.6, the peak current began to decrease.
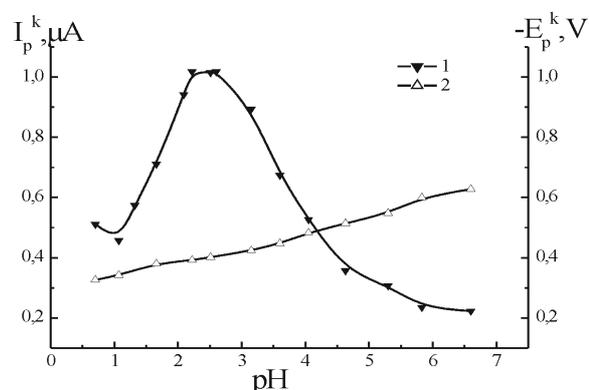

Fig. 1. Cyclic voltammograms of calcon in the absence (a) and presence (b) of Hf(IV) ions. C$_{Calc}$= 4·10^{-5} mol L^{-1}; C$_{Hf(IV)}$= 4·10^{-6} mol L^{-1}; pH 2.4; υ= 0.5 V s^{-1}.

Fig. 2. Effect of pH on I$_p^k$ (1) and E$_p^k$ (2) of Hf(IV) complex with calcon. C$_{Calc}$ = 4·10^{-5} mol L^{-1}; C$_{Hf(IV)}$ = 4·10^{-6} mol L^{-1}; φ$_{ethanol}$ = 36 vol. %, υ = 0.5 V s^{-1}.

Effect of ionic strength and ethanol content

The influence of the ionic strength (0.3–1.2) on the reduction peak of complex was studied. First, the current of the reduction peak increases and after it reaches the ionic strength 0.7; the current intensity remains almost constant. The potential of the reduced peak almost does not depend on its ionic strength. Therefore, all feature experiments were carried out with ionic strength of 0.85.

The addition of ethanol causes the decrease of the current of the hafnium complex. The potential of the reduced peak shifts in the cathode region of potentials.

Effect of calcon concentration

Fig. 3 shows the effect of variation of calcon concentration on the peak of the complex. The peak increases with calcon concentration up to $8.0 \cdot 10^{-5}$ mol L^{-1}, and at higher concentration of calcon, the peak decreases. A concentration of $8.0 \cdot 10^{-5}$ mol L^{-1} was found to be optimal.

Effect of scan rate

When the scan rate increases, the shift of the reduction peak of the complex in the cathode region of potential and the height of the peak grow. To assess the influence quantitatively, the rate criterion was calculated (Table 1). Values of the rate criterion $\lg i/\lg \upsilon > 0.5$ of the process under consideration serve as the proof of adsorption nature of the reduction peak.

The potential scan rate (υ) was performed in the range 0.12–6.00 V s^{-1}. Because the most distinct and high peaks were obtained at $\upsilon = 0.5$ V s^{-1}, all the following studies were carried out at this scan rate.
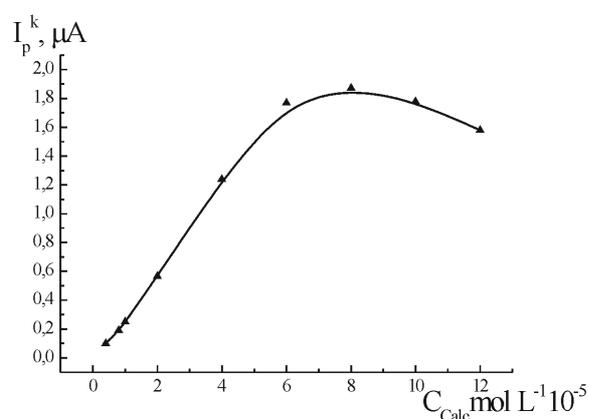
Table 1. Rate criterion values of the reduction process of Hf(IV) complex with calcon. $C_{Calc} = 8 \cdot 10^{-5}$ mol L^{-1}, pH 2.4.

$C_{Hf(IV)}$, µmol L^{-1}	$\lg i / \lg \upsilon$
4	0.77
8	0.61
4	0.51

Composition and stability of the complex

The voltammetric version of Job's method and modified method of DeFord and Hume [15] were used for finding the composition of the hafnium complex. The results indicated a molar ratio of Hf(IV)-Calc is 1:2. The modified method of DeFord and Hume has been used to determine the stability constant of the complex and it was found to be $4.6 \cdot 10^{12}$.

Linear range and detection limit

The reduction peak of the complex increases linearly with Hf(IV) concentration in the range $1.8 \cdot 10^{-7}$ to $8 \cdot 10^{-6}$ mol L^{-1} when $8.0 \cdot 10^{-5}$ mol L^{-1} calcon was used. The linear equation is $I = 0.22 + 2.24 \cdot 10^{5} C$ with r=0.999. Detection limit was estimated to be $1.99 \cdot 10^{-7}$ mol L^{-1}.

Effect of foreign ions

The effect of different ions on determination of Hf(IV) under the optimum conditions was investigated. The experimental results show that addition of $8 \cdot 10^{-6}$ Fe(III), Ti(IV), $1.2 \cdot 10^{-5}$ Pb(II), $1.6 \cdot 10^{-5}$ Cu(II), Pd(II), $8 \cdot 10^{-5}$ Mn(II), Co(II), $1.2 \cdot 10^{-4}$ Fe(II), Ni(II), $1.4 \cdot 10^{-4}$ Cd(II), $1.6 \cdot 10^{-4}$ Pt(IV), Tb(III), $3.2 \cdot 10^{-4}$Al(III), $8 \cdot 10^{-4}$ Zn(II), Mg(II), Ca(II) (mol L^{-1}) do not affect determination of $8 \cdot 10^{-6}$ mol L^{-1} Hf(IV) with an error of $\leq 5\%$. It was observed that Hf(IV) could not be determined in the presence of EDTA and SCN⁻. Accordingly, the above reagents could not be used as masking agents. In the presence of Ti(IV) ions the appearance of new peak at -0.27 V is observed on the voltammogram. It has more negative potential than reduction peak of the free reagent and less negative potential than reduction peak of the hafnium complex. But this separation peak only observed when the ratio of the hafnium and titanium is 1:1. Also it was established, that cadmium could be determined with Hf(IV) simultaneously, because cadmium reduce at -0.67 V and has more negative potential than the Hf(IV)-Calc complex (Fig. 4).

Under the experimental conditions used, zirconium behaves similarly to hafnium. Therefore, zirconium could not be determined with hafnium, but the sum of zir-
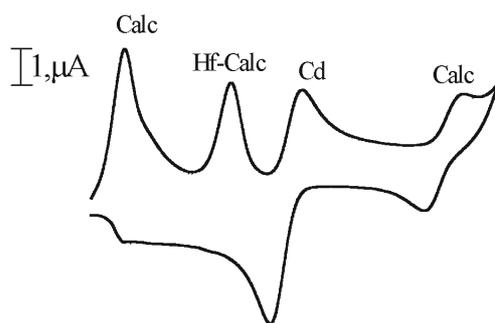

Fig. 3 Effect of calcon concentration on the Hf(IV)-Calc reduction peak. $C_{Hf(IV)} = 8 \cdot 10^{-6}$ mol L^{-1}, pH 2.4; $\upsilon = 0.5$ V s^{-1}.

Fig. 4. Cyclic voltammogram of Hf(IV)-Calc complex in the presence of Cd(II) ions. $C_{Calc} = 8 \cdot 10^{-5}$ mol L^{-1}; $C_{Hf(IV)} = 8 \cdot 10^{-6}$ mol L^{-1}; $C_{Cd(II)} = 8 \cdot 10^{-5}$ mol L^{-1}; pH 2.4; $\upsilon = 0.5$ V s^{-1}.

conium and hafnium can be determined. The sum zirconium and hafnium complex shows a linear relationship in the range $2 \cdot 10^{-7}$ to $6 \cdot 10^{-6}$ mol L^{-1} when $8.0 \cdot 10^{-5}$ mol L^{-1} calcon was used. The calibration graph can be described with the expression $I = 0.28 + 2.88 \cdot 10^5 C$ with r=0.999. Sum detection limit was estimated to be $2.16 \cdot 10^{-7}$ mol L^{-1}.

Application

The proposed method was tested on model solutions. The results are presented in Table 2. The relative standard deviation is less than 5%. Therefore, the obtained results are reproducible and satisfactory. Also, the proposed method was successfully applied to the determination hafnium in the terbium-base alloy (72% Tb(III), 9.5% Hf(IV), 18.5% Al(III)). The result obtained was 9.54±0.08% (RSD 0.28%), which confirms the validity of the procedure.

Conclusion

A new reagent, calcon, for the voltammetric determination of hafnium was proposed. This reagent permits the determination of hafnium and titanium (cadmium) simultaneously. It is very important, because titanium is a member of the hafnium group and behaves similarly to hafnium. The described method is high sensitive and has good selectivity. These facts are further confirmed by analyzing different samples of varying compositions.

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Table 2. Determination of Hf(IV) in model solution. $C_{Calc} = 8 \cdot 10^{-5}$ mol L^{-1}; pH=2.4.

C $_{Hf(IV)}$, µmol L^{-1}		RSD, %
Added	Found	
0.6	0.601 ± 0.006	0.38
1.0	0.99 ± 0.02	0.71
6.0	5.98 ± 0.02	0.12