

Piotr SZEFER

Medical Academy in Gdańsk
Department of Analytical Chemistry

EVALUATION OF SELECTED POLAROGRAPHIC TECHNIQUES FOR THE DETERMINATION OF URANIUM IN SEA AND INLAND WATERS

Contents: 1. Introduction, 2. Conventional polarography, 3. Square wave polarography, 4. Pulse polarography, 5. Differential — pulse polarography, 6. Oscillopolarography, 7. Single-sweep polarography, 8. General evaluation of selected polarographic techniques for the determination of uranium in natural waters; Streszczenie; References.

1. INTRODUCTION

The uranium level in natural waters ranges from several hundredths to several micrograms per litre. To assay such small quantities of the element, sensitive methods, usually preceded by concentration and separation from accompanying ions, have to be employed. The final determination of trace amounts of uranium in samples taken from the marine environment include polarographic and colorimetric methods. Isotopic dilution [16] and fluorimetric [15] methods were also employed to assay uranium in sea water. The polarographic method is particularly useful, as it is highly sensitive and the minimum detectable amount of an element depends upon the composition of the supporting electrolyte and the polarographic technique used. Initially, uranium in natural waters was determined by the conventional polarographic technique; later more sophisticated such as the square-wave and pulse polarography methods began to predominate.

2. CONVENTIONAL POLAROGRAPHY

This technique has gained widespread application in the assaying of components occurring over the concentration range 10^{-3} — 10^{-6} M. In some cases the minimum detectable amount of the ion could be decreased to 10^{-8} M. This is attained by means of such a supporting electrolyte

which is capable of chemical regeneration of a product of the electrode reduction of the depolariser determined. An example of such determinations is provided, for instance, by polarographic analysis of the Mo^{6+} and U^{6+} ions in a nitric acid supporting electrolyte.

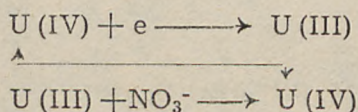
2.1. Determination of microgram amounts of uranium using a supporting electrolyte containing vat dye 2R

Ishibashi and associates [3, 7] found the blue vat dye 2R (sodium salt of 2-(5-chloro-3-sulpho-2-hydroxybenzoylazo)-5-sulpho-1-naphthol) in an acetate buffer of pH 5.3 to be the proper supporting electrolyte for assaying microgram amounts of uranium. The polarographic maxima appearing on the polarographic waves were suppressed by means of Triton X-100 (iso-octylphenoxypolyethoxyethanol). Such anions as SO_4^{2-} , NO_3^- and Cl^- did not affect the results, provided their concentrations did not exceed 0.1 M. The PO_4^{3-} ions interfered at concentrations higher than 0.05 M. Cations of Al, Fe, Co, Ni, Th, Ti, V, Pb, Cu and Zr interfered with the course of the analysis. To employ this method of assaying uranium in sea water, separation of the ions was necessary. The separation was accomplished by extraction of uranium with diethyl ether from a nitrate medium. For the uranium level of $2 \times 10^{-6} \text{M}$ the reported accuracy was ± 6 per cent.

2.2. Determination of nanogram amounts of uranium in 0.01 N HNO_3 supporting electrolyte using a uranium/nitrate catalytic wave

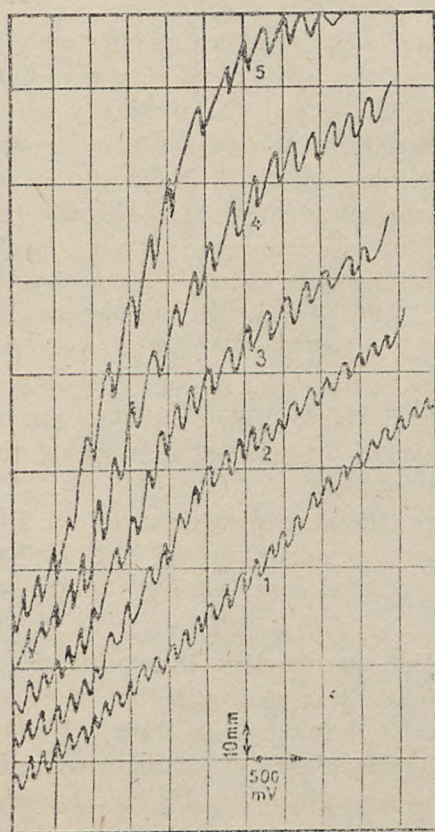
2.2.1. Sensitivity

Taking into account the sensitivity of the method as a basic criterion for the determination of uranium, a catalytic method reported in the literature is worth noting. The procedure consists in the catalytic oxidation of U(III) in a nitrate medium according to the following reaction



The 0.01 N HNO_3 supporting electrolyte used in this method enables the attaining of a sensitivity as high as $0.01 \mu\text{g}/\text{cm}^3$ [14]. The sensitivity is approx. 100 times higher than that attainable by other methods of conventional polarography and thus aroused the keen interest of analysts. Attempts were also made to achieve even better results by adding the

following compounds to the supporting electrolyte: HCl, H₂SO₄, H₃PO₄, KSCN, H₂S, H₂C₂O₄, alkali metal nitrates [12], HClO₄, NaClO₄, NaClO₃, TBP (tributyl phosphate), C₂H₅OH, LiNO₃, LiCl [18]. However, no progress has been achieved in terms of lowering the minimum detectable level or improving the quality of polarograms. As a matter of fact, the addition of sulphuric or hydrochloric acids with methyl red for suppressing polarographic maxima resulted in well-defined polarographic waves. However, this effect was achieved at the expense of a 5-fold increase of the minimum detectable amount, i.e. from 0.01 to 0.05 $\mu\text{g}/\text{cm}^3$ [12]. By lowering the pH of the HNO₃ solution from 2.0 to 1.7 with simultaneous reduction of the volume of polarographed sample from 1 to 0.5 cm³ it was possible to decrease the minimum detectable amount of uranium almost tenfold, i.e. to 0.001 $\mu\text{g}/\text{cm}^3$. The lowering of the pH of the solution, however, resulted in less distinct shape of the polarographic wave accompanied by generation of sharp peaks with an over oblique and over steep background curve outline. A well-defined shape was subsequently obtained (Fig.) by ensuring the following conditions [18].



Polarograms of UO_2^{2+} in HNO_3 of pH 1.7 — 1.8 1 — pure HNO_3 (pH 1.7 — 1.8); 2 — $2.1 \times 10^{-8}\text{M}$ UO_2^{2+} solution (2.5 ng U/0.5 cm³); 3 — $4.2 \times 10^{-8}\text{M}$ UO_2^{2+} solution (5 ng U/0.5 cm³); 4 — $6.3 \times 10^{-8}\text{M}$ UO_2^{2+} solution (7.5 ng U/0.5 cm³); 5 — $8.4 \times 10^{-8}\text{M}$ UO_2^{2+} solution (10 ng U/0.5 cm³). Sensitivity $s = 1/50$ (amplification 2); polarization rate 200 mV/min maximum compensation; chart speed 60mm/min; $t = 3.0$ s.

Polarogramy otrzymane dla roztworu UO_2^{2+} w HNO_3 o pH 1,7 — 1,8 1 — czysty HNO_3 (pH 1,7 — 1,8), 2 — $2,1 \cdot 10^{-8}\text{M}$ roztwór UO_2^{2+} (2,5 ng U/0,5 cm³), 3 — $4,2 \cdot 10^{-8}\text{M}$ roztwór UO_2^{2+} (5 ng U/0,5 cm³), 4 — $6,3 \cdot 10^{-8}\text{M}$ roztwór UO_2^{2+} (7,5 ng U/0,5 cm³), 5 — $8,4 \cdot 10^{-8}\text{M}$ roztwór UO_2^{2+} (10 ng U/0,5 cm³). Czulość $s = 1/50$ (wzmocnienie 2 \times), szybkość polaryzacji 200mV/min, maksymalna kompensacja, szybkość przesuwu taśmy 60 mm/min, $t = 3,0$ s.

(i) Both the polarographic cell and all glassware were carefully leached with aqua regia;

(ii) Both the supporting electrolyte and stock solutions of uranium were kept in polyethylene rather than in glass vessels. For each run, the nitric acid of pH 1.7 was freshly prepared;

(iii) For the preparation of fresh solutions immediately before runs, water double distilled in a quartz still was used;

(iv) Spectroscopic grade reagents were used throughout. Mercury was doubly distilled;

(v) Anodic mercury was added to the polarographic cell after de-aeration of a sample, otherwise interference due to hydrogen peroxide was observed;

(vi) Maximum compensation of the capacitive current was adopted with simultaneous 2-fold reduction of the polarization rate of the dropping electrode (from 400 to 200 mV per min). The chart speed was settled at 60 mm per min.

2.2.2. Selectivity

Prior to the application of a new method developed by using standards to assay an element in natural samples, the selectivity of the method should be estimated. The less selective the method, the more severe are the requirements for procedures employed for the preliminary separation of an element from accompanying ions. Antal [1] found that many ions occurring in the 0.01 N HNO₃ supporting electrolyte could interfere in the polarographic assay of trace amounts of uranium to a varying degree. At a uranium level of 0.2 µg/cm³ the results are affected by the ions of Cd, Co, Cr(III), Cu, Fe(III), Ni, Th, Ti, Zn and Zr present in concentrations higher than 10 µg/cm³, and those of Mo(VI), Sn(IV) and V(V) at concentrations exceeding 1 µg/cm³. Owing to their catalytic activity in the 0.01 N HNO₃ supporting electrolyte, the W(VI) ions distort strongly the shape of the polarographic wave of uranium at a concentration 100-fold lower than that of the uranium content.

The only anions which interfere are those complexing uranium. Fluoride and oxalate ions completely suppress the uranium wave. Phosphate and perchlorate ions reduce the height of the wave, while sulphate ions increase the limiting current [9].

The qualitative, and still more the quantitative interpretation of the polarograms can be rendered difficult or even impossible when the interfering ions occur in a sample at levels exceeding their allowable concentrations. As the 0.01 N HNO₃ was considered as a supporting electrolyte in the polarographic assay of uranium in natural waters, a separation procedure for this element was of paramount importance. Thiard [19] compared the following techniques of separating uranium from other ions: ethereal extraction, ion exchange and paper chromatography. Ion

exchange on a strongly basic anionite Amberlite IRA-400 was distinguished for its high selectivity and low time consumption. Taking into account the mean distribution of macro- and microcomponents in natural samples, less stringent requirements can be imposed on the separation process of uranium in natural waters than in solid natural samples. In inland waters, however, the levels of some elements can be increased by even several orders of magnitude. In this particular case, a very selective procedure has to be adopted for the separation of uranium, as is the case in the analysis of some Austrian spring waters and Australian ground waters containing considerable amounts of W and Mo [1, 5]. Further, when establishing preliminary conditions for the separation of uranium, an exceptional polarographic activity of tin occurring in the 0.01 N HNO₃ electrolyte, which acts as the activator of the reduction of uranium [1], should be taken into account. The effect of vanadium on the polarographic waves of uranium cannot be ignored. Vanadium can occur in enhanced concentrations in some inland waters in areas where deposits of the metal occur. It can also contaminate water bodies as a component of industrial waste waters. Trace amounts of platinum have also been found to interfere in the final assay of uranium in the 0.01 N HNO₃ supporting electrolyte. Although it is improbable that the rare metal will occur occasionally at levels exceeding the natural ones, interference in the polarographic curves due to this element cannot be ruled out. For this reason, platinum dishes should not be used for acid digestion of samples, as the metal can be leached out to some extent by oxidative acids thereby contaminating the solution with platinum ions. With the exception of the W (VI), Mo (VI), Sn (IV), V (V) and Pt (IV) ions, the remaining either do not produce any polarographic wave over the voltage range studied, or exhibit polarographic activity in the vicinity of the $E_{1/2}$ value for uranium at much more higher concentrations than that of uranium. In the latter case, interference due to the ions can be noted at concentrations at least 100-fold higher than that of uranium.

2.2.3. Comparison of the conventional polarographic technique with other methods

Owing to poor selectivity of the catalytic conventional polarography, it was compared with the fluorimetric [19] and photcolorimetric [17] methods. Although the fluorimetric method is characterised by a fairly low detection limit (0.001 µg U), its accuracy and time consumption are inferior to those of catalytic polarography. The fluorimetric method was employed by Antal [1] as the reference in the polarographic assay of uranium in natural waters using a catalytic nitrate wave. Analyses of water samples for uranium were run without interference and the

results obtained by using the two methods were comparable.

A photocolometric method with Arsenazo III was also employed as a reference, as this enables the assaying of uranium in the presence of a large excess of accompanying ions whose presence in the sample may affect the shape, height and position of the uranium wave. As the photocolometric method is less sensitive than the polarographic one, samples of water have to be increased from 0.5 to 2 dm³. The results obtained by using the photocolometric method conformed with those of the polarographic determinations [17].

3. SQUARE WAVE POLAROGRAPHY

Unlike conventional polarography, the square wave technique is characterised by a low detection limit, high separation performance and selectivity. The detection limit for reversible processes (two-electron) is 10⁻⁷M and for incompletely reversible 10⁻⁶M. The best selectivity is achieved for cathodic processes when the element to be determined undergoes reduction prior to that of a component present in excess. With a difference of the discharge potentials of two components amounting to 0.15 V, the concentration ratio of the ion to be determined/macrocomponent is 50,000.

To increase the sensitivity of determination of uranium by this technique, Milner and Nunn [13] studied the following supporting electrolytes: 0.5—1.5 M HCl, 0.25—1.5 M HNO₃, 1—3 M H₂SO₄ and 1—3 M HClO₄. The best results in terms of the detection limit (1 μg U/cm³) were obtained in the perchloric acid solutions. However, sodium tartrate had to be added to the supporting electrolytes to mask some interfering ions. The lowest detection limit of 0.6 μg/cm³ was achieved by using 2 M HClO₄ containing tartaric acid. At the same time, interfering effects due to the Bi ($E_{1/2} = -0.024$ V vs. SCE) and Fe (+0.10 V vs. SCE) ions were minimized. A chromium peak at $E_{1/2} = -0.43$ V vs. SCE can interfere with the uranium peak with a large excess of chromium to uranium. Similar interference can be due to Cu ions which produce a peak at the potential of the electrode reduction of chromium. Both the Mo ($E_{1/2} = -0.19$ V vs. SCE) and V ($E_{1/2} = +0.15$ V vs. SCE), even at low concentrations, make the quantitative recording of the uranium peak difficult or even impossible, as its half-wave potential is comparable with those of the electrode reduction of the two metals. On the other hand, the Zn, Ni, Cd, In, Co and Mn ions affect neither the shape nor the position of the uranium peak ($E_{1/2} = -0.225$ V vs. SCE). By using this supporting electrolyte the authors obtained an excellent detectable limit amounting to several tenths of a microgram of uranium in 1 cm³ of solution. The perchlorate electrolyte proved

useful for the polarographic determination of uranium in sewage.

The results obtained by the square-wave polarographic technique were subsequently checked by Milner and Nunn [13] by conventional polarography and neutron activation methods. Full conformity was achieved, thus confirming the suitability of this technique for assaying uranium in natural samples.

4. PULSE POLAROGRAPHY

The main advantage of pulse polarography lies in the very low limiting detectability. By using square-wave voltage with constant amplitude, detection limits of 10^{-8} M and 5×10^{-8} M for the reversible and irreversible processes, respectively, can be attained. By applying square wave voltage of increasing amplitude, the minimum detectable amount was increased to 10^{-7} M irrespective of the extent of reversibility of the reaction. Pulse polarography is less selective than square wave polarography.

In the pulse technique the supporting electrolyte had the same composition as that used in the square wave polarography. As the pulse technique is very sensitive, the detection limit when using perchlorate electrolyte was improved as compared with that of the square-wave technique. Whereas in the case of the latter technique no interference due to certain ions was observed, with the pulse technique their removal or masking is imperative. For this reason Milner et al. [4] reinvestigated the effect of foreign ions on the uranium peak recorded in a supporting electrolyte consisting of 2 M HClO_4 and 0.06 M sodium tartrate. The V(V), Cr(III), Mn(II), Ni(II), As(V), Ti(III) and Zn(II) ions did not produce peaks at concentrations of 10^{-3} , 6×10^{-5} , 3×10^{-5} , 8×10^{-5} , 6×10^{-5} , 4×10^{-5} and 3×10^{-5} M, respectively, in the vicinity of the uranium peak. The reason for this is either too high irreversibility of the reduction processes of the ions or appearance of their polarographic activity at too negative or too positive potentials lying beyond the operational scale of the instrument. The Fe(III) and Cd(II) ions developed peaks at $E_{1/2} = 0$ and -0.84 V vs. SCE, respectively, and their presence in a sample did not affect the results over a wide range of concentrations. The Cu(II) and Pb(II) ions did not interfere on the condition that the ratio of their concentration to that of uranium was less than 1. The strongest interference was due to the Mo(VI) ion which developed two peaks at $E_{1/2} = -0.18$ and -0.44 V vs. mercury pool anode.

Wilson and associates [2] compared results of analyses of sea water samples carried out by means of pulse polarography, fluorimetric and isotopic dilution methods. The authors evaluated carefully not only the accuracy of the methods, but also such important features of routine

analyses as time required for performing the appropriate procedures, total duration of analysis, the number of manhours per analysis and required sample size. The high precision of the pulse polarography and isotope dilution methods has been emphasized. The addition of an internal standard enables the elimination of errors due to losses during concentration and separation of uranium. This modification, however, extends the time required for analysis.

5. DIFFERENTIAL-PULSE POLAROGRAPHY

It is worthwhile mentioning the differential-pulse polarographic technique employed by Deutscher and Mann [5] for analysis of ground water for uranium. The minimum detectable amount achieved by the authors was $6 \mu\text{g U/dm}^3$ with 0.05 M TOPO (trioctyl phosphonium oxide) and 0.1 M LiClO_4 in an ethanol-cyclohexane (1:1) mixture as the supporting electrolyte. The ions of V(V), Cu(II), Fe(III), Ni(II) and Mo(VI) present in water samples at a concentration of $60 \mu\text{g/dm}^3$, as well as those of Ce(IV) and Pb(IV) at the $200 \mu\text{g/dm}^3$ level did not hinder uranium determination. Only those of Mo(VI) caused interference due to the development of a peak at -0.33 V vs. SCE colliding with that of uranium. The remaining ions were not extracted at all and ascorbic acid added before separation reduced the Ce(IV), Fe(III) and V(V) ions to forms non-coextractable with uranium.

Attempts to use the catalytic uranium/nitrate wave for assaying nanogram amounts of uranium by the differential pulse polarographic technique were successful.

Keil [8] found 0.02 N HNO_3 to be a suitable supporting electrolyte for assaying uranium in various natural waters and solid mineral samples. The isolation of uranium and simultaneous separation from accompanying ions was accomplished by extraction with a chloroformic solution of triphenylarsine oxide. An aqueous phase obtained after back extraction of uranium with 0.02 N Na_2CO_3 was acidified with such an amount of HNO_3 as to obtain a supporting electrolyte 0.01 N in HNO_3 and 0.02 N in NaNO_3 . Uranium peaks taken in this electrolyte were legible and reproducible, the extraction procedure employed making the method highly selective. Of 80 ions tested by the author, only three were found to affect the results, including Au(III) and Cr(VI) at 50-fold excess and Fe(III) ions at 1000-fold excess in relation to uranium.

6. OSCILLOPOLAROGRAPHY

A branch of polarography in which a cathode-ray oscillograph is em-

ployed is referred to as oscillopolarography. The technique has been used to observe the relation of three variables — voltage, current and time. In studies of electrode processes the most important is the relationship between voltage and time, $V=f(t)$, whilst in the quantitative analysis current intensity vs. voltage is of interest, $i=f(V)$. Unlike conventional polarography, variations of voltage in oscillopolarography occur very rapidly, reaching several tens of volt per s. With this technique, a component can be determined at lower concentrations, as the maximum current recorded in oscillopolarography is several times higher than diffusion current in d. c. polarography. The minimum detectable amount is about $10^{-7}M$.

Fauth [6] determined uranium levels in some 30,000 samples of inland waters collected in the Federal Republic of Germany, Peru, Mali, Togo, Ghana, Mozambique and Angola. The author concentrated uranium on $Fe(OH)_3$ from 2-litre samples. After the precipitate settled, the water was decanted and $Fe(OH)_3$ dissolved in nitric acid. Uranium was then selectively separated from this solution by tributyl phosphate and then back extracted. By using a $H_2SO_4-HClO_4$ supporting electrolyte, the author achieved a lower detection limit of about 0.2 ppb of uranium. The relative error was between 20 and 60 per cent depending on the working conditions. An average of 70—90 uranium analyses per man per working day can be made.

The oscillopolarographic technique was found by the author to be superior to the fluorimetric and colorimetric methods.

7. SINGLE-SWEEP POLAROGRAPHY

Single-sweep polarography is a simple, rapid and inexpensive method of trace element analysis in natural waters [20].

Whitnack [21] described polarographic determination of a variety of elements, including uranium, in river water, well and spring water, tap water, sea water and effluent waters from many sources. The elements were readily detected and measured to levels as low as 5 ppb. Well-defined uranium polarograms appeared at $-0.58V$ and $-0.72V$ in 0.05 M tartaric acid and in 0.05 M triethanolamine, respectively.

8. GENERAL EVALUATION OF SELECTED POLAROGRAPHIC TECHNIQUES FOR THE DETERMINATION OF URANIUM IN NATURAL WATERS

Results obtained by the pulse-polarographic technique revealed the source of variations in uranium levels in samples taken from the same areas

of the North Atlantic and North Pacific Oceans. Wilson and associates [2] and Milner and associates [4] showed that differences obtained by earlier workers were not primarily due to different analytical techniques employed, but rather by variations in the extraction and concentration steps in the actual analyses. To avoid the errors, the authors suggest to add a ^{237}U tracer to the original sea water. It is thus possible to account for losses of the natural uranium during individual analytical steps.

Taking into account sensitivity, accuracy and selectivity as basic criteria characterising various methods, the pulse technique [4], including preconcentration of uranium, can be considered to meet the principal requirements posed to methods of trace analysis (Table 1). This

Table 1. Evaluation of analyses of 4-litre sea water samples for uranium by the pulse polarographic technique [2, 4]

Tab. 1. Ocena analiz 4-litrowych prób wody morskiej na zawartość uranu techniką polarografii impulsowej [2, 4]

| No. Lp. | Analytical operation Rodzaj operacji analitycznej | Min. time for analysis Minimalny czas analizy | No. of man hours per sample Liczba osobogodziny na próbę | Std. dev of a single result Odchylenie standardowe pojedyn. wyniku | Overall coeff. of variation Całkowity współ. zmienn. |
|---------|--|--|---|---|---|
| 1 | Addition of indicator Dodanie wskaźnika | 1 day 1 dzień | — | | |
| 2 | Extraction of uranium (2 extractions, 1 back extraction, 2 evaporations; usually 6 samples simultaneously) Ekstrakcja uranu (2 ekstrakcje, 1 reekstrakcja, 2 odparowywania zazwyczaj 6 prób jednocześnie, | | 8 | 0.06—0.07 | 1.4% |
| 3 | Measurement of radiochemical yield Pomiary odzysku radiochemicznego | 2 days | 2 | | |
| 4 | Measurement of total uranium Pomiary zawartości uranu | | 5 | | |

conclusion was supported by full conformity of results obtained by this and the reference methods, fluorimetric and isotopic dilution [2].

On the other hand, the use of the nitrate catalytic method to assay uranium in natural waters may be cumbersome owing to poor selectivity, lower precision than that in the method developed by Milner

and associates [4] and a time-consuming step of separation preceding determination of uranium (cf. Table 2). For this reason the 0.01 N HNO₃ supporting electrolyte is not suitable for routine determinations. It may be useful in those cases where uranium concentration is very low, being below the detection limits of the element by other methods. When-

Table 2. Evaluation of the results of analyses of 2-litre samples of sea water for uranium by conventional polarography using the catalytic uranium/nitrate wave¹⁸⁾

Tab. 2. Ocena analiz 2-litrowych prób wody morskiej na zawartość uranu techniką polarografii klasycznej z wykorzystaniem katalitycznej fali uran/azotan¹⁸⁾

| No. Lp. | Analytical operation Rodzaj operacji analitycznej | Min. time for analysis Min. czas analizy | No. of man hours per sample Liczba osobo-godzin na próbę | Std. deviation of a single result Odchylenie standardowe poj. wyniku | Overall coeff. of variation Całkowity współczynnik zmienności |
|---------|--|---|---|---|--|
| 1 | Passage of the water sample through an ion-exchange column including prepn. of the ion exchange resin Przepuszczenie próby wody przez kolumnę jonowymienianą łącznie z uprzednim przygotowaniem żywicy | 1 day 1 dzień | 10 | | |
| 2 | Washing of the resin and elution of U; simultaneous evaporation of 3 samples Przemywanie żywicy oraz elucja U z odparowaniem 3 prób równocześnie | | 5 | | |
| 3 | Second sepn. of U; simultaneous evapn. of 3 samples Przeprowadzenie drugiej operacji rozdzielania U z odparowaniem 3 prób równocześnie | 2 days 2 dni | 4 | 0.027 | 11.2% |
| 4 | Polarographic detn. of U including prepn. of fresh supporting electrolyte of pH 2.0 each time. The pH was detd. electrometrically Oznaczenie polarograficzne U łącznie ze sporządzeniem zawsze świeżego elektrolitu podstawowego o pH=2,0 (pH wyznaczono elektrometrycznie) | | 4 | | |

analyzing Baltic Sea waters of lower salinity (ca. 7 per mille), it is advisable to add sodium chloride (p.a.) before separation in amounts ensuring about 5-fold increase in salinity. The purpose of this operation

is to attain an optimum concentration of chloride ions ensuring better sorption of uranium on Amberlite IRA-400 (Cl⁻).

The differential pulse polarography technique [8] in routine determinations of trace amounts of uranium by using the catalytic uranium/nitrate wave would appear to offer good prospects. The lowest detection limit achieved by the author is 1 ppb U and the relative standard deviation ± 2 per cent. In this relatively rapid analysis of 200-cm³ water samples, the extraction process with triphenylarsine oxide as the extractant afforded an 80 per cent uranium recovery.

The data given in Table 3 characterize methods of concentration of uranium and polarographic techniques used for its determination in natural waters.

Piotr SZEFER

Akademia Medyczna w Gdańsku
Zakład Chemii Analitycznej

CHARAKTERYSTYKA PRZYDATNOŚCI WYBRANYCH TECHNIK POLAROGRAFICZNYCH DO OZNACZANIA URANU W WODACH MORSKICH I ŚRÓDLĄDOWYCH

Streszczenie

W pracy dokonano przeglądu literatury na temat oznaczania śladowych ilości uranu, przy zastosowaniu technik polarografii klasycznej, prostokątnej, impulsowej, różnicowej polarografii impulsowej i oscylopolarografii. Wskazano na możliwość zaadaptowania tych technik do oznaczania mikro- i nanogramowych ilości uranu w różnego typu wodach naturalnych. Scharakteryzowano podstawowe kryteria ocenianych metod, jak wykrywalność, selektywność i precyzję z równoczesnym uwzględnieniem rodzaju zastosowanego sposobu zagęszczania i oddzielania uranu. Przy opisie metod polarografii klasycznej (stałoprądowej) zwrócono uwagę na możliwość zastosowania roztworu 0,01 HNO₃ jako elektrolitu podstawowego do oznaczania nanogramowych ilości uranu w wodach naturalnych. Spośród metod zmienoprądowych wyróżniono technikę polarografii impulsowej z zastosowaniem elektrolitu podstawowego składającego się z 2 M HClO₄ i 0,06 M winianu sodowego. Na szczególną uwagę zasługuje technika oscylopolarograficzna oznaczania uranu w wodach śródlądowych. Charakteryzuje się wysoką wykrywalnością i małą czasochołnością. Autor metody posłużył się nią w analizie 30 tys. prób wód śródlądowych na zawartość uranu i podkreślił wyższość metody oscylograficznej nad metodami fluorymetryczną i kolorymetryczną.

Na podstawie ogólnej oceny opisanych metod wskazano na możliwość zastosowania techniki oscylopolarograficznej i impulsowej w seryjnych analizach wód naturalnych na zawartość uranu.

Table 3. Data on procedures of concentration of uranium and polarographic techniques used for its determination in natural waters of various origin

Tab. 3. Dane dotyczące zastosowania metod zagęszczania uranu oraz techniki polarograficznej jego oznaczania w różnego typu wodach naturalnych

| Origin of water Rodzaj analizowanej wody | Uranium level found Oznaczone stężenie uranu w wodzie ($\mu\text{g}/\text{dlm}^3$) | Concentration and separation methods employed Zastosowana metoda zagęszczania i oddzielania uranu | Composition of supporting electrolyte Skład elektrolitu podstawowego | Half-wave potential Potencjał półfali (V) | Minimum detectable limit Wykrywalność (mol/dlm^3) | Reference Literatura |
|---|---|--|---|--|--|-------------------------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Conventional polarography Polarografia klasyczna | | | | | | |
| Coastal water the N.W. Pacific Woda z płn.-zach. wybrzeży Pacyfiku | 1.5 — 1.7 | Concentration of uranium on the Fe (OH) ₃ carrier followed by removing Fe by pptn. with carbonate. Uranium was separated from other ions by column chromatography using cellulose | The vat blue 2R in acetate buffer of pH 5.3 with Triton X-100 for suppressing maxima | -0.5 | 4×10^{-6} | 3,7 |
| | | Zagęszczenie U na Fe(OH) ₃ jako nośniku z następnym usunięciem Fe przez jego wytrącenie węglanem | Błękit zaprawowy 2R w zbuforowanym roztworze octanowym o pH 5,3 z Tritonem X-100 jako substancją tlumiącą maksima | | | |
| | | Oddzielenie U od innych jonów dokonano sposobem chromatografii kolumnowej z użyciem celulozy. | | | | |

| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|-------------|--|--------------------------|--------------------------------|----------------------|------------------|
| Coastal Baltic Sea water (Bay of Gdańsk) | 0.3 — 0.6 | Concentration and separation of U on a strongly basic Amberlite IRA-400 (Cl-) anion exchanger, performed in two steps from the Cl- and CH ₃ COO- media. Another procedure consisted in separation of U from Th on the Amberlite IRA-400 and Dowex-50 ion exchangers | 0.001 N HNO ₃ | —0.98 (vs. SCE) (wzgl. NEK) | 4.2×10^{-3} | 10, 11 17, 18 |
| Przybrzeżna woda bałtycka (Zatoka Gdańska) | | | | | | |
| Swedish river waters Wody rzeczne Szwecji | 0.21 — 1.86 | Zagęszczanie i oddzielenie U na silnie zasadowym anionie Amberlit IRA-400 (Cl-) przeprowadzone w dwóch operacjach rozdzielczych ze środowiska Cl- i CH ₃ COO-. Innym sposobem jest oddzielenie U od Th za pomocą jonitów Amberlit IRA-400 oraz Dowex-50. | | | | |
| Austrian spring waters Wody źródlane Austrii | 0.41 — 12.5 | | | | | |

Pulse polarography
Polarografia impulsowa

| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|--|----------|--|--|--|----------------------|---|
| Bay of Biscay waters Woda Zatoki Biskajskiej | 3.33 | Coprecipitation of U on AlPO_4 from water of pH 6; extraction of U in the form of 8-hydroxyquinoline or D_2EHPA in CCl_4 followed by back extraction of the element with conc. HCl . Współstrącanie U na AlPO_4 z wody o pH 6; ekstrakcja U w postaci 8-hydroksychinolinianu lub D_2EHPA w CCl_4 z reakcją pierwiastka stężonym HCl . | A 2 M solution in HClO_4 and 0.06 M in Na hydrogen tartrate Roztwór 2 M wzgl. HClO_4 i 0.06 M wzgl. wodorowinianu sodowego | -0.39 vs. mercury pool anode -0.39 wzgl. anodowej rtęci | 2×10^{-6} | 2 |
| Ground waters from the Murchison District of Western Australia Wody gruntowe z okręgu Murchison w zach. Australii | 42 — 215 | U was extracted from an acidified water sample with ascorbic acid by means of TOPO in cyclohexane Z zakwaszonej próby wody z dodatkiem kwasu askorbowego ekstrahowano U za pomocą TOPO w cykloheksanie | 0.05 M TO PO and 0.1 M LiClO_4 in 1:1 ethanol — cyclohexane Roztwór o składzie: 0.05 M TOPO, 0.1 M LiClO_4 w mieszaninie etanol — cykloheksan 1:1 | -0.30 vs. SCE wzgl. NEK | 3.5×10^{-7} | 5 |

Differential-pulse polarography
Różnicowa polarografia impulsowa

| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|--|---|---|---|---|--|---|
| <p>Ground, river and spring waters in the Federal Republic of Ghana, Mali, Mozambique, Peru, Togo and Angola</p> | <p>0.5 — 3.00 (in some reservoirs levels lower than 0.5 and higher 12 $\mu\text{g}/\text{dm}^3$)</p> | <p>Concentration of uranium ($\text{Fe}(\text{OH})_3$, dissolution of the precipitate in HNO_3 followed by extract of uranium with TBP and back extraction of the element.</p> | <p>Aqueous solution of $\text{H}_2\text{SO}_4 + \text{HClO}_4$ Wodny roztwór H_2SO_4 i HClO_4</p> | — | <p>8.4×10^{-7}</p> | 6 |
| <p>Wody gruntowe, rzeczne i źródlane w RFN, Gambia, Mozambiku, Peru, Togo i Angoli</p> | <p>(w niektórych zbiornikach oznaczano zawartość niższe niż 0.5 i wyższe niż 12 $\mu\text{g}/\text{dm}^3$)</p> | <p>Zagęszczenie uranu na $\text{Fe}(\text{OH})_3$, rozpuszczenie osadu w HNO_3, ekstrakcja uranu za pomocą TBP i re-ekstrakcja tego pierwiastka</p> | | | | |

Oscillopolarography
Polarografia oscylacyjna

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