



REVIEW ARTICLE

Various electroanalytical methods for the determination of uranium in different matrices

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Received 26 August 2012; accepted 23 September 2012

Available online 11 January 2013

KEYWORDS

Uranium and its compounds;
Electrophoresis;
Potentiometry;
Capillary electrophoresis;
Voltametric;
Polarography

Abstract Uranium is a toxic material hence numerous body systems such as the kidney, brain, liver, and heart can be affected by uranium exposure. The main effect is kidney toxicity. Uranium is a naturally occurring element found in low levels in all rock, soil, and water. All uranium isotopes may also cause radiation hazards, thus without any doubt an analysis of such materials in the surrounding environment is very important. The presented review is a summarization of all electroanalytical techniques for the determination of uranium and its compounds in various matrices. Totally 43 different methods are found in our literature survey. Out of these three are polarographic, 25 potentiometry, five capillary electrophoresis and 28 voltametric methods are available in the literature. Interferences of different ions and applications in different matrices are also given for each method.

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Peer review under responsibility of Faculty of Pharmacy, Cairo University.



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1. Introduction

Uranium is an element of the actinide series, has an atomic number of 92 and, in its refined state, it is metallic silver in color, malleable, ductile, slightly paramagnetic, and very dense. In rocks and ore, this element is not found in the metallic state but generally occurs in minerals such as carnotite, uraninite, and pitchblend. Uranium in the environment occurs naturally as three radioactive isotopes: ^{238}U (99.27%), ^{235}U (0.72%) and ^{234}U (0.005%), but other isotopes can be synthesized.¹ On average, the earth's crust contains nearly about 4 mg kg^{-1} uranium. ^{235}U is the only naturally occurring 'fissile' material.²

Uranium is an element that naturally presents various oxidation states (namely +2, +3, +4, +5 and +6), but uranium appears mostly in its hexavalent form. Usually in nature, uranium is associated with oxygen, forming the uranyl ion UO_2^{2+} . Uranium is also present often in a tetravalent state in nature on a strongly reducing medium, like water with a high amount of organic material.¹ Uranium behaves differently from many other metals due to its variable oxidation state and a tendency to form a wide variety of positive, neutral and negatively charged complexes, at approximately neutral pH. Unlike many other radioactive elements, its half life is commensurate with the age of the earth and, because of this, small amounts of uranium are found almost everywhere in soil, rock and water. The determination of uranium requires high selectivity due to its strong association with other elements.³

Uranium eventually reaches the top of the food chain causing severe damage to liver and kidneys, resulting in death. The World Health Organization has determined that hexavalent uranium is a carcinogen, and its concentration in water should not exceed 50 mg L^{-1} . The USA Environmental Protection Agency has recommended a drinking water standard of 20 mg L^{-1} for ^{238}U . In fact, uranium intake generates biochemical and genetic damages to the mammalian organisms.⁴

Uranium is an element of great commercial interest because of its use in the production of nuclear energy, in the manufacture of nuclear weapons, in the shielding of industrial radioactive sources and even as anti-tank ammunition. Unfortunately, human activities involving mining and milling activities, nuclear weapons and nuclear fuel fabrication have caused widespread environmental contamination. Additionally, contamination may be caused by catalysts, staining pigments, burning of fossil fuel (oil and coal) and the manufacture and use of phosphate fertilizers that contain uranium.¹ Thus there is a clear need for suitable analytical methods for its determination in various matrices.

Electrochemical methods are routinely used in analytical chemistry. Also known as electroanalytical techniques, they have been developed for measurements in the laboratory, mostly for fundamental research.⁵ Electroanalytical techniques

have undergone many important developments in recent decades.⁶

Modern electrochemical methods are now sensitive, selective, rapid and easy techniques applicable to analysis in the pharmaceutical fields, and indeed in most areas of analytical chemistry. They are probably the most versatile of all trace pharmaceutically active compound analysis. Electroanalytical methods are also widely used in specific studies and monitoring of industrial materials, biological samples and the environment. It is apparent that the electroanalytical techniques at varying levels of sensitivity are required to solve analytical-pharmaceutical problems. This kind of assays require high specificity, low detection and determination limits and capable of determining drugs and their metabolites with nanogram or picogram level simultaneously.

Electrochemistry has always provided analytical techniques characterized by instrumental simplicity, moderate cost and portability. Electroanalytical techniques can easily be adopted to solve many problems of pharmaceutical interest with a high degree of accuracy, precision, sensitivity and selectivity, often in a spectacularly reproducible way by employing this approach.⁷

Currently, the most widely used methods in the analysis of drugs are separation-based techniques. Examples are variants of chromatography and electrophoresis. These techniques are excellent, when dealing with complex samples like urine or when following the products of drug metabolism. In analyses of tablets or injection solutions, in particular of samples containing a single physiologically active component, electroanalytical techniques can, in some instances, offer some advantages, among them: (1) simple sample handling; (2) speed of analysis; (3) high sensitivity; (4) comparable or better accuracy; (5) cheaper instrumentation and lower cost of chemicals used; and (6) limited use of environmentally unfriendly organic solvents.⁸

There are some reviews already present in the current literature about various analytical methods available for the determination of uranium in various matrices^{1,2,9} but a description of electroanalytical methods was not attempted till date. Applications of these techniques are already discussed in the above paragraph and thus there is a clear need to summarize such excellent techniques for the determination of uranium both in the field and laboratory.

2. Electroanalytical methods

There are 25 studies found in the literature related to electroanalytical determination of uranium. Out of these three polarographic, 25 potentiometry, five capillary electrophoresis and 26 voltametric methods are available in the literature.

2.1. Polarography

Three polarographic methods were found. In the method developed by Dojozan et al.¹⁰ U(VI) oxinate is formed by the reaction of U(VI) with 8-hydroxyquinoline and adsorbed onto the octylsilane (C-8) SPE cartridge. The analyte is completely eluted with chloroform and determined by differential pulse polarography. By the proposed method a preconcentration factor of more than 100 was achieved. The reference, working and auxiliary electrode were Ag:AgCl (sat.), DME and platinum wire respectively. The supporting electrolytes used were tri-butylammonium perchlorate (tri-BAP) and tetrabutylammonium perchlorate (TBAP).

In another method reference electrode Ag/AgCl (satd.), tri-butylammonium perchlorate (satd.) and tetrabutylammonium perchlorate 0.5 M in chloroform in a separated compartment was directly immersed in the reaction cell. The working electrodes were DME (dropping mercury electrode) and HMDE (hanging mercury drop electrode) and the auxiliary electrode was a platinum wire. The supporting electrolytes used were 0.3 M tri-butylammonium perchlorate (tri-BAP), 0.5 M tetrabutylammonium perchlorate (TBA) or 0.75 M piperidinium perchlorate (PP) + 0.25 M piperidine (P).¹¹

In another method determination of U(VI) in organic extraction phases: hydrocarbon-diethyl-2-hexyl phosphoric acid-trioctylphosphine oxide and hydrocarbon-tri-*n*-octylamine, diluted by an alcohol have been studied by direct current polarography and differential pulse polarography (DPP).¹² An aqueous saturated calomel electrode (SCE) was used (without additional bridge) as a reference electrode, while the counter electrode was a platinum cylinder. Sulfuric acid (0.1 M) was chosen as supporting electrolyte. This study also includes miscibility tests of the supporting electrolyte with the alcohol-hydrocarbon system as well as conductivity measurements. The miscibility was increased with hydrocarbon diluent addition in the following order: *n*-dodecane < kerosene < *n*-hexane. For a given sulfuric acid concentration, the conductivity also increased in the same way.

2.2. Potentiometry

Potentiometric measurements are based on monitoring potential values under a zero current flow regime, in order to determine the analytical concentration of desired components in an analyte.¹³ In recent years, there has been considerable interest in the development of various types of solid-state electrochemical sensors (i.e., ion, gas, and biosensors), in which polymer membranes are cast on solid surfaces with no internal reference electrolyte solutions.¹⁴

There is a special interest for U(VI) analysis in nuclear industry, in particular for use in fuel separation and processing. Because Fe(II) is often used as a reducing agent, Fe(II) and Fe(III) are interfering ions of particular concern. Characteristic for the determination of uranyl is the small available pH range, which is limited by the occurrence of several U(VI) species in the aqueous solution. Besides the linear UO_2^{2+} species, UO_2OH^+ , $\text{UO}_2(\text{OH})_2$ dimers, and complexes of UO_2^{2+} with anions in solution are formed. While the above pH 3.5 $\text{UO}_2(\text{OH})_2$ starts to precipitate, at pH 3.5 or lower free UO_2^{2+} accounts for more than 96% of the uranyl species if the concentration of the total amount of uranyl is 10^{-4} M or smaller. However, the occurrence of other forms has usually not

been taken into account when calculating selectivity coefficients. Furthermore, activities and concentrations were used alternately to evaluate selectivities.¹⁵

Two recent publications are on the semi-automatic version of the potentiometric titration method for the characterization of uranium compounds.^{16,17} This method is used to determine the total uranium concentration, without chemical separation, in solutions containing iron, plutonium and nitrate. Both methods were applied with traceability assured by using a potassium dichromate primary standard. It was observed that the semi-automatic method, using the automatic buret, reduced the time required for titration from 15 to 20 min (manual) to 5 min (semi-automatic).

One of the simple determinations of uranium(IV) found is based on reduction to uranium(IV) with zinc metal in the acidic medium, and then oxidation by the addition of a known excess of peroxodisulfate. A measured excess of potassium bromide is added to reduce unreacted peroxodisulfate, and the excess bromide is titrated potentiometrically with silver. The amount of silver = bromide = peroxodisulfate = uranium is determined.

Another modified Davies and Gray method is based upon the reduction of U(VI) to U(IV) with a reductant (e.g. Fe^{++}) followed by a selective oxidation of the excess of reductant and subsequent titration of U(IV) with potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$).¹⁹

In a similar publication U(VI) was titrated with Fe(III), in the titration medium consisting of sulfamic acid, phosphoric acid, sulfuric acid, nitric acid and molybdenum(VI) as catalyst. Saturated calomel reference electrode and a platinum indicator electrode were used in the titration.²⁰

In two more recent publications the redox titration of U in H_3PO_4 solution with an automatic titrator for the determination of small amounts of U (0.1–0.2 mg) was studied. The choice of the oxidant appreciably affects the accuracy of the U determination, which decreases in the order $\text{KMnO}_4 > \text{K}_2\text{Cr}_2\text{O}_7 > \text{NH}_4\text{VO}_3 > \text{Ce}(\text{SO}_4)_2$. Publications on KMnO_4 as the most promising oxidant for the determination of small amounts of U by potentiometric titration in H_3PO_4 , as it ensures the smallest uncertainty of the analysis were studied.²¹

Another recent publication is the determination of 0.1–0.2 mg of U in mixed phosphoric–sulfuric acid solutions containing 6 M H_3PO_4 and 1.25 M H_2SO_4 , the titrant efficiency decreases in the order $\text{NH}_4\text{VO}_3 > \text{KMnO}_4 > \text{Ce}(\text{SO}_4)_2 > \text{K}_2\text{Cr}_2\text{O}_7$. In 2 M H_2SO_4 , the use of KMnO_4 as titrant allows the determination of 0.02–0.1 mg of U with the uncertainty within 10%. Uranium can be determined > 0.1 mg.²²

The summary of different potentiometric sensors used for the determination of uranium^{23–39} is presented in Table 1.

2.3. Electrophoresis

CE techniques constitute a very attractive alternative to more common methods of determining inorganic cations (spectroscopy, chromatography), primarily because of a high resolution and possibility of multicomponent separation using simple and rapid procedures. On the other hand, the limits of detection and quantitation often compare with those attained in spectroscopy and chromatography.⁴⁰ Capillary electrophoresis (CE) is an establishing separation technique of choice effective for a wide spectrum of analytes, ranging from small inorganic ions to DNA macromolecules as it provides reliable data,

Table 1 Different potentiometric sensors for the determination of uranium.

Sensor membrane	Range (mol L ⁻¹)	Detection limit (μM)	Interfering ions	References
Bis(2-ethylhexyl)phosphoric acid + tributylphosphate	10 ⁻¹ –10 ⁻⁴	< 100	Cu ²⁺ , Fe ³⁺ , NO ³⁻ , ClO ⁴⁻ , PO ₄ ³⁻ , I ⁻	23
Bis{di[4-(1,1,3,3-tetramethyl butyl)phenyl]phosphate} + dioctylphenylphosphonate	9 × 10 ⁻² –10 ⁻⁴	< 100	Fe ³⁺	24
Tris(chloroethyl or propyl)phosphite	10 ⁻¹ –10 ⁻⁴	< 100	Cr ³⁺ , Fe ³⁺ , Ce ⁴⁺ , U ⁴⁺	25
Tri- <i>n</i> -butylphosphate + tri- <i>n</i> -octyl phosphine oxide	10 ⁻¹ –10 ⁻⁴	< 100	Ni ²⁺	26
Tetraphenyl- <i>o</i> -xylyldiphosphine dioxide	10 ⁻¹ –10 ⁴	< 100	NM	27
1,11-Bis(2-benzylox-5-formylphenoxy)-3,6,9-trioxaundecane + nitrophenyloctyl ether	10 ⁻² –2.5 × 10 ⁻⁴	< 100	Fe ³⁺	28
<i>O</i> -Methyldihexyl phosphine oxide <i>O'</i> -hexyl-2-ethyl-phosphoric acid + bis(2 ethyl hexyl)sebacate	2 × 10 ⁻²	3.0	Fe ³⁺ , Al ³⁺ , Mn ²⁺ , F ⁻ , PO ₄ ³⁻	29
<i>N,N'</i> -Diheptyl- <i>N,N'</i> ,6,6-tetramethyl-4,8-dioxaundecanediamide + 1-chloronaphthalene	10 ⁻² –10 ⁻⁵	NM	Th ⁴⁺	30
<i>N,N'</i> -Heptyl- <i>N,N'</i> ,6,6-tetramethyl-4,8-dioxaunde-	10 ⁻¹ –10 ⁻⁵	< 10	NM	31
Di-(4- <i>n</i> -octylphenyl) phosphate + bis(2-ethylhexyl)phosphate	10 ⁻¹ –5 × 10 ⁻⁵	NM	Sr ²⁺ , Ca ²⁺ , Ba ²⁺ , F ⁻	32
Tris(2-ethylhexyl)phosphate	1 × 10 ⁻¹ –2 × 10 ⁻⁵	1.3 × 10 ⁻⁵	Fe ³⁺ , Ca ²⁺ , V ⁴⁺ , F ⁻	33
<i>O</i> -(1,2-dihydro-2-oxo-1-pyridyl)- <i>N,N,N'</i> -bis(tetra-methylene)uronium hexafluorophosphate + dioctyl phenylphosphonate	1 × 10 ⁻¹ –5 × 10 ⁻⁵	2.7 × 10 ⁻⁵	Fe ³⁺ , Th ⁴⁺ , F ⁻	
Bis(2-hydroxyacetophenone) ethylenediimine	5.0–10 ⁻⁶ –0.05	approx. 2.0 μM	Zn ²⁺ , Co ²⁺ , Cd ²⁺ , Pb ²⁺ , Ag ⁺ , Fe ³⁺ , Cu ²⁺ , Ni ²⁺ , K ⁺ , Th ³⁺	34
Ion imprinted polymer (biomimetic) in polyvinyl chloride matrix.	2.0 × 10 ⁻⁸ –1.0 × 10 ⁻²	2.0 × 10 ⁻⁸	No interference	35
Polymeric membrane (PME) and coated graphite (CGE)	(1.0 × 10 ⁻⁶ –1.0 × 10 ⁻¹ M for PME and 1.0 × 10 ⁻⁷ –1.0 × 10 ⁻¹ M for CGE)	8.0 × 10 ⁻⁷ M for PME and 7.3 × 10 ⁻⁸ M for CGE	Selectivity coefficients between 10 ⁻² –10 ⁻⁴ [negligible interference]	36
5,6,7,8-Tetrahydro-8-thioxopyrido[4',3',4,5]thieno[2,3-d]pyrimidine-4(3H)one	1.0 × 10 ⁻¹ –2.0 × 10 ⁻⁵	1.0 × 10 ⁻⁵ mol l ⁻¹	No interference	37
<i>N,N'</i> -4,5-(ethylenedioxy)benzenebis(salicylideneimine)	1.0 × 10 ⁻² –1.0 × 10 ⁻⁶	3.2 × 10 ⁻⁷	No interference	38
5,11,17,23,29,35-hexa- <i>tert</i> -butyl-37,38,39,40,41,42-hexahydroxy calix[6]arene (calixarene I) and tri- <i>n</i> -octyl phosphine oxide (TOPO)	10 ⁻¹ –10	NM	Cu ²⁺ , Ni ²⁺ , Co ²⁺ and Al ³⁺ , while Fe ³⁺ , Th(IV), EDTA and F ⁻ interfered seriously	39

NM: not mentioned.

*Minimized by using diethylenetriaminepenta acetic acid (DTPA) masking agent followed by re-extraction of uranium from the solvent by stripping with water.

Table 2 Summary of various electroanalytical methods reported for the determination of uranium and compounds.

References	Method	Principle	Linearity range	LOD	Interference tolerance	Application
[10]	Differential pulse polarography	U(VI) oxinate is formed by the reaction of U(VI) with 8-hydroxyquinoline and adsorbed onto the octylsilane (C-8) SPE cartridge. Uranium oxinate shows good electrochemical behaviors in chloroform. Analyte is completely eluted with chloroform and determined by differential pulse polarography	0.5–80 μM	0.4 μM	Ca ⁻² , Mg ⁻² and Fe ⁻³ , Cu ²⁺ were masked with EDTA	Caspian Sea and Persian Gulf water samples
[11]	Adsorptive pulse polarographic determination	Measurement of voltammetric characteristics of uranium(W) oxinate in chloroform at a mercury electrode	0.5–80 μM	0.5 μM	Among the metal ions Fe(III), Bi(III), Cd(II), Zn(II), Co(II), Ni(II), Cu(II), Pb(II), Al(III), In(III), Ga(III), Tl(III) and V(V), potentials of the Cu(II) and V(V) reduction are sufficiently different and hence do not cause any severe interference. Presence of Fe(III) is undesirable but extraction at pH 6 with 0.05 M oxine solution in the presence of 0.05 M EDTA masks Fe(III), Cu(II) and V(V), and prevents the interference of 1000-fold molar excesses of iron	Uranium mineral ores
[12]	Direct current polarography (DCP) and differential pulse polarography (DPP)	Determination of U(VI) in organic extraction phases: hydrocarbon-diethyl-2-hexyl phosphoric acid-trioctylphosphine oxide and hydrocarbon-trin-octylamine, diluted by an alcohol. The dropping mercury electrode had the following characteristics: mercury flow-rate $m = 1.8 \text{ mg s}^{-1}$ and drop lifetime $t = 1.0 \text{ s}$	2×10^{-6} and $2 \times 10^{-3} \text{ M}$	$3 \times 10^{-7} \text{ M}$ (DPP) and $8 \times 10^{-6} \text{ M}$ (DCP)	Not defined	Routine analytical procedure
[16]	Semi-automated potentiometric titration	Titration with potassium dichromate. Near to the end point titration, a standard solution with $1.67 \times 10^{-3} \text{ M}$ of $\text{K}_2\text{Cr}_2\text{O}_7$ (=0.01 No. of $\text{K}_2\text{Cr}_2\text{O}_7$) was added until the potential of 130 mV. The automatic titration system consisted of a Pt–Rh wire (90:10) used as an indicator electrode and a reference electrode of mercurous sulfate ($\text{Hg}/\text{Hg}_2\text{SO}_4$)	NM	NM	NM	Certification and characterization of uranium compounds. To determine uranium without chemical separation in solutions containing iron, plutonium and nitrate

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Table 2 (continued)

References	Method	Principle	Linearity range	LOD	Interference tolerance	Application
[17]	Semi-automated potentiometric titration	Titration with potassium dichromate. Near to the end point titration, a standard solution with 1.67×10^{-3} M of $K_2Cr_2O_7$ (=0.01 No. of $K_2Cr_2O_7$) was added until the potential of 130 mV. The automatic titration system consisted of a Pt–Rh wire (90:10) used as an indicator electrode and a reference electrode of mercurous sulfate (Hg/Hg ₂ SO ₄)	NM	NM	NM	Characterization of uranium compounds applied in inter comparison programs
[18]	Potentiometry	Based on reduction to uranium(IV) with zinc metal in acidic medium, and then oxidation by addition of a known excess of peroxodisulfate. A measured excess of potassium bromide is added to reduce unreacted peroxodisulfate, and the excess bromide is titrated potentiometrically with silver. Silver = bromide = peroxodisulfate = uranium	NM	NM	NM	Determination of uranium
[19]	Potentiometry	It is based upon the reduction of U(VI) to U(IV) with a reductant (e.g. Fe ⁺⁺) followed by a selective oxidation of the excess of reductant and subsequent titration of U (IV) with potassium dichromate (K ₂ Cr ₂ O ₇).	NM	NM	NM	Routine analysis
[20]	Potentiometric titrations	Davies and Gray method, saturated calomel reference electrode and a platinum indicator electrode was used	NM	NM	NM	Routine analysis
[21]	Potentiometry	Redox titration of U in H ₃ PO ₄ solution with an automatic titrator. Titration efficiency decreases in the order $KMnO_4 > K_2Cr_2O_7 > NH_4VO_3 > Ce(SO_4)_2$. Excess TiCl ₃ was added until a violet color appeared (i.e., to reduce all the present components). Then 5 ml of a 5% NaNO ₂ solution was added to oxidize TiCl ₃ . Excess NaNO ₂ was decomposed by adding 10 ml of a 30% urea solution. The equivalence point was determined from the maximum of the derivative of the potential with respect to the volume (mV ml ⁻¹).	NM	NM	NM	Determining low quantity (0.1–0.2 mg) of U

[22]	Potentiometry	Redox titration of U mixed phosphoric–sulfuric acid systems with an automatic titrator. The titrant efficiency decreases in the order $\text{NH}_4\text{VO}_3 > \text{KMnO}_4 > \text{Ce}(\text{SO}_4)_2 > \text{K}_2\text{Cr}_2\text{O}_7$. Titrant efficiency decreases in the order $\text{NH}_4\text{VO}_3 > \text{KMnO}_4 > \text{Ce}(\text{SO}_4)_2 > \text{K}_2\text{Cr}_2\text{O}_7$. Rest is same as ²¹	NM	NM	NM	Determining low quantity (0.1–0.2 mg) of U
[46]	Capillary electrophoresis with direct UV \pm Vis detection	2-[(2-Arsenophenyl)-azo]-1,8-dihydroxy-7-[(2,4,6-tribromophenyl)-azo]-naphthalene-3,6-disulfonic acid (chelating agent). 30 mM NaAc–HCl (sodium acetate solution and hydrochloric acid) buffer containing 0.5 mM cetyltrimethylammonium bromide and 0.2 mM chelating reagent, pH 4.30, 12 kV, 635 nm as detection wavelength	0.8–100 mg L ⁻¹	39 $\mu\text{g/ml}$	NM	Separation of thorium, uranium and rare-earth elements
[56]	Adsorptive stripping voltammetry	Uranium–chloranilic acid complex (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone	0.5–1.5 mg L ⁻¹	24 ng L ⁻¹	Some metals and organic contaminants (Not specified)	Analysis of natural water and drainage water from a uranium slag heap
[47]	Capillary electrophoresis	Arsenazo III, a metallochromic ligand with metal complex. Detection of the arsenazo III metal complexes is achieved using a red light emitting diode (LED) light source and a photodiode array detector. Carbowax 20 M is used as background electrolyte, pH conditions utilized here (pH 3.4–6.3)	NM	23 ppb U(VI)	Nd^{3+} , Eu^{3+} , Er^{3+} , Gd^{3+} , La^{3+} , Pr^{3+} , and Ce^{3+}	Uranium(VI) in the presence of seven lanthanide impurities
[68]	Cyclic voltametry	The working electrode of the cell was 1 mm diam. wire made of the test metal (Pt, W, Mo). The glassy carbon container was used as the auxiliary electrode. The quasi-reference platinum, molybdenum or tungsten electrode was 1 mm diam. wire semi-immersed in the test melt	0.1–2.1 mol% (UF_4)	NM	NM	Determination of [U(IV)]/[U(III)] ratio in the Molten salt reactor (MSR) fuel salt
[67]	Adsorptive stripping voltammetric	Chelating agent: cupferron. Acetate buffer solution 0.2 mol L ⁻¹ of pH 4.2 at the potential –0.65 V. A glassy carbon electrode of diameter 1 mm was polished daily using 0.3 μm alumina slurry. Pt wire and Ag/AgCl were used as auxiliary and reference electrodes, respectively	5×10^{-10} – 2×10^{-8} mol L ⁻¹	2×10^{-10} mol L ⁻¹	The determination of U(VI) at concentration of 2×10^{-8} mol L ⁻¹ is not influenced by a 100-fold excess of Cu(II), Zn(II), Fe(III), Ni(II), Mn(II), Al(III) and V(V). Interference was observed in the presence of Mo(VI) and it was found that a 10-fold excess of Mo(VI) causes a decrease of the U(VI) signal to 20% of its original value	U(VI) determination in water certified reference materials

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Table 2 (continued)

References	Method	Principle	Linearity range	LOD	Interference tolerance	Application
[44]	Capillary zone electrophoresis (CZE)	The potential applied was 10 kV and the injection time (by a pressure of 0.5 psi) was 3 s. A capillary (75 μm I.D., 375 O.D.) made from fused silica of length 31.2 cm and an effective separation length of 21 cm. The reverse polarity mode was applied. The calibration curves were plotted at 190 nm for oxalate and 230 nm for the other ions (trimellitate, mellitate and benzoate)	Two ranges of concentration for U(VI) ($\sim 1 \times 10^{-5}$ – 1×10^{-3}), mellitate and trimellitate ($\sim 5 \times 10^{-6}$ – 5×10^{-4}), and about one range ($\sim 1 \times 10^{-4}$ – 5×10^{-3}) for oxalate and benzoate	At 230 nm are 2×10^{-6} M for U(VI), 5×10^{-7} M for mellitate, 1×10^{-6} M for benzoate, at 210 nm to 4×10^{-7} M for trimellitate and at 190 nm to 5×10^{-6} M for oxalate	Not defined	Studying the kinetic mechanism of UC dissolution (influence on dissolution of different parameters: temperature, nitric acid concentration, etc.) and to control for soluble species formation
[68]	Linear sweep voltammetry	1 mm diameter tungsten, molybdenum and platinum electrodes with respect to a glassy carbon rod as a quasi-reference electrode and versus the silver–silver chloride reference electrode	NM	Up to 10^{-4} mol cm^{-3} (UCl_3)	NM	The diffusion coefficients of U(III), standard rate constants of charge transfer for electroreduction of U(III) to U and formal standard potentials
[70]	Adsorptive cathodic stripping voltammetry	Uranium(VI) complexed with aluminon (3-[bis(3-carboxy-4-hydroxy-phenyl)methylene]-6-oxo-1,4-cyclohexadiene-1-carboxylic acid triammonium salt)	2–33 ng ml^{-1}	0.2 ng ml^{-1}	30 ng ml^{-1} additions of Cd(II) and Ge(IV) in 20 ng ml^{-1} U(VI) resulted in 20% enhancement of the U(VI)–aluminon peak, and Sc(III) was the only major interference ($\sim 50\%$ diminution of the U(VI) peak). Gd^{3+} , Tb^{3+} , Yb^{3+} , Y^{3+} , Sm^{3+} , Eu^{3+} , Al^{3+} , Zn^{3+} , La^{3+} , Th^{4+} , Ga^{3+} , Fe^{3+} , Bi^{3+} , Cu^{2+} , Pb^{2+} , Ce^{4+} did not interfere	Simultaneous determination of U(VI) and Zn(II)
[57]	Adsorptive stripping voltammetry associated with square wave measurements (SWAdSV)	Accumulation of the uranium complexed with propyl gallate on a working SPE microelectrode, then reduction of the adsorbed complex	5 ng L^{-1} to 10 $\mu\text{g L}^{-1}$	0.5 ng L^{-1}	No interference in 1 $\mu\text{g L}^{-1}$ of cadmium, copper, lead, zinc, cobalt and iron. But 10 $\mu\text{g L}^{-1}$ of cadmium, copper, zinc, cobalt, iron and lead resulted in a 25%, 75%, 15%, 50%, 40% decrease and 20% increase, respectively of the original value of U–PG peak	Detection in waters

[48]	Capillary zone electrophoresis	Carrier electrolyte carbonate buffer (ionic strength of 0.1 M), pH 9.8, 0.15 mM of tetradecyltrimethylammonium bromide, 25% (v/v) of methanol reverse polarity mode was applied (the injection is performed at the negative end). The potential applied was 10 kV. The injection was done by a pressure of 0.5 psi. U(VI) was detected at 230 nm	Two ranges of concentration from $\sim 1 \times 10^{-5}$ – $\sim 1 \times 10^{-3}$ M for oxalate, acetate, propionate, U(VI) and $\sim 1 \times 10^{-4}$ – $\sim 1 \times 10^{-3}$ for formate	5×10^{-6} M at 190 nm for U(VI), it is 1×10^{-6} M at 230 nm	When the perchlorate concentration is 2.5×10^{-3} M, a negative peak appears near the oxalate peak. With an increase in the perchlorate concentration up to 1×10^{-2} M the oxalate peak is disturbed, and its determination becomes impossible. With 25% (v/v) methanol addition in electrolyte can solve this problem Table 4	Sorption studies on silica and rutile
[58]	Cathodic adsorptive stripping	Complex of uranium with a 3-hydroxy-2-naphthoic hydrazide at a hanging mercury drop electrode (HMDE)	1–500 nM	0.75 nM.		Determination of uranium in the analytical grade of tap water, seawater, sodium nitrate, and potassium chloride samples
[59]	Adsorptive stripping voltammetric	Uranium form a ML ₂ complex with L-3-(3,4-dihydroxy phenyl) alanine (LDOPA) in solution	0.5–300 ng ml ⁻¹	0.27 ng ml ⁻¹	Table 4	Determination of uranium in different water and food samples
[60]	Differential pulse adsorptive cathodic stripping voltammetry	Uranium(VI) determination in the presence of chloranilic acid as a complexing agent. voltammetric determination of uranium(VI) by application of cylindrical mercury film electrode formed on the silver wire, refreshed before each measurement. Cyclic renewable mercury film silver based electrode (Hg(Ag)FE) was used	0.4 nM (95 ng L ⁻¹) to 250 nM (60 mg L ⁻¹)	12 ng L ⁻¹	Cl ⁻ in a 10000-fold excess, and Pb(II), Cd(II), Zn(II) in a 100-fold excess did not interfere. Antimony(III) ions in a concentration of 10 nM, the uranium(VI) peak current decreased by 11%, for a 10-fold excess by 40%, and for a 100-fold excess by 85%. Copper (II) ions (a 10-fold excess), the uranium peak decreased by 10%, while for a 50-fold excess decreased by 30%. For 15 mg L ⁻¹ of Triton X-100 concentration, the signal was suppressed by only 15%, and in the case of humic acid a concentration of 0.25 mg L ⁻¹ was enough to suppress the signal completely Table 4	River water and sediment samples
[61]	Adsorptive cathodic stripping	Uranium-pyromellitic acid (benzene-1,2,4,5-tetracarboxylic acid) complex onto a hanging mercury drop electrode, followed by reduction of the adsorbed species by voltammetric scan using differential pulse modulation	1.19–40.46 ng mL ⁻¹ and 0.238–20 ng mL ⁻¹ for 120 and 300 s accumulation times respectively.	0.136 ng mL ⁻¹ 0.058 ng mL ⁻¹	Table 4	Salts, seawater and in synthetic samples, some uranium alloys

(continued on next page)

Table 2 (continued)

References	Method	Principle	Linearity range	LOD	Interference tolerance	Application
[45]	Capillary electrophoresis	Strongly absorbing complexes with arsenazo III (AIII). Back ground electrolyte citrate at pH 4.7 and III containing 0.1 mM AIII was used for the separation of uranium(VI) and La. Capillary, FS 0.480 × 0.400 m	NM	0.25 mM (60 ppb)	NM	Separation of lanthanides and uranium(VI)
[62]	Adsorptive stripping voltammetry	Supporting electrolyte of 0.1 M KCl + HCl (pH 1.8) containing arsenazo III (5.7×10^{-7} mol L ⁻¹), an accumulation potential of 0 V (vs. SCE), and a scan range from -0.4 V to 0 V using a hanging mercury drop electrode	Up to 8×10^{-7} mol L ⁻¹	1×10^{-8} mol L ⁻¹	Bivalent cations, such as Ca ²⁺ , Ni ²⁺ , Zn ²⁺ , Ba ²⁺ , Mn ²⁺ when present in the solution can influence the current response in similar way. At pH 3, an increase of their concentration up to 50 mM reduces the signal to almost 25%. At pH 1.8 this change is very less significant	Uranium traces in water and soil samples
[63]	Adsorptive stripping voltammetry	Complexation of U(VI) ions with cupferron and the subsequent adsorptive accumulation of the complex on the surface of the preplated rotating-disk bismuth-film electrode BiFE	1–9 µg ⁻¹	0.1 mg L ⁻¹	Reduction peaks of U(VI) → U(V) [Pb(II), Hg(II), Cu(II), Fe(II), Cd(II), Ti(IV), Ca(II) and Mn(II) added at a 10-fold mass concentration excess over U(VI) did not interfere but U(V) → U(III) number of cations did interfere; for example Al(III) and Zn(II) interfered at mass concentration ratios over U(VI) of 1 and 10, respectively, by producing peaks overlapping with that of uranium	Sea water
[64]	Adsorptive Stripping Voltammetry	Complexation of U(VI) ions with cupferron using hanging mercury drop electrode	1.7×10^{-10} – 2.0×10^{-8} mol L ⁻¹	1.7×10^{-10} mol L ⁻¹	Not defined	Certified reference material NASS-5 and river water samples
[71]	Square-Wave Stripping Voltammetry	Chelate compound formed between U(VI) and [4-(2-hydroxyethyl)-1-piprazine ethane sulfonic acid] on glassy carbon electrode	At three different accumulation times: (a) 0 s, (b) 60 s, and (c) 180 s, Limit of linearity 0.6×10^{-5} , 1.2×10^{-5} and 1.2×10^{-5} , respectively	1×10^{-9} M	Cd(II), K(I), Na(I), Mg(II), Ba(II), Ca(II), Mn(II) and Zn(II) did not interfere on 1×10^{-6} M U(VI) + 5×10^{-6} complexing agent until their concentrations exceed 500 times that of U(VI). Metal affected the current by suppressing it more than 5% are Fe(III), Pb(II), Al(III), Cu(II) in concentration range 4×10^{-6} – 4×10^{-7} M at two different accumulation times: 0 and 180 s	Fertilizers, cement and sugar samples

[67]	Adsorptive stripping voltammetric techniques	Interfacial activity of uranium(VI)-cupferron and uranium(VI)-chloranilic acid (CAA) complexes (in 0.1 M acetate buffer pH 4.6 or 0.1 M NaClO ₄ respectively) on polarized mercury electrode at 110 mV, 10 mV or -240 mV respectively vs. saturated calomel electrode (SCE)	3×10^{-4} – 3×10^{-4} mol ⁻¹	3×10^{-5} mol L ⁻¹	Metal ions not specified, claimed that nonionic organic contaminants are not adsorbed on the mercury/solution interface	Interfacial activity
[55]	Cathodic adsorptive stripping voltammetric	Complex with dipicolinic acid (2,6-pyridinedicarboxylic acid) using a hanging mercury drop electrode (HMDE)	1×10^{-9} – 1.2×10^{-7} M	0.27×10^{-9} M	Table 4	Synthetic and natural water samples
[54]	Adsorptive stripping voltammetry	Complex forming reagent 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid) was used. For the auto-batch determination of uranium, a pH 2.5 hydrochloric acid supporting electrolyte containing 1.5×10^{-4} mol L ⁻¹ chloranilic acid was used. In the flow-through determination, the supporting electrolyte solution, unless otherwise mentioned, had a pH of 2.5 (HCl or any other acid) and contained 1×10^{-5} mol L ⁻¹ chloranilic acid. The sample solution usually contained chloranilic acid (1×10^{-5} mol L ⁻¹) and was set to pH 2.5	10–30 µg L ⁻¹	0.5 µg L ⁻¹	Not defined	Water samples originating from a uranium slag heap
[53]	Cathodic stripping voltammetry	Acidifying the sample with HCl from its natural pH to pH 3 under a nitrogen atmosphere in order to purge out the CO ₂ and destroy the uranyl-carbonate complexes. After that the pH has to be adjusted with NaOH to a pH of between 6.5 and 7.0 to enable formation of uranyl-hydroxo complexes which are adsorbable on the working electrode [static mercury drop electrode (SMDE)]	0.4 – 3.3×10^{-8} mol l ⁻¹	11.0 ± 0.5 A mol ⁻¹	Not defined	Natural water samples taken from the Krka river estuary

(continued on next page)

Table 2 (continued)

References	Method	Principle	Linearity range	LOD	Interference tolerance	Application
[52]	Adsorptive stripping voltammetric	U(VI) complex with cupferron was accumulated from an acetate buffer solution of pH 4.2 at the potential -0.65 V. The measurements were carried out from undeaerated solutions	5×10^{-10} – 2×10^{-8} mol L $^{-1}$	2×10^{-10} mol L $^{-1}$	The determination of U(VI) at concentration of 2×10^{-8} mol L $^{-1}$ is not influenced by a 100-fold excess of Cu(II), Zn(II), Fe(III), Ni(II), Mn(II), Al(III) and V(V). Interference was observed in the presence of Mo(VI) and it was found that a 10-fold excess of Mo(VI) causes a decrease of the U(VI) signal to 20% of its original value. The influence of surfactants on the U(VI) peak was investigated by an addition of Triton X-100 to the concentration 1 mg L $^{-1}$ to the studied solution. It was observed that the U(VI) peak decreases to 9% of its original value.	In situ plated lead film electrode
[51]	Cathodic adsorptive stripping voltammetric	Potassium hydrogen phthalate as complexing agent to form a uranium complex. Solutions of 0.1 mol dm $^{-3}$ sodium perchlorate, potassium nitrate, potassium chloride and 0.2 mol dm $^{-3}$ sodium dihydrogen phosphate were used as supporting electrolytes	0.5–4.8 μg^{-1}	–	Table 3	Superphosphate fertilizer
[69]	Linear sweep voltammetry (LSV), cyclic voltammetry (CV), steady-state voltammetry (SSV), chronopotentiometry (CP), chronoamperometry (CA) and impedance spectroscopy (IS)	Electrochemical curves were determined with a 1 mm diameter tungsten, molybdenum and platinum electrodes with respect to a glassy carbon rod as a quasi-reference electrode and versus the silver–silver chloride reference electrode. The counter electrode was constituted of either glassy carbon plate or ampoule	NM	NM	NM	Electrochemical behavior of UCl $_3$ in LiCl–KCl melt. The diffusion coefficients of U(III), standard rate constants of charge transfer for electroreduction of U(III) to U and formal standard potentials $E^*_{\text{U(III)/U}}$ were determined

[66]	Differential pulse voltammetric	Preconcentrating sensor based on 6- <i>O</i> -palmitoyl-l-ascorbic acid (PAA) (a water insoluble compound of ascorbic acid) modified graphite (GRA) electrodes. Uranium was accumulated by heterogeneous complexation (10 min, in 0.1 M H ₃ BO ₃ , pH 4.3) and then, it was reduced by means of a differential pulse voltammetric scan in 0.1 M H ₃ BO ₃ , pH 3.4	2.7–67.5 μg L ⁻¹	1.8 μg L ⁻¹ and 0.26 μg L ⁻¹ at preconcentration time 10 and 30 min respectively	As(V), Cd(II), Cr(VI), Fe(III), La(III), Mn(II), Pb(II), Sb(V) not interfere. Hg(II), Ni(II), Se(IV) and Th(IV) ($I_p(\text{ion})/I_p(\text{U(VI)}) > 0.15$). Cu(II) and vanadyl ions are potential interference	Tap and lake water samples
[72]	Cyclic voltametry and differential pulse voltametry	A modified carbon electrode incorporating benzo-15-crown-5 used to evaluate charge transfer reaction. The three electrode system used for the study consisted of a plain carbon paste electrode or chemically modified electrode with 5% modifier in a graphite paraffin matrix and used in conjunction with an Ag/AgCl/3 mol dm ⁻³ KCl reference electrode and platinum as auxiliary electrode	0.04–278 and 0.002–0.2 μg ml ⁻¹ respectively	0.03 and 0.0011 μg ml ⁻¹ respectively	Cs ⁺¹ , Sr ²⁺ , Th ⁴⁺ , La ³⁺ , Pb ²⁺ , Cd ²⁺ and Zn ²⁺ did not interfere	Trace level determination of UO ₂ ²⁺ in industrial effluents
[65]	Square wave voltammetry	Electrodes were prepared via electrochemically reduction of the diazonium salt of 4-carboxyphenyl (4-CPSPEs). Uranium detection was then achieved by immersing the grafted electrode into the sample solution	8.5 × 10 ⁻¹⁰ –10 ⁻⁷ mol L ⁻¹	7 × 10 ⁻¹⁰ mol L ⁻¹	Among Cu(II), Cd(II), Pb(II), Zn(II), M(II) ions, only in the case copper, peak current remained unchanged as long as the concentration of Cu(II) remained three times higher than that of U(VI). For higher concentrations, Cu(II) induces a decrease of the U(VI) analytical response correlated to an increase of Cu(II) peak current showing the competition between U(VI) and Cu(II) at the working surface	Natural water samples

Table 3 Interference studies reported by Farghaly and Ghandour.⁵¹

Experiments	Effects
In the presence of 1×10^{-4} mol dm ⁻³ potassium hydrogen phthalate and fertilizer phosphate sample solution in 0.01 mol dm ⁻³ NaClO ₄ (pH: 3.95), 1×10^{-7} and 1×10^{-6} mol dm ⁻³ of each metal ions viz; Cu(II), Pb(II), Cd(II), Zn(II), Ni(II) and Mn(II) ions	Slight decrease in the current signal was observed. In the case of 1×10^{-6} mol dm ⁻³ Bi(III) decreases the peak height of uranium ion by about one-sixth of its value
Small increments of HF up to 5×10^{-4} mol dm ⁻³ fluoride ions concentration	No change in the current signal. But, series interferences has been observed if the concentration of fluoride added to the superphosphate fertilizer sample exceed 1×10^{-3} mol dm ⁻³ , where a diminution of the current was noticed and eventually vitiated at concentration 8×10^{-3} mol dm ⁻³ fluoride ions
Synthetic solution 1×10^{-3} mol dm ⁻³ potassium hydrogen phthalate and 1×10^{-6} mol dm ⁻³ uranyl ion with 0.01 mol dm ⁻³ NaClO ₄ (pH~7), up to fivefold concentration of Pb(II), Cu(II), Ni(II), Zn(II), and Fe(III) 20-fold Cd(II) concentration	No change in the current signal
Half concentration of Bi(III)	No effect
2000 fold of PO ₄ ³⁻ , ClO ₄ ⁻ , NO ₃ ⁻ , Cl ⁻ and 1000 of F ⁻ anions	Decreases the peak height of uranyl complex to half its value Do not interfere, a slight decrease in the current has been observed in the presence of 2×10^{-3} mol dm ⁻³ fluoride ions concentration

Table 4 The magnitude of tolerance of some reported methods toward some interferents.

Species	Tolerance concentration (M _{ion} /M _{uranium})	References
K ⁺ , NO ⁻³ , Ca ²⁺ , Mg ²⁺ , Li ⁺ , Ba ²⁺ , ClO ⁻³ , BrO ⁻³ , NO ⁻² , NH ⁺⁴ , ClO ⁴⁻	3000	[58]
Mn ²⁺	1000	
V ⁵⁺ , Mo ⁶⁺ , Fe ³⁺	500	
Cu ²⁺ , Cd ²⁺ , Cr ³⁺	300	
Co ³⁺ , Pb ²⁺ , Bi ³⁺	200	
Ni ²⁺ , Cr ⁶⁺	60	
Zn ²⁺	10	
Ce ³⁺ , Ba ²⁺ , Mo ⁴⁺ , Mg ²⁺ , Na ⁺ , Bi ³⁺ , Li ⁺ , Cr ³⁺ , K ⁺ , Ca ²⁺ , Mn ²⁺ , Cl ⁻ , Ag ⁺ , F ⁻ , HPO ₄ ²⁻ , SO ₄ ²⁻ , CO ₃ ²⁻ , CN ⁻	1000 ^a	[59]
Cu ²⁺ , Co ²⁺	10	
Fe ³⁺ , Pb ²⁺ , Cd ²⁺	1	
Sb ³⁺	500	
Zn ²⁺ , ^b Cu ²⁺ , ^b Co ²⁺	100	
^b Fe ³⁺ , ^b Pb ²⁺ , ^b Cd ²⁺	50	
K ⁺ , NO ⁻³ , Ca ²⁺ , Mg ²⁺ , Sr ²⁺ , Li ⁺ , Ba ²⁺ , SO ₄ ²⁻ , Br ⁻ , ClO ⁻³ , BrO ⁻³ , NO ⁻	20,000	[61]
Ni ²⁺ , Zn ²⁺ , Mo ⁶⁺	1200	
Mn ²⁺	500	
Fe ³⁺ , Cu ²⁺ , V ⁵⁺ , Co ²⁺ , Cd ²⁺ , Cr ³⁺ , Th ⁴⁺	300	
Bi ³⁺	200	
Pb ²⁺	40	
Na ⁺ , Cl ⁻ , K ⁺ , NO ³⁻ , CN ⁻ , SO ^{42-a} , K ⁺ , HPO ^{42-a} Ca(II), Ba(II), Mg(II), Li ⁺ , Cs ⁺	20,000 ^a	[55]
Ag(I)	5000	
Cu(II), Co(II), Cd(II), Cr(III), Ni(II)	2000	
Mn(II), Br ⁻	1000	
Zn(II), Fe(II), Hg(II), Tl ⁺	500	
Pb(II)	10	
Pb(II) ^c , V(III), Cr ₂ O ⁷⁻²	300	
Fe(III), Al(III)	150	

^aMaximum concentration of foreign species tested.

requires minimal sample preparation and offers a high degree of automation. CE is an alternative to more traditional methods such as gel electrophoresis and liquid chromatography and is employed to detect both high and low affinity molecular interactions, and separation of both charged and non-charged molecules.⁴¹

Electrophoretic separation techniques are at least as widely distributed as chromatographic methods. High separation efficiency can be achieved using a relatively little number of equipment.⁴² More highly charged ions and ions of smaller size, which means they have a higher charge-to-size ratio, migrate at a faster rate than larger ions, or ions of lower charge.

Neutral species do not experience the electric field and remain stationary. The resulting electropherogram looks similar to the chromatograms obtained in GC or HPLC and provides both qualitative and quantitative information.⁴³

Separation and simultaneous determination of a number of organic acid anions (oxalate, mellitate, trimellitate and benzoate) and U(VI) with direct UV detection is developed⁴⁴ for the analysis of uranium carbide (UC) dissolution products by capillary zone electrophoresis (CZE). Authors claimed that their method can be utilized on experimental data on dissolution product quantities. Dissolution is an important step in the reprocessing of used fuel in the nuclear energy industry, especially in the case of uranium based carbide, which is a potential fuel for gas-cooled fast reactors of generation IV.

In another method⁴⁵ several carboxylic acids were compared as back ground electrolyte competing ligands and citrate provided the best selectivity and peak shapes. A citrate back ground electrolyte at pH 4.7 and containing 0.1 mM arsenazo III was used for the separation of uranium(VI) and LaIII while, to separate most lanthanides and uranium(VI), a similar BGE with a lower (0.03 mM) arsenazo III concentration was used. Seventy-five micrometre I.D. fused-silica (FS) separation capillary in 0.480-m (0.400 m to detector) or 0.600-m lengths (0.520 m to detector) was used. The separation of thorium, uranium and rare-earth elements (RE) as their 2-[(2-arsenophenyl)-azo]-1,8-dihydroxy-7-[(2,4,6-tribromophenyl)azo]-naphthalene-3,6-disulfonic acid complexes by capillary electrophoresis with direct UV-vis detection at 635 nm⁴⁶ is also reported. The influences of pH value and concentration of electrolyte, voltage and surfactant on separation were investigated and optimized. Under the selected conditions (30 mM NaAc-HCl buffer containing 0.5 mM cetyltrimethylammonium bromide and 0.2 mM chelating reagent, pH 4.30, 12 kV), the coexisted ions were separated within 4 min, and limits of detection of 37, 39 and 199 $\mu\text{g L}^{-1}$ for RE, thorium, uranium with a linear dynamic range of over two orders of magnitude were achieved, respectively. This method was applied for the determination of these metal ions in ore samples.

In the method developed by Collins and Qin⁴⁷, arsenazo III, a metallochromic ligand which selectively reacts with the actinide and lanthanide metal ion series under acidic conditions, was chosen for the application to a CE microchip on the basis of its (1) large molar extinction coefficient for binding uranium(VI), a characteristic making absorbance detection through the microchannel a viable option, (2) large bathochromic shift in absorbing wavelength which results from the complexation of uranium(VI), a factor which permits a red LED to be utilized in the detection scheme, and, finally, (3) demonstrated success on benchtop CE instruments for the separation of uranium(VI) from numerous lanthanide metal ions.

Detection of the arsenazo III metal complexes was achieved using a red light emitting diode (LED) light source and a photodiode array detector. Carbowax 20 M was incorporated into the background electrolyte in order to eliminate the electroosmotic flow and prevent dye adsorption on the microchannel walls. Separation of uranium from four lanthanide metal ions was then demonstrated in under 2 min. The addition of diethylenetriaminepentaacetic acid (DTPA) to the background electrolyte was found to be an effective means for eliminating any interference from lanthanide, transition and alkaline earth metal ions.

Recent publication is separation and the simultaneous determination (in a single run) of a number of short chain carboxylic acids (oxalic, formic, acetic and propionic) and U(VI) with direct UV detection. U(VI) was detected at 230 nm.⁴⁸ The pH in the range from 9.8 to 10.4 can be suitable for U(VI) determination. Thus the carbonate buffer with pH 9.8 is used in this study.

2.4. Voltammetry

Analytical chemists routinely use voltammetric techniques for the quantitative determination of a variety of dissolved inorganic and organic substances.⁴⁹ The characteristics of voltammetric techniques make them particularly well suited for automatic (thus low cost) in situ speciation measurements, with no or minimum sample change, i.e., under conditions that dramatically minimize contaminations by reagents or losses by adsorption on containers. Voltammetric techniques are based on the recording of the current, i , which flows between the working electrode (WE) and an auxiliary electrode (AE), due to the reduction or oxidation of the test element, as function of the potential, E , imposed on the WE and expressed with respect to that of a reference electrode (RE).⁵²

Twenty-two voltammetric methods were found in various journals. Methods were applied in different matrices such as the determination of uranium in superphosphate fertilizer⁴³ determination in water of different sources,⁵⁰⁻⁶⁶ interfacial activity of uranium complexes with cupferron or chloranilic acid,⁶⁷ study of the oxidation and dissolution of uranium dioxide in deaerated acidic and noncomplexing media,⁶⁸ determination of U(VI) at an in situ plated lead film electrode,⁵² diffusion coefficients of U(III),⁶⁹ simultaneous determination of U(VI) and Zn(II),⁷⁰ synthetic alloys,⁵⁹ analytical grade salts,⁶¹ soil samples,⁶² niobium ores⁷¹ and industrial samples, e.g. fertilizers, cement and sugar samples.⁷²

3. Conclusion

Uranium is a naturally occurring radioactive metal, interesting from an ecotoxicological perspective because it can have both chemical and radiological toxicities. Uranium's environmental prominence is currently increasing because of new mining and milling activities to support the resurging commercial nuclear power industry (in response to energy production needs with low carbon output). Such anthropogenic activities can increase environmental concentrations of U.⁷³ Thus uranium monitoring in environment is of a great importance because of its chemical and radiologic toxicities. Moreover, such interest is the need of today's world due to safety, regulatory compliance and disposal issue of uranium in the environment. One potentiometry,³⁶ one polarography,¹² five capillary electrophoresis^{44,45,47,48,67} and some methods based on voltammetry^{52,55,61,62,64,65,70,71} found in our literature search are of high sensitivity. Summary of all electroanalytical methods reported is presented in Table 2. Interference study reported by Farghaly and Ghandour is presented in Table 3 and magnitude of tolerance of some reported methods toward some interferents is provided in Table 4. In this way all of the electroanalytical methods are summarized and presented here. The presented review is a valuable source of information for the researchers involved in the development of analytical methods

for the determination of analytical methods of uranium in different matrices.

4. Conflict of interest

None.

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