Geochemistry and Determination Possibilities of Uranium in Natural Waters

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Abstract: Uranium concentration levels in aquatic environment are of great importance for environmental and safety assessment. In this work the chemical properties of uranium ions and complexes in aqueous solutions especially in geological environment are presented. Different methods for uranium determination in water samples are also discussed. The chemical behaviour of uranium species in aqueous solutions can be influenced by several factors such as the inclination of uranium towards complex formation (in the presence of inorganic and organic ligands), the hydrolytic processes and the redox properties. In natural waters it is also dependent on sorption processes to surfaces of minerals and/or colloids. Four different oxidation states of uranium (U^{3+} , U^{4+}, UO_2^+ and UO_2^{2+}) are soluble and therefore can be studied in aqueous solutions. The most dominant form of uranium in aqueous solutions is the uranyl cation (UO_2^{2+}).

Keywords: uranium, aqueous solution, uranyl ion, analytical methods

1. Introduction

Uranium is a very dense, highly reactive, metallic element that has the highest atomic mass of the naturally occurring elements [1-4]. Uranium is found in Earth's crust at an average concentration of about 3 mg/kg [5]. The formation of uranium accumulations is a normal geological process, especially in granites and sedimentary rocks, two widely occurring rock types. The most common uranium-containing mineral is uraninite (a complex uranium oxide). Examples of other uranium-containing minerals are autunite (a hydrated calcium uranium phosphate), brannerite (a uranium calcium cerium titanium iron oxide) and carnotite (a hydrated potassium uranium vanadate) [4].

Surface waters and especially groundwater play the main role in the migration of radionuclides in the earth's crust. Concentrations of uranium in waters are influenced by the chemical and physical characteristics of the aquifer and by the uranium content of the geological formation involved. In systems where the rocks are exposed to

weathering and the circulation of water, separation of the uranium series isotopes occurs [6]. It is well-known that in many locations very small amounts of uranium are also present in drinking and mineral waters. Uranium is transferred to plants, food supplements and to humans. The average uranium concentration in ocean water, plants, and animal organism is around 10^{-7} g/g, as a result of the solubility of uranium compounds in water [7]. It must be noted that mineral phosphate fertilizers can also contain uranium and are therefore a possible source of this element [8-9]. In addition, uranium enters the environment as a result of other human activities such as nuclear weapon tests, the use of uranium ammunition, the uranium mining as well as the manufacture and processing of fuel rods [1-2, 10].

Naturally occurring uranium nominally consists of two long-lived radioactive isotopes: ^{238}U (99.28%) and ^{235}U (0.72%). A very small amount of ^{234}U (0.005%) occurs in secular equilibrium with ^{238}U. The main type of radiation emitted by uranium is the alpha particle. The ratio of ^{234}U to ^{238}U would be expected to be unity as long as the uranium stays locked inside undisturbed crustal rock in secular equilibrium with its progeny, but measurements show that the ratio is typically different than unity. This disequilibrium occurs when the rock is disturbed by chemical or physical changes involving water. These processes can change the uranium isotope ratios in air, soil and water [6, 10-12].

Assessment of the impact risk in connection with most radionuclides is based on the total radiological dose rate. However, for uranium, there can be a greater risk from chemical toxicity than radiological toxicity, presumably because of the relatively low specific activity of this mixture of uranium radionuclides [5, 13]. High intake of uranium may lead to harmful effects in humans (damage the kidneys, lungs and bone marrow). According to estimates food contributes about 15% of ingested uranium while drinking water contributes about 85% [14]. The exposure limits for soluble uranium compounds are related to a maximum concentration of 3 μg uranium per gram of kidney tissue [13].

The maximum admissible concentrations of uranium for drinking water depend on each public authority and it is not yet defined within the European Union [5, 15]. However, various organizations recommend guideline values. While the World Health Organization (WHO) assumes that the uranium content of up to 15 μg/L can be tolerated by adults in drinking and mineral waters, the German Federal Environment Agency recommends a guideline value of only 10 μg/L [15]. In the USA the maximum permitted uranium content of drinking water has been stipulated as being 30 μg/L [16]. It has to be noted that according to the Hungarian Standard, the maximum U concentration of mine water that can be released into natural water streams is 2 mg/L, and the limiting value of U concentration in drinking water is 0.4 mg/L [13].

In the light of the above facts the measurement of uranium levels in aquatic environments is of great importance for environmental and safety assessment, especially in nuclear devices and plants or in regions of uranium mines. The aim of this article is to provide an overview on the chemical properties of uranium ions and complexes in aqueous solutions (especially in geological environment), particularly considering the most dominant form of uranium (uranyl ion (UO_2^{2+})). In addition, methods for uranium determination in water samples are discussed as well.

2. Chemical properties of uranium ions and complexes in aqueous solutions

2.1. Uranium ions properties

The chemical behaviour of uranium species in aqueous solutions can be influenced by several factors such as the inclination of uranium towards complex formation (in the presence of inorganic and organic ligands), hydrolytic processes (often leading to polymeric ion species) and the redox properties [3, 17-18]. In naturally occurring waters it is also dependent on the sorption processes to surfaces of minerals and/or colloids, etc. [10, 19].

In accordance with the relevant Pourbaix diagrams (Fig 1a and 1b) ions of four different oxidation states of uranium are soluble and therefore can be studied in aqueous solutions [17]. They are: oxidation states of uranium (U^{3+}, U^{4+}, UO_2^+) (representing the uranium(V) state) and UO_2^+ (representing the uranium(VI) state). In aqueous media U(IV) and U(VI) are stable, although the tetravalent ion is only stable under reducing conditions [3]. A few solid and semi-metallic compounds such as UO and US exist in the formal oxidation state U(II), but no simple ions are known to exist in solution for that state.

The most prevalent form of uranium in aqueous solution is the light yellow, fluorescent uranyl ion (UO_2^{2+}). The U^{4+} cation (green in solution) can be obtained by strong reduction of U(VI), but in air it readily oxidizes back to UO_2^{2+} . The pentavalent ion UO_2^+ can be reversibly formed by reduction of UO_2^{2+} , but it readily disproportionates into U(IV) and U(VI). The trivalent U^{3+} can be formed by reduction of U(IV) but it is unstable as it oxidizes in aqueous solution [1, 4].

2.2. Complexation

In the light of the previous facts in aqueous solutions the uranyl cation is a dominant feature of uranium chemistry. It is well-known that the UO_2^{2+} species can form compounds such as the carbonate, chloride and sulphate. It also forms complexes with various organic chelating agents, the most commonly encountered of which is uranyl acetate [1]. The main characterizing data of the uranyl cation can be described as follows: [20-23].

- Its chemical structure is linear and symmetric $(O=U=O)^{2+}$ (owing to the role of 5f atomic orbital in the formation of the chemical bond). The hexavalent U atom in the linear $(O=U=O)^{2+}$ is only partially shielded by the two oxygen atoms; thus in the equatorial plane the effective charge of the uranium may be more than 3 (ca. 3.3±0.1).
- UO_2^{2+} can coordinate several donor atoms in the equatorial plane and hereby can produce wide variety of complexes. As uranyl cations - like other actinide ions - are strong acids, the electrostatic model can be used to describe their chemical bonds in the above complexes. Moreover, uranyl ions display strong preference to oxygen donors; accordingly, the chemical bonds formed exhibit predominantly ionic character.

The hydrolysis of uranyl ion is an especially important factor in aqueous solutions. The references on this subject [20, 24-25] and Fig. 1 provide evidences on the formation of the following complexes:

- mononuclear complexes: $UO_2(OH)^+$, $UO_2(OH)_2$, $UO_2(OH)_3^-$, $UO_2(OH)_4^{2-}$
- polynuclear complexes: $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_4(OH)_7^+$, $(UO_2)_3(OH)_4^{2+}$, $(UO_2)_3(OH)_5^+$, $(UO_2)_3(OH)_7^-$.

In concentrations below 10^{-6} M, $UO_2(OH)^+$ is the dominant hydrolysis species in solution while above this concentration, polymeric forms such as $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_4^{2+}$ and $(UO_2)_3(OH)_5^+$ form [19]. Besides the hydrolytic processes the strong carbonate complexation producing carbonate (UO_2CO_3, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$) and mixed hydroxo carbonate ($(UO_2)_2CO_3(OH)_3^-$) complexes are also considered, especially in geological environments [20, 26-27]. Carbonate complexes are estimated to account for 90–100% of the uranium dissolved in ocean waters [19]. Fig. 2 presents the speciation of UO_2^{2+} as a function of pH. It is of special interest to emphasize that CO_2 in the air or in a closed ground water system can also take part in the formation of the above carbonate and hydroxo carbonate complexes [10, 26].

Some experimental data [24-25] reveal that the hydrolysis of uranyl cations in aqueous solutions begins at pH > 3.5. Moreover, at open to air condition the formation of hydroxo carbonate complexes commences at pH≈5.5. Simultaneously, the solution may become oversaturated and uranyl hydroxide (schoepit, $UO_2(OH)_2 \cdot H_2O$) is precipitated in the pH range of 5.3–7.3. The relatively high solubility of uranium at higher pH is due to the negatively charged carbonate complexes dominating in the solution at pH > 8. It is also remarkable that under reducing conditions, the speciation of U(IV) is dominated by the neutral aqueous species $U(OH)_4$ at pH values greater than 2 [10].

At the same time, it must be noted that the dissolved carbonate, uranium can also form stable complexes with other naturally occurring inorganic and organic ligands such as phosphate complexes [$UO_2HPO_4(aq)$ and $UO_2PO_4^-$] (Fig. 3) [10]. Complexes with sulfate (Fig. 4), fluoride and possibly chloride are potentially important uranyl species where concentrations of these anions are high. However, their stability is considerably less than the carbonate and phosphate complexes [28]. The uncomplexed uranyl ion also has a greater tendency to form complexes with fulvic and humic acids than many other metals with a +2 valance [10].

The basic thermodynamic principles of advanced aquatic chemistry including modelling methods are fairly discussed in a series of recent textbooks and monographs [76, 77, 78]. Important thermodynamic data concerning aqueous uranium hydroxide complexes, crystalline and amorphous uranium oxides and hydroxides, uranium hydrides as well as uranium halogen- and chalcogen compounds and complexes are published in [79]. To uranium compounds and complexes with organic ligands, namely to uranium oxalate-, citrate-, and EDTA-compounds and complexes another notable publication is devoted [80]. For quick answers of uranium speciation problems and chemical equilibrium

calculations in natural waters a series of computer programs are available, e.g. MINEQL, GEOCHEM and MINTEQ.

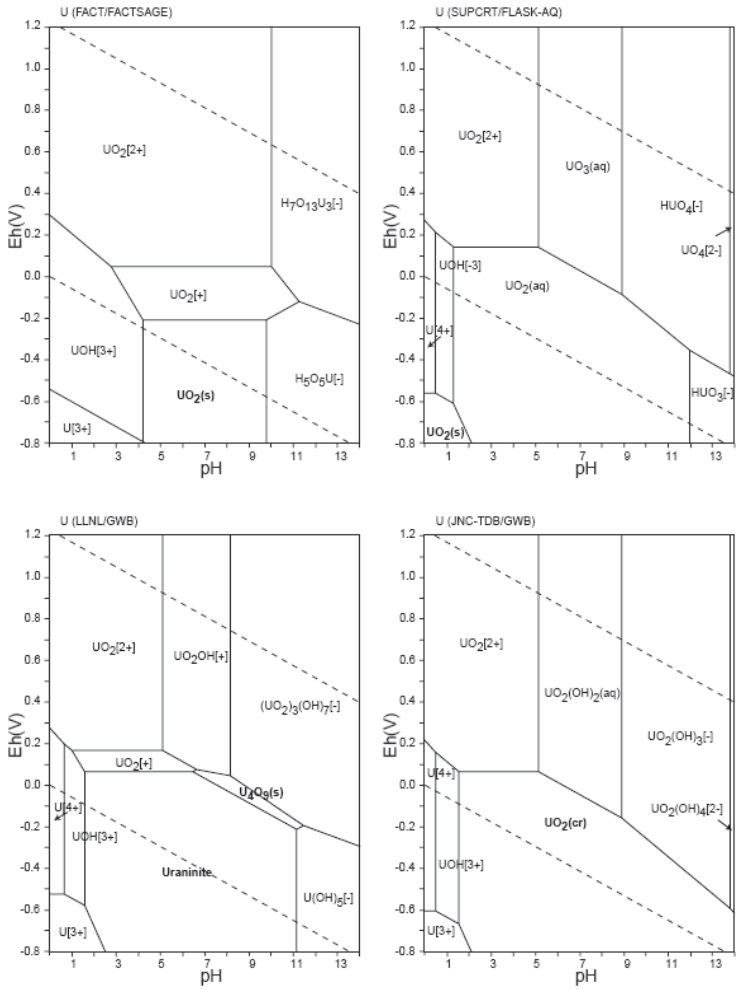

Figure 1. Eh-pH diagrams of the system U-O-H [17]. ∑U = 10^{-10}, 298.15K, 10^5 Pa

On the top of the diagrams after the U symbol the database and the software is marked:

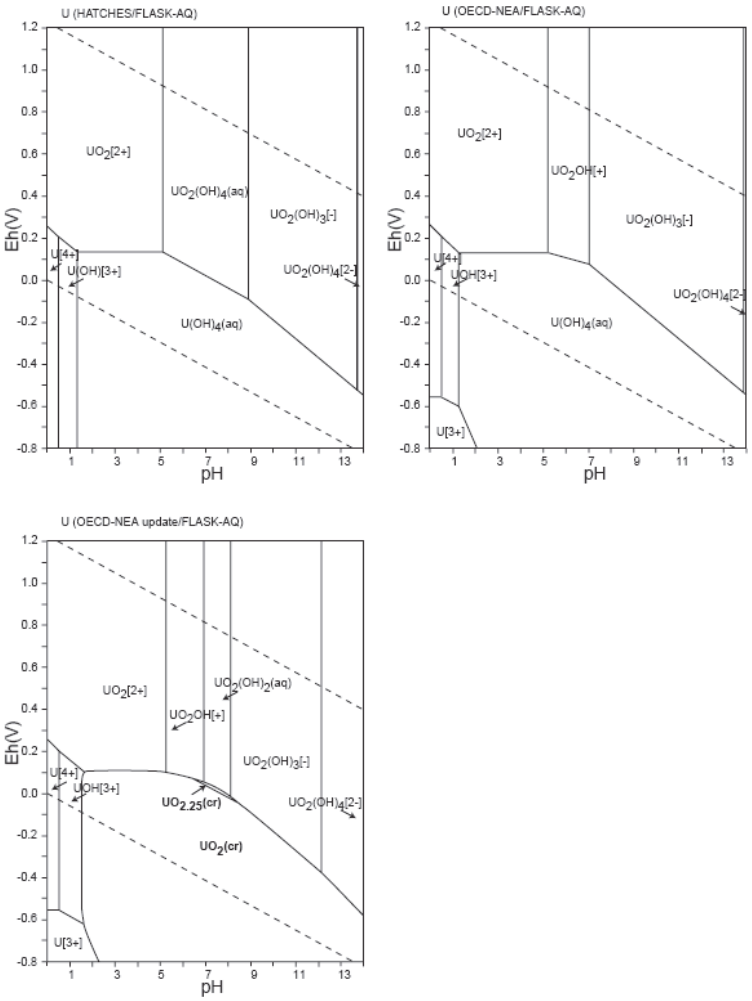

Figure 1 (continued). Eh-pH diagrams of the system U-O-H [17]. $\sum U = 10^{-10}$, 298.15K, 10^5 Pa

On the top of the diagrams after the U symbol the database and the software is marked:

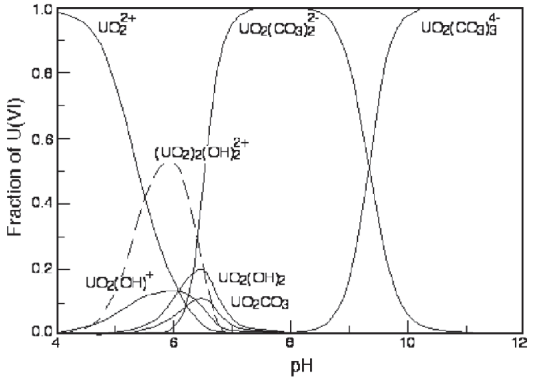

Figure 2. Speciation diagram of UO_2^{2+} *as a function of pH in natural waters [19]*

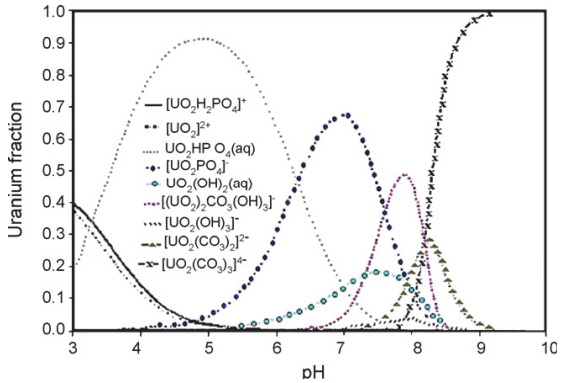

Figure 3. Calculated uranium speciation in the system UO_2–PO_4–CO_3–OH–H_2O *at over-saturation at 298.15 K [10]*

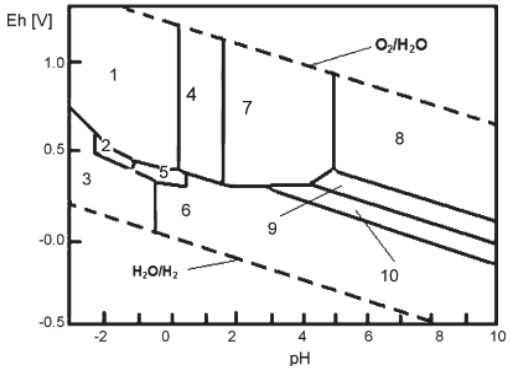

Figure 4. Eh–pH diagram and uranium speciation in present of sulfates at 298.15 K (concentration of U-ions: 0.01mg/L; concentration of sulfate-ions: 0.1mg/L) [10]

(1) UO_2^{2+}; (2) USO_4^{2+}; (3) U^{4+}; (4) $UO_2(SO_4)$; (5) $U(SO_4)_2$; (6) UO_2;

(7) $UO_2(SO)^{2-}$; (8) $UO_2(OH)_2H_2O$; (9) U_3O_8; (10) U_4O_9

2.3. Sorption

The uranium sorption (like other actinides sorption) is influenced by the charge of the cations as well as by steric effects and the sorption strength follows the same trend as complexation. In neutral and basic media, actinides interact with hydroxyl moieties of polysilicic acid, hydrated iron oxides, as well as the surface hydroxyl groups of colloidal materials. Particles may have net positive or negative surface charges depending on the pH [19].

The literature data [10, 20, 29-31] reveal that the U(VI) sorption onto the soil are the iron and manganese oxide coatings and the clay fraction are based on the assumption that surface OH−sites are formed on the oxide/water interface and they are considered as proton donors as well as proton acceptors, respectively, depending on pH. Specifically, hydroxyl groups on the oxide surface, -SOH, are expected to be the dominant sorption site. Hydroxylated groups (–SiOH and –AlOH) situated along the edges of clay minerals can also be significant sorption sites. Consequently, these surface sites are positively or negatively charged, and electrostatically interact with anions or cations in the aqueous solution. If no specific adsorption phenomena occur, the electrostatic interactions (non-specific adsorption processes) between the oppositely charged surface and solution species determine the formation of surface complexes.

3. Methods for uranium measurement in water samples

There are several methods for determination of uranium concentration in water. Uranium can be measured in mass units using chemical analytical methods and in activity units using radiochemical analysis [32]. For most frequently applied laboratory methods the following basic steps are included: pre-concentration or vaporization; acidification; co-precipitation; calcification; acid or carbonate separation; extraction and preparation for measuring [33-35].

Uranium in water is commonly measured by fluorimetry with either laser excitation or ultraviolet light following fusion of the sample with a pellet of carbonate and sodium fluoride (detection limit in the μg/L range). This method is based on the measurement of the fluorescence intensity of the UV irradiated uranyl ion. Fluorimeter is suitable to determine the concentration of uranium in drinking waters, groundwater, surface waters, as well as wastewater of the uranium industry [13, 36-37].

Uranium can also be determined by inductively coupled plasma mass spectrometry (ICP-MS), which has its detection limit in the ng/L range and a between-run precision of less than 6%. It is a routine method for quantitative analysis of uranium in environmental samples [38-44]. The U.S. Environmental Protection Agency (EPA) suggested that ICP-MS analytical methods could be more cost-effective, less labor-intensive or more sensitive than some of the technologies (fluorometric and laser phosphorimetry methods) previously approved [45]. In contrast, determination of dissolved uranium in the form of U(VI) in different water samples by voltammetric method show that this analysis technique is just as accurate and efficient as current ICP-MS methods [15].

Alpha spectrometry has been used for the determination of uranium in bottled waters and environmental media, although the recovery is often highly variable owing to the low specific activity of natural uranium [11, 33, 46-51]. The advantages of alpha spectroscopy are the precise measurement of uranium isotope concentration in water, the excellent energy resolution (15–30 keV) and the negligible background. The disadvantages of alpha spectrometry are as follows: not so good counting efficiencies, a required sample preparation with a series of steps including ion-exchange chromatography and electrodeposition as a thin layer to reduce problems of self-absorption. Also, the addition of a tracer is necessary to measure chemical recovery.

One of the references on this subject [33] compares the capabilities of five different methods (photometry, laser photometry (laser fluorimetry), liquid scintillation (LSC), gamma spectrometry and alpha spectrometry) for uranium determination and limits of application for the purposes of environmental monitoring. Samples included surface and underground waters, mineral, drinking and drilled well waters and water from areas with potential pollutants such as the locations of former uranium mines and miles. The main characteristic of the applied methods can be described as follows:

- For fairly low concentrations, liquid scintillation and laser photometry are equally applicable and the results do not show significant differences. The advantage of the applied laser photometry against other methods is the high measuring precision with the possibility of detecting fairly low concentrations down 0.2 μg/L. Laser photometry has accuracy comparable to that of liquid scintillation, it is fast and avoids organic waste as in the case of LSC. Furthermore, there is no need for a specific sample preparation. It uses modern technology and is easy to use even in the field. For mineral and natural waters, laser photometry is the best opportunity.
- For the determination of samples with higher uranium concentrations (e.g. samples from the region around the former uranium mines), the classical photometry is suitable. Photometry is applicable practically up to 10 mg/L and also for acidified samples. The main disadvantage of photometry comes from the colour quenching and the heavy metals content of the solution.
- Uranium isotopes determination can be carried out by alpha and gamma spectrometry or LSC. Alpha and gamma spectrometry resolve the problem of precise isotope determination, but with the disadvantage of hard chemical preparation and long measurement times. An intermediate method is LSC, with the problem of isotope estimation, due to poor energy resolution. Gamma spectroscopy is usually applied for rough estimation and it may be used successfully for samples with high uranium content.

It is also remarkable that different X-ray spectroscopic techniques (e.g. total reflection X-ray fluorescence spectrometry (TXRF), microbeam X-ray fluorescence (μ-XRF)) are promising but not usual methods for uranium determination in liquid samples [13]. It is also important to notice that kinetic phosphorescence analysis shows promise as a sensitive and selective method for the analysis of uranium and other lanthanides in drinking water and other media. This technique utilizes a laser source to excite an aqueous solution of uranium, and measures the emission luminescence intensity over time to determine the luminescence decay profile [52-54].

Recently, numerous studies concerning electrochemical analysis of uranium in environmental samples have been published. The use of stripping analysis has been expanded greatly, owing to the growing needs for one-site environmental monitoring or clinical testing of trace metals. Adsorptive cathodic stripping voltammetry (ACSV) is a technique in which the analyte is pre-concentrated first by adsorption onto a working electrode surface followed by voltammetric measurements of the electro-active species. Advantages of ACSV for trace analysis predominantly are high sensitivity, low instrumentation and running costs as well as the possibility of analysis matrices without the need of prior separation. This method has been applied to the stripping voltammetric determination of uranium in the absence or in the presence of various complexing reagents [60, 62]. The most common used chemical reagent, for forming a complex with uranium before particular electrochemical analysis, is chloranillic acid [56, 67-71]. Cupferron is also very frequently utilised for this purpose [63, 65-66, 72, 74]. However, many other complexing reagents have already been studied such as potassium hydrogen phthalate [60], dipicolinic acid [62], pyromellitic acid [61], 4-(2-pyridylazo)resorcinol [59], N-benzoyl-N-phenylhydroxylamine and propyl galate [73], aluminon [55], oxine [75], Mordant red 19 [57], HEPES [58] and arsenaso III [64]. Except the selection of the proper chemical reagent its concentration is also essential. Electro-chemical behaviour of such systems is primarily dependent on used supporting electrolyte. Acetate solution (0.02 - 1 mol/L) buffered on pH range 4.2 to 7.0 tends to be the most favourable. Also, sodium perchlorate solutions (0.01 – 0.02 mol/L) buffered in wider pH range (2.5 – 7.0) has been often applied. The type of electrode utilised during the pre-concentration step of ACSV plays a key role as well. Hanging mercury drop electrode (HMDE) [55-57, 59, 60-62, 64, 67, 69-71, 74-75] or its modification, such as mercury film silver based electrode [68], mercury-coated screen-printed carbon electrode [72] and pre-plated mercury film covering glassy carbon electrode [73] is very often used. The bismuth-film electrode [63], bismuth-coated carbon-fiber electrode and plated lead film electrode [65] seem to be environmentally friendly alternatives for uranium electrochemical determination. Further important parameters for ACSV analysis are determination of preconcentration respectively accumulation potential of uranium in particular studied electro-system and estimation of necessary accumulation time, which is very closely connected to uranium concentration in the sample.

After optimization of the individual electro-parameters there is still a requirement to assess the most significant interferences for the uranium analysis. Generally, cations of heavy and toxic metals, a number of anions (Cl^-, F^-, NO_3^-, BrO_3^-, ClO_4^-, SO_4^{2-}, PO_4^{3-}, CO_3^{2-}, HCO_3^-, $Cr_2O_7^{2-}$) as well as surfactants, dissolved organic carbon (DOC) or humic and fulvic acids in the system are investigated with this aim. The majority of ion influences may be eliminated by adding of strong complexing agent (e.g. EDTA). On the other hand, samples rich in organic compounds are recommended to mineralize for obtaining correct and accurate results.

4. Conclusions

Uranium is found in virtually all rocks and soils (being derived from erosion of the rocks) and it is essentially present in surface waters and groundwater. Concentrations of uranium in waters are influenced by the chemical and physical characteristics of the aquifer and by the uranium content of the geological formation involved. In systems where the rocks are exposed to weathering and the circulation of water, separation of the uranium series isotopes occurs.

The chemical behaviours of uranium species in aqueous solution can be influenced by several factors such as the inclination of uranium towards complex formation (in the presence of inorganic and organic ligands), the hydrolytic processes (often leading to polymeric ion species) and the redox properties. In the natural waters it's presence is also dependent on the sorption processes to surfaces of minerals and/or colloids, etc. The most prevalent form of uranium in aqueous solutions is the uranyl cation UO_2^{2+}. It is usually present in forms of uranyl hydroxyl carbonate complexes in natural waters. In the same time, it must be noted that uranium can also form stable complexes with other naturally occurring inorganic and organic ligands containing in water. The U(VI) sorption onto the soil are the iron and manganese oxide coatings and the clay fraction are based on the assumption that surface OH−sites are formed on the oxide/water interface and they are considered as proton donors as well as proton acceptors, respectively, depending on pH.

It is well-known that the general medical and scientific consensus is that in cases of high intake, uranium is likely to become a chemical toxicology problem before it is a radiological problem. Ingested or inhaled uranium can be harmful because of its chemical toxicity, excess uranyl ions depress renal function (i.e., affect the kidneys). It is straightforward that the measurement of uranium levels in aquatic environment is of great importance for environmental and safety assessment, especially in nuclear devices and plants or in the region of uranium mines. There are several analytical and radiochemical methods for the determination of uranium concentration in water. In accordance with literature data fluorimetry, ICP-MS, alpha spectrometry as well as electro-chemical determination of uranium are the most commonly applied methods.

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