



## Design of an electrochemically assisted radiation sensor for $\alpha$ -spectrometry of actinides traces in water



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### HIGHLIGHTS

- The method allows to find trace of actinides in water.
- The method allows direct  $\alpha$  spectrometry of actinides in aqueous solutions.
- Alpha spectrometry is performed without the use of a vacuum chamber.
- Decontamination of the sensor before re-use is very fast and efficient.
- Detection limit is lowered by concentration of actinides at the detector entrance window.

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### ABSTRACT

We describe a new approach for the detection and identification of actinides at low activity levels directly in aqueous solution. The measurement consists initially, in immobilizing alpha emitters in the form of insoluble hydroxides onto the entrance window of an immersed alpha particles detector. For this, a boron doped diamond detector window is negatively polarized to produce a basic layer on its surface by water decomposition. Actinides elements that are known to be very sensitive to hydrolysis are precipitated as solid hydroxides onto the entrance window of the sensor. Due to the absence of an air layer between the radioactive source and the detector, there is no need for vacuum during the alpha spectrometry measurement. After analysis, the detector can be easily cleaned by anodization in the aqueous medium to be reused at once. The minimum detectable activity concentration (MDA) of the system has been evaluated with <sup>241</sup>Am at 0.5 Bq/L for a 0.33 cm<sup>2</sup> area Si PIN diode.

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### 1. Introduction

The quality of the water we use every day is an essential governing parameter of the public health. In our societies, the preservation of the integrity of the drinking water supply is considered as a major stake. The quality of this water can be affected more or less durably by numerous pollutants. Beside usual contaminants such as organic products (solvents...), heavy metals, and bacteriological pollutants, the quality of water can also be severely affected by radioactivity and should be controlled (European Commission, 2011). Radioactivity in water has mainly three origins. It can be either from natural, anthropogenic or could also result from hostile terrorist activity.

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Among the multiple radionuclides, the actinide elements are of major importance due to their long half-lives of hundreds to hundred thousands of years, their radiation emission as well as their chemical toxicity to humans (Lizon and Fritsch, 1999). The light actinide elements, namely U, Np, Pu, Th, and Am, can exist in multiple oxidation states, (III–VI/or IV for Th and III–VII for Np), with each forming behaviorally distinct molecular species that can differ by orders of magnitude in reactivity, stability, and solubility (Vitorge, 1999). The range of potential reactions in natural aquifer systems is extremely broad because of the great variety of chemically active compounds in nature and the rich chemistry actinide elements exhibit (Choppin, 2003,2007). The conditions of the aquifer, such as pH, redox potential, complexing agent concentrations, and colloid concentration, determine the predominant actinide species and their transport characteristics in the environment (Silva and Nitsche, 1995; Maher et al., in press).

The analytical determination of actinide concentration levels in water by alpha spectrometry usually requires very long operations

that involve the following sequence: (i) separation, (ii) purification, (iii) preparation of solid sources and (iv) counting and spectrometric detection (Holm and Fukai, 1977; de Regge and Boden, 1984; Bickel et al., 2000; Diakov et al., 2001; Ayranov et al., 2005; Salar Amoli and Barker, 2007). Under such operating conditions, the time required from sampling to the analytical result delivery extends over several days. Also, clearly the sample if evaporated can be considered as lost, thus it remains a test sample approach. In the proposed approach, the detection of actinides is much faster, the sample is not destroyed, thus this becomes a real breakthrough for the consumer.

We propose to realize a novel sensor enabling to probe the activity concentration of trace levels of actinide contaminants in water. To date, there is no system enabling evaluation of water activity using a portable, easy to handle system that can be established for early stage detection of nuclear accidents as well as for continuous water quality control. Primary target is fresh water control, but in the future the detection system could be also used for water reservoir monitoring, for waste water assessment, for soils as well as for drinking products.

Water immersed detectors for  $\alpha$  activity monitoring in solutions containing traces of actinides ions have been addressed for a long time. In fact, as early as in 1977, natural diamond had already been successfully tested as detector material of  $\alpha$  particles in concentrated plutonium solutions in nitric acid media (2 M) with concentrations ranging from 10 to 100 mg/L of  $^{239}\text{Pu}$  (Kozlov et al., 1977). In this configuration the volume probed by the active surface of the device corresponds to the volume of liquid through which alpha particles can penetrate, thus it is limited to typically a few tens of micrometers. Although this technique allows getting round the delicate problem of the  $\alpha$ -source preparation, it can only probe in real-time extremely high activity levels, and therefore is not suitable for monitoring traces in fresh water. Later in 2000, the detection technique was improved at CEA (French Atomic Energy Commission) by the use of synthetic diamond as active alpha-sensor which was deposited on silicon substrate using Plasma Enhance Chemical Vapor Deposition (PECVD). Prototypes were fabricated for monitoring alpha activity in acids and concentrated solutions in nuclear reprocessing plants (Bergonzo et al., 2000). Some of these devices are currently in use at the Rakkasho Mura reprocessing plant (Japan) under operation by Japan Nuclear Fuel Limited (JNFL). More recently, PIPS<sup>®</sup> detectors (Passivated Ion Implant Planar Silicon—a Canberra Silicon based technology for radiation detection) have been used to detect  $\alpha$  particles on the surface of a liquid (Egorov et al., 2005). Although these devices are not a part of the family of immersed detectors, the experimental purpose remains similar: direct detection conducted without any pre-enrichment and reduction of the corrosion degradation from the radionuclide acidic solution. In 2005, Addleman and co-workers proposed a chemically enhanced alpha-energy spectroscopy in liquids based on extraction of actinides at pH 2 by a thin polymer film composed of di-2-ethylhexylphosphoric acid (HDEHP) and PVC deposited on a silicon diode (Addleman et al., 2005). In spite of this clever approach and consistent data collected with  $^{241}\text{Am}$ , the reversibility of the membrane seemed to be not achieved for all actinides in particular when extraction is not pH dependent ( $^{239}\text{Pu}$ ). In this case, decontamination of the sensor by pH variation is not possible and the membrane should be stripped off and renewed before being used again. Furthermore, no kinetics data on actinides extraction by the membrane sensor were given by the authors.

We will introduce another innovative approach that will be a real breakthrough for sensitive detection consisting of depositing actinides using an electrochemical technique directly onto a boron doped diamond entrance window of an alpha sensor acting as an electrochemical cathode. On the one hand, diamond is a low

atomic number material convenient for detector window fabrication with respect to alpha lines attenuation. On the other hand, boron doped diamond is a very attractive material for electrochemists. It possesses several interesting properties and namely hardness, high resilience to corrosion and radiation damage in harsh environment (Bergonzo et al., 2003) combined with very particular electrochemical properties. Highly doped diamond exhibits a large potential window (3.2 V in aqueous solution), high electron transfer rate ( $k_0 > 0.1$  cm/s) with outer sphere redox couples combined with low backing currents (Van hove et al., 2007,2009). Boron is by far the most widely used doping agent to produce conducting p-type semi-conductor diamond (Thonke, 2003). This is because boron has a low charge carrier activation energy of 0.37 eV (Haenni et al., 2004). At high doping levels ( $> 3 \times 10^{20}$  boron atoms  $\text{cm}^{-3}$ ) the material acts as a semimetal (Lagrange et al., 1998). If boron doped diamond electrodes are fouled in dirty environments (biological fluids...), they can be electrochemically re-activated by cyclic (de Sanoit and Van Hove, 2007), pulsed (Mahé et al., 2005), or pulsed in situ (Kiran et al., 2011,2013) electrochemical methods within several media. Thin electroactive films of synthetic boron doped nanocrystalline diamond (B-NCD) can be synthesized at rather low cost using a mixture of hydrogen/methane as carbon precursor and trimethyl-boron (TMB) as doping agent, at temperatures from 500 °C to 800 °C, by microwave assisted chemical vapor deposition (CVD) on silicon substrates.

It is known that the electrodeposition of actinides, i.e. their reduction at the metallic state with a charge transfer, is impossible with respect to the very negative standard potentials of these elements (Vitorge, 1999). However, in aqueous acid solution, the potential window is limited by the electrochemical water decomposition (on the reduction side through the system  $\text{H}_2/\text{H}^+$  and on the oxidation side through the system  $\text{H}_2\text{O}/\text{O}_2$ ). In addition, no electrochemical activity can be undertaken beside the electrochemical decomposition of the solvent. The whole current crossing the electrode being used for these reactions building what the electrochemists call the “solvent wall”. One can overcome this experimental difficulty by taking into account that actinide ions are very sensitive to hydrolysis (Altmaier et al., 2013). By increasing the pH of an aqueous solution containing actinide ions, the structure of ions is modified: protons become expelled by water hydration molecules towards non-binding water, the actinide ions accumulate hydroxyl ions ( $\text{OH}^-$ ) in the internal sphere and form hydroxo mono or polynuclear complexes (Baes and Mesmer, 1986) with solid hydroxides as final products. As a result, ion hydrolysis of actinides will not take place as long as they are kept in acidic solutions with concentration above 1 M or/and by the addition of complexing ions which will delay the aforementioned hydrolysis reactions. It is easy to locally modify the pH near the surface of the working electrode by electrochemical water reduction, a reaction that results in the formation of a basic layer (pH 12–13) according to the following reaction:



For example, the electroprecipitation of insoluble trivalent actinide hydroxide onto the cathode can thus be carried out even in slightly acidic solution according to reaction



More information on actinides insoluble hydroxide compounds versus oxidation states has been discussed by Vitorge in a review (Vitorge, 1999).

When the reduction current is switched off, the basic layer disappears and the actinide hydroxide can dissolve more or less quickly in the acid liquid medium. This can be avoided by adding ammonia into the electrolyte just before switching off the current.

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