

Electrochemically assisted precipitation of actinides on B-NCD/Si pin diode sensors for α -spectroscopy in solution

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Abstract: α -detection in liquid media is an extremely tedious issue since α -particles are self-absorbed by a few microns of liquid. Conventional techniques rely on the complete evaporation of the solvent, a long and energetically demanding process. We have developed novel devices enabling the electrochemically assisted precipitation of actinides on diamond sensors for α -spectroscopy. This approach enables to directly probe the α -activity in a sample solution. Our work focused on the optimization of the experimental parameters for ²⁴¹Am electro-precipitation: pH of electrolyte, nature of the supporting electrolyte Na₂SO₄ or NaNO₃ and current density value. This study therefore allowed to determine the best conditions for electro-precipitation of ²⁴¹Am, which leads a maximum precipitation yield of 37.6 %. The result also demonstrated that α -spectroscopy measurements could be practically performed, for the first time, on diamond/silicon pin diode based sensors immersed in aqueous solution after deposition process. High decontamination yields (≥ 99 %) of the sensors have been obtained by applying an anodic current density (6 mA/cm² for 10 minutes) on the B-NCD entrance window of the detector in an aqueous solution of Na₂SO₄ 0.3 M at pH 3.

Keywords: boron doped diamond, silicon sensor, actinides deposition, α -spectroscopy

1 - Introduction

Nuclear power plant provides the important part on world's energy about 6 %. As another industry, the development of nuclear industry generates non negligible amount of radioactive waste as by-product which is very hazardous. It requires different managements in order to protect the human life and the environment. This radioactive waste demands the strict control and treatment before dispersion in the environment. Otherwise, the nuclear industry, nuclear accidents (Tchernobyl 1986 and Fukushima 2011), terrorism potential attacks with dirty bombs as well as natural radioactivity can spread non negligible quantity of radioactive elements in the environment which could contaminate water resources. The α -particles detection of actinide at tracer levels in water is an extremely tedious issue since α -particles are self-absorbed by a few microns of liquid. The α -particles determinations usually requires very long operations that consist of a succession in a) separation, b) purification, c) preparation of liquid or solid sources and d) counting and spectrometric detection. Under such operating conditions, the time required from the moment a sample is taken for analysis to the result of the measurement may extend over several days. Moreover, α -particles

measurement absolutely requires the sophisticated condition such as vacuum condition, solid source preparation....

We have developed a device enabling the electrochemically assisted precipitation of actinides on diamond sensors for α -spectroscopy. Our approach is unique and applies for the first time electro-precipitation of actinides directly on the entrance window of the sensor as initial step.¹ The diamond material possesses unique properties such as chemical inertness, extreme hardness, thermal conductivity, corrosion hardness,....² Bergonzo *et al.* demonstrated that the diamond material could be used as corrosion hard material for α -particle monitoring in highly corrosive media.³ The sensor structure was previously detailed consisting of a 200 nm of thick boron doped nanocrystalline diamond layer (B-NCD) deposited onto a 200 μ m of thick silicon substrate with a 100 nm of thick aluminium layer on the back side.⁴ The protocole to use the sensor involves two steps (i) the first is the electro-precipitation in the aqueous medium of the actinides as insoluble hydroxide forms onto the negatively polarized B-NCD layer (entrance window of the sensor) and (ii) the second is the α -particle measurement of actinides deposited on the sensor by α -spectrometry. In the approach chosen,

the detection of actinides is shortened which will be a real time breakthrough for assessment of α -particles.

Electro-precipitation is a very efficient method commonly applied to the source preparation for α -spectrometric determination early pioneered by *Talvitie* in the 1970.⁵ Then, this method was modified by using Na_2SO_4 as electrolyte buffer as described by *Hallstadius*.⁶ The latter is very efficient and the most used by many authors for electro-precipitation of actinides such as ^{237}Np , ^{239}Pu , ^{241}Am .^{7,8,9} During electrolytic water decomposition under current, hydroxyl anions are adjacently generated at the cathode as well as hydrogen gas as side-product. In contact with the basic layer produced, actinides ions form low solubility solid hydroxides at the cathode (in **Fig 1**). Otherwise, the nitrate solutions are the reference media in the nuclear industry for fuel reprocessing and actinides separation chemistry, and there is little data on the actinides electro-precipitation in this medium.¹⁰ Interest of nitrate electrolyte buffer is the generation of hydroxyl layer by nitrate reduction reactions which leads to produce more hydroxyl anion while limiting hydrogen gas side-product evolution than in sulfate (in **Fig 2**).¹¹

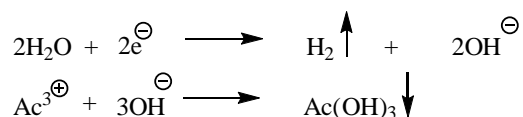


Fig 1: Reactions at the cathode during the electro-precipitation in Na_2SO_4 electrolyte

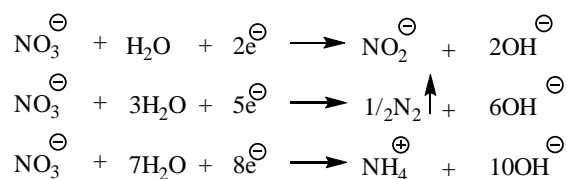


Fig 2: Nitrate reduction at the cathode during the electro-precipitation in NaNO_3 electrolyte

Following our previous work demonstrating the possibility of actinide electro-deposition for alpha-spectroscopic measurement in aqueous solution,¹ we report herein the study for improving the actinides precipitations yields. In a first approach, we studied the variation of some electro-precipitation parameters such as pH (range 2 to 4), electrolyte composition (Na_2SO_4 , NaNO_3 or

mixture) and current density over the range 1 - 20 mA/cm^2 on the deposition yield using ^{241}Am 5.96 Bq as radioactive tracer.

2 - Experimental section

2.1 - Chemical and apparatus

Chemical products NaNO_3 , Na_2SO_4 , HNO_3 , H_2SO_4 and NaOH were purchased from Sigma Aldrich. Actinides stock solution ^{241}Am 238.4 Bq/ml was supplied by LNHB (France) and activities were measured by liquid scintillation counting using Ultimagold (Packard) as scintillation cocktail. The pH of solution were adjusted to necessary value by diluted solutions of HNO_3 , H_2SO_4 and NaOH and controlled by a pH meter (Metrohm).

Electro-precipitation experiments are carried out for 90 minutes using ^{241}Am 5.96 Bq as radioactive tracer. The first geometry total in a 100 ml beaker containing 60 ml of electrolyte is studied on a sensor with active area 0.33 cm^2 (in **Fig 3a**). The magnetic stirring speed is adjusted at 700 rpm. The current density applied to B-NCD of sensor as the cathode is $9 \text{ mA}/\text{cm}^2$. The pH of solution was controlled and adjusted to basic pH 9-10 by ammonia diluted solution 2 % one minute before switching off the current. Second geometry for the electrochemical cell is developed in the framework of this study. A glass funnel is stuck on the sensor for promoting gravimetric deposition and reducing electrolyte volume to 15 ml (in **Fig 3b**). The B-NCD active area in this geometry is 0.25 cm^2 after sealing the device with epoxy resin. The mass transport was maintained by magnetic stirring at the rate 1500 rpm. The sensor decontamination was performed by positive polarization in Na_2SO_4 0.3 M pH 3 at a current density of $6 \text{ mA}/\text{cm}^2$.

2.2 - Alpha-spectroscopy

After electro-precipitation of actinides, the sensor is connected to an α -spectrometry chain composed of a signal amplifier (Amptek 250), followed by an amplifier (Ortec). The signal is digitalized and stored on a Digital Storage Oscilloscope (DSO) LeCroyWaverunner. This experimental arrangement allows us to record the counting rate (counts per second) involved in the radioactive

deposition onto the sensor. The acquisition time was adjusted to obtain a 3 % statistical counting uncertainty. The efficiency of electro-precipitation was calculated according **Eq 1**.⁴

$$R (\%) = 2 * \frac{\text{counting rate } (\frac{\text{counts}}{\text{second}})}{\text{activity in solution (Bq)}} * 100 \quad (\text{Eq1})$$

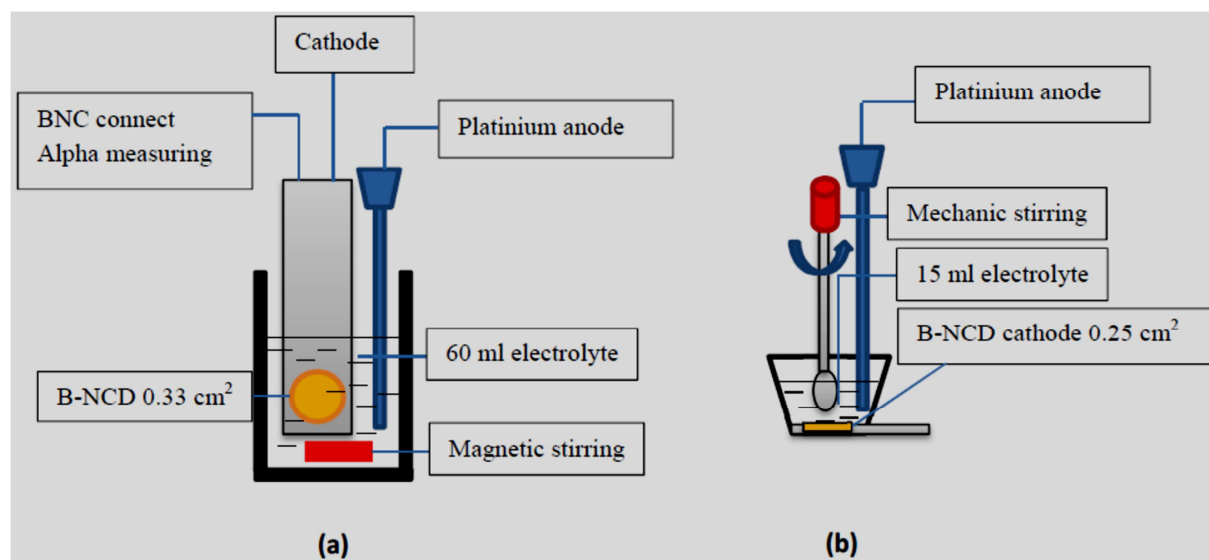


Fig 3: Electrochemical cell for electro-precipitation (a) Beaker geometry (b) Funnel geometry

3 - Results and discussion

3.1 - pH and electrolyte composition

Actinides are very sensitive to hydrolysis reactions and they can form insoluble hydroxides directly in aqueous solution. An important consequence is that actinides standard solution should be stored in acid medium before use. During electro-precipitation reactions, complexing agents nature and concentration (sulfate, nitrate) and pH should be adjusted to avoid hydrolysis of actinides before deposition onto the cathode. The electro-precipitation of ²⁴¹Am is studied at the constant activity of 5.96 Bq, at the constant current density $j_c = 9 \text{ mA/cm}^2$, in 60 ml electrolyte buffer, on the B-NCD sensor with active area of 0.33 cm^2 for 90 minutes. The pH of the electrolyte is studied at three levels in Na_2SO_4 and $[\text{Na}_2\text{SO}_4 + \text{NaNO}_3]$ mixture electrolytes. The experimental data are reported in **Table 1**.

After electro-precipitation of ²⁴¹Am on the sensor, two different ways for alpha-measurement were undertaken: either (i) keeping the sensor immersed in solution or (ii) drying the sensor after washing in deionized water. The data shows that the two

methods give the same counting rate excepting for these experiences 1 and 4 in **Table 1** due to high measurement uncertainties in correlation with the poor precipitations yields. Nevertheless, this work clearly demonstrated that α -spectroscopy can be performed directly (and for the first time) with a sensor directly immersed in the electrolyte.

In **Table 1**, we observe that the precipitation yield is very poor with values below 1 % at pH 2.17 in Na_2SO_4 or in $\text{Na}_2\text{SO}_4 + \text{NaNO}_3$ mixture electrolytes. This poor ²⁴¹Am deposition efficiency is linked to the fact that the electrolyte is too acidic and disturbs the generation of the hydroxyl layer adjacent at the cathode. For Na_2SO_4 at pH 3.17 and 4.20, the precipitation yields increase to 6.7 and 9.4 % respectively. This increase is attributed to the improvement of the hydroxyl layer formation by increasing of pH electrolyte solution. Contrary to Na_2SO_4 electrolyte, the deposition yield in $\text{Na}_2\text{SO}_4 + \text{NaNO}_3$ mixture solution at pH 4.20 is 8.2 % whereas the maximum ²⁴¹Am precipitation yield was obtained at pH 3.17 with 10.1 %. This can be explained by generating more hydroxyl in the nitrate reduction reactions. The hydroxyl layer at pH 4.20 could be thicker and more stable than in pH 3.17 (see section 3.2). The best precipitation

yield 10.1 % is obtained in NaNO₃ electrolyte. Otherwise, the electro-precipitation of ²⁴¹Am is also attempted in the pure NaNO₃ buffer leading to 11.0 % of the precipitation yield which is the same order of magnitude efficiency in Na₂SO₄ + NaNO₃ mixture solution. The electro-precipitation is

subsequently carried out in the pure NaNO₃ buffer instead of Na₂SO₄ + NaNO₃ mixture buffer for simplicity. The result shows that appropriate pH for the electro-precipitation of ²⁴¹Am in Na₂SO₄ and NaNO₃ buffer was 4.20 and 3.15 respectively.

Table 1: Parametric study of electro-precipitation of ²⁴¹Am 5.96 Bq in 60 ml electrolyte

Experiment	Electrolyte composition	pH initial	Counting rate immersion(s ⁻¹)	Counting rate dried(s ⁻¹)	Deposition yields (%)	decontamination yields (%)
1	Na ₂ SO ₄ 0.3M	2.17	0.0056	0.0067	0.2	76.51
2	Na ₂ SO ₄ 0.3M	3.13	0.204	0.200	6.7	99.35
3	Na ₂ SO ₄ 0.3M	4.20	0.281	0.279	9.4	99.74
4	Na ₂ SO ₄ 0.25M NaNO ₃ 0.05M	2.17	0.0085	0.0097	0.3	85.68
5	Na ₂ SO ₄ 0.25M NaNO ₃ 0.05M	3.17	0.304	0.301	10.1	99.81
6	Na ₂ SO ₄ 0.25M NaNO ₃ 0.05M	4.15	0.230	0.244	8.2	99.51

Otherwise, decontamination is an important aspect for reusing sensor. This work is efficiently done with positive polarization of the sensor according the mechanism described in **Fig 4**. Electro-decontamination procedure shows a high efficiency greater than 99 % in the most cases expecting of these experiments 1 and 4 with the poor precipitation yield in **Table 1**.

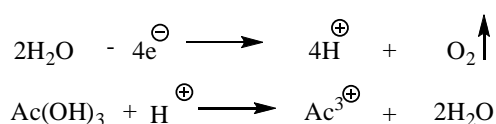


Fig 4: Mechanism for desorption of actinides hydroxides on the sensor

3.2 – Current density

Current density is a very important parameter affecting both the electro-precipitation efficiency and the quality of deposition layer.⁹ Indeed, the current density directly relates to the hydroxyl layer playing the kinetic of actinide hydroxyl formation. In general, the quality of electro-precipitated layers is improved with the decrease of the current density.¹² Nevertheless, we are herein interested in improving the electro-precipitation at level of

recovering efficiency. One of the main equation showing the relation between the thickness of the hydroxyl layer and the current for electro-precipitation is based on Hansen's theory where l_{OH} is the thickness of hydroxyl layer adjacent at the cathode, j is the current density applied to the cathode, δ is the thickness of the diffusion layer, and C and D_H are the hydrogen ion in bulk solution and the diffusion coefficient (in **Eq 2**). According to this theory, there is a minimum value of the current density (j_{min}) allowing reaching the highest electro-precipitation yield. Above this value, the precipitation yield lightly decreases due to thicker hydroxyl layer formation and more than difficult diffusion of actinides to the cathode. And under this value, the precipitation yield significantly decreases because of the absence of hydroxyl layer generation.

$$l_{OH} = \delta - \frac{CD_H}{j} \quad (\text{Eq 2})$$

Electro-precipitation is carried out in 15 ml electrolyte solution in the funnel cell described in **Fig 3b**. The experiments are performed in the Na₂SO₄ buffer at pH 4.05 and the NaNO₃ buffer at pH 3.10 for comparison purpose. In **Fig 5**, the black curve shows the precipitation yield according to the current density over the range 0.5 - 18.0 mA/cm².

The optimum current density obtained was 1 mA/cm² revealing a good agreement with the value at 0.6 mA/cm² determined by *Tsouko-Sitnikov*.⁹ The difference could be from the experimental setup at pH 4.30 and rotating disk electrode condition. The best precipitation yield reaches up to 25 % in Na₂SO₄ buffer. In general, the precipitation yield slightly decreases above 1 mA/cm². Limiting current density is 3 mA/cm² for NaNO₃ pH 3.10 electrolyte buffer. This value is higher than those of Na₂SO₄ buffer which could be related to the difference of electrolyte pH. Nevertheless, the best

precipitation yield of 36.7 % was obtained at the current 5 mA/cm². This result could be explained by complex reactions involved in nitrate reduction. The studying allows reaching to the better deposition yield even at less current density. Experimentally, electro-precipitation prefer to low current by breaking of araldite resin sealing. We observed also that the precipitation in NaNO₃ buffer usually is more efficient than in Na₂SO₄ due to more hydroxyl generation and limitation of hydrogen gas generation.

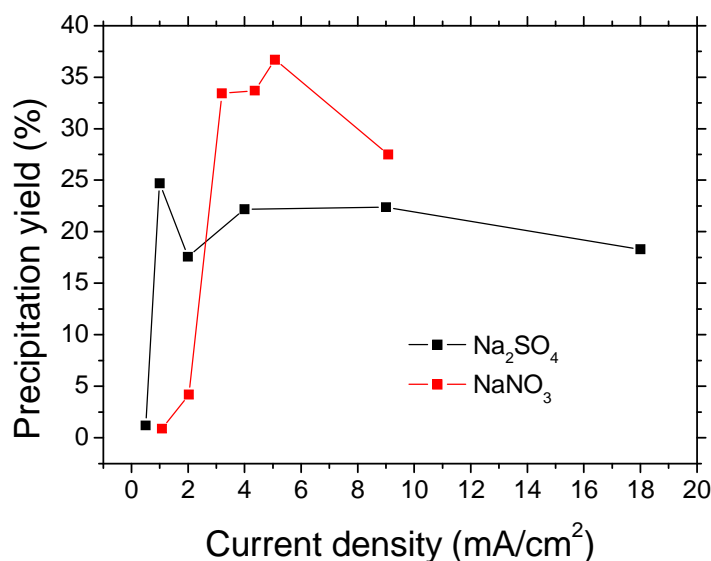


Fig 5: Precipitation yield versus current density for electro-precipitation of ²⁴¹Am 5.96 Bq in 15 ml electrolyte

4 - Conclusion

This study allowed us to demonstrate the possibility to significantly improve the efficiency of actinide collection reaching values of 36.7 % for ²⁴¹Am electro-precipitation by optimizing the pH of electrolyte buffer, the current density applied to the cathode and the cell geometry. The conditions for best electro-precipitation yield are to use a current density of 5 mA/cm², in an NaNO₃ electrolyte solution of pH 3. Decreasing the electrolyte volume results in the increasing ²⁴¹Am concentration in the solution that improves the electro-precipitation

yield. The result shows that the NaNO₃ electrolyte leads to a better precipitation yield than the Na₂SO₄ due to enhancement of the hydroxyl layer generation and a limitation of the hydrogen gas generation. The actinides desorption is rapidly carried out by applying a positive current density at 6 mA/cm². The coupling of silicon pin diode α -particles sensor with boron doped diamond layer therefore enables a straightforward and direct alpha-measurement in solution while conventional α -spectrometry requires a vacuum chamber for measurement. Other sensors with larger surface area are current developed in the laboratory for improving the deposition yield.

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