



# Determination of $^{227}\text{Ac}$ in water by alpha spectrometry after purification with titanium phosphate and DGA resin

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## Abstract

A new routine method to measure  $^{227}\text{Ac}$  in water samples was developed. Actinium-227 was separated from potential radioactive and matrix interferences using a DGA resin (Eichrom) at optimal extraction and elution conditions (2 M and 15.7 M  $\text{HNO}_3$ , respectively). This was possible because Ac was pre-concentrated and separated from Ca using titanium phosphate co-precipitation at pH 3.5. Finally,  $^{227}\text{Ac}$  was counted by alpha spectrometry for 48 h after a cerium fluoride micro-precipitation. A minimal detection limit of  $0.03 \pm 0.01 \text{ Bq l}^{-1}$  was obtained. The method was validated using spiked water samples.

**Keywords** Actinium · Water · DGA resin · Titanium phosphate · Analytical method

## Introduction

Actinium-227 is present at trace level in the environment as part of the  $^{235}\text{U}$  decay series. It has a radiological half-life ( $t_{1/2}$ ) of  $21.772 \pm 0.003 \text{ y}$  [1], and decays mainly through beta emission to  $^{227}\text{Th}$  (98.58%) ( $t_{1/2} = 18.7 \text{ d}$ ) and slightly through alpha emission to  $^{223}\text{Fr}$  (1.42%) ( $t_{1/2} = 22.00 \pm 0.07 \text{ min}$ ) [1]. Actinium-227 is considered a very toxic radionuclide because it deposits into the skeleton and liver following ingestion [2] and then decays to a series of short-lived alpha emitters [1]:  $^{223}\text{Ra}$ ,  $^{219}\text{Rn}$ ,  $^{215}\text{Po}$ , and  $^{211}\text{Bi}$ , which have radiological half-lives of  $11.43 \pm 0.03 \text{ d}$ ,  $3.98 \pm 0.03 \text{ s}$ ,  $1.781 \pm 0.004 \text{ ms}$ , and  $2.15 \pm 0.02 \text{ min}$ , respectively.

Actinium-227 monitoring could be needed for drinking, waste, and environmental waters in the vicinity of some uranium, rare-earth, and radiopharmaceutical facilities to ensure public health and to comply with national regulations. Actinium-227 is a waste product of the uranium and rare-earth mining and purification industries [3–6]. Also,  $^{227}\text{Ac}$  is of great importance in the medical field for the production of  $^{223}\text{Ra}$ , a medical isotope used for the treatment of

some advanced prostate cancers [7–9]. The highest activity concentration guidance value issued by the World Health Organization (WHO) for safe consumption of drinking water for  $^{227}\text{Ac}$  is  $0.1 \text{ Bq l}^{-1}$  [10]. The exemption quantities for  $^{227}\text{Ac}$  in waste water in Canada [11] and the United Kingdom [12] are 10 and  $0.1 \text{ Bq l}^{-1}$ , respectively. A method to monitor  $^{227}\text{Ac}$  activity in water with a minimum detectable activity (MDA) concentration of  $0.1 \text{ Bq l}^{-1}$  would be sufficiently sensitive for most routine monitoring applications and would safeguard public health.

Actinium-227 can be measured by alpha spectrometry [13], liquid scintillation counting (LSC) [14], and gas flow proportional counting [15]. Alpha spectrometry is the preferred method because it is more sensitive, there are fewer spectral interferences, and  $^{225}\text{Ac}$  can be used as a recovery tracer. To measure  $^{227}\text{Ac}$  by alpha spectrometry,  $^{227}\text{Ac}$  is pre-concentrated (e.g., with  $\text{MnO}_2$ ), purified, and deposited as a thin layer (e.g., electroplated) [13, 15]. Then, the  $^{225}\text{Ac}$  tracer is measured shortly after separation because it decays relatively quickly ( $t_{1/2} = 10.0 \pm 0.1 \text{ d}$ ). The progenies of  $^{227}\text{Ac}$  are measured about 100 days after separation, when they reach their maximum activity, to obtain an optimal sensitivity. Most analytical methods to determine  $^{227}\text{Ac}$  in water have been developed to measure very low traces of  $^{227}\text{Ac}$  in sea water ( $\sim 0.8\text{--}80 \mu\text{Bq l}^{-1}$ ), mainly for oceanographic studies [13, 15–18]. These methods are too tedious and time-consuming for routine monitoring because a large volume of sea water ( $> 50 \text{ l}$ ) and a long time for the progenies to

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grow are needed [13]; thus, new routine monitoring methods more adapted to the routine determination of  $^{227}\text{Ac}$  in water samples are needed.

Precipitation [19], solvent extraction [6], ion exchange chromatography [16], and extraction chromatography (EXC) [20] can be used to separate Ac from potential matrix and radiological interferences. The commercially available EXC resin DGA [21] is commonly used to purify trivalent actinides and lanthanides. Dulaiova et al. [20] extracted Ac(III) in 4 M HCl (retention capacity ( $k'$ ) of  $\sim 20$ ) on the DGA resin (normal), as Ca(II) and Ra(II) are less retained ( $k' < 1$ ). Then Ac(III) was eluted with 2 M HCl ( $k' = 0.5$ ) while the other actinides remained on the resin ( $k' > 20$ ). The main disadvantage of this method is that the retention capacity for Ac(III) is very low in 4 M HCl ( $k' = 20$ ), which could lead to poor recoveries in some environmental water samples due to the presence of organic ligands. Actinium extraction on DGA resin differs significantly in nitric acid solutions from other actinides and lanthanides extraction: the Ac(III) retention capacity is optimal at 2 M  $\text{HNO}_3$  ( $k' = 2000$ ) and decreases at higher  $\text{HNO}_3$  molarities, whereas for other actinides and

lanthanides the  $k'$  increases with acid molarity to reach a maximum value at 10 M  $\text{HNO}_3$  [21]. The extraction of Ac(III) in 2 M  $\text{HNO}_3$  on the DGA resin would be ideal for its purification, but to our knowledge no such method has been developed because Ca(II) is also strongly extracted on the resin under the same conditions. Calcium interferes with Am(III) uptake on the DGA resin [21], and this is expected to be similar for Ac(III). Also, if the thin layer source of Ac for alpha spectrometry measurement is prepared using  $\text{CeF}_3$  micro-precipitation, Ca(II) will precipitate as  $\text{CaF}_2$  and directly decrease the alpha spectrometry resolution.

A novel and rapid method to purify and determine  $^{227}\text{Ac}$  in water samples using DGA resin was developed. Actinium was pre-concentrated with titanium phosphate at pH 3.5 from a 1 l water sample, which left Ca(II) in solution and prevented it from interfering with the purification and measurement steps (Fig. 1, steps 15–18). Then, the precipitate was dissolved in 2 M  $\text{HNO}_3$  and passed through a DGA resin. Actinium was eluted from the resin using 15.7 M  $\text{HNO}_3$ , which left the other actinides and lanthanides strongly retained on the resin. Finally, Ac(III) was co-precipitated with  $\text{CeF}_3$  and immediately measured by alpha spectrometry for 48 h.

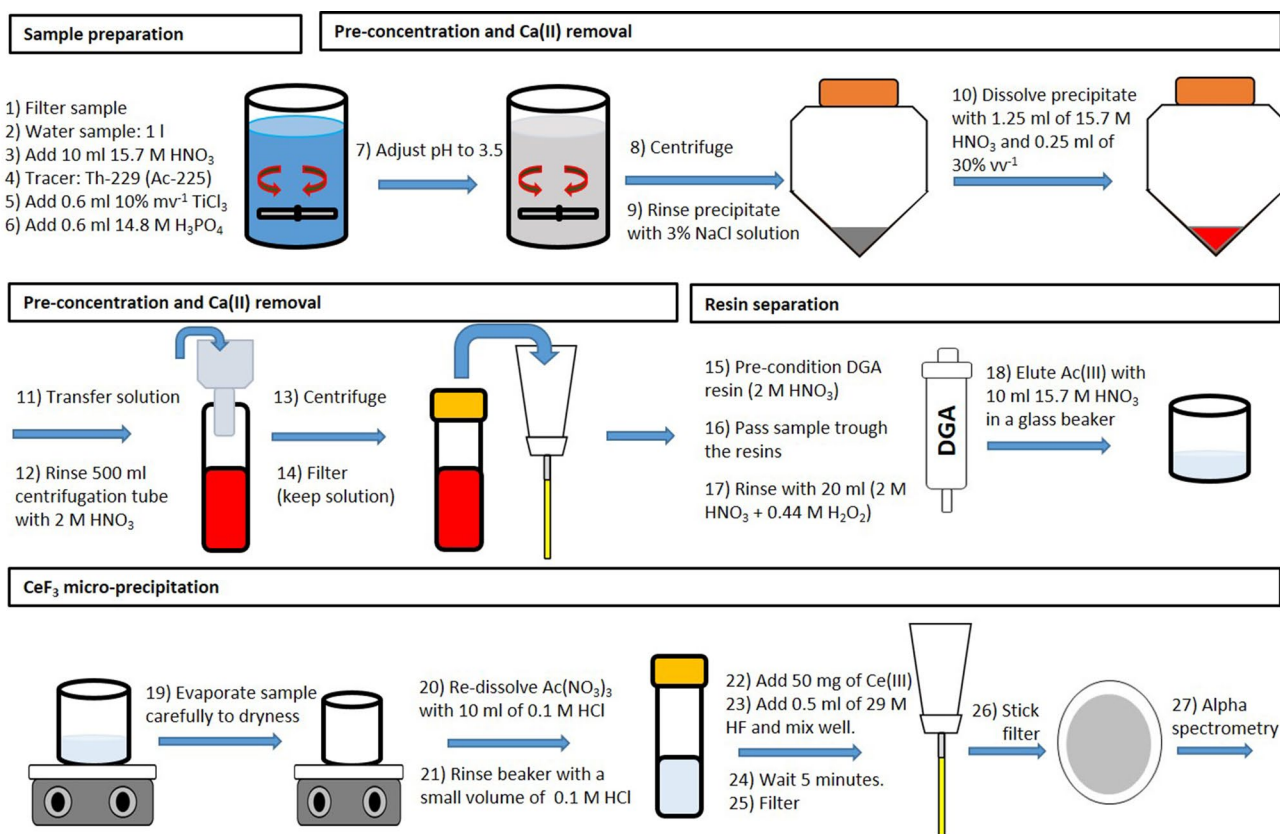


Fig. 1 Schematic representation of the method

## Experimental

### Reagents and standards

All solutions used for this work were prepared using ultrapure water from a Millipore Direct-Q5 water purification system (Billerica, MA, USA). Trace metal grade acids (phosphoric acid ( $\text{H}_3\text{PO}_4$ ), nitric acid ( $\text{HNO}_3$ ), hydrochloric acid ( $\text{HCl}$ ), and hydrofluoric acid ( $\text{HF}$ )), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), sodium hydroxide ( $\text{NaOH}$ ), sodium chloride ( $\text{NaCl}$ ), and cerium nitrate  $\text{Ce}(\text{NO}_3)_3$  were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Titanium trichloride ( $\text{TiCl}_3$ ) and zirconyl chloride ( $\text{ZrOCl}_2$ ) in  $\text{HCl}$  were obtained from Sigma Aldrich (Oakville, ON, Canada). DGA® extraction chromatography resin (normal, 50–100  $\mu\text{m}$ ) containing N,N,N,N'-tetra-n-octyldiglycolamide and pre-packed in 2 ml cartridges was purchased from Eichrom Technologies (Lisle, IL, USA). Ethanol was obtained from Commercial Alcohols (Mississauga, ON, Canada). Certified solutions of  $^{90}\text{Sr}$ ,  $^{209}\text{Po}$ ,  $^{147}\text{Pm}$ ,  $^{226}\text{Ra}$ ,  $^{227}\text{Ac}$ ,  $^{231}\text{Pa}$ ,  $^{229}\text{Th}$ ,  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$ , and  $^{244}\text{Cm}$  were obtained from Eckert and Ziegler (Valencia, CA, USA). Solutions of natural Th and U were obtained from SCP Science (Baie d'Urfé, QC, Canada).

### Instruments

All samples measurement were performed using an Octete Plus® alpha spectrometer with eight 450  $\text{mm}^2$  ULTRA-AS ion-implanted silicon detectors (AMETEK/ORTEC, Oak Ridge, TN, USA). For method development, some beta emitters were measured using a Hidex 300 SL liquid scintillation counter (Hidex Oy, Turku, Finland).

### Procedure

#### Sample preparation

A 1 l water sample was filtered using a 45  $\mu\text{m}$  pore size filter to remove suspended particles and acidified with 10 ml of 15.7 M  $\text{HNO}_3$  (Fig. 1, steps 1 and 2). Actinium adsorbed on the suspended particles is not considered for this method. The filtered water sample and 20 mBq of  $^{229}\text{Th}$  tracer, in equilibrium with its daughter  $^{225}\text{Ac}$ , were weighed in a glass beaker (Fig. 1, steps 3 and 4). To the water sample, 0.6 ml of  $\text{TiCl}_3$  10%  $\text{mv}^{-1}$  in  $\text{HCl}$  and 0.6 ml of 14.8 M  $\text{H}_3\text{PO}_4$  were added (Fig. 1, steps 5 and 6). The sample was mixed using a magnetic stirrer and a stirring plate until Ti(III) was fully oxidized to  $\text{TiO}^{2+}$  (absence of purple color), which took only a few minutes (Fig. 1, step 5). Note that it was preferable to add Ti(III) from a solution and oxidize it with  $\text{HNO}_3$  instead

of adding Ti(IV) from a solution or salt, because Ti(III) solution is much easier to obtain commercially.

#### Actinium pre-concentration and calcium removal

The sample pH was adjusted to 3.50 with a 40%  $\text{NaOH}$  solution and mixed for 5 min to co-precipitate  $\text{AcPO}_4$  with titanium phosphate (Fig. 1, step 7). The pH was adjusted to 3.50 to optimize the precipitation of  $\text{AcPO}_4$  and minimize the precipitation of  $\text{CaHPO}_4$ . The precipitate was isolated by centrifugation (3500 rpm for 3 min) using 500 ml centrifugation tubes (Fig. 1, step 8). The precipitate was rinsed and re-centrifuged three times with 100 ml of a 3%  $\text{NaCl}$  solution to remove as much Ca(II) as possible (Fig. 1, step 9). A  $\text{NaCl}$  solution was used instead of water to minimize the dispersion of the precipitate in solution during the centrifugation step, which increased the method's recovery.

After centrifugation, the precipitate was dissolved with 1.25 ml of 15.7 M  $\text{HNO}_3$  and 0.25 ml of 30%  $\text{v}^{-1}$   $\text{H}_2\text{O}_2$  (Fig. 1, step 10) ( $\text{H}_2\text{O}_2$  is used to complex Ti(IV)). This solution was transferred to a 50 ml plastic centrifugation tube using a funnel, and the volume was completed to 10 ml with water to adjust the acid molarity to 2 M  $\text{HNO}_3$  (Fig. 1, steps 11). The transfer was necessary because the gradation on the 500 ml centrifugation tube was not precise enough to adjust the acid molarity. The 500 ml centrifugation tube was rinsed twice with about 5 to 10 ml of 2 M  $\text{HNO}_3$  and the rinsing solution transferred to the 50 ml centrifugation tube to minimize transfer losses (Fig. 1, step 12). The dissolved sample in the 50 ml centrifugation tube was centrifuged for 1 min at 3700 rpm and the supernatant filtered through a 0.1  $\mu\text{m}$  pore size filter to remove remaining particles that could clog the resin (Fig. 1, steps 13 and 14).

#### Resin purification

Actinium was separated from potential interferences using a DGA resin in a 2 ml cartridge. The resin was put on top of a multi-hole vacuum box using the appropriate connectors and reservoirs. The resin was conditioned with 5 ml of 2 M  $\text{HNO}_3$  (Fig. 1, step 15) and the sample was passed through the resin at a flow rate of about 1 to 2  $\text{ml min}^{-1}$  (Fig. 1, step 16). The resin was rinsed with 20 ml of 0.44 M  $\text{H}_2\text{O}_2$  in 2 M  $\text{HNO}_3$  solution to remove  $\text{TiO}^{2+}$  and elements that were weakly retained on the resin (Fig. 1, step 17). Actinium was selectively eluted using 10 ml of 15.7 M  $\text{HNO}_3$  into a glass beaker (Fig. 1, step 18) and the elution time was recorded.

#### micro-precipitation

The eluate containing Ac was carefully evaporated to dryness on a hot plate to avoid losses by splattering (Fig. 1,

step 19). The residue was re-dissolved with about 10 ml of 0.1 M HCl and transferred into a 50 ml plastic centrifuge tube (Fig. 1, steps 20 and 21). The nitric acid solution was evaporated to dryness because the yield of the CeF<sub>3</sub> micro-precipitation is poor in highly acidic solutions. For each sample, 50 µg of Ce(III) and 0.5 ml of 29 M HF were added to co-precipitate AcF<sub>3</sub> with a micro-precipitate of CeF<sub>3</sub> (Fig. 1, steps 22 and 23). The solution was shaken, left aside for 5 min, and filtered through a 0.1 µm pore size filter (Fig. 1, steps 24 and 25). The filter was rinsed with 1 ml of ethanol and placed on a sticky metal planchet (Murphy Die & Machine, North Quincy, MA, USA) with the precipitate on top (Fig. 1, step 26). The filter was left to dry for a few minutes and then counted by alpha spectrometry for 48 h (Fig. 1, step 27).

### Counting and activity calculation

The <sup>227</sup>Ac activity concentration ( $A_{Ac227}$ ) in Bq l<sup>-1</sup> was calculated using Eq. 1:

$$A_{Ac227} = \frac{A_{Ac225} CR_{Ac227}}{bVACR_{Ac225}} \quad (1)$$

where  $A_{Ac225}$  is the activity of <sup>225</sup>Ac tracer added (from <sup>229</sup>Th) in Bq,  $CR_{Ac227}$  the net count rate of <sup>227</sup>Ac (count·s<sup>-1</sup>),  $b$  the fraction of <sup>227</sup>Ac that decays through alpha emission (e.g., 0.0142) [1], and  $V$  the sample volume in liters. Note that the sample volume can be replaced by the sample mass.  $ACR_{Ac225}$  is the corrected net count rate of <sup>225</sup>Ac (count·s<sup>-1</sup>), calculated according to Eq. 2:

$$ACR_{Ac225} = \frac{CR_{At217} \lambda_{Ac225} t_2 e^{(\lambda_{Ac225} t_1)}}{(1 - e^{(-\lambda_{Ac225} t_2)})} \quad (2)$$

where  $CR_{At217}$  is the net count rate of <sup>217</sup>At in Bq,  $\lambda_{Ac225}$  is the decay constant of <sup>225</sup>Ac ( $\ln(2)/t_{1/2}$ ),  $t_1$  is the time elapsed between separation and counting in seconds, and  $t_2$  is the counting time in seconds. The count rate of <sup>225</sup>Ac needs to be corrected because the isotope decays significantly while it is counted. The net count rate of <sup>225</sup>Ac is obtained indirectly from <sup>217</sup>At because the <sup>217</sup>At peak is free from interferences. Astatine-217 is in transient equilibrium with <sup>225</sup>Ac after about 30 min. The decay of <sup>227</sup>Ac can usually be neglected if the sample is counted within a few days following the separation. The <sup>227</sup>Ac activity measured should be decay-corrected to the sampling date.

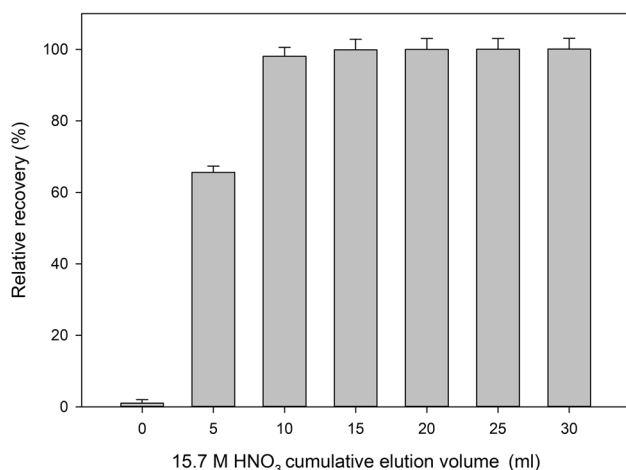
### Method development

#### Actinium elution profile from DGA Resin

To determine the elution profile of Ac(III) on the DGA resin, a 20 ml solution of 2 M HNO<sub>3</sub> containing 100 mBq of <sup>229</sup>Th (<sup>225</sup>Ac) was prepared. A DGA resin was conditioned with 5 ml of 2 M HNO<sub>3</sub>. The <sup>299</sup>Th (<sup>225</sup>Ac) solution was passed through the resin and the resin was rinsed with 20 ml of 2 M HNO<sub>3</sub>. Actinium was eluted from the resin by fractions of 5 ml with 15.7 M HNO<sub>3</sub>. Each fraction was collected in an individual glass beaker. The load and rinse solutions were also collected to ensure that Ac(III) was completely retained by the resin under these conditions. The fractions eluted were evaporated to dryness and re-dissolved in 10 ml of 0.1 M HCl. The CeF<sub>3</sub> micro-precipitation steps described in the procedure section (Fig. 1, steps 22–26) were performed and the test samples were measured by alpha spectrometry. The elution profile test was performed three times.

#### Purification and isolation of Ac

The method decontamination factor (DF) was determined by spiking water samples with a known activity or amount of an element (<sup>232</sup>Th, <sup>238</sup>U, and <sup>231</sup>Pa (1 Bq); <sup>209</sup>Po, <sup>226</sup>Ra, <sup>237</sup>Np, <sup>239</sup>Pu, and <sup>244</sup>Cm (0.1 Bq); <sup>90</sup>Y (10 Bq); <sup>147</sup>Pm (100 Bq); and Ca (13.5 g)) that could potentially interfere. The method was then applied. The DF was calculated by dividing the activity or amount added by the activity or amount measured. Each test was repeated twice. The isotopes were measured by alpha spectrometry after the micro-precipitation step (Fig. 1, step 27), except for <sup>90</sup>Y, <sup>147</sup>Pm, and Ca. The isotope <sup>90</sup>Y was obtained by purifying a <sup>90</sup>Sr solution using a Sr resin (2 ml cartridges, 50–100 µm, 4,4'(5')-di-*t*-butylcyclohexano-18-crown-6 in 1-octanol) (Eichrom, Lisle, IL, USA) [21].



**Fig. 2** Elution profile of Ac(III) on the DGA resin (extraction, 2 M HNO<sub>3</sub>; elution, 15.7 M HNO<sub>3</sub>)

**Table 1** Potential radioactive interferences [1]

Isotope to measure			Potential interferences			DF
Isotope	Energy (keV)	Intensity (%)	Isotope	Energy (keV)	Intensity (%)	
$^{227}\text{Ac}$	5042	0.658	$^{209}\text{Po}$	4977	79.2	$1900 \pm 300$
	5029	0.546		4979	19.8	
			$^{226}\text{Ra}$	4871	94.0	$3000 \pm 1000$
			$^{229}\text{Th}$	4845	56.2	$2700 \pm 800$
				4901	10.2	
			$^{231}\text{Pa}$	5104	25.3	$1250 \pm 30$
				5040	22.5	
				5120	20.0	
				5150	11.7	
			$^{234}\text{U}$	4858	71.4	$\geq 5000 \pm 2000$
			$^{237}\text{Np}$	4872	47.6	$\geq 6410 \pm 4$
				4855	23.0	
			$^{242}\text{Pu}$	4985	76.5	$\geq 5100 \pm 100$
				4940	23.4	
			$^{247}\text{Cm}$	4870	71.0	$390 \pm 20$
				5267	13.8	
				4985	2.00	
			$^{248}\text{Cm}$	4943	1.60	
				5078	75.0	
				5035	16.5	
$^{217}\text{At}$	7200	99.9	–	–	–	–

**Table 2** Potential matrix interferences

Potential interference	DF
$\text{Ca}^{2+}$	$6000 \pm 2000$
$\text{Y}^{3+}$	$400 \pm 70$
$\text{Pm}^{3+}$	$170 \pm 10$

The isotopes  $^{90}\text{Y}$  and  $^{147}\text{Pm}$  were measured by dissolving the  $\text{CeF}_3$  precipitate on the disc used for alpha spectrometry measurement (Fig. 1, step 26) in 10 ml of 0.1 M HCl. The solution was transferred to an LSC vial, and 10 ml of Ultima Gold AB (PerkinElmer, Guelph, ON, Canada) liquid scintillation cocktail were added. The  $^{90}\text{Y}$  and  $^{147}\text{Pm}$  were then counted by LSC. Calcium was determined by measuring the mass of  $\text{CaF}_2$  on the final alpha disc (Fig. 1, step 26).

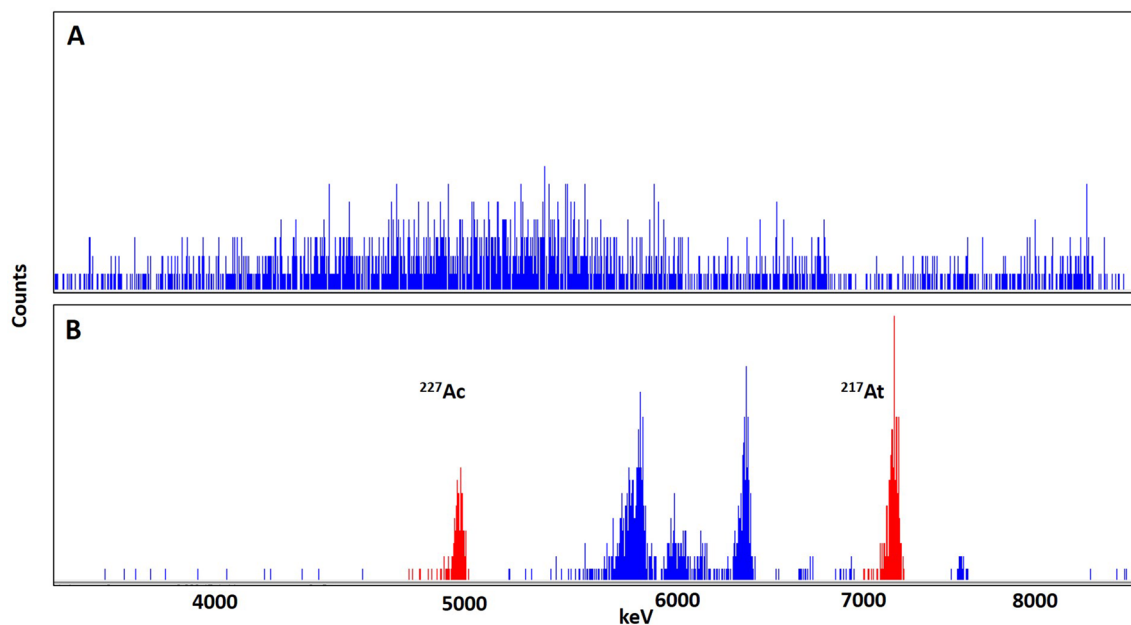
The optimal co-precipitation pH of Ac(III) with titanium phosphate (Fig. 1, step 7) was studied. Test samples were prepared with ultrapure water (1 l water and 30 mBq  $^{229}\text{Th}$ ). The method procedure described above was applied, but the precipitation pH was varied between 0 and 7 at the titanium phosphate precipitation step (Fig. 1, step 7). The test was repeated twice.

### Titanium phosphate

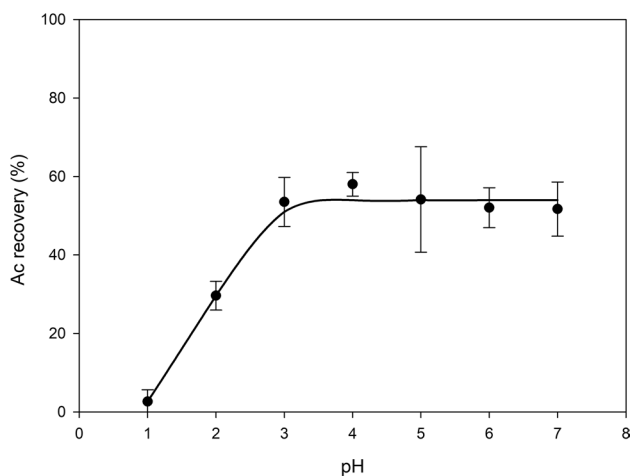
A rapid qualitative test was done to determine whether the salt obtained at the titanium phosphate co-precipitation step (Fig. 1, step 7) was a phosphate salt or a titanium oxide/hydroxide salt. In two separate 50 ml centrifuge tubes, 40 ml of water, 1 ml of 15.7 M  $\text{HNO}_3$ , and 0.6 ml of a 10%  $\text{TiCl}_3$  solution were combined. In one of the tubes, 0.6 ml of 14.8 M  $\text{H}_3\text{PO}_4$  was added. The pH was adjusted to 4. The precipitate obtained was centrifuged and rinsed three times with a 3% NaCl solution. The precipitate obtained was dissolved with 5 ml of 15.7 M  $\text{HNO}_3$  and 0.1 ml of 30%  $\text{ZrOCl}_2$  was added.

### Figures of merit

The MDA was determined using 10 method blanks. The MDA was calculated using the Currie equation [22]. The MDA, relative bias (accuracy), and relative standard deviation (precision) were calculated as described in previous work [23]. The method was validated using river water and artificial sea water samples. The water samples were filtered and a known amount of  $^{227}\text{Ac}$  was added. The artificial sea water was prepared according to the method by Kester et al. [24] and the river water was collected at the Chalk River Laboratory site (Ottawa River, ON, Canada).



**Fig. 3** Example of alpha spectrum of  $^{225}\text{Ac}$  ( $\sim 0.01$  Bq) and  $^{227}\text{Ac}$  ( $\sim 1$  Bq) for an artificial sea water sample at **A** pH 3.8 (poor resolution) and **B** pH 3.5 (good resolution)



**Fig. 4** Ac(III) recovery as a function of the pH at the titanium phosphate co-precipitation step

## Results and discussion

### Method development

#### Actinium extraction and elution on DGA resin

The elution profile of Ac(III) on the DGA resin using 15.7 M  $\text{HNO}_3$  is shown in Fig. 2. Most of the Ac(III) was eluted from the DGA resin using 10 ml of 15.7 M  $\text{HNO}_3$  ( $98 \pm 3\%$ ). This volume was considered optimal to elute Ac(III) from the resin because it saved time during the elution and evaporation steps that followed (Fig. 1, steps 18 and 19), with only minor losses ( $\sim 2\%$ ). About 95% ( $94 \pm 5\%$ ) of the Ac(III) added was recovered and only  $1 \pm 1\%$  of the Ac(III) passed through the resin (Fig. 2), which confirmed that Ac(III) was well retained by the resin in 2 M  $\text{HNO}_3$  and well eluted with 15.7 M  $\text{HNO}_3$ .

#### Actinium purification

The DFs measured for potential radioactive and matrix interferences are presented in Tables 1 and 2, respectively. These DFs are high for all the radionuclides tested, including elements with oxidation state +3, such as Am, Cm, Pm, and Y. This is in agreement with the retention capacity graphs published by Eichrom [21], which show that the retention capacity of elements of oxidation state +3 increases when

**Table 3** Figures of merit

Average chemical recovery (%)	$67 \pm 8$
MDA ( $\text{Bq l}^{-1}$ )	$0.03 \pm 0.01$
Reference level ( $\text{Bq l}^{-1}$ ) (WHO)	0.1
Mean relative bias (accuracy) (%)	-0.35
Relative standard deviation (precision) (%)	7.15
Samples per workday per person	4

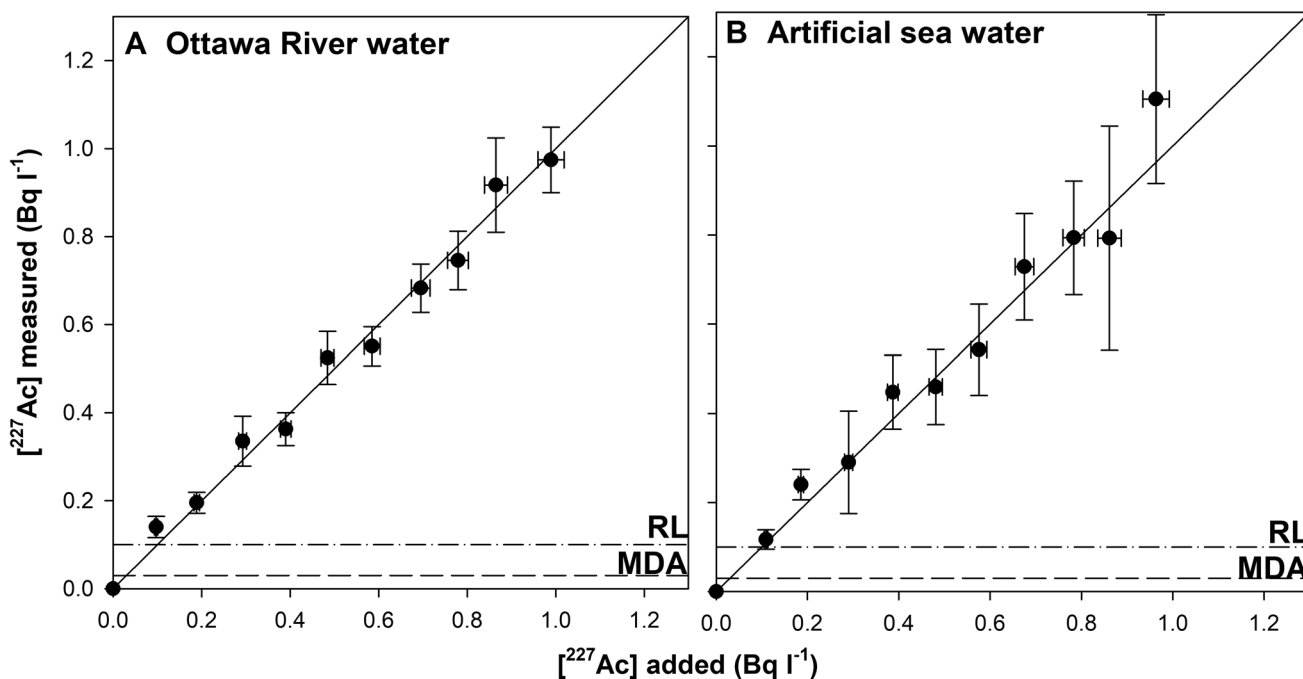


Fig. 5 Spiked samples of **A** Ottawa River water and **B** artificial sea water (RL, reference level)

increasing the acid molarity, except for Ac(III). This new simple purification method allowed the efficient isolation of Ac(III) from potential interferences, and led to a very pure Ac fraction. The strategy could have further applications such as the separation of Ac(III) from lanthanides(III).

A high DF of  $6000 \pm 2000$  was obtained for Ca(II) by co-precipitating Ac(III) at pH 3.5 with titanium phosphate (Table 2). The precipitation pH of  $\text{CaHPO}_4$  is about 4. Artificial sea water samples were prepared, and the method was first tested at pH 3.8 for the titanium phosphate co-precipitation step (Fig. 1, step 7). A small precipitate of  $\text{CaF}_2$  was randomly observed on some filters after the  $\text{CeF}_3$  micro-precipitation step (Fig. 1, step 26), which led to a poor alpha resolution (Fig. 3A). We chose to lower the precipitation pH of the titanium phosphate co-precipitation step to 3.5 to ensure a consistently good alpha resolution for all samples (Fig. 3B).

The Ac(III) recovery as a function of the pH at the titanium phosphate co-precipitation step (Fig. 1, step 7) is shown in Fig. 4. The chemical recovery was constant at  $\text{pH} \geq 3$  ( $54 \pm 3\%$ ) and decreased significantly at lower pH. A pH of 3.5 was chosen for the titanium phosphate co-precipitation step because Ac was effectively co-precipitated without  $\text{CaHPO}_4$  and without affecting the chemical recovery.

### Titanium phosphate

Titanium was precipitated at pH 4 with and without  $\text{H}_3\text{PO}_4$ . Then, the salt obtained was rinsed and was dissolved with

$\text{HNO}_3$ , and Zr(IV) was added. A precipitate was observed only in the tube in which  $\text{H}_3\text{PO}_4$  was added.  $\text{Zr}_3(\text{PO}_4)_4$  is a very insoluble salt that precipitates in very acidic solutions. This test demonstrated that the precipitate obtained at the titanium phosphate co-precipitation step (Fig. 1, step 7) is in great part a phosphate salt, but this simple test does not exclude the possibility that some titanium oxide could also be present in the precipitate.

### Figures of merit

#### Minimal detectable activity

An approximate MDA of  $0.03 \pm 0.01$  Bq l $^{-1}$  was obtained (Table 3). The MDA obtained is below the expected level of 0.1 Bq l $^{-1}$ , and is likely sufficient for assessing the safety of drinking and environmental waters.

River water and artificial sea water samples were spiked with a known amount of  $^{227}\text{Ac}$  and then measured using the developed method. The activity added as a function of the activity measured is shown in Fig. 5. In both cases, the activity measured corresponds to the activity added within the experimental uncertainty, which validates the method. The mean relative bias and the relative precision (all samples) were  $-0.35\%$  and  $7.15\%$ , respectively, and an average overall recovery of  $67 \pm 8\%$  was obtained for these samples (Table 3). Note that the recovery could vary depending on the nature of the sample due to many factors

such as particles in suspension ( $\leq 45 \mu\text{m}$ ), salinity, and ligands present.

### Method throughput

Four samples can be comfortably performed in one workday using this method (Table 3).

### Conclusions

A new method was developed to measure  $^{227}\text{Ac}$  in water samples. A titanium phosphate co-precipitation was performed at pH 3.5 to pre-concentrate Ac(III) and separate it from Ca(II) interference. Then, Ac(III) was effectively separated from potential interferences, including lanthanides and actinides of oxidation state + 3, using a DGA resin. The method was validated using spiked river and artificial sea waters. The method is sufficiently sensitive to assess the safety of drinking water and to evaluate whether effluents can be released to the environment.

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### Declarations

**Conflict of interest** The authors have no relevant financial nor non-financial interests to disclose. The authors have no conflict of interest to disclose. The authors have no competing interests to declare that are relevant to the content of this article.

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