

*Full Length Research Paper*

# Extracting $^{226}\text{Ra}$ from sand filter samples using $\text{MnO}_2$ impregnated resin and determination by sector field inductively coupled plasma mass spectrometry

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An analytical procedure was proposed for the determination of  $^{226}\text{Ra}$  at ultratrace levels in sand filters using sector field inductively coupled plasma mass spectrometry (ICP-MS). Radium was pre-concentrated using an impregnated manganese dioxide filter and separated from strontium using Eichrom "Sr-resin." Following the extraction chromatography, polyatomic ions of Pb and W were eliminated by optimizing the operation parameter of ICP-MS. The detection limit of  $^{226}\text{Ra}$  was found to be  $0.9 \text{ fg ml}^{-1}$  ( $33 \text{ mBq kg}^{-1}$ ). Underground water samples and sands of the filters were analyzed for  $^{226}\text{Ra}$ . Furthermore, radium removal from sand filters was studied using inorganic acids.  $^{226}\text{Ra}$  was measured in the precipitation of dissolved oxide layers from the sand filters.

**Key words:**  $^{226}\text{Ra}$ , ICP-MS, sand filter.

## INTRODUCTION

Underground water is pumped to the surface and distributed to consumers as bottled water or through pipe networks. Sand filters are used as a filter bed in many underground water treatment stations to remove the physical contaminants and oxidation products from underground water. If uranium-rich ores are located near the source of the underground water, an elevated concentration of radium is expected (Al-Hobaib et al., 2006). A build-up of radioactivity may take place on the granules, where iron and manganese oxides are deposited and form thin films coating the granules of the filter. The oxides of iron and manganese play an important role in adsorbing radium from underground water. Consequently, radium removal from water is performed by sorption of radium on iron and manganese oxides up to 96% (Al-Hobaib et al., 2006). Iron and manganese oxides adsorb 30 and 95% of radium respectively (Martin and Akber, 1999). After a period of station operation, radium concentrations increase such that the level of radioactivity inside the station becomes

critical, owing to the high specific activity of radium ( $\sim 3.7 \times 10^{10} \text{ Bq g}^{-1}$ ). The disposal of those granules poses a significant problem (Shabana and Al-Jaseem, 1995).

Because of the high sensitivity, short analysis time and relatively easy operation, inductively coupled plasma mass spectrometry (ICP-MS) has been widely used for the determination of isotopes of uranium, thorium, and plutonium,  $^{79}\text{Se}$ ,  $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$ ,  $^{129}\text{I}$ ,  $^{135}\text{Cs}$ ,  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{231}\text{Pa}$ ,  $^{237}\text{Np}$ ,  $^{241}\text{Am}$ ,  $^{243}\text{Am}$  and  $^{244}\text{Cm}$  in environmental and waste samples (Amr and Abdel-Lateef, 2011). However, due to the multitude of possible polyatomic interferences at the  $m/z$  226, as well as relatively low concentration of  $^{226}\text{Ra}$ , selective separation and pre-concentration of radium prior to the measurements is required (Larivière et al., 2005; Hou and Roos, 2008).

The aim of the work is to extract  $^{226}\text{Ra}$  from sand filter samples using  $\text{MnO}_2$  impregnated resin and determine the sector field inductively coupled plasma mass spectrometry.

## EXPERIMENTAL

### Instrumentation

A sector field inductively coupled plasma mass spectrometer

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**Table 1.** The experimental conditions of ICP-MS used for radium measurements.

Parameter	Value
Forward RF power	900 W for radium and 1300 W for trace elements
Reflected RF power	< 2 W
Coolant gas flow rate	14 L/min
Auxiliary gas flow rate	0.3 L/min
Sampling depth	5 mm
Nebulizer gas flow rate	0.95 L/min for radium and 0.85 L/min for trace elements
Sample uptake rate	0.1 L/min
Accelerating voltage	6 kV applied on the sampler and skimmer
Mass resolution (m/ $\Delta$ m)	300
Optimization	Maximum ion intensity of 10 pg ml <sup>-1</sup> of <sup>226</sup> Ra

(JMS-PLASMAX2) was used for the determination of radium and other trace elements. The optimization of ICP-MS was performed using a <sup>226</sup>Ra standard solution of 10 pgml<sup>-1</sup> in 2 % HNO<sub>3</sub>. An identical 2% HNO<sub>3</sub> blank solution was used both as a background sample and to clean the tubes between the measurements. A microconcentric nebulizer with a desolvation introduction system (ARDIUS, CETAC, USA) was used in the measurements; the argon gas used was 99.9999% pure. The experimental conditions used for radium determination by ICP-MS are shown in Table 1. The detection limit was calculated from the calibration curve using standard solutions of <sup>226</sup>Ra (5, 50 and 100 fg mL<sup>-1</sup>). The detection limit (Blank + 3 $\mu$ -criterion, n = 5) for <sup>226</sup>Ra in deionized water was found to be 0.9 fg ml<sup>-1</sup> (33 mBq L<sup>-1</sup>). For validation of the ICP-MS measurement, the activity of <sup>226</sup>Ra was measured using a high-purity germanium detector (EG&G ORTEC Model GEM20180) at the 186.21 keV peak for 1000 s.

#### Standard and reagents

Multielement standard solutions of Sr, Ba, Mo, La, Ce, Pb, W, Bi and U were obtained from Merck (Darmstadt, Germany). <sup>226</sup>Ra (SRM 4695) and <sup>133</sup>Ba (SRM 4251C) standard solutions were purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). <sup>130</sup>Ba was purchased from Isoflex USA (San Francisco, USA). All solutions were diluted with high-purity deionized water (18 M  $\mu$ m<sup>-1</sup>) and then acidified to 2% HNO<sub>3</sub> with ultrapure nitric acid (Merck, Germany). Two commercially available ionic resins (AG 1-X4 and Sr\*Spec) were used for radium separation. Extraction resins were purchased from Eichrom Technologies (Darien, IL, USA).

#### Sand filters and samples

Standard sand filters were prepared from a tank with a capacity of 200 m<sup>3</sup> of water per hour. Four layers of sands were used as a bed. The granules sizes, in mm, were 52>X>26, 13.2>X>6.7, 4.7>X>2.6, and 1.2>X>0.6. Samples were collected from three underground water treatment stations located in El-Sharkia governorate, Egypt. Each station was given a code, namely: SI, SII, and SIII.

When the amount of impurities and oxide layers increase, the sand filter may be blocked or the rate of water output may decrease. In this case, changing the sand bed is required. The samples collected for the present study were collected from previously removed sands.

#### Measurement of <sup>226</sup>Ra in underground water by $\gamma$ -ray spectrometry

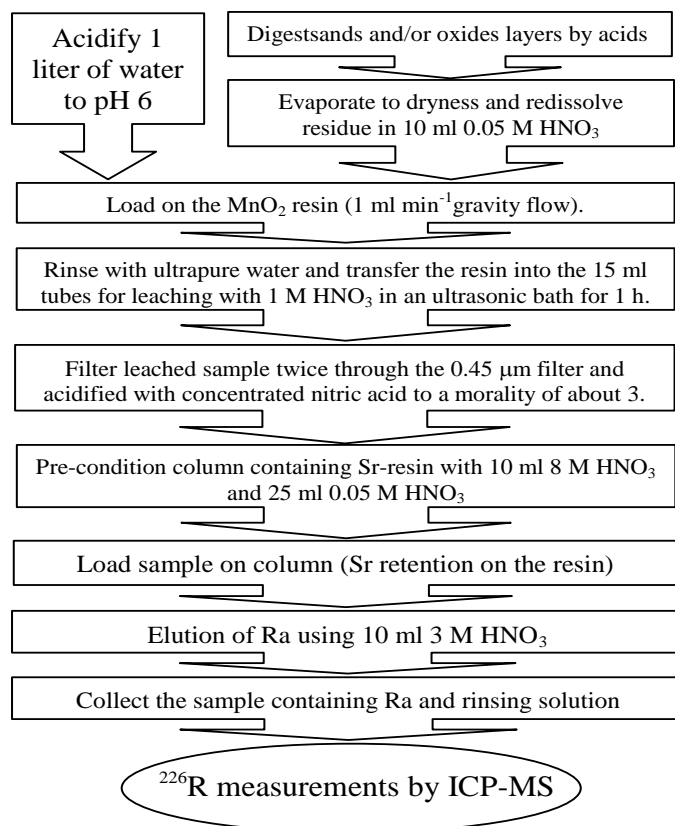
The activity due to <sup>226</sup>Ra was measured in water, as reported by Küsters and Schraven (2009). Namely, 5 liters of underground water were collected and weighed. The sample was boiled and gently stirred using a magnetic stirrer. A total of 10 ml of a barium carrier (10 mg Ba<sup>2+</sup> ml<sup>-1</sup>) and 20 ml 25% hydrochloric acid were added, and the solution was heated under intense stirring for an additional 5 min. To precipitate barium sulfate, 40 ml of sulfuric acid (50%) was pipetted to the solution and mixed vigorously for 30 min while being heated. The precipitate was allowed to settle over night. The supernatant was decanted carefully up to approximately 900 ml. Subsequently, 10 to 15 g of xanthan gum (suspended in ethanol) was added and mixed for approximately 30 min to form homogeneous gelatin. The thickened sample was filled to a total volume of 1 liter, transferred quantitatively into a Marinelli beaker and stored locked for progeny ingrowth for at least one month. The sample was measured thereafter for 1000 s.

#### Preparation of MnO<sub>2</sub> impregnated resin

Manganese dioxide impregnated resin was prepared as reported by Varga (2007). Namely, 40 g of AG 1-X4 anion exchange resin (chloride form: 100 to 200 mesh) was placed in a 250 ml centrifuge tube with twice the volume of high-purity water and mixed thoroughly. About 40 ml of saturated KMnO<sub>4</sub> solution was added to the resin and mixed vigorously. After 15 min, the sample was centrifuged and the supernatant was discarded. The resin was rinsed three times with 80 ml of high-purity water with successive centrifugation discarding the rinsing solution. The resin obtained was filtered gravimetrically through a Whatman filter and quantitatively transferred to a 250 ml plastic container with water. The resin was dried at 70°C overnight. After drying, the resin was thoroughly homogenized with a plastic rod.

#### Pre-concentration of <sup>226</sup>Ra on MnO<sub>2</sub> impregnated resin for ICP-MS measurements

One liter of underground water was acidified to pH 6 with concentrated HNO<sub>3</sub>. The prepared MnO<sub>2</sub> resin was transferred into a column for filtering and the sample was loaded at a rate of 1 ml min<sup>-1</sup> (Zoriy et al., 2005). The filter was then rinsed with ultrapure water and transferred into the 15 ml tubes for leaching with 1 M HNO<sub>3</sub> in an ultrasonic bath for 1 h. The leached sample was filtered twice through the small Teflon filter and acidified with concentrated



**Figure 1.** Scheme for radium pre-concentration and separation from strontium.

nitric acid to a molarity of about 3. Then, the sample (final volume ~ 15 ml) was used for separation on the Eichrom “Sr-specific” resin.

#### Chemical separation of radium from strontium on the Sr-resin

Because the  $\text{MnO}_2$  filter is also selective for strontium (Larivière et al., 2007), which forms polyatomic ions at  $m/z = 226$ , it was further separated from the analyte by means of extraction chromatography using the commercially available Eichrom Sr-resin. The resin was washed with 10 ml of 8 M  $\text{HNO}_3$  and 25 ml of 0.05 M  $\text{HNO}_3$  to elute residual strontium, and it was conditioned with 3 ml of 3 M  $\text{HNO}_3$ . Next, the sample was loaded (assuming retention of the Sr) and the resin was rinsed with 3 ml of 3 M  $\text{HNO}_3$ . The sample and rinse solutions that had passed through the resin were then collected in the 50 ml tube and diluted to 20 ml. The samples prepared in this manner were then used for the determination of  $^{226}\text{Ra}$  using ICP-MS. A scheme for radium pre-concentration and separation from strontium is shown in Figure 1. The scheme was applied for radium pre-concentration and separation from underground water and digested soil samples.

## RESULTS AND DISCUSSION

### Polyatomic ions at $m/z$ 226

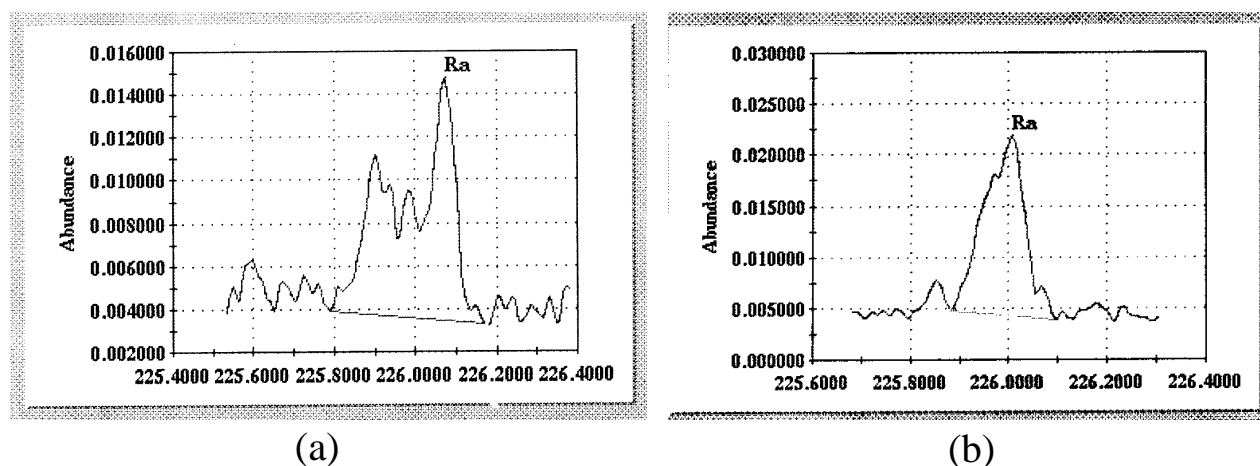
Clean nickel cones were used for the sample analysis to

avoid memory effects. The possible formation of polyatomic interferences between inert gases (other than Ar) present as impurities in the plasma (Xe and Kr) and some transition (Mo) and lanthanide elements (Ce and Nd) was studied. At concentrations of  $1 \mu\text{g ml}^{-1}$ , no change in the background signal at  $m/z = 226$  was detected. Therefore, the formation of  $^{92}\text{Mo}^{134}\text{Xe}$ ,  $^{94}\text{Mo}^{132}\text{Xe}$ ,  $^{95}\text{Mo}^{131}\text{Xe}$ ,  $^{96}\text{Mo}^{130}\text{Xe}$ ,  $^{97}\text{Mo}^{129}\text{Xe}$ ,  $^{98}\text{Mo}^{128}\text{Xe}$ ,  $^{100}\text{Mo}^{126}\text{Xe}$ ,  $^{140}\text{Ce}^{86}\text{Kr}$ ,  $^{143}\text{Nd}^{83}\text{Kr}$ ,  $^{144}\text{Nd}^{82}\text{Kr}$ ,  $^{146}\text{Nd}^{80}\text{Kr}$ ,  $^{148}\text{Nd}^{78}\text{Kr}$  and  $^{146}\text{Nd}^{40}\text{Ar}^{40}\text{Ar}$  were not detected. A background equivalent concentration (BEC) was measured when  $1 \mu\text{g ml}^{-1}$  of single solutions composed of W, Bi, Pb, Sr/La, SrCe, and Sr/Ba were aspirated, as shown in Table 2. The results are in concordance with data previously published (Epov et al., 2003; Larivière et al., 2007; Park et al., 1999).

The ionization energies of elements (Lias et al., 1988) that likely form polyatomic ions that interfere with  $^{226}\text{Ra}$  are divided to two groups. The ionization energies of Ba, Ce, La, and Sr are 5.212, 5.539, 5.58 and 5.695 eV respectively, and these ionization energies are close to the ionization energy of Ra, 5.278 eV. Meanwhile, the ionization energies of Mo, Bi, Pb, W and Xe are 7.092, 7.286, 7.417, 7.864 and 12.13 eV respectively. These energies are 2 eV, or greater than the ionization energy

**Table 2.** Background equivalent concentration ( $\text{fgml}^{-1}$ ) generated by aspiration  $1 \mu\text{g ml}^{-1}$  solutions of W, Bi, Pb, Sr/La, Sr/Ce and Sr/Ba.

Polyatomic ion	BEC	Required resolution
$^{88}\text{Sr}^{138}\text{Ba}^+$	4.8	1054
$^{87}\text{Sr}^{139}\text{La}^+$	3.8	1076
$^{86}\text{Sr}^{140}\text{Ce}^+$	4.3	1072
$^{186}\text{W}^{40}\text{Ar}^+$	42	2080
$^{209}\text{Bi}^{16}\text{O}^1\text{H}^+$	76	5347
$^{208}\text{Pb}^{18}\text{O}$	10.2	4556



**Figure 2.** Mass spectrum at mass  $m/z$  226; (a) before radium separation (b) after radium separation.

of radium. By decreasing the radio frequency power (RF) to 900 W, the degree of ionization of the Bi and Pb was minimized so that their polyatomic ions were nearly eliminated. Meanwhile, the polyatomic ions of Ba, Ce, La and Sr were observed, as shown in Figure 2a, when  $1 \text{ ng ml}^{-1}$  of multielement solution comprising W, Bi, Pb, Sr, La, Ce and Ba spiked with  $10 \text{ pg ml}^{-1}$  was aspirated. Although, the Sr-based interferences can be successfully separated from the  $^{226}\text{Ra}$  ions by measuring at a resolution of 1100, the loss of sensitivity in comparison to a low-resolution mode could not be afforded for the low concentration level of  $^{226}\text{Ra}$  in analyzed samples. Therefore, a separation of strontium, or rare earth elements, was required. Radium was pre-concentrated and separated from strontium using the procedure shown in Figure 1. A Gaussian shape of the  $^{226}\text{Ra}$  peak was observed after radium separation at low-resolution mode, as shown in Figure 2b.

#### Concentration of $^{226}\text{Ra}$ in underground water

Trace element concentrations, including the alkaline earth elements (Mg, Ca, Sr and Ba) and rare earth elements (La, Ce, Nd, Sm, Eu, Gd and Eu) were

measured in three underground water samples from three different regions. The results are shown in Table 3. Trace elements were measured in order to estimate the level of interference with  $m/z = 226$ . The concentration of  $^{226}\text{Ra}$  was measured by ICP-MS after pre-concentration and separation from strontium using the scheme shown in Figure 1. One liter of underground water was passed through the columns and the final solution was reduced by evaporation to 50 ml. The recovery of  $^{226}\text{Ra}$  was evaluated using  $10 \text{ pg ml}^{-1}$  of  $^{130}\text{Ba}$  as a tracer. Ba was used for recovery calculations, because it behaves chemically similar to Ra (Lasheen et al., 2007). Concentrations of  $^{226}\text{Ra}$  in water samples were found to be in the range from 0.62 to  $1.01 \text{ fgml}^{-1}$  (0.022 to  $0.041 \text{ mBqml}^{-1}$ ), taking into account a 20-fold pre-concentration.  $^{226}\text{Ra}$  concentrations found in this work were compared with other results reported in Egypt. Hilal (2002) measured the radioactivity levels in three underground drinking water samples collected from localities in the Eastern Nile Delta area at Inshas and found  $^{226}\text{Ra}$  levels ranging from 3.9 to  $4.9 \text{ Bq l}^{-1}$ . Lasheen et al. (2007) measured the  $^{226}\text{Ra}$  in several types of bottled drinking water originating from three different areas in Egypt and reported that the mean levels of  $^{226}\text{Ra}$  activity range from 0.44 to  $0.92 \text{ Bq l}^{-1}$ . Water types originating from the Eastern

**Table 3.** Concentrations of metals in underground waters measured by ICP-MS.

Elements	Unit	SI	SII	SIII
Na	$\mu\text{g ml}^{-1}$	$655 \pm 17$	$645 \pm 26$	$408 \pm 5$
Mg	$\mu\text{g ml}^{-1}$	$175.9 \pm 4.74$	$97 \pm 3$	$58 \pm 1$
Al	$\mu\text{g ml}^{-1}$	$66.42 \pm 0.7$	$487 \pm 13$	$61 \pm 2$
K	$\mu\text{g ml}^{-1}$	$33.3 \pm 1.7$	$25 \pm 2$	$29 \pm 2$
Ca	$\mu\text{g ml}^{-1}$	$587 \pm 46$	$675 \pm 52$	$259 \pm 11$
V	$\text{ng ml}^{-1}$	$146 \pm 4$	$124 \pm 8$	$43 \pm 2$
Cr	$\text{ng ml}^{-1}$	$275 \pm 24$	$173 \pm 5$	$153 \pm 3$
Mn	$\text{ng ml}^{-1}$	$243 \pm 40$	$67 \pm 2$	$260 \pm 9$
Fe	$\mu\text{g ml}^{-1}$	$8.76 \pm 0.3$	$9.4 \pm 0.8$	$9.8 \pm 0.4$
Sr	$\mu\text{g ml}^{-1}$	$82 \pm 4$	$46 \pm 1$	$17 \pm 1$
La	$\text{ng ml}^{-1}$	$636 \pm 29$	$971 \pm 42$	$808 \pm 35$
Ce	$\text{ng ml}^{-1}$	$233 \pm 14$	$138 \pm 0.2$	$34 \pm 2$
Nd	$\text{ng ml}^{-1}$	$479 \pm 11$	$282 \pm 4$	$831 \pm 23$
Sm	$\text{ng ml}^{-1}$	$41 \pm 2$	$18.7 \pm 0.8$	$120 \pm 3$
Eu	$\text{ng ml}^{-1}$	$239 \pm 13$	$149 \pm 6$	$24 \pm 1$
Gd	$\text{ng ml}^{-1}$	$35 \pm 2$	$19.5 \pm 1$	$94 \pm 2$
Er	$\text{ng ml}^{-1}$	$60 \pm 3$	$36 \pm 0.2$	$16 \pm 0.4$
Ba	$\text{ng ml}^{-1}$	$551 \pm 40$	$397 \pm 6$	$278 \pm 11$
U	$\text{ng ml}^{-1}$	$65 \pm 3$	$46 \pm 0.9$	$5.7 \pm 0.1$
Ra-226*	$\text{fg ml}^{-1}$	$0.71 \pm 0.04$	$1.01 \pm 0.02$	$0.62 \pm 0.07$
Ra-226 measured by $\gamma$ -ray spectrometry	$\text{fg ml}^{-1}$	$0.74 \pm 0.03$	$1.11 \pm 0.08$	$0.60 \pm 0.07$

\*Taking into account a 20-fold pre-concentration.

Nile Delta area are characterized by low  $^{226}\text{Ra}$  levels and relatively high  $^{228}\text{Ra}$  activity, presumably due to the muddy agricultural nature of this area, which is subject to water from several surface resources for irrigation (Lasheen et al., 2007). The United States Environmental Protection Agency (US-EPA) regulates the amount of combined  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in community water systems, so that it will not exceed  $5 \text{ pg l}^{-1}$  ( $0.185 \text{ Bq l}^{-1}$ ) (Park et al., 1999).

### Radium-226 concentration in sands

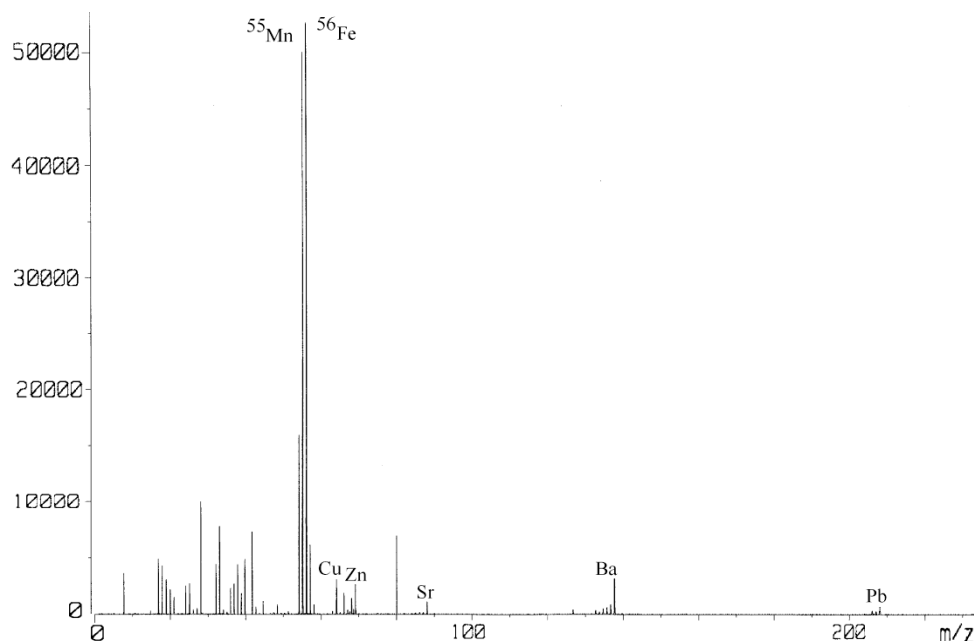
Five grams from each sand layer were collected together. Sand samples were dried overnight at  $105^\circ\text{C}$  and the sand mixture was then grinded. The sand was weighed and transferred into polytetrafluoroethylene (PTFE) beaker and moisten with a few milliliters of deionized water. A total of 10 ml HF and 4 ml  $\text{HClO}_4$  were slowly added and evaporated on a hot plate at  $200^\circ\text{C}$  until a crystalline paste was formed. This took an order of 2 to 3 h. Four milliliters of  $\text{HClO}_4$  was added to each sample and evaporated to incipient dryness, to remove any HF residue present. A total of 10 ml of 5 M  $\text{HNO}_3$  was added and warmed gently until a clear solution was obtained. The clear solutions of samples were allowed to cool down and were diluted to 100 ml in polypropylene bottles (producing a 0.05 M  $\text{HNO}_3$  solution). To estimate radium

recovery, the solution was spiked with  $10 \text{ pg ml}^{-1}$  of  $^{130}\text{Ba}$ . The concentrations of  $^{226}\text{Ra}$  in the samples were measured using ICP-MS after pre-concentration and separation from strontium using the scheme shown in Figure 1. A sediment standard reference material (IAEA-313), which contains  $9.38 \text{ pg g}^{-1}$  ( $343 \text{ Bq kg}^{-1}$ ) of  $^{226}\text{Ra}$ , was used for quality assurance. The recoveries obtained were about 71% and was further used to correct the measured radium concentrations in unknown sand samples. Concentrations of  $^{226}\text{Ra}$  were  $0.87 \pm 0.08 \text{ pg g}^{-1}$  ( $31.5 \pm 3 \text{ Bq kg}^{-1}$ ),  $1.08 \pm 0.06 \text{ pg g}^{-1}$  ( $39.5 \pm 2 \text{ Bq kg}^{-1}$ ) and  $0.97 \pm 0.06 \text{ pg g}^{-1}$  ( $35.5 \pm 2 \text{ Bq kg}^{-1}$ ) in the sands of stations SI, SII and SIII respectively.

Furthermore, 50 g from each sand layer was collected and dried overnight. The total amount of sand was 200 g. The sand were transferred into a Marinelli beaker and locked for progeny in-growth for one month. The samples were measured thereafter for 1000 s. Concentrations of  $^{226}\text{Ra}$  were  $29.8 \pm 2.3 \text{ Bq kg}^{-1}$  ( $0.81 \pm 0.06 \text{ pg g}^{-1}$ ),  $37.5 \pm 3.1 \text{ Bq kg}^{-1}$  ( $1.02 \pm 0.09 \text{ pg g}^{-1}$ ) and  $34.5 \pm 2.8 \text{ Bq kg}^{-1}$  ( $0.94 \pm 0.08 \text{ pg g}^{-1}$ ) in the sands from stations SI, SII, and SIII respectively.

### Removal of radium by dissolving the oxide layers

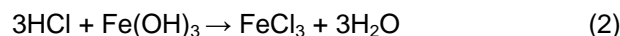
Radium removal from sand filters was tested by washing sands with inorganic acids  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$



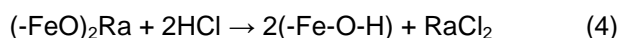
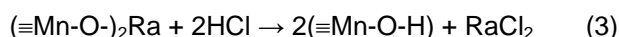
**Figure 3.** Mass spectrum of sample SII, where iron and manganese are the main peaks.

with concentrations of 0.05, 0.5, 1 and 2 M of acids. The  $\text{H}_2\text{SO}_4$  process demonstrated low efficiency, due to low solubility and the thermodynamic formation of sulfate salts. Sulfate formed an insoluble layer from cations of alkaline metals that grow on the outer surface of oxides. Consequently, these sulfates prevent  $\text{H}_2\text{SO}_4$  from attacking the inner layer of oxides, which cover granules. Washing with  $\text{HNO}_3$  and  $\text{HClO}_4$  showed good removal of radium, compared with  $\text{H}_2\text{SO}_4$ . Moreover,  $\text{HCl}$  acid showed good efficiency in removing radium (68% using 2 M  $\text{HCl}$ ) because radium chloride has good solubility (245 g/L) in water (Sedlet, 1974). The relationships between radium removal by acids and solubility of radium salts are arranged in the following manner,  $\text{RaCl}_2 > \text{Ra}(\text{ClO}_4)_2 > \text{Ra}(\text{NO}_3)_2 > \text{RaSO}_4$ .

Depending on the previous results,  $\text{HCl}$  acid was used to dissolve the layers of oxides. Five grams of granules from each sand layer were treated by impressing them in 20 ml of 2 M  $\text{HCl}$  acid for two hours with a shaking speed of 300 rpm and a temperature of  $25^\circ\text{C}$ . The chemical reactions describing radium removal processes are shown below (Equation 1 to 4), where Equation 1 and 2 show removal of 67 and 93% of  $\text{MnO}_2$  and  $\text{Fe}(\text{OH})_3$  layers using 2 M  $\text{HCl}$ , respectively.



Equation 3 and 4 show competition of proton to be adsorbed on the undissociated oxide layers, which will result in radium removal (Al-Hobaib et al., 2006):



Precipitated oxides were analyzed by ICP-MS. Figure 3 shows the mass spectrum of sample SII. Iron and manganese are the most prominent peaks, while traces of Mg, Ca, Sr, Ba and Pb are shown in the spectrum.

Radium activity, before and after treatment, was measured by  $\gamma$ -ray spectrometry at the 186.21 keV peak for 1000 s. The efficiency of this method was calculated using Equation 5.

$$\text{Removal}(\%) = \left( \frac{A_o - A}{A_o} \right) \times 100 \quad (5)$$

Where  $A_o$  is the radium activity before treatment,  $A$  is the radium activity after treatment.

### Radium concentration in the oxide precipitate

Precipitates of oxides were dried overnight at  $105^\circ\text{C}$ . One gram of precipitate was weighed and transferred into a PTFE beaker. A total of 10 ml  $\text{HF}$  and 4 ml  $\text{HClO}_4$  were slowly added and evaporated on a hot plate at  $200^\circ\text{C}$  for several hours, and 4 ml of  $\text{HClO}_4$  was added to each sample and evaporated to incipient dryness to remove any  $\text{HF}$  residue. A total of 10 ml of 5 M  $\text{HNO}_3$  was added and warmed gently until a clear solution was formed. The clear solutions of the samples were allowed to cool down

**Table 4.** Concentrations of  $^{226}\text{Ra}$  ( $\text{pg g}^{-1}$ ) in oxide precipitate measured by ICP-MS and  $\gamma$ -ray spectrometry.

Sample	ICP-MS		$\gamma$ -ray spectrometry	
	Sub-samples (Mean $\pm$ SD) <sup>#</sup>	Mean $\pm$ SD <sup>*</sup>	Sub-samples (Mean $\pm$ SD) <sup>#</sup>	Mean $\pm$ SD <sup>*</sup>
SI-1	121.4 $\pm$ 4.5		121.8 $\pm$ 5.7	
SI-2	134.5 $\pm$ 7.4	130.5 $\pm$ 7.9	136.1 $\pm$ 5.4	131.3 $\pm$ 8.3
SI-3	135.7 $\pm$ 6.2		136.1 $\pm$ 5.8	
SII-1	281.0 $\pm$ 6.6		278.6 $\pm$ 2.8	
SII-2	270.2 $\pm$ 5.2	274.4 $\pm$ 5.8	282.5 $\pm$ 3.1	280.6 $\pm$ 2.0
SII-3	272.1 $\pm$ 5.3		280.7 $\pm$ 3.2	
SIII-1	209.2 $\pm$ 11.1		192.1 $\pm$ 2.3	
SIII-2	187.1 $\pm$ 6.8	201.4 $\pm$ 12.4	193.8 $\pm$ 2.2	192.4 $\pm$ 1.3
SIII-3	207.9 $\pm$ 7.5		191.2 $\pm$ 2.2	

<sup>#</sup>The mean and the standard deviation of each measurement by ICP-MS or  $\gamma$ -ray spectrometry. <sup>\*</sup>The mean and the standard deviation of the three sub-samples from the filters SI, SII and SIII.

and were diluted to 1000 ml in polypropylene bottles (producing a 0.05 M  $\text{HNO}_3$  solution). To estimate the radium recovery, the solution was spiked with  $10 \text{ pg g}^{-1}$  of  $^{130}\text{Ba}$ .  $^{226}\text{Ra}$  concentrations were measured by ICP-MS after pre-concentration and separation from strontium using the scheme shown in Figure 1. Furthermore, the oxide precipitates were transferred into a Marinelli beaker and stored locked for progeny ingrowth for one month. The samples were measured by  $\gamma$ -ray spectrometry.

Table 4 shows the concentrations of  $^{226}\text{Ra}$  in precipitates dissolved from three filters of the three treatment stations.  $^{226}\text{Ra}$  concentrations are  $130.5 \pm 7.9 \text{ pg g}^{-1}$  ( $4870 \pm 289 \text{ Bq kg}^{-1}$ ),  $274.4 \pm 5.8 \text{ pg g}^{-1}$  ( $10050 \pm 212 \text{ Bq kg}^{-1}$ ) and  $201.4 \pm 12.4 \text{ pg g}^{-1}$  ( $7400 \pm 461 \text{ Bq kg}^{-1}$ ) in the sand filters of SI, SII, and SIII treatment stations, respectively. The measured concentrations of  $^{226}\text{Ra}$  by ICP-MS were in agreement with the measured concentration of  $^{226}\text{Ra}$  by gamma-ray spectrometry within  $\pm 2.5\%$ . US-EPA regulations stipulate that the maximum concentration in soil should not be than  $1.38 \text{ pg g}^{-1}$  ( $50 \text{ Bq kg}^{-1}$ ) (PHS and EPA, 1990; EPA, 1996). The measured  $^{226}\text{Ra}$  concentrations were between 130 and 274 times the maximum concentration limit suggested by US-EPA. Therefore, it is recommended that the oxide precipitations be treated as radioactive waste and be disposed of safely according to the national regulations.

## Conclusion

Extraction chromatography was shown to eliminate possible polyatomic interferences from Sr, Ba, La and Ce. Polyatomic interferences formed by Pb and W were successfully eliminated by measurements at a low RF, namely, 900 W. A comparison of  $\gamma$ -spectrometry and ICP-MS measurements indicates that for the range of samples activities tested, both methods provide comparable results. The overall time requirement for the

measurement of  $^{226}\text{Ra}$  by ICP-MS is 2 days, which is significantly shorter than any radioanalytical protocol currently available. Washing the sand filters with 2 M HCl could be dissolving the oxide layers. Washing solution must be evaporated in open air and its precipitate disposed of safely, because it contains high amount of  $^{226}\text{Ra}$ .

## REFERENCES

- Al-Hobaib AS, Al-Sulaiman KM, Al-Dhayan DM, Al-Suhybani AA (2006). Removal of radium from sand filters by inorganic acids. *J. Radioanal. Nucl. Chem.*, 268: 425-431.
- Amr MA, Abdel-Lateef AM (2011). Comparing the capability of Collision/reaction Cell Quadrupole and Sector Field Inductively Coupled Plasma Mass Spectrometers for interference removal in different matrices. *Int. J. Mass spectrum*, 299: 184-190.
- EPA (1996). Drinking Water Regulations and Health Advisories (EPA 822-B-96-002), US Environmental Protection Agency, Washington, DC, USA.
- Epov VN, Larivière D, Evans RD, Li C, Cornett RJ (2003). Direct determination of  $^{226}\text{Ra}$  in environmental matrices using collision cell inductively coupled plasma-mass spectrometry. *J. Radioanal. Nucl. Chem.*, 256: 53-60.
- Hilal MA (2002). Nuclear spectroscopic measurements for different environmental radiation. Ph.D. thesis (Physics), Faculty of Science, Mansoura University, Egypt.
- Hou X, Roos P (2008). Critical comparison of radiometric and mass spectrometric methods for the determination of radionuclides in environmental, biological and nuclear waste samples. *Anal. Chim. Acta.*, 608: 105-139.
- Küsterns M, Schraven W (2009). Determination and differentiation of  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  by gamma-ray spectrometry in drinking water. *J. Radioanal. Nucl. Ch.*, 280: 475-480.
- Larivière D, Brownell DK, Epov VN, Cornett RJ, Evans RD (2007). Determination of  $^{226}\text{Ra}$  in sediments by ICP-MS: A comparative study of three sample preparation approaches. *J. Radioanal. Nucl. Chem.*, 273: 337-344.
- Larivière D, Epov VN, Reiber KM, Cornett RJ, Evans RD (2005). Micro-extraction procedures for the determination of Ra-226 in well waters by SF-ICP-MS. *Anal. Chim. Acta*, 528: 175-182.
- Lasheen YF, Seliman AF, Abdel-Rassoul AA (2007). Simultaneous measurement of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in natural water by liquid scintillation counting. *J. Environ. Radioact.*, 95: 86-97.
- Lias SG, Bartmess JE, Liebman JF, Holmes JL, Levin RD, Mallard WG

- (1988). Gas-phase ion and neutral thermochemistry. *J. Phys. Chem. Ref. Data. Suppl.*, 1, (17): 1-861.
- Martin P, Akber RA (1999). Radium isotopes as indicators of adsorption-desorption interactions and barite formation in ground water. *J. Environ. Radioact.*, 46: 271-286.
- Park CJ, Oh PJ, Kim HY, Lee DS (1999). Determination of  $^{226}\text{Ra}$  in mineral waters by high-resolution inductively coupled plasma mass spectrometry after sample preparation by cation exchange. *J. Anal. At. Spectrom.*, 14: 223-227.
- PHS, EPA (1990). Toxicology profile for radium, agency for toxic substances and disease registry U.S. public health service in collaboration with US Environmental Protection Agency, Washington, DC, USA. pp.1-69.
- Shabana EI, Al-Jaseem Q (1995). Removal of radium from filter sands of a conventional ground water treatment station. *J. Radioanal. Nucl. Chem.*, 189: 35-43.
- Sedlet J (1974). Radon and radium, in: Kolthoff, J. M., Elving, P. J. (Eds), *Treatise on Analytical Chemistry, Part II*, Interscience, New York. pp. 219-366.
- Varga Z (2007). Preparation and characterization of manganese dioxide impregnated resin for radionuclide pre-concentration. *Appl. Radiat. Isot.*, 65: 1095-1100.
- Zoriy MV, Varga Z, Pickhardt C, Ostapczuk P, Hille R, Halicz L, Segald I, Becker JS (2005). Determination of  $^{226}\text{Ra}$  at ultratrace level in mineral water samples by sector field inductively coupled plasma mass spectrometry. *J. Environ. Monit.*, 7: 514-518.