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The importance of radiochemistry for the characterization of NORM and of environments contaminated by NORM

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Naturally occurring radioactive materials (NORM) are present in the environment and they can be concentrated by technical activities, particularly those involving natural resources. This article describes radioanalytical problems arising in the accurate determination of natural radionuclides in NORM and in the environment contaminated by NORM. The solution of these problems is of particular importance since the results can be used to estimate the dose to workers and to the population. A special emphasis is given to the reliability of the radiochemical methods and procedures applied for the detection and measurement of alpha or beta emitters by radiometric or non-radiometric techniques.

Keywords: NORM; Radioanalytical methods; Radiochemical separation

1. Introduction

Naturally occurring radioactive materials (NORM) have been a part of our world. Approximately 70 naturally occurring radionuclides have been found in the earth's crust and soil, in water, food, air and human tissues. The primordial radionuclides, ^{238}U , ^{235}U and ^{232}Th , and their daughters associated with underground geological formations, as well as ^{40}K , regardless of their source, are called NORM.

It is possible to distinguish between “normal” NORM and “elevated” NORM. “Normal” NORM contain a radioactivity concentration near to the mean value of crustal rocks; “elevated” NORM contain a radioactivity concentration significantly higher.

The “elevated” NORM origin can be natural or technologically enhanced. As a matter of fact, the cause for such elevations can be due to the geological and geochemical nature of the soil. Examples of “elevated” NORM are monazite sands, alum shale and phosphate bearing rocks which contain significantly higher concentrations of

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uranium, and waters with high ^{226}Ra contents flowing from hot springs into the surrounding region [1–5].

Moreover, in many cases some of the naturally occurring radionuclides are concentrated by industrial processes, achieving relatively high activity concentrations. The problems associated with the build up of NORM in oil industry are well known [6–13] and a wide variety of other industries also use feed material containing NORM. Ores, such as ilmenite and phosphate rocks [14,15], are used for the manufacture of titanium dioxide pigment and phosphoric acid, respectively; baddeleyite is used in the production of zirconia, and zircon is used both as a refractory and in the manufacture of refractories [16]. Rare earths are used in the manufacture of glass polishing compounds, catalysts and special glasses. Pyrochlore is used in the production of niobium alloys [17]. In these applications the feed material is used because of its chemical properties rather than its radioactive content, and yet the activity concentrations can exceed the reference levels [5].

The two primary routes of exposure for workers are inhalation of dusts and external exposure to gamma radiation from bulk storage of the material. Doses from ingestion are several orders of magnitude lower, and hence the ingestion pathway is not considered to be significant. The inhalation pathway has been conventionally assumed to dominate [4].

The potential pathways of exposure for the population to NORM [18–20] contained in surface soil are shown in figure 1 [18]. These exposure pathways include: (a) direct exposure to external radiation from radioactive contaminants in the soil; (b) internal radiation from inhalation of airborne radionuclides and radon progeny; and (c) internal dose from ingestion of contaminated food, soil and water.

Therefore it is very important to have reliable radioanalytical methods for the accurate determination of natural radionuclides concentration in NORM and in the environment contaminated by NORM: in fact these values can be used to estimate the dose to workers and to population [20–22].

2. Radioanalytical methods

For NORM characterization both non-destructive and destructive methods can be used. The principal non-destructive method is the gamma spectrometry that involves

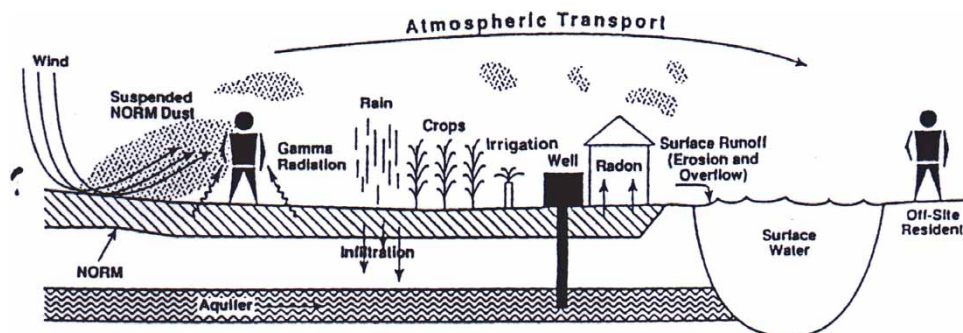


Figure 1. Potential pathways for exposure to NORM contained in surface soil [18].

a direct determination of radionuclides in the original samples; the destructive methods (radiochemical analyses) consist of measurements of the radionuclides after their separation from the solution coming from the dissolution of the sample.

2.1 Gamma spectrometry

By gamma spectrometry measurements it is possible to determine simultaneously many radionuclides without any specific pre-treatment. However, standard sampling and sample pre-treatment procedures are needed to obtain accurate results. Nevertheless it is impossible to determine directly all the radionuclides of interest because some of them, e.g. ^{232}Th and ^{210}Po , are not gamma emitters.

Particular care must be taken to ensure that the overall analytical procedure does not give erroneous results. The principal cause of error is that some procedures automatically assume secular equilibrium for all members of the series. On the contrary, NORM often results from complex processes that cause breaks in the radioactive equilibria. If the daughters are long lived radionuclides, it is impossible to restore these equilibria in the laboratory [23]. For example, in the ^{232}Th family the equilibrium breaks occur between ^{232}Th and ^{228}Ra , ^{228}Ac and ^{228}Th , ^{224}Ra and ^{220}Rn . So it is possible to determine ^{228}Ra by its short lived daughter gamma emitter ^{228}Ac , and ^{228}Th by gamma emission of its short lived daughters from ^{224}Ra to ^{208}Tl , but it is not possible to determine ^{232}Th .

As an example, Spezzano [24] reports the ^{228}Th and ^{232}Th activity concentrations obtained by alpha spectrometry in two zircon sands of different origin and different chemical composition: in an Australian sample (zirconium silicate) there is the equilibrium between ^{228}Th and ^{232}Th , in an African sample (zirconium oxide) the activity ratio $^{228}\text{Th}/^{232}\text{Th}$ is nearly 11; therefore in the second case, the value of ^{232}Th activity, calculated from the measured gamma activity of ^{228}Th , would be overestimated.

In the ^{238}U family the equilibrium breaks between ^{234}Pa and ^{234}U , ^{234}U and ^{230}Th , ^{230}Th and ^{226}Ra , ^{226}Ra and ^{222}Rn can be found. For ^{226}Ra and ^{222}Rn the equilibrium can be restored in the laboratory. So it is possible to determine ^{238}U by its daughter gamma emitters ^{234}Th , $^{234\text{m}}\text{Pa}$ and ^{234}Pa , and ^{226}Ra by ^{214}Pb and ^{214}Bi , but it is impossible to determine by this way the activity of ^{234}U and ^{230}Th activities.

In table 1 the concentrations of ^{238}U , ^{232}Th and ^{226}Ra concentrations in low specific activity scales (LSA scales) of some oil and gas plants are reported. These values show a relevant disequilibrium between ^{238}U and ^{226}Ra [25]. ^{226}Ra plays a fundamental role in the radioactive scale where it is incorporated by co-precipitation with barium, strontium and calcium salts during hydrocarbon production; this precipitation is caused mainly by solubility changes due to the injection of incompatible waters and pressure changes in the aqueous solution where the metal ions are present [25].

2.2 Radiochemical methods

Radiochemical separations [26] play an important role when alpha and beta emitting natural radionuclides must be determined in complex matrices as NORM, and in the environment contaminated by NORM. The typical radiochemical methods are based on the radioisotopes determination after their selective separation from the solution obtaining from the dissolution of the sample.

Table 1. ^{238}U , ^{232}Th and ^{226}Ra concentrations (Bq kg^{-1}) in scales [25].

Plant features	Extracted hydrocarbon	Depth (km)	^{238}U	^{232}Th	^{226}Ra
Extraction plant (Po Valley, Italy)	Liquid	6	<0.9	<0.8	$2,890 \pm 578$
Extraction plant (Po Valley, Italy)	Liquid	5	<0.9	<0.8	$1,126 \pm 225$
Extraction plant (Po Valley, Italy)	Mixed	5	<0.9	<0.8	120 ± 24
Collection plant (Po Valley, Italy)	Gaseous	–	23.8 ± 4.3	18.9 ± 3.8	30 ± 6
Collection plant (Po Valley, Italy)	Gaseous	–	53.8 ± 10.8	<0.8	<2.7
Collection plant (Southern Italy)	Liquid	–	11.3 ± 2.3	<0.8	110 ± 22
Offshore platform (Northern Sea)	Liquid	3	<0.9	<0.8	780 ± 156
Extraction plant (Tunisia)	Liquid	1	1.2 ± 0.2	<0.8	$1,189 \pm 238$
Treatment plant (Tunisia)	Liquid	1	<0.9	<0.8	31 ± 6
Phase separation plant (Tunisia)	Liquid	1	7.6 ± 1.5	5.1 ± 1.0	64 ± 12
Phase separation plant (Congo)	Liquid	1	<0.9	<0.8	97 ± 20
Oil storage reservoir (Congo)	Liquid	1	2.7 ± 0.5	2.2 ± 0.4	151 ± 30

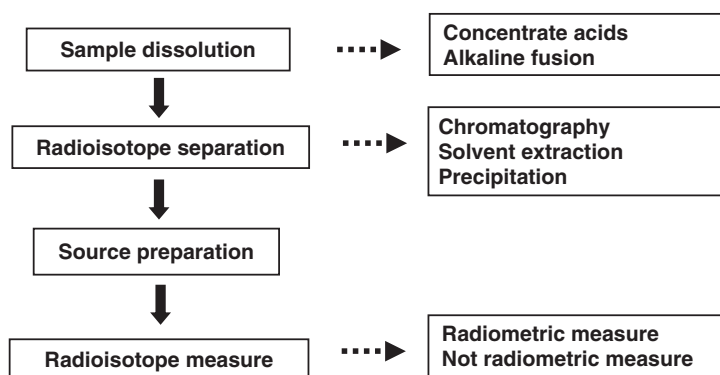


Figure 2. Flow sheet of a typical radiochemical method.

This technique is certainly more sensitive in comparison to the gamma spectrometry and it can detect radioactivity at very low levels. However, an extensive sample preparation, together with separation and purification procedures is often required to achieve accurate results. When the matrix is very complex (sediments, soils, rocks, etc.) many separation steps must be followed to achieve the complete purification of a radionuclide to be determined from interfering elements whose weight is often 10^{10} – 10^{12} times greater than that of the radionuclide. In these quite complex radiochemical procedures it is necessary to add a stable or radioactive tracer to calculate the final chemical yield, sample by sample. Generally, ^{232}U , ^{236}U , ^{229}Th , ^{209}Po , ^{133}Ba are used as radioactive yield tracers.

In addition, it is often required to set up a specific method for each particular radioisotope in each type of matrix. However, all the radiochemical methods, even if different, are based mainly on the chemical steps shown in figure 2.

2.2.1 Sample dissolution. The first step is to achieve the complete dissolution of the sample. The chemical digestion may differ depending on the radioisotope and on the type of matrix.

Table 2. The influence of the chemical treatment for the dissolution of zircon sand and refractory material samples containing ^{210}Po and ^{210}Pb .

Matrix	Recovery of ^{210}Po (Bq kg^{-1})	Recovery of ^{210}Pb (Bq kg^{-1})
Zircon sand	487 ± 195 (concentrated acids + HF) $2,109 \pm 527$ (fusion)	493 ± 197 (concentrated acids + HF) $2,506 \pm 626$ (fusion)
Refractory material	845 ± 338 (concentrated acids + HF) $1,453 \pm 363$ (fusion)	834 ± 334 (concentrated acids + HF) $1,075 \pm 269$ (fusion)

Some matrices can be dissolved by a simple leaching with 6M HNO_3 (phosphorites, carbonatic scales). Other matrices need a sequential dissolution with concentrated. HCl , HNO_3 , HClO_4 and HF . Refractory materials can be dissolved by a fusion with Na_2O_2 , Na_2CO_3 , KNO_3 , borax, etc. For zircon sand it is necessary to use a method developed by Sill [27], which insures that all the refractory solids are completely dissolved by using a sequential treatment based on a fusion with KF and a digestion with H_2SO_4 .

This first step is very important because an incomplete dissolution can determine an underevaluation of the radioisotope concentration. As an example table 2 shows the ^{210}Pb and ^{210}Po concentrations determined by the authors using two different dissolution methods: a sequential digestion with concentrated acids (HNO_3 , HCl , HClO_4 and HF) and an alkaline fusion. The results show that the first method is not sufficient to dissolve the radioisotopes completely, whereas the second method supplies higher and reproducible results.

2.2.2 Radioisotope separation. The natural radionuclides have to be separated from the matrix solution before the final measurement. This is mandatory for some important natural alpha and beta emitters which present severe self-absorption problems [26].

The separation techniques used for the determination of alpha and beta emitters in NORM and in the environment contaminated by NORM are generally those used for the analyses of stable trace element, such as: co-precipitation, selective liquid-liquid extraction, extraction chromatography, ion exchange chromatography and electroplating.

2.2.2.1 Co-precipitation Multiple selective or semi-selective precipitations can be used as pre-concentration and separation methods: sometimes one or two precipitations are not sufficient to obtain the desired decontamination factor.

Thorium and uranium can be co-precipitated with $\text{Fe}(\text{OH})_3$, LaF_3 and BiPO_4 ; radium can be co-precipitated as $\text{Ba}(\text{Ra})\text{SO}_4$ [25], lead as sulphide or sulphate [28], bismuth as sulphide [29].

2.2.2.2 Liquid-liquid extraction Solvent extraction deals with two liquid phases and the distribution of solutes, which usually are electrolytes, between them. One of the phases is generally an aqueous solution of electrolytes, the other phase is a non-aqueous one, usually an organic solvent immiscible with water [30].

Some examples are those concerning the separation of thorium and uranium from soil contaminated by NORM: thorium can be separated from a nitric solution with tributylphosphate (TBP) [30] and recovered by 8M HCl , uranium can be extracted

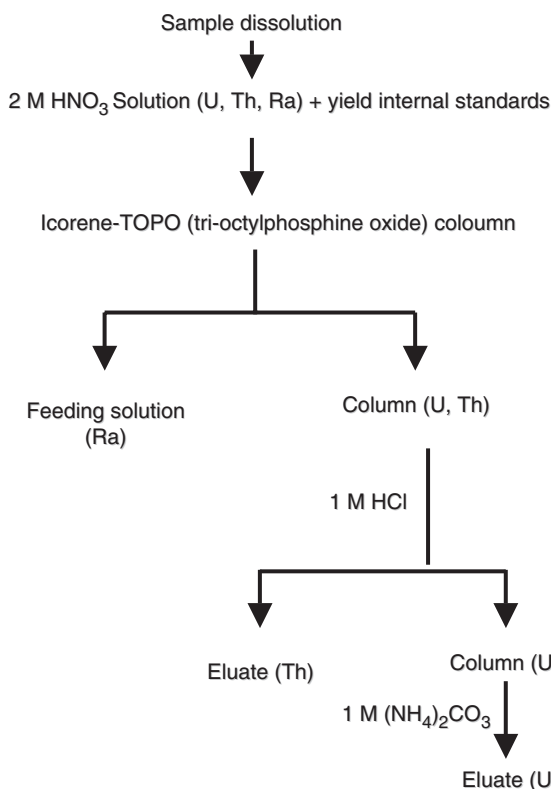


Figure 3. Flow sheet of U, Th and Ra separation from a phosphorite sample [36].

from $\text{Ca}(\text{NO}_3)_2$ solution with methyl isobutylketon (MIBK) and then stripped by 0.001M HNO_3 [12].

2.2.2.3 Extraction Chromatography Extraction chromatography combines the power and selectivity of solvent extraction with the ease of using a chromatographic technique. This unique combination allows radiochemists and other analysts to perform rapid, single-step separations of complex mixtures of radionuclides.

In extraction chromatography the stationary phase consists of a non-polar extractant adsorbed on an inert support (microporous polyethylene, Kel-F, etc.) while the mobile phase is a polar aqueous solution [31,32].

Tri-octyl-phosphine oxide (TOPO), di(2-ethylhexyl)phosphoric acid (HDEHP) and tri-n-octylamine (TNOA) are often used as the stationary phase. More recently, extraction chromatographic stationary phase as TRU-Spec [octyl(phenyl)-*N,N*-diisobutylcarbamoyl-methylphosphine oxide (CMPO) dissolved in tributyl phosphate (TBP) supported on an inert polymeric substrate called Amberlite XAD-7] [33,34] and TEVA-Spec [diamyl amylphosphonate supported on Amberlite XAD-7] [35] are commercially available.

An example of this technique is the separation of uranium, thorium and radium from phosphorite [37] (figure 3) and zircon sand [37] (figure 4) samples.

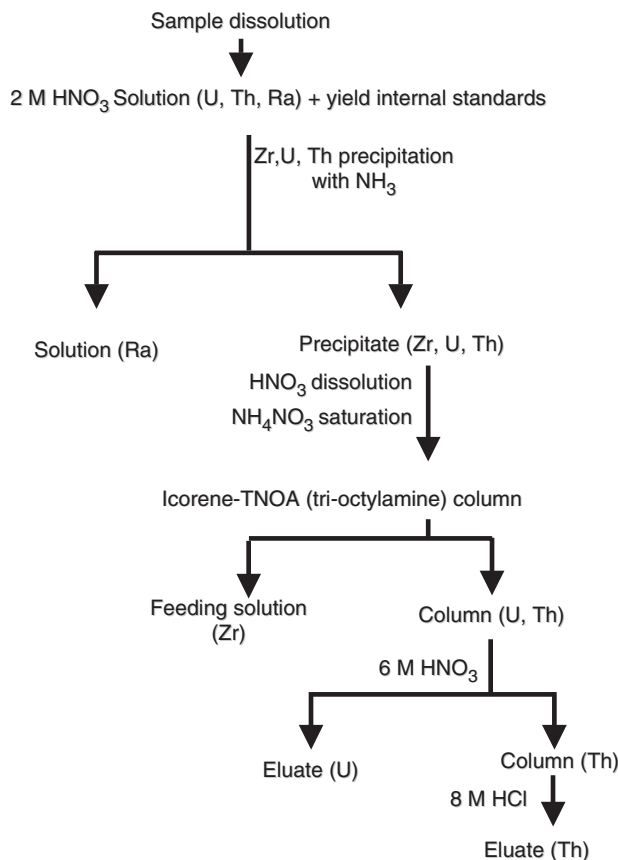


Figure 4. Flow sheet of U, Th and Ra separation from a zircon sand sample [37].

For phosphorite it is sufficient to use a column of microporous polyethylene (Icorene) supporting TOPO. This column retains uranium and thorium but it does not retain radium and calcium.

For zircon sand it is necessary to eliminate Zr^{4+} and the interfering anions (F^- , SO_4^-) used in the fusion. A column of microporous polyethylene supporting TNOA retains uranium and thorium from a NH_4NO_3 solution but it does not retain zirconium.

2.3 Radioisotope measurements

After separation, the radioisotope has to be determined: the measurement technique can be radiometric or non-radiometric if the alpha and beta particle radiation or other physical properties are taken into account respectively. In any case, all samples must be conveniently prepared for the final measurements.

2.3.1 Source preparation and radiometric techniques. ^{238}U (E_α : 4.19), ^{234}U (E_α : 4.77 MeV), ^{232}Th (E_α : 3.99 MeV), ^{230}Th (E_α : 4.68 MeV), and ^{228}Th (E_α : 5.42 MeV)

are electroplated from ammonium sulphate solution at pH 4; then the source is counted by alpha spectrometry with a silicon detector [38].

^{210}Po ($E_a = 5.30\text{ MeV}$) is deposited spontaneously at 85–90°C and at pH 1–2 onto a silver disk; the source can then be counted by alpha spectrometry [39,40].

^{226}Ra can be co-precipitated as $\text{Ba}(\text{Ra})\text{SO}_4$ and then counted by an alpha-counting system with a $\text{ZnS}(\text{Ag})$ detector, repeating the counting up to 30 days to check the growth of its daughters [25].

^{210}Pb ($E_{\beta\text{max}}: 0.016\text{ MeV}$) can be precipitated as sulphate and counted by a low background beta counter repeating the counting in order to verify the growth of ^{210}Bi ($E_{\beta\text{max}}: 1.161\text{ MeV}$) [40].

Figure 5 shows the alpha spectra [24] of thorium separated from a zirconium silicate (A) and a zirconium oxide (B) (section 2.1). In the spectrum A ^{228}Th and ^{232}Th are in secular radioactive equilibrium as concluded from their activity ratio equal to 1 whereas in the spectrum B this ratio is as high as 11.

Figure 6 shows the alpha spectra [25] of thorium separated from two samples of scales coming from two different hydrocarbon extraction plants. In the spectrum A ^{228}Th and ^{232}Th are in secular radioactive equilibrium whereas in spectrum B the activity ratio is about 700. The excess of ^{228}Th is due to the presence of high concentrations of the parent ^{228}Ra in the original waters from which the scale is derived.

2.3.2 Non-radiometric techniques. The radiometric measurements need a long time to prepare and to count the source, moreover the samples with low activity present poor counting statistics. Radioisotopes can be measured by non-radiometric techniques such as fluorimetry and spectrophotometry [12,36,37]. However, these techniques allow to determine the mass and, by using the specific activity, the activity concentration of ^{232}Th and ^{238}U but they do not supply any information about ^{228}Th and ^{234}U .

The use of inductively coupled plasma mass spectrometry (ICP-MS) is well-suited to measure the concentration of long lived radionuclides [41–43]. In particular, this technique allows the investigations of releases of naturally occurring radioactive material to the environment through the measurements of the ratios $^{232}\text{Th}/^{230}\text{Th}$, $^{230}\text{Th}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$. Each ratio measurement may indicate the contrast between the geochemical background and the contaminated environment [41].

Thorium isotope ratios represent a mean to discriminate “natural background” and U-affected environments, particularly when they are applied to studies of accumulation of ^{230}Th in phosphate-fertilized lawns [41]. The $^{232}\text{Th}/^{230}\text{Th}$ mass ratio in typical unmineralized crustal materials is approximately 200,000. Mixing U-bearing NORM wastes with material resembling crustal background will lower the bulk $^{232}\text{Th}/^{230}\text{Th}$ ratio towards intermediate values (10^3 – 10^5). Table 3 compares Th isotope ratios of two never-fertilized soils (Forest 1 and 2 soil) with five soil samples obtained from golf course fairways having more than a thirty-year history of continuous fertilization. Each fairway soil has the $^{232}\text{Th}/^{230}\text{Th}$ ratio significantly lower than either of the control locations because ^{230}Th is added along with U as a concomitant in phosphate fertilizers.

Also the ratio $^{230}\text{Th}/^{238}\text{U}$ (expressed as an activity ratio, $\text{AR}_{230/238}$) may additionally be used as a measure of influence from certain types of NORM wastes [41]. Chemical separation processes, such as uranium milling, disrupts the secular equilibrium between ^{230}Th and ^{238}U , owing to the differences in the properties of elements. In uranium milling,

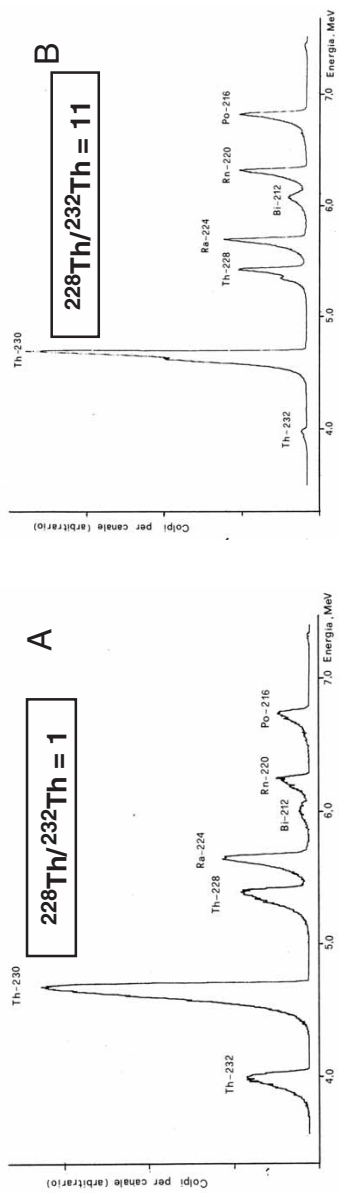


Figure 5. Alpha spectra of thorium separated from (A) zirconium silicate (Zircon) and (B) zirconium oxide (Baddeleyite) [24].

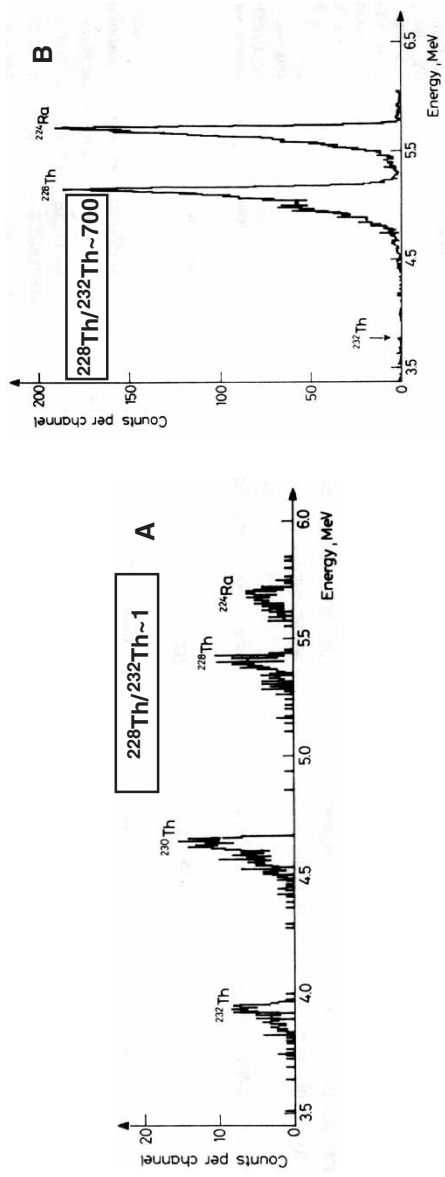


Figure 6. Alpha spectra of thorium separated from hydrocarbon plant scales: (A) Italian plant and (B) African plant [25].

Table 3. $^{232}\text{Th}/^{230}\text{Th}$ ratios of fertilizer and soil samples [41].

Sample	Preparation	$^{232}\text{Th}/^{230}\text{Th}$
Agrium monoammonium phosphate	KOH fusion	$1,010 \pm 10$
Agrium monoammonium phosphate	KOH fusion	$1,030 \pm 30$
Dragon triple superphosphate	KOH fusion	$2,480 \pm 30$
Espoma rock phosphate	KOH fusion	$5,200 \pm 200$
Scotts turf builder	KOH fusion	$3,200 \pm 100$
Fairway-1 soil	DTPA extraction	$69,000 \pm 7,000$
Fairway-2 soil	DTPA extraction	$87,000 \pm 7,000$
Fairway-3 soil	DTPA extraction	$73,000 \pm 3,000$
Fairway-4 soil	DTPA extraction	$54,000 \pm 5,000$
Fairway-5 soil	DTPA extraction	$50,000 \pm 9,000$
Forest-1 soil	DTPA extraction	$160,000 \pm 20,000$
Forest-2 soil	DTPA extraction	$110,000 \pm 10,000$
Lawn-1 soil	DTPA extraction	$18,000 \pm 1,000$

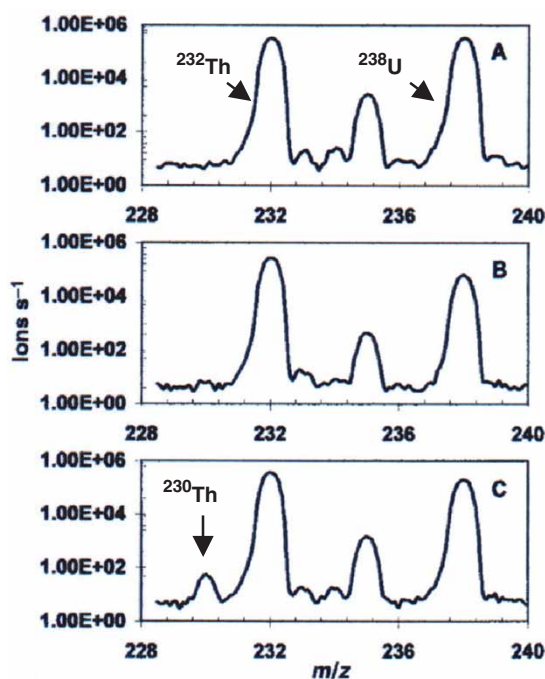


Figure 7. ICP mass spectra: (A) Th–U mixed standard solution; (B) and (C) Th and U separated from two river sediments [41].

a great majority of ^{238}U is removed as a product, while most of the ^{230}Th and other daughters are discharged with tailings. Therefore, $\text{AR}_{230/238} \gg 1$ is expected for uranium mill tailings wastes; on the contrary, $\text{AR}_{230/238} \sim 1$ is observed for most U ores as well as in many “background” environments.

ICP mass spectra for anomalous and background sediments are shown in figure 7. Spectrum A is a Th–U mixed standard solution; spectra B and C are obtained from two river sediments after Th and U recovery with TRU-Spec resin [41]; spectrum B

is typical of uncontaminated background sediments and spectrum C is an example of sediments containing high levels of unsupported ^{230}Th , evidently arising from input of mill tailings.

Another method for the evaluation of the difference between the geochemical background and the contaminated environment is to examine the ratio $^{234}\text{U}/^{238}\text{U}$ [41]. The unit activity ratio, corresponding to mass ratio of 0.00005472, is referred to as “secular” equilibrium. The activity ratio $^{234}\text{U}/^{238}\text{U}$ in surface and ground water exceeds unity, as exemplified by the activity ratio of 1.148 ± 0.002 for uranium in sea water. Introduction of NORM wastes (ores, mill tailings, fertilizers, etc.) in the aquatic environment, however, may bring about the addition of large amounts of material with $\text{AR}_{234/238} \sim 1$; consequently, waters contaminated by NORM wastes exhibit an activity ratio $^{234}\text{U}/^{238}\text{U}$ of ~ 1.0 , while “background waters” have significantly higher $\text{AR}_{234/238}$ values of 1.3–1.5.

3. Conclusion

By taking into account the described examples it clearly appears that chemical separation chemistry is the necessary and irreplaceable tool when alpha or beta emitters need to be detected by radiometric or non-radiometric techniques in NORM and in environmental samples contaminated by NORM. In fact, it is impossible to determine directly all the radionuclides of interest by gamma spectrometry because some of these are not gamma emitters.

Particular care must be taken to ensure that the adopted analysis package is specific and selective in order to avoid any erroneous results. The principal error is that some analytical procedures automatically assume that equilibrium exists with all the members of the series. In fact, NORM often derive from complex processes that cause the equilibria breaks impossible to restore in laboratory.

As far as radiochemical methods are concerned, it has to be pointed out that the same radioanalytical procedure cannot be used for all the matrices, each requiring the most appropriate conditions. A selective choice of all the operation parameters must be applied: the size of the column, the flow rate, the kind of stationary phase, the number of precipitations steps which are necessary for a good separation etc. In addition other chemical factors have to be considered: the quantity and kind of sample, the ionic strength, the concentration of the interfering ions and radionuclides, the presence of chelating substances, of silica, of oxidizing or reducing agents, the hydrolysis or adsorption processes, the necessity to fix a certain oxidation state of the ion, etc.

Furthermore, when it is required to use a gamma spectrometry procedure and not the radiochemical methods, it is always important to verify the equilibrium grade between the members of natural series by using the radiochemical methods described above.

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