

# DETERMINATION OF URANIUM ISOTOPES IN FOOD AND ENVIRONMENTAL SAMPLES BY DIFFERENT TECHNIQUES: A COMPARISON

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## INTRODUCTION

In recent years, the determination of natural series radionuclides played an outstanding role in our activity. This was partly due to the growing concern, from both a scientific and an institutional point of view, about significant exposure from NORM (Naturally Occurring Radioactive Material).

On the other hand, the Council Directive 98/83/EC on the quality of water intended for human consumption has pointed out the question of evaluating natural radionuclides water content. Moreover, the recent Balkan conflict posed the problem of possible environmental contamination by depleted uranium.

A comparison among different analytical methods for uranium isotopes determination is the aim of the present work. Both liquid and solid samples are concerned. Particular attention was paid to situations where radioactive secular equilibrium conditions were not assured.

## WATER SAMPLES ANALYSIS

We analyzed 59 water samples, mainly from Lombardia (Italy), concerning bottled waters, tap waters and some thermal waters. Inductively coupled plasma-mass spectrometry (ICP-MS), semiconductor alpha spectrometry and low-level liquid scintillation counting (LSC) were used for uranium determinations.

ICP-MS analysis was performed on all the samples with a Finnigan Mat ITS 40 instrument without any preconcentration. Results are reported in fig. 1.

Samples measured by alpha spectrometry (18 bottled waters) were firstly preconcentrated by ionic chromatography on a chelating resin (Chelex). This procedure allowed to get rid of the majority of lighter cations <sup>(1)</sup>. Uranium was then separated by anionic exchange on Dowex 1X8 resin following a modified HASL-300 <sup>(2)</sup> procedure and electrodeposited on stainless steel discs. Internal standard <sup>232</sup>U has been added as yield tracer. Alpha counting was performed with a 450 mm<sup>2</sup> surface-barrier detector equipped with Canberra Genie 2000 software for Alpha Acquisition and Analysis.

LSC analysis was carried out by direct uranium extraction from water using a lipophylic toluene-based scintillation solution mixed with bis(2-ethylhexyl) phosphoric acid (HDEHP) <sup>(3)</sup>. Samples were counted by a Wallac Quantulus 1220 liquid scintillation counter with alpha/beta discrimination. Only few results have been obtained up to now (7 samples of bottled water). At present we are improving the extraction technique by comparing different extractants performances. Spectral analysis and <sup>238</sup>U plus <sup>234</sup>U peak deconvolution were obtained by means of Canberra Genie 2000 Interactive Peak Fit Software (v. 1.0) which is designed for gamma and alpha spectrometry; the software parameters have been adjusted to closely fit the less resolved LSC spectra (fig. 2).

In order to compare the characteristics of the different techniques used, the requirements and the performances of each of them (table 1) are summarized in table 1.

ICP-MS is certainly the quickest way for measuring uranium in water since no pretreatment is needed and the analysis is very fast, but it allows a reliable determination only for the most abundant uranium isotope <sup>238</sup>U.

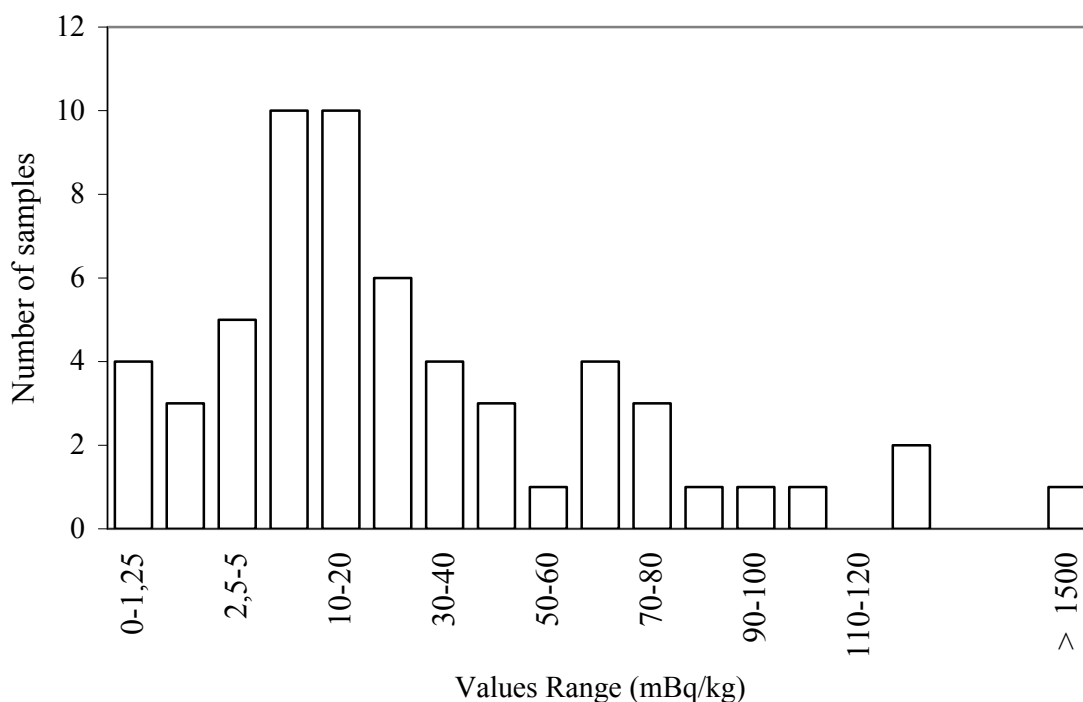


Figure1. Frequency distribution of  $^{238}\text{U}$  concentrations in bottled water samples.

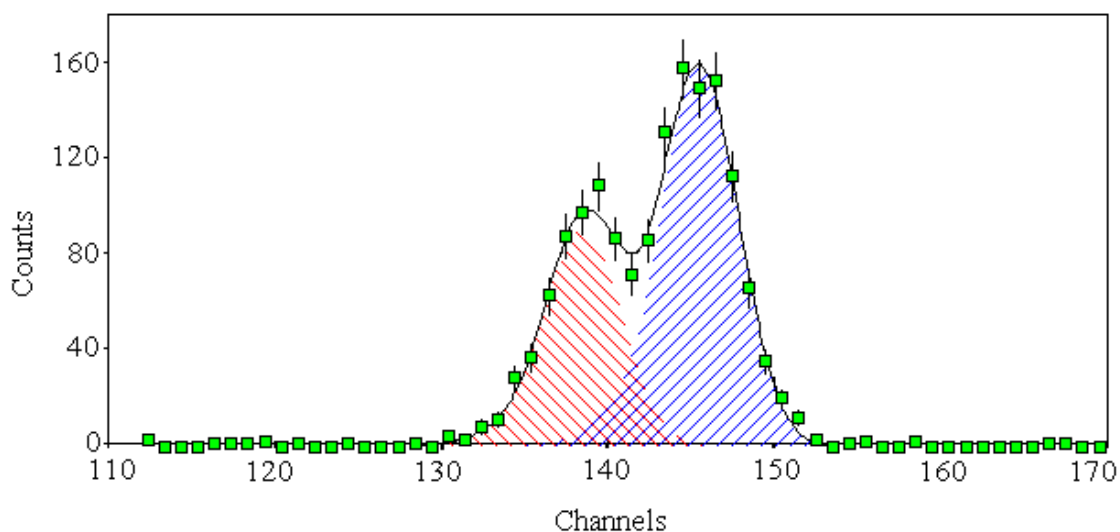


Figure2. Alpha spectrum of uranium by liquid scintillation of bottled water samples.

The semiconductor alpha spectrometry is relatively cumbersome but it gives complete information on concentrations and isotopic ratios of  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{234}\text{U}$ . The use of Chelex selective preconcentration allows to shorten the treatment and to achieve clean chemical separations.

Liquid scintillation counting coupled with selective solvent extraction is a very attractive technique since it is reasonably quick. Moreover it gives reliable information on total uranium content and, to some extent (in the hypothesis of negligible  $^{235}\text{U}$  concentration), on  $^{234}\text{U}$  and  $^{238}\text{U}$  contents and ratios.

**Table 1. Requirements of performances of techniques for uranium determination in water samples.**

	sample amount (kg)	preconcentration	treatment time (hrs)	counting time (hrs)	<sup>238</sup> U	<sup>235</sup> U	<sup>234</sup> U	<sup>238</sup> U sensitivity (mBq/kg)
ICP-MS	< 0,01	no	0	< 0,1	yes	yes	no	1
Alpha Sp.	1	yes	30	66	yes	yes	yes	1
LSC	0,1	no	1	66	yes	no	yes	4

A good agreement is generally found for the results obtained with the three different techniques (table 2).

**Table 2. Uranium concentration in bottled water samples measured by different techniques. Error indicated is one standard deviation. Lower limit of detection is expressed at the 95% confidence level.**

Bottled Water Sample	U-238 (ICP-MS) mBq/kg	err.	U-238 (Alpha Sp.) mBq/kg	err.	U-238 LSC mBq/kg	err.	U-234 (Alpha Sp.) mBq/kg	err.	U-234 LSC mBq/kg	err.
San Carlo Spinone	9	0,9	8,6	0,5	10	2	13	0,8	14	4
Tavina	22	2	21	1,4	17	4	21	1,4	25	6
St. Yorre	26	3	26	1,9	20	5	162	10	176	40
Frisia	34	3	20	1,3	20	3	21	1,3	27	4
Badoit	100	10	103	7	70	11	268	16	237	36
S. Pellegrino	122	12	99	8	87	7	101	8	107	9
Lurisia Garbarino	1798	180	1936	123	1595	132	2842	179	2730	226
Orobica	25	3	21	1,4	n.a.	n.a.	28	2	n.a.	n.a.
Pracastello	89	9	73	4,4	n.a.	n.a.	85	5	n.a.	n.a.
Bracca	102	10	97	6	n.a.	n.a.	120	8	n.a.	n.a.
Gaverina	4	0,4	3,1	0,3	n.a.	n.a.	5,0	0,4	n.a.	n.a.
Bernina	< 6,2		3,3	0,3	n.a.	n.a.	3,1	0,3	n.a.	n.a.
S. Francesco	7	0,7	7,2	0,8	n.a.	n.a.	8,5	0,9	n.a.	n.a.
S. Antonio	7	0,7	5,6	0,4	n.a.	n.a.	7,5	0,5	n.a.	n.a.
Gajum	5	0,5	3,9	0,4	n.a.	n.a.	5,6	0,5	n.a.	n.a.
Obernauer	9	0,9	10	0,9	n.a.	n.a.	17	1,3	n.a.	n.a.
Valser	18	2	25	2	n.a.	n.a.	34	2,5	n.a.	n.a.

n.a. : not available

Ratio data are markedly important for water because isotopic secular equilibrium is not generally attained. In 18 samples analyzed (semiconductor alpha spectrometry) <sup>234</sup>U/<sup>238</sup>U values lie between 1 and 1.3 in 7 cases, between 1.3 and 2 in 9 cases and are higher than 2 in 2 cases. A ratio value of 6.2 is reached. Ratio values obtained by both semiconductor alpha spectrometry and liquid scintillation counting agree within the experimental error.

## SOLID SAMPLES ANALYSIS

We compared results obtained with both gamma and alpha spectrometry on soil, bicalcic phosphate and zirconium silicate samples; we also analyzed shellfish samples from Adriatico Sea to detect depleted uranium.

The analysis of  $^{238}\text{U}$  by gamma spectrometry relies on the hypothesis of equilibrium conditions between parent nuclide  $^{238}\text{U}$  and short-lived daughters  $^{234}\text{Th}$  e  $^{234\text{m}}\text{Pa}$ .  $^{234}\text{U}$  can hardly be detected due to its low emission probability direct gamma rays.  $^{235}\text{U}$  determination is affected by heavy interference from  $^{226}\text{Ra}$  which often can't be suppressed.

$^{234}\text{Th}$  gamma peaks (63 and 93 keV) are usually considered useful for analytical purposes. The real sample density and chemical composition, however, should be taken into account when evaluating the system detection efficiency; self-absorption of low energy gamma rays strongly depends on them. Furthermore the 93 keV peak (which is actually a doublet) suffers of possible overlap of  $^{228}\text{Ac}$  93 keV X-ray peak (often occurring in natural samples).

$^{234\text{m}}\text{Pa}$  gamma peaks (766 and 1001 keV) are higher in energy than  $^{234}\text{Th}$  ones. Their detection efficiency is less dependent on the sample density and chemical composition; detection limits, however, are higher due to their low emission probabilities.  $^{234\text{m}}\text{Pa}$  can thus be successfully used only when measuring samples with medium to high uranium concentration. Special attention has to be paid in selecting emission probabilities since recently accepted values <sup>(4)</sup> are about 40% higher than formerly given ones <sup>(5)</sup>.

**Table 3. Extracted results for solid samples; values are referred to dry weight. Error indicated is one standard deviation. Lower limit of detection is expressed at the 95% confidence level.**

	Semiconductor Alpha Spectrometry						High Resolution Gamma Spectrometry					
	$^{238}\text{U}$ Bq/kg	err.	$^{234}\text{U}$ Bq/kg	err.	$^{235}\text{U}$ Bq/kg	err.	$^{234}\text{Th}$ Bq/kg	err.	$^{234\text{m}}\text{Pa}$ Bq/kg	err.	$^{235}\text{U}$ Bq/kg	err.
<b>Soil Samples</b>												
Bergamo	27	2	23	2	1,0	0,2	36	3	49	5	1,9	0,3
Chernobyl	5,1	0,1	5,3	0,7	0,3	0,1	< 32,5		< 160		< 3,20	
Chiesa V.M.	139	2	122	1	6,3	0,6	168	6	160	10	7,5	0,7
Cremono	49	6	47	7	2,3	0,3	54	7	62	7	6,3	0,7
Kosovo	18	1	18	1	1,0	0,2	17	2	19	4	0,7	0,2
Romagnese	28	2	24	2	1,3	0,2	25	10	31	5	1,3	0,3
Valbrona	21	1	20	1	1,1	0,2	21	2	31	2	1,8	0,2
Valfurva	28	11	27	14	1,3	0,3	52	4	56	6	3,1	0,4
Varese C.F.	24	9	22	10	1,2	0,2	19	2	21	2	2,0	0,2
<b>Other Inorganic Samples</b>												
Bicalcic Phosphate	1819	109	1914	114	106	14	1873	53	2094	105	90	2
Refractory Material	978	69	1008	70	< 100		618	24	1042	58	59	3
Zirconium Silicate	n.a.		n.a.		n.a.		899	37	3600	133	164	5
<b>Shellfish Samples</b>												
Edible + Sand	13	1	13	1	0,42	0,14	51	3	39	6	1,03	0,29
Edible Cleaned	4,3	0,5	4,8	0,6	0,38	0,20	103	4	56	16	0,72	0,121
Shells	0,62	0,06	0,76	0,07	0,06	0,02	2,0	0,4	< 14		0,09	0,023

Gamma spectrometry was performed by high purity germanium detector equipped with Canberra Genie 2000 software for Gamma Acquisition and Analysis. The calibration source was a multigamma solution in HCl 0.2 M (density 1 g/cm<sup>3</sup>). No self-absorption correction has been applied, as generally done in routine laboratory work for time and cost reasons.

Pretreatment and electrodeposition techniques have been tailored in order to reduce preparation time and improve spectral resolution in alpha spectrometry measurements. The measuring system is the same previously described for water samples analysis. Results are summarized in table 3.

As far as gamma spectrometry results are concerned, a general agreement is found between <sup>234</sup>Th concentrations (based on 63 keV gamma line) and <sup>234m</sup>Pa ones (based on recently reported values for its gamma rays emission probabilities <sup>(4)</sup>); agreement is not found for samples with density and, most of all, chemical composition different from the calibration standard. As an example, calculated concentration of <sup>234</sup>Th in zirconium silicates is about four times lower than <sup>234m</sup>Pa; <sup>234m</sup>Pa value is confirmed by mass spectrometry <sup>238</sup>U analysis. In such cases the use of <sup>234m</sup>Pa activity values is recommended; methods for self-absorption correction of 63 keV <sup>234</sup>Th gamma line <sup>(6)</sup> are needed when <sup>234m</sup>Pa concentration is lower than minimum detectable activity.

In measured biological samples (*Pecten Opercularis* shellfish) a general agreement is found between <sup>234</sup>Th and <sup>234m</sup>Pa activity values. On the other hand <sup>238</sup>U activities measured by alpha spectrometry are lower showing the lack of equilibrium between <sup>238</sup>U e <sup>234</sup>Th. This could be related to different metabolic behaviours of uranium and thorium and shows the importance of the direct uranium measurement when equilibrium conditions are not attained.

Alpha spectrometry provides the best sensitivity for accurate evaluations of isotopic ratios, which is necessary for the detection of low amounts of depleted uranium in environmental samples. The more reliable indicator is <sup>238</sup>U/<sup>234</sup>U ratio rather than the less accurate <sup>238</sup>U/<sup>235</sup>U.

## FURTHER PROGRAMS

As far as water results are concerned, a detailed statistical analysis of data is currently under development in order to investigate relationship among uranium and other parameters (gross alpha and beta activity, <sup>226</sup>Ra concentration, chemical-physical and hydro-geological properties).

A particular effort is devoted in developing quick methods for water analysis by LSC and optimizing liquid scintillation extractors and measurement conditions.

The above described methods are presently being employed for depleted uranium assessment in environmental samples from Garda Lake and Adriatico Sea as a part of a national monitoring program.

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