

NATURAL RADIONUCLIDES MONITORING IN LOMBARDIA DRINKING WATER BY LIQUID SCINTILLATION TECHNIQUE

Maurizio Forte¹, Rosella Rusconi¹, Silvia Bellinzona² and Giuseppe Sgorbati³

Abstract

Gross α/β and uranium measurement methods on drinking water by liquid scintillation counting coupled to extractive techniques and α/β discrimination have been optimized; special regard has been reserved to reduce pretreatment times and to increase sensitivity and reproducibility. Measurements were performed using Wallac Quantulus 1220 ultra low level liquid scintillation counter. Procedures have been tested by comparison with other methods and repeatability has been evaluated. These techniques have been applied to radiometric measurements in tap water samples drawn in 13 Lombardia centers in order to check compliance with the more recent national and international regulations concerning drinking water quality. A preliminary identification of areas where ground waters exhibit higher radioactivity content has been made; further investigations demonstrated that in all examined cases the major contribution to the radioactivity content is due to uranium.

Introduction

Concern about total radionuclides content in water intended for human consumption has been brought to public attention by the recent Council Directive 98/83/EC, subsequently enforced through an Italian law (DL 31, February 2nd, 2001). Parameter values have been fixed for Tritium content and total indicative dose: the Directive points out that the total indicative dose must be evaluated excluding Tritium, ⁴⁰K, ¹⁴C, Radon and its decay products, but including all other natural series radionuclides. Maximum concentration values for Radon are separately proposed in Commission Recommendation 2001/928/Euratom.

Tritium determination follows a well established procedure, standardized by International Standard Organization (ISO 9698, 1989). On the contrary, total indicative dose evaluation requires more specific and cumbersome procedures for the measurement of radioactivity content, with special regard to natural series radionuclides. The large number of possibly involved radionuclides and the good sensitivities required make the application of traditional analytical techniques unsuitable in view of a large scale monitoring program.

World Health Organization (WHO 1993 and 1996) guidelines for drinking water suggest performing an indirect evaluation of committed dose by measuring alpha and beta gross radioactivity and checking compliance to derived limit values; the proposed limit values are 0,1 Bq/l for gross alpha and 1 Bq/l for gross beta radioactivity. Nevertheless, it is desirable to identify single radionuclides contribution to alpha and beta activity in order to perform more accurate measurements of committed dose.

Ultra-low level liquid scintillation counting coupled to extractive techniques and alpha-beta discrimination allows rapid and simple determination of all radiometric parameters relevant to dose evaluation, namely gross alpha and beta activity, uranium and radium isotopes content.

¹ ARPA Lombardia, Dipartimento sub-provinciale Città di Milano, Sezione Radioprotezione - Via Juvara 22, 20129 Milano (Italy) - crr.lombardia@sanita.it

² Università degli Studi di Milano, Facoltà di Fisica – Via Celoria 16, 20133 Milano (Italy)

³ ARPA Lombardia, Settore Agenti Fisici – Via Restelli 1, 20124 Milano (Italy) - g.sgorbati@arpalombardia.it

These techniques were applied to a preliminary monitoring program of tap waters in Lombardia; up to now, total alpha and beta activity and uranium isotope concentration have been measured. Some brands of bottled water were examined too, both for testing methods and because of the widespread use of mineral water by the Italian population. Mineral water brands are not reported here.

Gross alpha and beta

Gross alpha and beta activity is usually measured by counting the dry residue of a water sample. In US-EPA and ASTM methods (ASTM D 1943-96 and 1890-96; EPA 00-01) an acidified amount of water is reduced in volume and evaporated to dryness on a steel planchet. In ISO method 9696 and 9697 the residue is first sulphated by addition of sulphuric acid; a fixed amount of dry salts is then evenly dispersed on a steel planchet and counted by a proportional counter or other suitable counter (zinc sulfide scintillation counter for α emissions, plastic scintillation counter for β emissions).

The availability of low-background liquid scintillation counters equipped with alpha-beta discrimination device provides an alternative for gross alpha and beta determination (Salonen, 1989 and 1990; Sanchez-Cabeza, 1993 and 1995). The LSC method offers several advantages over the traditional procedure: 1) simultaneous alpha and beta measurement through alpha-beta discrimination technique - reduced counting times; 2) high (close to 100%) and rather constant detection efficiency for alpha emitters and for high energy beta emitters; 3) faster and more reproducible sample preparation; 4) spectral energy response through inspection of emission spectra.

It is possible, in principle, to verify compliance with WHO recommended values for alpha and beta activity content in water by ultra low level liquid scintillation counting without any previous treatment. Water is added to the scintillation cocktail in a proper amount, generally in a 8:12 ratio (Sanchez-Cabeza, 1993) and counted for the time necessary to achieve desired sensitivity (1000 minutes): LLD of 80 mBq/l and 250 mBq/l for α and β activity respectively can be attained. A key point is the proper setting of the α/β discrimination parameter based on pulse shape analysis (PSA).

Better sensitivities and reduced counting time can be achieved by sample preconcentration; both freeze drying technique (Salonen, 1990) and evaporation by heating (Sanchez-Cabeza, 1995) have been used.

In the present work water samples were acidified (to avoid losses due to precipitations, polymerizations, colloid formations) and preconcentrated by slow evaporation on hot plate. 15 M bidistilled nitric acid was added to a 200 g sample up to pH 2,5 and the volume was reduced ten fold by heating; pH drops to 1,5 and in the same time all the dissolved radon is desorbed. Finally 8 g of the concentrated sample is transferred in the scintillation vial and 12 ml of Optiphase Hisafe 3 (Wallac) cocktail is added. No quenching effect of nitric acid was observed.

Detection efficiency was evaluated by measuring degassed pH 1,5 nitric solutions traced with ^{241}Am and $^{90}\text{Sr}/^{90}\text{Y}$ with activity concentrations similar to those of real samples. The alpha beta discrimination parameter (PSA) was set using the same standards: measurements were repeated increasing PSA value by 5 each time and α/β interference was calculated by the following expressions (Sanchez-Cabeza, 1993).

$$\text{alpha interference:} \quad \tau_{\alpha} = \frac{\beta}{\alpha + \beta}$$

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Alpha interference (τ_α) is the fraction of counts observed in the beta window (β) with respect to the counts observed in alpha and beta windows ($\alpha+\beta$) when a pure alpha emitter is measured; the beta interference (τ_β) is the fraction of counts observed in the alpha window (α) with respect to the counts observed in alpha and beta windows ($\alpha+\beta$) when a pure beta emitter is measured.

Since alpha and beta interference depends on sample quenching, interference curves were evaluated at different quenching values obtained by adding increasing amounts of CCl_4 to traced samples; quenching variation in real samples, however, was limited and had no influence on alpha-beta discrimination parameter setting.

LSC method was tested by comparing its outcomes with ISO procedure results for 9 water samples, 8 from bottled mineral waters and 1 from tap water (Tab. 1): a good agreement can be observed.

Tab. 1: Gross alpha and beta activities comparison

Water sample	GROSS α (mBq/kg)		GROSS β (mBq/kg)	
	LSC	ISO	LSC	ISO
Mineral water 1	346 ± 23	393 ± 51	467 ± 43	402 ± 84
Mineral water 2	334 ± 43	281 ± 49	210 ± 53	294 ± 47
Mineral water 3	59 ± 5	59 ± 7	158 ± 16	163 ± 15
Mineral water 4	38 ± 4	29 ± 9	100 ± 14	154 ± 37
Mineral water 5	12 ± 3	15 ± 4	45 ± 12	< 35
Mineral water 6	29 ± 4	28 ± 6	62 ± 12	< 55
Mineral water 7	99 ± 7	80 ± 9	135 ± 15	140 ± 13
Mineral water 8	13 ± 3	16 ± 4	66 ± 13	< 33
Milano (tap)	70 ± 6	71 ± 12	116 ± 14	146 ± 34

Repeatability was tested in a ten fold replication experiment; alpha measurement repeatability, as expressed by values distribution width, resulted to be 9 %; beta measurement repeatability resulted to be 16 %.

Uranium

A number of methods have been devised for total or isotopic determinations of uranium in water. Most widely used non-radiometric methods are fluorimetry, X rays fluorescence, ICP atomic emission or ICP mass spectrometry; the last one is growing in importance due to its rapidity, sensitivity and the possibility to perform isotopic composition evaluations. The main limitation is the cost of instruments, especially if extra sensitivity is needed for the more difficult determination of ^{234}U and ^{235}U isotopes besides the more abundant (in mass) ^{238}U .

In water analysis this is a quite crucial problem since isotopic equilibrium between ^{234}U and ^{238}U is generally not attained; uranium isotope disequilibrium can be due to transfer mechanisms from rocks to water and to the less stable position of ^{234}U in the lattice after recoil following alpha decay. The activity ratio $^{234}\text{U}/^{238}\text{U}$ generally varies between 1 and 1,5 but can reach much higher values, up to 7-8. The evaluation of total uranium activity from ^{238}U concentration can thus lead to underestimate total uranium content.

Radiometric methods, like semiconductor alpha spectrometry on electrodeposited samples, allow accurate determinations of all isotope concentrations thanks to good spectral resolution. They are nevertheless too cumbersome for a wide scale monitoring application.

LSC also offers an attractive option, especially when coupled to direct uranium extraction. Since '80s several researchers exploited the complexing power of phosphor or nitrogen compounds like TOPO (trioctyl-phosphin oxide), HDEHP (bis-2-ethylhexyl-orthophosphoric acid) or TNOA (tris-N-octyl amine). These compounds can be added to a non water soluble scintillation cocktail giving an "extractive cocktail". By simply shaking the extractive cocktails with the water sample, the uranium moves into the organic phase. After phase separation, the extractive cocktail is ready to be counted.

Other actinides like thorium, plutonium and americium can be co-extracted; if necessary, complexing agents can be added to the water sample to suppress such interferences (Abuzeida, 1987).

Liquid scintillation counting coupled to selective uranium extraction was used in this work to assess uranium content in waters. Experimental conditions were optimized with regard to the cocktail selection, pretreatment and counting procedure. Extractive performances of four different scintillation cocktail were compared, two of them (C1 and C2) used by others researchers (Yu Yu Fu, 1990; Cadieux, 1994), the third realized in our laboratory (C 3), the fourth (C 4) prepared by adding HDEHP to the commercial Wallac cocktail (Optiphase Hisafe 3). HDEHP has always been used as the uranium complexing agent because of its low effect on quenching, especially when added to the scintillation cocktail in small amounts (YuYu Fu, 1990). Except C4, extractive scintillation cocktails were prepared by adding a fluorescent substance (or a mixture of them), naphthalene (to enhance alpha-beta separation) and 5% HDEHP to an aromatic solvent (toluene or xilene) (Tab. 2).

Tab. 2: Composition of 1 liter extractive cocktail

Cocktail	Solvent	Fluo	Naphtalene	HDEHP
C 1	Toluene	PPO 4 g Bis-MSB 0,5 g POPOP 0,05 g	35 g	50 g
C 2	Xilene	PBBO 4 g	180 g	50 g
C 3	Toluene	PBBO 4 g	35 g	50 g
C 4 (Optiscint)	Diisopropilnaphtalene	PPO* Bis-MSB*	-	50 g

PBBO: 2-(4-biphenylyl)-6-phenyl-benzoxazole; **PPO:** 2,5-diphenyloxazole;

Bis MSB: 1,4-bis(2-methystiryl)benzene; **POPOP:** 1,4-bis(5-phenyloxazol-2-yl)-benzene.

* composition registered by Perkin Elmer-Wallac

Extraction yields were evaluated by measuring water samples acidified with nitric acid (0,7 M) and spiked with a known amount of natural uranium; the extraction yield was calculated as percentage of extracted uranium.

Extraction procedures were further investigated; different amounts of sample and cocktail were mixed and extraction conditions were slightly modified. Yields not far from 100 % were obtained by extracting in a separatory funnel (2 minutes shaking) 20 ml of test solution with 20 ml of cocktail. Extraction efficiency drops when using greater test solution volumes. Better results were obtained with a two-step extraction of 100 ml of test solution in 10+10 ml cocktail volume; similar extraction yields were obtained with the four cocktails (Tab 6).

Since it is known that dissolved oxygen seriously affects both resolution and α/β discrimination, all samples were degassed after the extraction by sparging them with argon. This procedure could

not be applied to the extractive cocktail C4 since gas bubbling caused foaming and subsequent cocktail spillover.

Counting characteristics of the four cocktails are summarized in Tab. 3. Besides background, optimal discrimination parameter setting (PSA) and alpha resolution, PSA plateau (PSA values range in which α and β interferences are lower than 1%) is also listed.

Tab. 3 : Extractive cocktails features

Scintillation Cocktail	Argon fluxed	Extraction yields	Background α window cpm *	PSA	PSA plateau	Resolution (%)	
						^{234}U	^{238}U
C1	no	98.6 +/- 0.5	0,012	90	25	4.7	4.9
	yes	98.6 +/- 0.5	0,010	110	40	3.5	4.8
C2	no	98.2 +/- 0.8	0,026	130	55	3.3	4.9
	yes	98.2 +/- 0.8	0,009	130	70	2.7	3.7
C3	no	98.0 +/- 0.5	0,040	120	50	4.1	4.9
	yes	98.0 +/- 0.5	0,036	130	55	3.2	4.4
C4	no	98.4 +/- 0.8	0,053	130	55	3.6	3.9

Resolution was calculated by the following formula (Horrocks, 1964):

$$R(\%) = \frac{2 * \left| \left(x_m - x_{1/2} \right) \right|}{x_m} * 100$$

$$x_m = \text{peak channel} \quad x_{1/2} = \text{half height channel}$$

The C2 scintillation cocktail, which combines low background, good resolution and discrimination and a wide PSA plateau, was selected as the optimum cocktail.

Performances of glass, polyethylene, teflon and teflon coated polyethylene vials (20 ml) were compared. Glass vials gave poor results both for background and spectral alpha resolution; best results were obtained when using teflon and polyethylene vials. Teflon vials were discarded because of their high cost, while polyethylene vials are permeable to cocktail solvent. The best results were obtained with teflon coated polyethylene vials, which exhibit good resolution, low background and no solvent permeability.

In order to raise the analytical sensitivity, a sample preconcentration method was adopted too. One liter samples were first acidified with 5 ml of 14 M in order to avoid uranium losses, then slowly evaporated on a hot plate to 100 ml; the final HNO_3 concentration is 0,7 M. Uranium was finally extracted by the selected procedure.

Uranium measurements were made considering the alpha discriminated spectrum component (channels range 600-800).

^{238}U and ^{234}U content was evaluated applying spectral deconvolution of uranium alpha peaks; Canberra Genie 2k Interactive Peak Fit software was used to this purpose (Fig. 1). ^{235}U contribution to total uranium was estimated to be lower than 2.5%, and was neglected when performing alpha spectra deconvolution.

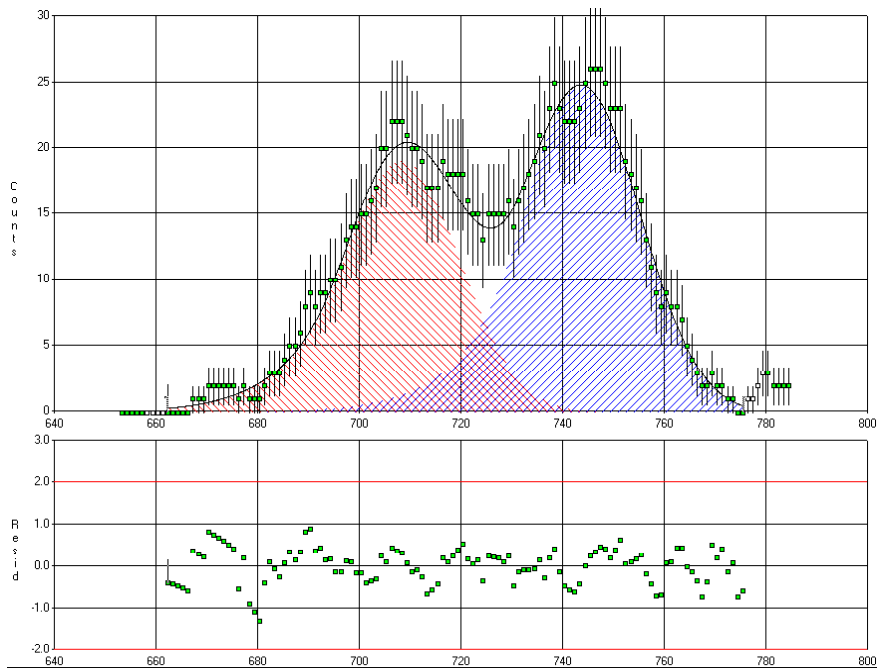


Fig. 1: ^{238}U and ^{234}U α peaks deconvolution

The method was tested, with good results, by comparison with values obtained by two independent methods on some bottled water samples, namely: 1) semiconductor alpha spectrometry on electrodeposited samples; 2) ICP mass spectrometry (^{238}U alone). Results are shown in Tab.4.

Tab. 4: Uranium activities comparison

Water sample	^{238}U mBq/kg			^{234}U mBq/kg	
	LSC	Semiconductor spectrometry	ICP-MS	LSC	Semiconductor spectrometry
Mineral water 1	97 ± 11	99 ± 8	122 ± 12	113 ± 13	101 ± 8
Mineral water 2	87 ± 10	96 ± 6	102 ± 10	123 ± 14	120 ± 7
Mineral water 3	31 ± 4	20 ± 1	34 ± 3	30 ± 4	21 ± 1
Mineral water 4	22 ± 3	21 ± 1	22 ± 2	23 ± 3	21 ± 1
Mineral water 5	$5,3 \pm 1,3$	$7,2 \pm 0,8$	$7,3 \pm 0,7$	$7,8 \pm 1,5$	$8,5 \pm 0,9$

Test methods summary

Tab. 5 resumes the main features of the above described test methods. Teflon coated polyethylene vials were always used.

A mixture of 8 ml of radon free HNO_3 solution (pH 1.5) and 12 ml of Optiphase Hisafe 3 was used as a background sample to determine gross alpha and beta. A 20 ml sample of argon fluxed C2 cocktail was used for uranium background.

Tab. 5: Test methods performances

	Sample volume (g)	Measure time (min)	Measure window (channels)	Spectrum	Background (cpm)	Efficiency (%)	LLD (mBq/kg)
Gross α	80	1000	500-1000	α	$0,099 \pm 0,007$	102 ± 1	8
Gross β	80	1000	500-1000	β	$0,960 \pm 0,020$	69 ± 1	25
Total U	1000	1000	600-800	α	$0,087 \pm 0,004$	98 ± 5 *	0,4

* combined efficiency (extraction + counting)

Measurement uncertainty was evaluated according to ISO Guide to the Expression of Uncertainty in Measurement. Uncertainty on sample amounts, on calibration standard activity as well as counting uncertainty were considered in the evaluation of the combined standard uncertainty; uncertainty on measurement results is always expressed in terms of expanded uncertainty (obtained by multiplying the combined standard uncertainty by a coverage factor $k=2$).

Applications to environmental samples

We used the above described methods to carry out radioactivity measurements of different water samples: bottled, surface and tap waters.

First results of tap waters monitoring program are presented in Tab. 6. Samples were drawn in 13 of the largest Lombardia centers; gross alpha and beta activity and uranium isotope concentration were measured. Chemical analysis of potassium was performed by ionic chromatography and ^{40}K activity calculated taking into account its natural abundance (30,3 mBq per mg of potassium).

Tab. 6: Tap waters results

ARPA Department	Gross α mBq/kg	U total mBq/kg	^{234}U mBq/kg	^{238}U mBq/kg	Gross β mBq/kg	^{40}K mBq/kg
Parabiago	349 ± 41	372 ± 41	211 ± 24	161 ± 18	273 ± 48	46 ± 2
Lodi	94 ± 16	110 ± 12	59 ± 7	52 ± 6	239 ± 45	100 ± 5
Milano	91 ± 16	105 ± 12	59 ± 7	46 ± 6	118 ± 37	46 ± 2
Monza	78 ± 14	97 ± 11	50 ± 6	47 ± 6	132 ± 38	46 ± 2
Sondrio	55 ± 12	55 ± 6	30 ± 4	26 ± 4	140 ± 38	76 ± 4
Lecco	36 ± 11	38 ± 4	20 ± 3	18 ± 3	136 ± 38	100 ± 5
Brescia	27 ± 10	43 ± 5	25 ± 3	18 ± 3	81 ± 35	30 ± 2
Bergamo	23 ± 10	25 ± 3	14 ± 2	11 ± 2	< 25	7.0 ± 0.3
Varese	20 ± 10	21 ± 3	11 ± 2	10 ± 2	88 ± 35	61 ± 3
Como	< 8	4.7 ± 0.8	3 ± 1	1.6 ± 1.0	81 ± 35	42 ± 2
Pavia	< 8	0.6 ± 0.4	< 0.4	< 0.4	78 ± 35	48 ± 2
Cremona	< 8	< 0.4	< 0.4	< 0.4	65 ± 34	30 ± 2
Mantova	< 8	< 0.4	< 0.4	< 0.4	88 ± 35	64 ± 3

Southern Lombardia cities (Pavia, Cremona, Mantova) exhibit the lowest radioactivity concentrations, while northern (Sondrio, Lecco, Varese, Como) and north-eastern ones (Brescia, Bergamo) exhibit medium-low levels. Higher values were found in Milano and surrounding areas (Parabiago, Lodi, Monza). Northern Lombardia is an alpine district; previous works (Sgorbati, 1998) showed a relevant dishomogeneity for both tap and bottled water produced in that area (52 samples were analyzed). Thus samples collected in the main city should not be considered representative of the whole district.

A more detailed monitoring of waters from Milano and surrounding area is currently underway; a complete chemical and radiometric analysis (gross α and β , uranium, radium, tritium and radon) is being performed on samples drawn directly at wells; preliminary results show remarkable chemical and radiological differences in waters from same area wells; in 7 main wells from a small area, for instance, α activity ranges from 23 to 410 mBq/kg. Differences could be due to different wells depth; further analysis are still in progress.

Results in Tab. 6 show that α activity is mainly due to uranium isotopes: $^{234}\text{U}/^{238}\text{U}$ ratio is generally close to 1.

Gross beta activity shows a more limited range of values; a major contribution to beta activity is due to ^{40}K , especially in low activity waters. ^{40}K is not to be considered in committed dose evaluation, therefore, alpha activity values are more useful to identify critical situations.

Conclusions and further developments

Liquid scintillation has proven to be a quick, versatile and accurate tool for radiometric investigation on both surface and drinking water. Gross α and β and uranium isotope activity can be measured with quick and simple procedures; method sensitivity is adequate to check compliance to Italian law parameters.

Preliminary results on Lombardia tap waters show the existence of critical areas where water radionuclide content can exceed WHO proposed values: high values are usually due to uranium isotopes.

Nevertheless previous works (Sgorbati, 1998) showed that, in specific areas, a relevant dose contribution is due to radium isotopes, for which dose conversion factors are higher than uranium ones.

A more detailed survey should therefore consider radium isotopes concentrations. Methods for simultaneous determination of ^{226}Ra and ^{228}Ra by liquid scintillation counting are currently under development: they should be applied to samples that approach gross α and β WHO proposed values.

Bibliography

- Abuzeida M., Arebi B.H., Zolotarev Y.A., Komarov N.A.: Selective liquid scintillation method of uranium α -spectrometry J. of Radioanal. and Nucl. Chem., Articles 116 2, 285-289 (1987)
- ASTM D 1890-96: Standard test method for beta particle radioactivity of water
- ASTM D 1943-96: Standard test method for alpha particle radioactivity of water
- Cadieux J.R., Clark S., Fjeld R.A., Reboul S., Sowder A.: Measurement of actinides in environmental samples by photon-electron rejecting alpha liquid scintillation. Nucl. Instr. and Meth. in Phys. Res. A 353, 534-538 (1994)
- D. Lgs. 2 febbraio 2001 n. 31: Attuazione della direttiva 98/93/CE relativa alla qualità delle acque destinate al consumo umano. G. Uff. 52, 3/3/2001
- EEC: Council Directive 98/93/EC of 3 november 1998 on the quality of water intended for human consumption. Off. J. L330, 05/12/98
- EEC: Commission Recommendation of 20 December 2001 on the protection of the public against exposures to radon in drinking water supplies. 2001/928/Euratom
- EPA 00-01: Radiochemical determination of gross alpha and gross beta particle activity in water. Radiochemistry Procedure Manual. USEPA 520/5-84-006
- Horrocks D.L.: Alpha particle energy resolution in a liquid scintillator. Rev. of Scientific Instr. 35 3, 334-340 (1964)
- ISO Guide to the expression of uncertainty in measurement (1992)
- ISO 9696: Measurement of gross alpha activity in non saline water. Thick source method (1992)
- ISO 9697: Measurement of gross beta activity in non saline water. Thick source method (1992)
- ISO 9698: Water quality: Determination of tritium activity concentration – Liquid scintillation counting method (1989)
- Salonen L.: Simultaneous determination of gross alpha and beta in water by liquid scintillation counting. 2^o International Conference on Analytical Chemistry in Nuclear Technology; Karlsruhe 5-9/6/1989
- Salonen L.: Monitoring of natural radionuclides in water by low level liquid scintillation counting. First-Joint Finnish-Soviet Symposium on Radiochemistry; Helsinki 16/5/1990
- Sanchez-Cabeza J.A. et al. : Optimization and calibration of a low-background liquid scintillation counter for the simultaneous determination of alpha and beta emitters in aqueous samples. Liquid Scintillation Spectrometry 1992 edited by J.E. Noakes, F. Schonhofer and H.A. Polach.; Radiocarbon, 43-50 (1993)
- Sanchez-Cabeza J.A. and Pujol Ll.: A rapid method for the simultaneous determination of gross alpha and beta activities in water sample using a low background liquid scintillation counter. Health Physics 68 (5), 674-682 (1995)
- Sgorbati G., Forte M., Gianforma G., Rusconi R., Margini C.: Rilevazione delle concentrazioni di uranio-238 e radio-226 in acque destinate al consumo umano in Lombardia. A.S.L. Milano Città, 1998
- WHO: Guidelines for drinking water quality 2nd Edition Vol. 1 (1993) Vol.2 (1996)
- Yu Yu Fu, Salbu B., Bjornstad H.E., Lien H.: Improvement for α -energy resolution in determination of low level plutonium by liquid scintillation counting. J. of Radioanal. and Nucl. Chem., Letters 145 5, 345-353 (1990)