NATURAL RADIONUCLIDES MEASUREMENTS IN DRINKING WATER BY LIQUID SCINTILLATION COUNTING. METHODS AND RESULTS

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1 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,[1] subsequently enforced through an Italian law.[2] Parameter values have been fixed for Tritium content (100 mBq/l) and total indicative dose (0,1 mSv/year): the Directive points out that the total indicative dose must be evaluated excluding Tritium, ^{40}K, ^{14}C, 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.[3]

Tritium determination follows a well established procedure, standardized by International Standard Organization.[4] 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 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;[5] 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. For tritium and radon determination well established procedures, based on LSC, can also be used.

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. A Quantulus-Wallac scintillation counter has been used in this work. 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.

2 METHODS AND RESULTS

2.1 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 an acidified amount of water is reduced in volume and evaporated to dryness on a steel planchet.[6, 7, 8] 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.[9, 10, 11, 12] 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 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).[11]

Better sensitivities and reduced counting time can be achieved by sample preconcentration; both freeze drying technique and evaporation by heating have been used.[10, 12]

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}Sr/^{90}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; optimum PSA value was found, corresponding to minimum α and β interference.

Alpha interference is the fraction of counts observed in the beta window with respect to the counts observed in alpha and beta windows when a pure alpha emitter is measured; the beta interference is the fraction of counts observed in the alpha window with respect to the counts observed in alpha and beta windows 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.
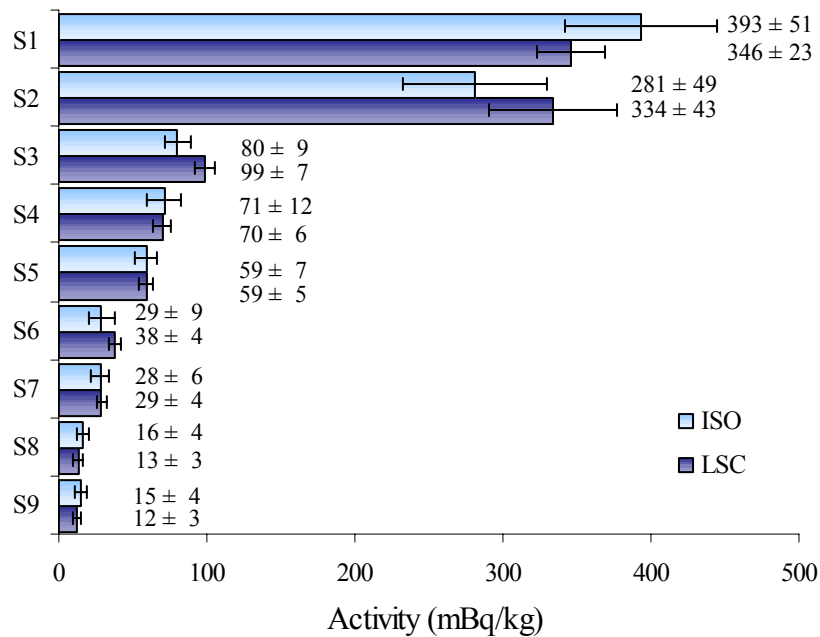
Figure 1 Gross alpha activities comparison
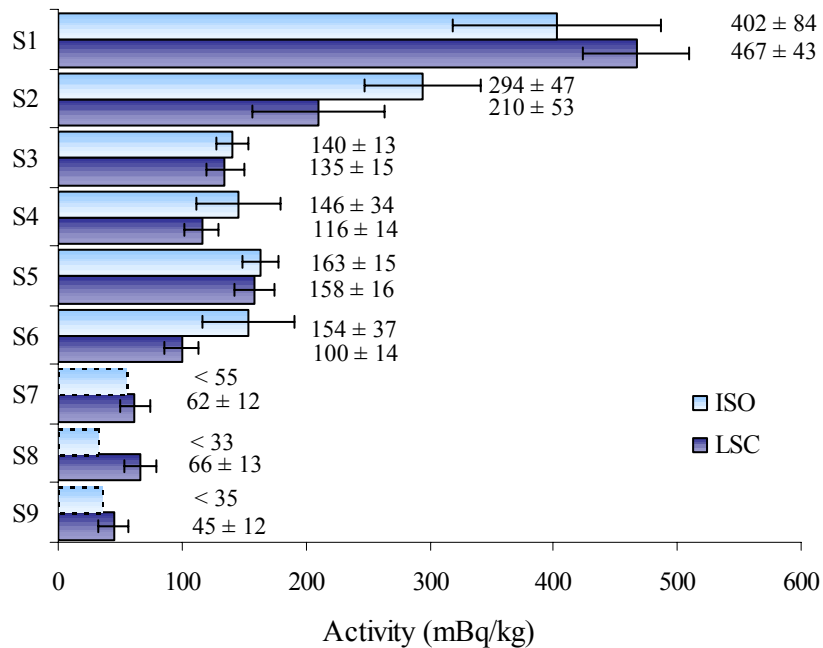
Figure 2 *Gross beta activities comparison*

LSC method was tested by comparing its outcomes with ISO procedure results for 9 water samples, 8 from bottled mineral waters and 1 from Milano tap water (S4) (Figures 1 and 2): a good agreement can be observed.

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 %.

2.2 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}U/^{238}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-etilhexyl-ortophosphoric 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.[13]

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) respectively used by others researchers[14, 15], the third realized in our laboratory (C3), the fourth (C4) 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[14]. 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) (Table 1).

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 (Table 2).

Table 1 *Composition of 1 liter extractive cocktail*

Cocktail	C1	C2	C3	C4* (Optiscint)
Solvent	Toluene	Xilene	Toluene	Diisopropil naphtalene
Fluo	PPO 4 g Bis-MSB 0,5 g POPOP 0,05 g	PBBO 4 g	PBBO 4 g	PPO Bis-MSB
Naphtalene	35 g	180 g	35 g	-
HDEHP	50 g	50 g	50 g	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

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 Table 2. 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.
Resolution was calculated by the Horrocks formula.[16]

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 HNO_3 14 M in order to avoid uranium losses, then slowly evaporated on an hot plate to 100 ml; the final HNO_3 concentration is 0,7 M. Uranium was finally extracted by the selected procedure.

Table 2 *Extractive cocktails features*

| 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
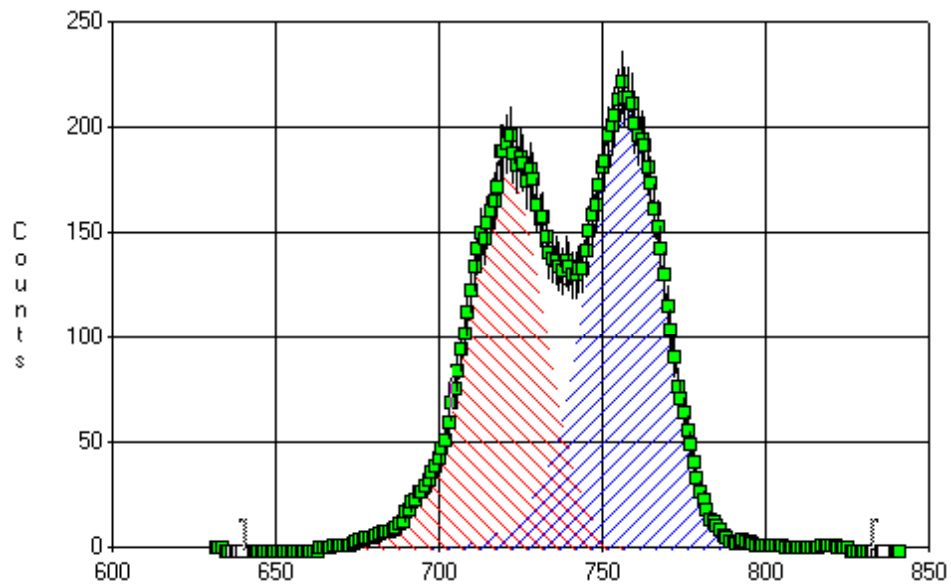
Figure 3: ^{238}U and ^{234}U $\alpha-$ peaks deconvolution

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 (Figure 3). ^{235}U contribution to total uranium was estimated to be lower than 2.5%, and was neglected when performing alpha spectra 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 Figures 4 and 5.
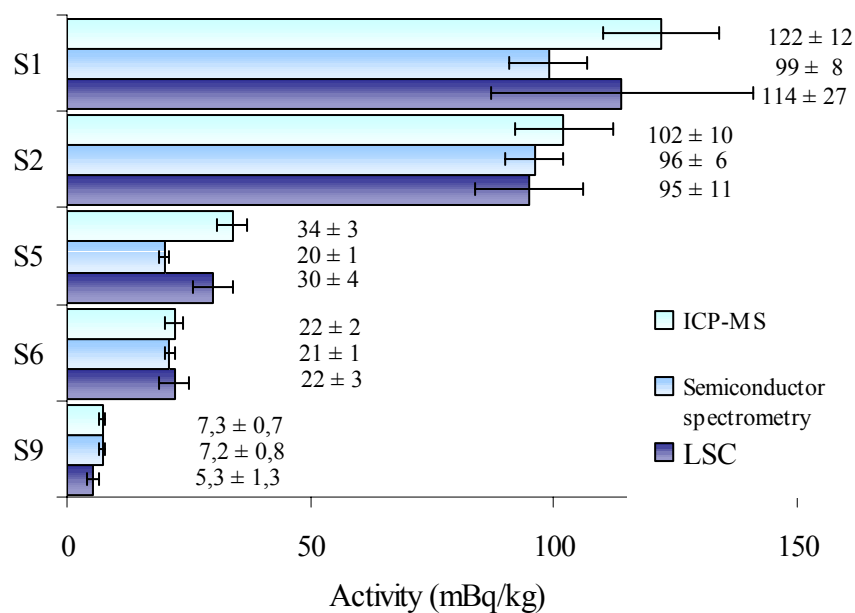
Figure 4: ^{238}U activities comparison
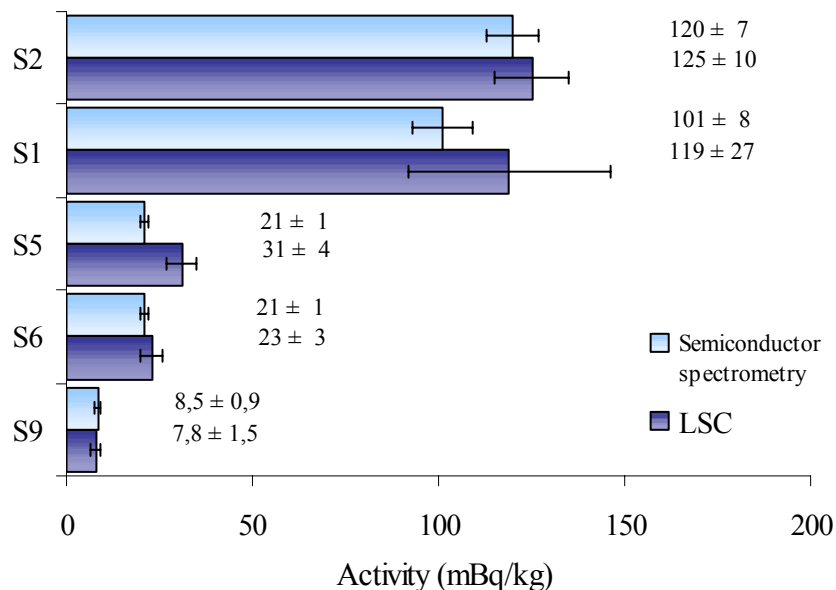
Figure 5: ^{234}U *activities comparison*

2.3 Tritium

ISO 9698 method was used for tritium measurement. Water samples were distilled with a Vigreux apparatus in the presence of sodium carbonate and sodium tiosulphate. 8 ml of distilled water were then transferred in a teflon coated polyethylene vial, mixed to 12 ml of scintillation cocktail (Optiphase Hisafe 3 – Wallac) and stored for one day in the liquid scintillation counter sample holder to allow full decay of chemi-luminescence and photo-luminescence.

Detection efficiency was determined by measuring tritium standards (tritiated fructose pellets – Wallac) of different activity. Measurements performed at different times showed no change in efficiency, so internal standard technique was not used. The stability of instrumental response was checked in general periodic controls. One hour counting was considered enough to achieve the desired sensitivity levels of 5 Bq/l vs. a 100 Bq/l recommended value. (EEC Counc. Dir. 98/93/EC).

2.4 Radon

Radon measurements were realized by the widely used double-phase method.[17, 18, 19] According to this procedure an unaerated water sample is injected in a scintillation vial containing a water-immiscible scintillation cocktail. The favorable distribution coefficient causes the selective absorption of radon in the organic phase. After three hours the secular isotopic equilibrium between radon and short term daughters is attained and the sample can be counted.

Since in our experimental conditions it was not possible to prepare samples for scintillation counting straight on the field, we collected water in glass bottles.[20] A plastic tube was attached to the faucet and inserted in the bottle; a slow flux of water was maintained for about 10 minutes till no bubbles were present in the tube, leaving the water to spill over the bottle top. The bottle was tightly sealed, carried to the laboratory and analyzed within 24 hours.

Table 3 *Radon cocktails features*

Scintillation cocktail	Resolution %			Efficiency (%) average	Background cpm
	^{222}Rn	^{218}Po	^{214}Po		
Optifluor O	not resolved		1,58	415 +/- 20	2,62 +/- 0,05
NEF	3,01	2,92	1,71	475 +/- 25	2,25 +/- 0,05
Optiscint	0,98	0,96	0,44	430 +/- 20	2,26 +/- 0,05

Table 4 *Radon activities in directly measured and transported samples*

Container	Sampling	1° meas. Bq/kg	2° meas. Bq/kg	3° meas. Bq/kg	Mean value Bq/kg	Std. Dev. of mean value
None	immediate	5,82 ± 0,91	5,83 ± 0,92	5,57 ± 0,88	**5,74**	0,17
Glass	24 h	5,13 ± 0,88	4,93 ± 0,86	5,58 ± 0,94	**5,21**	0,38
Polyethylene	24 h	4,97 ± 0,85	4,39 ± 0,78	4,45 ± 0,78	**4,60**	0,37

Once in the laboratory, 10 ml of sample were drawn by a gas-tight syringe and delivered in a vial preloaded with 10 ml of scintillation cocktail and tared with an analytical balance. The exact sample amount was then determined by weighing.

Previous studies showed that teflon coated polyethylene vials were tight enough for radon especially when an organic solvent is present.[21, 22, 23]

Some different lipophilic scintillation cocktails are available; we compared performances of three of them, namely Optifluor O (Packard), Optiscint (Wallac) and NEF 957A (Packard). Results are reported in Table 3.Resolution was calculated by the the Horrocks formula.[16]

NEF cocktail has excellent counting properties (efficiency and background) and gives a quick and sharp phase separation. Optiscint adds some other useful characteristics to good detection features: like all di-isopropyl naphtalene (DIN) based cocktails, it exhibits low permeation through plastic vials, it is virtually odorless and gives little disposal problems because of its biodegradability; for these reasons it has been chosen for the present work.

Overall efficiency was calculated by measuring a vial filled with 10 ml of a ^{226}Ra standard solution and lipophilic cocktail after the radon buildup was complete (20 days) (ASTM 5072-98). Efficiency was evaluated as the average value of four different standards with activity ranging from 0,02 to 1 Bq.

It is well known that a main source of inaccuracy comes from radon leakage that may occur when sample transportation is involved[20, 24]. Analytical results of direct sampling and vial filling were compared to those obtained by collecting water in glass or plastic bottles, transporting them by car and analyzing them after 24 hours.

Results in Table 4 show an appreciable radon leakage in polyethylene bottle while the decrease of radon concentration in the glass bottle is smaller than experimental error.

2.5 Radium-226 and Radium-228

Radium isotopes determination is important because of their radiotoxicity and subsequently high contribution to committed dose.

Usually the most diffused isotope is alpha emitter ^{226}Ra, but relevant amounts of beta emitter ^{228}Ra and, sometimes, of alpha emitter ^{224}Ra can also be present.

LSC based techniques can be successfully applied in this field. Two strategies are possible: 1) radium purification and homogeneous phase counting; 2) sample preconcentration and heterogeneous phase counting.

The first approach allows in principle the measurement of all radium isotopes.

Radium purification can be accomplished with different methods: barium sulphate coprecipitation, selective scintillation cocktail extraction, filtration on selective membranes.[25, 26, 27, 28, 29, 30, 31]

The second method consists in an indirect measurement of ^{226}Ra alone through its short term decay products. As in radon measurement (see 2.4), the water sample is transferred to a scintillation vial preloaded with a water immiscible cocktail. ^{222}Rn produced by ^{226}Ra is absorbed in the organic phase and counted after the isotopic equilibrium is attained. The water sample can be preconcentrated by various techniques or analyzed without any previous treatment.[32, 33, 34, 35]

For ^{226}Ra measurement, in order to minimize pretreatment time the indirect method based on radon measurement was preferred for our routine controls.

An aliquot of the 10 fold preconcentrated water sample, previously prepared for gross alpha and beta measurement, was used for this purpose: 10 ml of preconcentrated sample were transferred in a teflon coated polyethylene vial and 10 ml of water immiscible cocktail Optiscint (Wallac) was added. The sample was measured after 21 days ingrowth without shaking the vial: radon diffusion was demonstrated to be quick enough to cause no differences between shaked and non shaked samples (< 3%). All vials were kept at constant temperature in the counter sample holder for the whole ingrowth period.

The method was tested on two water samples only. All other bottled water samples, previously measured by emanometry,[36] showed a radium content lower than minimum detectable activity (Table 5).

A preliminary work has been done to identify a method suitable for the contemporary measurement of ^{226}Ra and ^{228}Ra.

Previous studies showed that most Lombardia waters exhibit ^{226}Ra concentrations between 0,2 and 10 mBq/l.[36] Routine controls in Milano laboratory by γ spectrometry on resin concentrated 200 l tap water samples display ^{228}Ra medium concentrations of 1,2 mBq/l.

To increase the sensitivity of LSC analysis to a sufficient extent, preconcentration of at least 2 liters samples is necessary. To this purpose three different pretreatment methods have been compared:

   a. Radium absorption by lead rhodizonate supported on charcoal;[38]
   b. Filtration on Radium Rad Empore disks;[30, 31]
   c. Selective absorption on cationic resins from a pH 5,5 EDTA (ethylen diammino tetra acetic acid) solution.

First tests gave high yields (near 100%) for a 2 liters spiked water preconcentration by using the three methods. The first two are not selective towards lead, so ^{210}Pb is observed in concentrated samples. The third one allowed isolation of radium isotopes only after pH 10 EDTA elution.

Concentrated samples were then purified by chromatography on a small cationic resin like in method c. and counted by LSC. α/β discrimination was also applied to achieve simultaneous ^{226}Ra and ^{228}Ra determination.

Table 5 *^{226}Ra activities comparison*

Water sample	LSC mBq/l	Emanometry mBq/l
Mineral water S1	188 ± 24	200 ± 40
Mineral water S2	104 ± 16	140 ± 28

Table 6 *Test methods performances*; * *combined efficiency (extraction + counting)*

	Sample volume (g)	Meas. time (min)	Measure window (channels)	Spectrum	Background (cpm)	Efficiency (%)	LLD (mBq/kg)
Gross α	80	1000	500-1000	α	0,099 ± 0,007	111 ± 2	**8**
Gross β	80	1000	500-1000	β	0,960 ± 0,020	73 ± 1	**24**
Total U	1000	1000	600-800	α	0,087 ± 0,004	98 ± 5 *	**0,4**
Tritium	8	60	1-250	α+β	1,8 ± 0,1	25 ± 1	**5000**
^{222}Rn	10	60	100-1000	α+β	2,5 ± 0,1	428 ± 20	**250**
^{226}Ra	100	1000	100-1000	α+β	2,5 ± 0,1	428 ± 20	**14**

2.6 Test methods summary

Table 6 resumes the main features of the above described test methods. Teflon coated polyethylene vials were always used.

Background samples were prepared in the following way:

- Gross α/β: 8 ml of radon free HNO_3 solution (pH 1.5) + 12 ml of Optiphase Hisafe 3
- Uranium: 20 ml of argon fluxed C2 cocktail
- Tritium: 8 ml of distilled dead water + 12 ml of Optiphase Hisafe 3
- ^{222}Rn and ^{226}Ra: 10 ml of boiled ultrapure (MilliQ) water + 10 ml Optiscint

Measurement uncertainty was evaluated according to ISO Guide to the Expression of Uncertainty in Measurement.[37] Uncertainty on sample amounts and 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).

2.7 Applications to Environmental Samples

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

Only some representative examples are reported in this work (Figures 6-7 and Tables 7-8). Tap water samples were drawn in 13 of the largest Lombardia centers; gross alpha and beta activity and uranium isotope concentration were measured. Potassium chemical analysis was performed by ionic chromatography, ^{40}K activity was calculated taking into account its natural abundance (30,3 mBq per mg of K).

Southern Lombardia cities (Pavia, Cremona, Mantova) exhibited the lowest radioactivity concentrations, while northern (Sondrio, Lecco, Varese, Como) and north-eastern ones (Brescia, Bergamo) displayed medium-low levels. Higher values were found in Milano and surrounding areas (Parabiago, Lodi, Monza). Northern Lombardia is an alpine district; previous works showed a relevant dishomogeneity for both tap and bottled water produced in that area (52 samples were analyzed).[36] Thus samples collected in the main city should not be considered representative of the whole district.
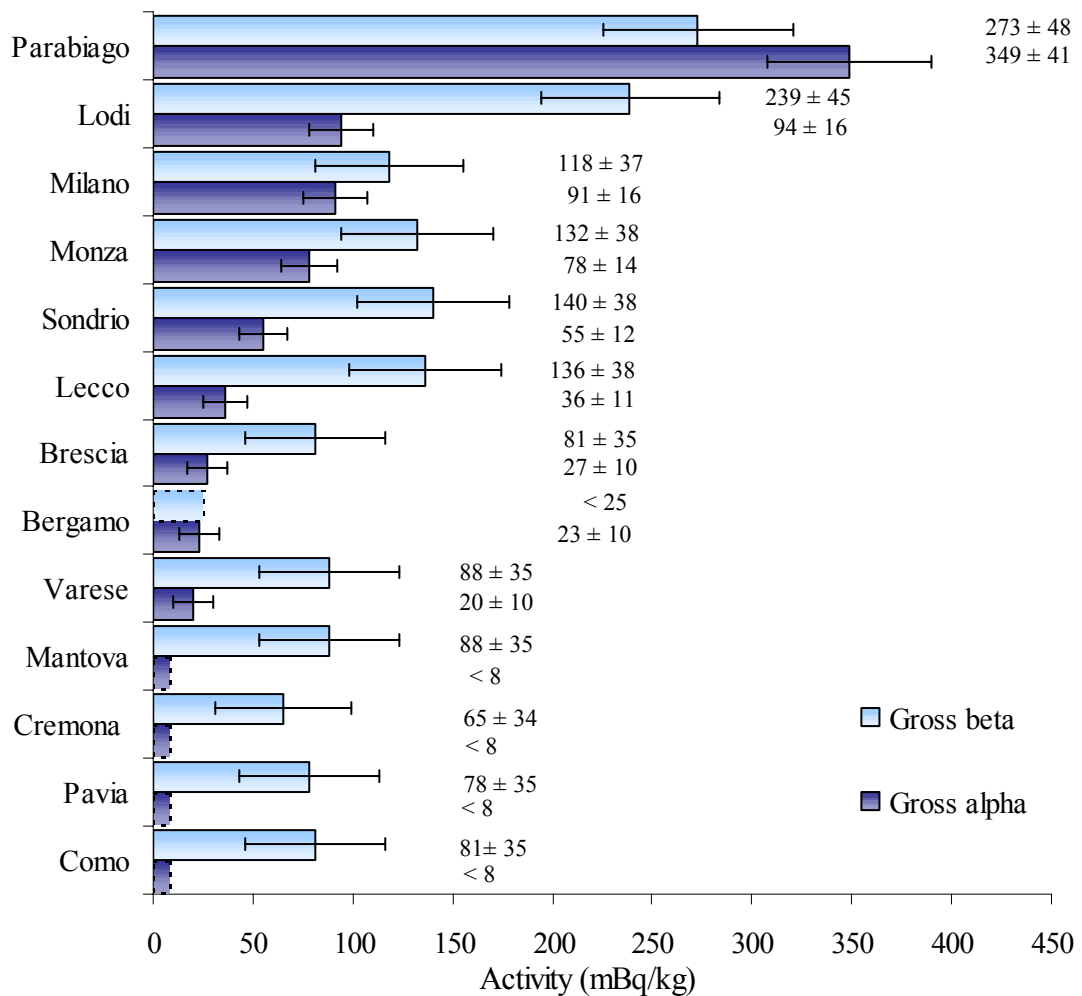
**Figure 6:** *Tap waters results – Alpha and beta activities*

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 the wells depths; further analysis are still in progress.

Results in Figures 6 and 7 show that α activity in tap water is mainly due to uranium isotopes: $^{234}U/^{238}U$ 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 (Table 7), 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.

Bottled mineral waters are mainly produced in northern and north-eastern part of Lombardia. Two of them, Mineral Water S1 and S2 exhibited high gross α activities which can not be entirely attributed to uranium isotopes (Table 8). In such cases ^{226}Ra measurements give concentration values consistent with the encountered difference (Table 5). This situation is rather common in water samples drawn in small towns of alpine districts.[36]

Table 7 *Gross beta and Potassium content; * after subtracting* ^{40}K *activity*

Tap water sample (departement)	Gross β mBq/kg	^{40}K mBq/kg	Residual Gross β* mBq/kg
Parabiago	273 ± 48	46 ± 2	227 ± 48
Lodi	239 ± 45	100 ± 5	139 ± 45
Milano	118 ± 37	46 ± 2	72 ± 37
Monza	132 ± 38	46 ± 2	86 ± 38
Sondrio	140 ± 38	76 ± 4	64 ± 38
Lecco	136 ± 38	100 ± 5	36 ± 38
Brescia	81 ± 35	30 ± 2	51 ± 35
Bergamo	< 25	7,0 ± 0,3	-
Varese	88 ± 35	61 ± 3	27 ± 35
Como	81 ± 35	42 ± 2	39 ± 35
Pavia	78 ± 35	48 ± 2	30 ± 35
Cremona	65 ± 34	30 ± 2	35 ± 34
Mantova	88 ± 35	64 ± 3	24 ± 35
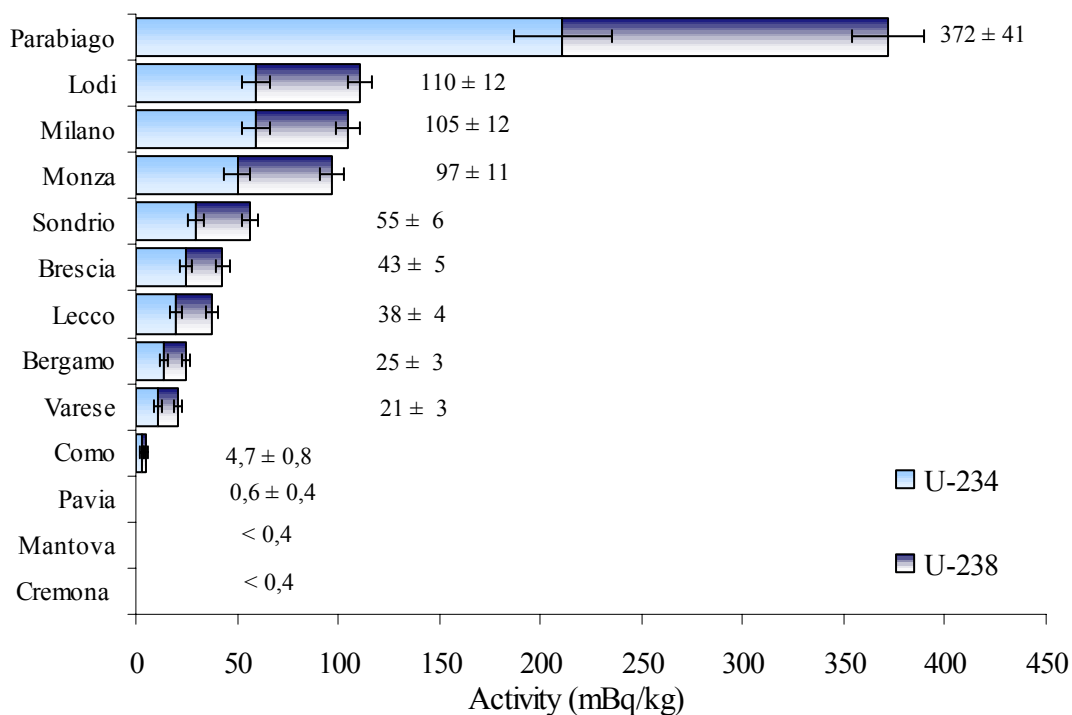
Figure 7: *Tap waters results-Total Uranium activities*

Table 8 *Bottled waters results*

Bottled water sample	Gross α mBq/kg	U total mBq/kg	^{234}U mBq/kg	^{238}U mBq/kg	Gross β mBq/kg	^{40}K mBq/kg
Min. water S1	346 ± 23	233 ± 29	119 ± 27	114 ± 27	467 ± 43	82 ± 4
Min. water S2	334 ± 43	220 ± 24	125 ± 10	95 ± 11	210 ± 53	48 ± 2
Min. water S5	59 ± 5	61 ± 7	31 ± 4	30 ± 4	158 ± 16	88 ± 4
Min. water S6	38 ± 4	44 ± 5	23 ± 3	22 ± 3	100 ± 14	64 ± 3
Min. water S9	12 ± 3	13 ± 2	7,8 ± 1,5	5,3 ± 1,3	45 ± 12	24 ± 1

Tritium and radon concentration values are not reported here in detail. Up to now tritium measurement always gave results lower than LLD (5 Bq/kg). Radon determination displayed high variability; values from 5 to 15 Bq/kg have been measured in Milano and surrounding area. Particular attention has to be paid to the presence of treatment water plants (by active charcoal for instance) which can strongly influence radon concentration.

3 CONCLUSIONS AND FURTHER DEVELOPMENTS

Liquid scintillation has proven to be a quick, versatile and accurate tool for radiometric investigation both on surface and on drinking waters. Thanks to high detection efficiency and low instrument background, alpha and beta emitting isotope activities can be measured with good sensitivities.

Small differences in sample chemical properties (e.g. pH value, amount of oxygen present, etc.) can modify scintillation yields and, as a consequence, measurement outcomes. Great care must be paid in defining sample treatment and counting procedures: in order to maintain control of relevant parameters (e.g. quenching value, chemiluminescence intensity, etc.), suitable validation criteria should be identified.

World Health Organization proposes derived limits for gross alpha and beta activities; compliance to these limits should ensure compliance to committed dose value enforced by Italian law. In order to check full compliance to Italian law requirements, the following analytical scheme may be adopted:

a. Tritium (LSC), radon (LSC), potassium (Ionic Chromatography) measurements
b. Sample preconcentration – gross α and β measurements (LSC)
c. Sample preconcentration – uranium measurements (Extraction + LSC)
d. If gross α > 100 mBq/kg or if α > total U, ^{226}Ra measurements (^{222}Rn ingrowth from preconcentrated solution b + LSC)

Preliminary results on Lombardia tap waters show the existence of sites where water radionuclide content exceed WHO proposed values; this is generally due to high uranium isotopes concentrations.

Previous works showed that,[36] in specific areas, a relevant dose contribution is due to radium isotopes for which dose conversion factors are higher than uranium ones. In some of these critical situations WHO proposed derived limits are not exceeded but committed dose is higher than 0.1 mSv/y with special regard to group age < 1 year.

Pre-existent data on water radionuclide content are incomplete, and often do not consider ^{228}Ra contribution to committed dose. It is therefore desirable to perform a full preliminary screening on Lombardia tap waters, in order to check suitability of WHO proposed derived limits to our local situation.

Therefore in order to:
- check adequacy of WHO gross alpha and beta derived limits to our situation
- identify correlations between waters radioactivity content and aquifers characteristics to identify critical areas

we are planning to apply the above described methods to a monitoring program on the whole Lombardia area.

References

1 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.

2 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.

3 EEC, Commission Recommendation of 20 December 2001 on the protection of the public against exposures to radon in drinking water supplies. 2001/928/Euratom

4 ISO 9698, Water quality: Determination of tritium activity concentration – Liquid scintillation counting method -1989

5 WHO, Guidelines for drinking water quality 2nd Edition Vol. 1 (1993) Vol.2 (1996).

6 ISO 9696, Measurement of gross alpha activity in non saline water. Thick source method - 1992.

7 ISO 9697, Measurement of gross beta activity in non saline water. Thick source method - 1992.

8 EPA 00-0, Radiochemical determination of gross alpha and gross beta particle activity in water. *Radiochemistry Procedure Manual*. USEPA 520/5-84-006.

9 L. Salonen, *2° International Conference on Analytical Chemistry in Nuclear Technology*; Karlsruhe 5-9/6/1989

10 L. Salonen, *First-Joint Finnish-Soviet Symposium on Radiochemistry*, Helsinki 16/5/1990.

11 J.A. Sanchez-Cabeza et al., *Radiocarbon*, 1993, 43.

12 J.A.Sanchez-Cabeza and L. Pujol, counter. *Health Physics*, 1995, **68 (5),** 674.

13 M. Abuzeida, B.H. Arebi, Y.A. Zolatarev, N.A. Komarov, *J. of Radioanal. and Nucl. Chem., Articles,* 1987, **116**, 285.

14 Yu-fu Yu, B. Salbu, H.E. Bjornstad, H. Lien, *J. of Radioanal. Nucl. Chem. Letters*, 1990, **145**, 345.

15 J.R.Cadieux, S. Clark, R.A. Fjeld, S. Reboul, A. Sowder, *Nucl. Instr. and Meth. in Phis. Res.*, 1994, **A353**, 534.

16 D.L. Horrocks,. *the Review of Scientific Instr.*, 1964, **35**, 334.

17 H.M. Prichard, T.F. Gesell, *Health Physics*, 1977, **33**, 577.

18 ASTM D 5072-98, Standard test method for radon in drinking water.

19 E. Vitz, *Health Physics*, 1991, **60**, 817.

20 N. Kinner et al., *Env. Science and Techn.,* 1991, **25**, 1165.

21 P. Belloni al., *7th International Symposium on Environmental Radiochemical Analysis*, Bournemouth, Sept. 1994.

22 P. Belloni, G. Ingrao, G.P. Santaroni, R. Vasselli, Urbino, giugno 1995.

23 F. Schönofer, technical sheet, Wallac Oy - Sept 1989.

24 J.H. Hightower, J.E. Watson, *Health Physics,* 1995, **69**, 219.

25 S. Chalupnik, J.M. Lebecka, *Radiocarbon,* 1993, 397.

26 K. Sato, T. Hashimoto, *J. of Environm. Radioact.,* 2000, **48**, 247.

27 Yong-Jae Kim, Chang-Kyu Kim, Jong-In Lee, *Appl. Rad. Isotopes,* 2001, **54**, 275.

28 S. Möbius et al., *Radiocarbon,* 1993, 413.

29 M.P. Blanco Rodriguez, F.Vera Tomè, J.C. Lozano, V. Gomez Escobar, *Appl. Rad. Isotopes,* 2000, **52**, 705.

30 S.Möbius, K.Kamolchote, T.Rakotoarisoa, *Advances in Liquid Scintillation Spectrometry,* Karlsruhe, May 2001.

31 F. Schönofer, *Radioact. Radiochem.,* 2001, **12**, 33.

32 Kuo et al., *Appl. Rad. Isotopes*, 1997, **48**, 1245.

33 H. Higuchi et al., *Anal. Chem.*, 1984, **56**, 761.

34 M. Roveri, Enel CRTN, Servizio Ambiente, E0/87/01/MI −1987.

35 F. Schönofer, *Analyst,* 1989, **114**, 1345.

36 G. Sgorbati, M. Forte, G. Gianforma, R. Rusconi, C. Margini, A.S.L. Milano Città − 1998.

37 ISO Guide to the expression of uncertainty in measurement -1992

38 M.T. Valentini-Ganzerli, L. Maggi, V. Crespi Caramella, G. Premoli, *J. Radioanal. Nucl. Chem.*, 1997, **221**, 109.