

ASSESSMENT OF DRINKING WATER RADIOACTIVITY CONTENT BY LIQUID SCINTILLATION COUNTING: SET UP OF HIGH SENSITIVITY AND EMERGENCY PROCEDURES

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Abstract

In our institute different procedures have been developed to measure the radioactivity content of drinking water both in normal and in emergency situations, as those arising from accidental and terroristic events. A single radiometric technique, namely low level liquid scintillation counting (LSC), has been used. In emergency situations, a gross activity screening is carried out without any sample treatment by a single and quick liquid scintillation counting. Alpha and beta activities can be measured in more than one hundred samples per day with sensitivities of few Bq/kg. Higher sensitivity gross alpha and beta, uranium and radium measurements can be performed on water samples after specific sample treatments; the sequential method proposed is designed in such a way that the same water sample can be used in all the stages, with slight modifications. Reduced equipment requirements and relative readiness of radiochemical procedures make LSC an attractive technique which can be applied also by laboratories lacking specific radiochemistry facilities and experience.

1. INTRODUCTION

Drinking and fresh waters usually contain many natural radionuclides: tritium, radon, radium and uranium isotopes, etc. Their concentrations are highly variable since they depend on the nature of the aquifer and namely the prevailing lithology and the presence of air in it. Radon occurrence is not due to rocks erosion but mainly to permeation from inner soil layers, so its concentration is not normally related to other natural series radionuclides.

Concern about radioactivity content of water intended for human consumption has been brought to public attention by recent international regulations (see Table I):

- EU Council Directive 98/83/EC requires the member states to monitor the concentrations of radionuclides in public drinking water [1] and fixes parameter values for tritium content and indicative dose.
- For practical purposes, the World Health Organization guidelines recommends activity concentrations for gross alpha and for gross beta activity [2];
- Commission Recommendation 2001/928/Euratom proposes maximum concentration values for Radon and its long lived daughters [3];
- WHO (1998) guidelines [4], suggest a maximum uranium concentration of 2 $\mu\text{g/L}$ in drinking water. This value takes into account mainly chemical toxicity effects, since they are generally considered higher than radiological ones as far as uranium is concerned;
- single radionuclides reference values are being discussed by EU at present. They shall be reported in the Annex 2 to the EU Council Directive 98/83/EC, not issued yet.

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In case of radiological emergency, European Union fixes maximum permitted levels of radioactive contamination of foodstuffs; maximum reference levels are proposed separately for alpha and beta emitting artificial radionuclides in drinking water [5].

TABLE I. REFERENCE VALUES FOR RADIOACTIVITY CONCENTRATION IN DRINKING WATER

Reference values				
Normal situations				
EU, 1998	[1]	Tritium:	100 Bq/L	Indicative Dose: 0.1 mSv/y
Euratom, 2001	[3]	Radon 222 :	100 Bq/L	Polonium 210: 0.1 Bq/L Lead 210: 0.2 Bq/L
WHO, 1998	[2-4]	Gross alpha:	0.1 Bq/L	Gross beta: 1 Bq/L Uranium: 2 µg/L
Emergency situations				
Euratom, 1989	[5]	Gross alpha :	20 Bq/L	Gross beta: 125 Bq/L
		(transuranic elements)		(strontium isotopes)

In recent years an additional concern arose in relation to international political problems. The widespread use of depleted uranium (DU) ammunition may have caused ground waters and fresh waters contamination. Moreover the risk of terrorism acts involving voluntary radiocontamination of water resources or the use of “dirty bombs” is considered not negligible by public authorities.

Assessment of drinking water radioactivity content is therefore a main topic, both in normal and in emergency situations. Thus laboratories should be able to carry on all required measurements, with reduced equipment requirements and relative readiness of radiochemical procedures.

2. MEASUREMENT TECHNIQUE AND METHODS

In our laboratory both emergency and high sensitivity measurements have been performed by liquid scintillation counting (LSC). This technique involves mixing the sample with a proper detection cocktail to be counted in a liquid scintillator. Under these conditions, problems relating to sample self-absorption and attenuation of particles by detector windows are completely avoided. Detection efficiencies approach 100 percent for alpha particles and vary from about 20 to 100 percent for beta particles with different endpoint energies; each natural and artificial radionuclide can therefore be detected. Furthermore, alpha and beta events can be simultaneously recorded in separated counting channels by pulse shape analysis (PSA), which is based on the difference between the delayed component of their fluorescent decay [6].

Ultra low-level LSC coupled to proper sample treatment and extractive techniques allows rapid and simple determination of many radiometric parameters, e.g. gross alpha and beta activity, uranium, radium, radon and tritium content.

2.1. Instrumental setup

An ultra-low level Wallac Quantulus 1220 liquid scintillation counter has been used for all measurements. This instrument is specifically designed for the determination of very low level activities, using both an anticoincidence active and a passive shield and low background construction materials. It also includes a pulse shape analyzer which separates pulses produced by alpha and beta radiations into different spectra. An automatic sample changer allows to measure up to 60 samples

sequentially.

For each selected procedure, LS counter PSA parameter, background, efficiency and minimum detectable activity (MDA) were measured as follows:

- PSA parameter: an alpha (^{241}Am) and a beta emitter ($^{90}\text{Sr}/^{90}\text{Y}$) are separately measured and the interference between both spectra was determined for different PSA values; the best PSA parameter is determined by minimizing the sum of alpha and beta interference. Because quenching can significantly alter the pulse shape and therefore affect the pulse discrimination effectiveness, strict control of quenching values is always required. All subsequent measurements must be performed by using the optimum PSA values previously defined; quenching affecting factors, as pH of the sample and presence of dissolved oxygen, must be controlled;
- background: background count rate was determined by measuring dead water samples and scintillation cocktail in the same proportions and conditions as real samples. Background measurements should be repeated in order to take account of its statistical and seasonal fluctuations; mean count rate and standard deviation are then used in calculations;
- efficiency: detection efficiency is evaluated by measuring solutions traced with ^{241}Am and $^{90}\text{Sr}/^{90}\text{Y}$ with activity concentrations and chemical composition similar to those of real samples. Counting windows must be properly set: the alpha counting window should be wide enough to take into account all alpha events; the beta counting window depends on the energy of the radionuclide under investigation and a lower threshold may be fixed to discard lower energy events;
- MDA: the minimum detectable activity was evaluated using Currie formula [7]:

$$\text{MDA (Bq/kg)} = L_d(\varepsilon TQ)^{-1}$$

with

$$L_d (\text{counts}) = 2.71 + 4.65 (BT)^{-1/2}$$

where

- ε is the detection efficiency,
- T is the counting time (s),
- Q is the sample quantity (kg),
- B is the background count rate (s^{-1})

2.2. Methods

2.2.1. Emergency procedure

In emergency situations many samples have to be analysed quickly and with sufficient sensitivities; all artificial radionuclides should be detected, and detection limits should be lower than reference levels fixed for countermeasures adoption. Therefore, in this case, LSC is employed as a screening technique in order to identify samples containing more radioactivity than the expected one (on the basis of natural radionuclides concentration).

Background in liquid scintillation is more significant than in many others radiometric techniques, due to specific interfering chemical-physical phenomena (e.g. photo- and chemiluminescence). They can produce signals exceeding those due to the radioactive decay of the sample. Many others factors contribute to background counts, as phototubes electronic noise, cosmic radiation and so on. As a result, background counts distribution will not necessarily be a normal one, in particular when measurement times are very short. The behaviour of background counts should be re-analysed and the actual distribution of data should be determined.

In emergency situations counting time must be kept as low as possible, so that many samples per day can be analysed. Notwithstanding detection limits are higher than natural radioactivity content of most drinking waters, MDA values useful for radioprotection purposes can still be achieved.

Furthermore, a decision limit must be arrived at, based on knowledge of the background count rates and the confidence that one wishes to place on the outcome. For radioprotection purposes, the probability of getting false-negative response should be kept as low as possible.

2.2.1.1. Emergency sample preparation

The gross activity screening is carried out without any sample treatment by a single and quick (10 minutes) liquid scintillation counting. 8 ml of water sample are transferred in a 20 ml teflon coated polyethylene vial and vigorously shaken in order to assure radon elimination. Afterwards 12 ml of PerkinElmer Optiphase Hisafe 3 cocktail are added and sample is shaken again. Sample is measured after a 3 hours rest in the dark to allow a decrease of photo- and chemi-luminescence and the decay of short lived radon progeny.

2.2.1.2. Emergency decision limits

Background count rate was determined measuring 50 samples of different tap waters prepared and analyzed as described. In this situation counts are almost completely due to instrumental background; the distribution of experimental data has been analyzed both for alpha and for beta spectral components.

The distribution of alpha background counts is not normal (test Shapiro-Wilk: 0.881, $p < 0.01$), even if mean and median values are very similar. An unbiased estimator for the central tendency can be obtained after removing values falling in distribution tails, and a new mean value B_α is calculated as the 5% trimmed mean. A 99.9% confidence interval can then be defined, centered in B_α and whose half-width is equal to by 3.5 times the standard error s_{B_α} of the full set of data.

The distribution of beta background counts is normal, and 99.9% confidence interval centered in mean value B_β and with half-width $3.5s_{B_\beta}$ has been calculated as previously described.

In emergency situations each sample is measured once; its gross counts G_α and G_β are recorded, and their percent standard errors $s_{G_\alpha}\%$ and $s_{G_\beta}\%$ are supposed to be the same previously determined for background counts distributions.

The conditions are defined as follows (see Table II):

TABLE II. EMERGENCY DECISION CRITERIA

Condition	Comments
- $G_\alpha < B_\alpha$ ($G_\beta < B_\beta$)	sample data is not significantly different from background. No further investigation is required
- $B_\alpha < G_\alpha < B_\alpha + 3.5s_{G_\alpha} = DL_\alpha$ ($B_\beta < G_\beta < B_\beta + 3.5s_{G_\beta} = DL_\beta$)	there is some indication that sample data exceeds background counts, but result needs to be confirmed; the sample should be analysed with better sensitivity, e.g. increasing counting time or by sample preconcentration
- $G_\alpha > DL_\alpha$ ($G_\beta > DL_\beta$)	sample data is significantly different from background. Further investigation is required to identify radionuclides actually present in the sample. Adoption of proper countermeasures should be considered

Radioactivity concentration values corresponding to the above decision limits are 0.7 Bq/L for gross alpha and 8 Bq/L for gross beta activity, which are much lower than maximum permitted levels of drinking water contamination in emergency situations (20 Bq/L for alpha emitters and 125 Bq/L for beta emitters, with special regard to strontium isotopes). For practical purposes higher decision limits were adopted, i.e. $DL_\alpha = 10$ counts (equivalent to 2 Bq/L of alpha emitters) and $DL_\beta = 60$ counts (equivalent to 12.5 Bq/L of beta emitters).

More details of counting setup are given below (see Table III):

TABLE III. EMERGENCY COUNTING SETUP AND DECISION LIMITS

Acquisition parameters	Alpha	Beta
Counting window (channels)	500-1000	100-1000
Efficiency	(1.02 ± 0.04)%	(1.05 ± 0.03)%
Background counts		
mean	2.34	36.34
median	2.00	36.00
5% trimmed mean	2.20	-
standard error	0.32	0.93
Statistical decision limit (counts)	3.30 (0.7 Bq/L ^a)	39.60 (8 Bq/L ^a)
Working decision limit (counts)	10 (2 Bq/L ^a)	60 (12.5 Bq/L ^a)

^a Corresponding activity concentration.

2.2.2. High sensitivity procedures

In normal situations drinking waters monitoring aims to verify compliance to EU Council Directive 98/83/EC, with special regard to tritium content and indicative dose. Tritium determination follows a well established procedure, standardized by International Standard Organization [8]. On the contrary, indicative dose evaluation requires more specific and cumbersome procedures for the measurement of radioactivity content, with special regard to natural series radionuclides.

WHO guidelines propose a derived parameter based on gross alpha and beta activity. If 0.1 Bq/L of gross alpha activity or 1 Bq/L of gross beta activity are exceeded, further investigations and single radionuclides determinations (with special regards to radium and uranium isotopes) are needed.

In a survey of 80 sites in our region, Lombardia, run during the last two years, the average gross alpha activity concentration was 108 ± 9 mBq/kg, with single values ranging from 18 to 410 mBq/kg. Alpha activity was mostly due to uranium isotopes contribution, while ²²⁶Ra concentrations are lower by 1-2 orders of magnitudes [9-10]; the average gross beta concentration was 91 ± 7 mBq/kg, with single values ranging from 24 to 326 mBq/kg. Gross alpha activity was higher than 0.1 Bq/kg WHO guideline value in 44% of cases, while gross beta was always lower than 1 Bq/kg WHO proposed guideline value; therefore no specific procedures for beta emitting nuclides have been considered.

The proposed sequential procedure has been designed to minimize sample pretreatment (i.e. the same pretreatment is used for both gross alpha/beta and ²²⁶Ra analysis). If reference values at any stage are exceeded the next analytical step is performed (see Figure1).

All procedures are described in detail elsewhere [11]. A summary is given below.

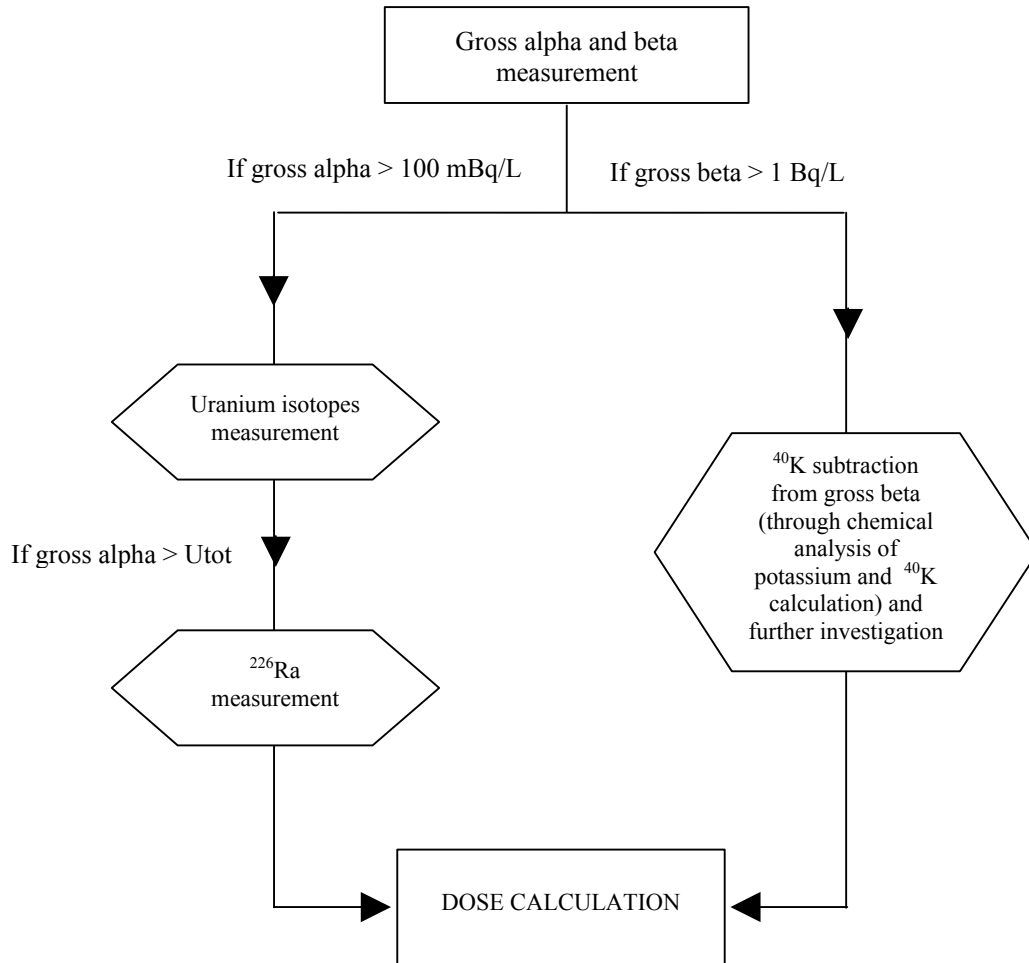


FIGURE 1. SEQUENTIAL METHODOLOGY FOR HIGH SENSITIVITY SCREENING

2.2.2.1. Gross alpha and beta measurement

1 liter of water sample was acidified to pH 2.5 with high purity nitric acid (to avoid losses due to precipitations, polymerizations, colloid formations) and preconcentrated by slow evaporation on a hot plate. After a ten-fold volume reduction the pH dropped to 1.5 and in the same time all the dissolved radon was desorbed. After cooling to room temperature, 8 g of the concentrated sample were transferred in the scintillation vial and 12 ml of Optiphase Hisafe 3 (PerkinElmer) cocktail were added. Samples were counted for 1000 minutes. The MDA for gross alpha and gross beta activity were, respectively, 8 mBq/kg and 25 mBq/kg.

Results of LSC procedure were compared to those obtained with ISO methods [12-13] for about 30 water samples and a good agreement was found.

TABLE IV. IRC-CEC INTERCOMPARISON RESULTS

	Gross alpha Act. ± Uncert. (Bq/L)	Gross beta Act. ± Uncert. (Bq/L)
Our laboratory results	0.051 ± 0.010	0.519 ± 0.063
IRC reference values	0.057 ± 0.008	0.520 ± 0.047

Moreover this procedure was used with good results (see Table IV) in IRC-CEC Intercomparison concerning the measurement of the gross alpha, gross beta, tritium activities and potassium concentration in a drinking water sample – August 2002 [14].

2.2.2.2. Uranium isotopes measurement

1 liter of water sample was acidified with 5 ml of 15 M high purity nitric acid and reduced by slow evaporation on a hotplate to 100 ml. After cooling, the sample was transferred in a separatory funnel and extracted twice by 10 ml each portions of specially designed scintillation cocktail. The extractive scintillation cocktail was prepared by adding a fluorescent substance (PBBO, 2-(4-biphenyl)-6-phenyl-bezoxazole), naphthalene (to enhance alpha-beta separation) and 5% complexing agent (HDEHP, bis-2-ethylhexyl-orthophosphoric acid) to xylene. Extraction yields not far from 100% were obtained with this procedure. The sample was then fluxed with argon to remove dissolved oxygen. Uranium measurements were made by considering the alpha discriminated spectrum component; ^{238}U and ^{234}U content and their ratio were evaluated by applying spectral deconvolution of uranium alpha peaks. Canberra Genie2k Interactive Peak Fit software was used to this purpose. ^{235}U contribution to total uranium was estimated to be lower than 2.5%, and was neglected when performing alpha spectra deconvolution. Each sample is counted for 1000 minutes; the MDA for total uranium content is 0.4 mBq/kg.

The method was tested, with good results, by comparison with values obtained by two independent methods on 15 different water samples, namely: 1) semiconductor alpha spectrometry on electrodeposited samples; 2) ICP mass spectrometry [9]. It was also used in the recent Interlaboratory Study promoted by IAEA ‘Determination of radium and uranium radionuclides in water’; performance evaluation report is not yet available.

2.2.2.3. ^{226}Ra measurement

^{226}Ra was indirectly determined by daughter ^{222}Rn measurement. A portion of the ten 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 a water immiscible cocktail (Optiscint – Perkin Elmer) were added. After a 21 days ingrowth the vial was vigorously shaken to extract radon in the cocktail phase and let to stand for 4 hours to allow the ingrowth of radon short lived progeny. Samples were counted for 1000 minutes and the undiscriminated alpha + beta spectrum were considered; the MDA was 14 mBq/kg. Higher sensitivities could be achieved by increasing sample preconcentration.

The method was tested with good results on two water samples by comparison with values obtained by emanometry [9] and used in the above mentioned Interlaboratory Study promoted by IAEA.

3. APPLICATION TO ENVIRONMENTAL SAMPLES

3.1 Tap waters survey

High sensitivity techniques have been applied to a preliminary monitoring program of tap waters samples drawn in 13 of the largest Lombardia towns; first results have been reported in full detail elsewhere [10]. Gross alpha activity ranges from values lower than minimum detectable activity (8 mBq/kg) to about 350 mBq/kg; 38% of values was higher than WHO reference level. Alpha activity was always due mainly to uranium isotopes, so no ^{226}Ra measurement was required.

Gross beta activity ranges from values lower than minimum detectable activity (25 mBq/kg) to about 280 mBq/kg; WHO proposed guideline value was never exceeded.

Southern Lombardia towns (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 neighboring towns

(Parabiago, Lodi, Monza). A more detailed monitoring of waters from Milano and its surrounding area has therefore been performed and results are reported (see Table V).

21 tap water samples have been collected in Milano and Lodi districts, including Parabiago and Monza towns. Both areas are highly populated, therefore drinking water quality is of special significance for radioprotection purposes. Results of gross alpha and gross beta measurement are reported in Table V.

TABLE V. GROSS ALPHA-BETA ACTIVITIES IN MILANO AND LODI TAP WATERS

Distr.	Towns	Gross Alpha (mBq/kg)	±	Gross Beta (mBq/kg)	±
Milano	Parabiago (ARPA)	349	41	273	48
Milano	Milano-v. Cusago-v.Assiano	135	20	125	38
Milano	Liscate (MI)	111	17	138	38
Milano	Zibido S. Giacomo (MI) - A	110	17	75	35
Milano	Milano-v. Don Orione-C.Crescenzero	100	16	141	38
Milano	Zibido S. Giacomo (MI) - B	100	16	121	37
Lodi	Lodi (ARPA)	94	16	239	45
Milano	Milano (ARPA)	91	16	119	37
Milano	Noviglio (MI) – B	88	15	101	36
Milano	Noviglio (MI) – A	81	15	110	37
Milano	Monza (ARPA)	78	14	132	38
Milano	Segrate (MI)	60	13	84	35
Milano	Milano-v. Aristotele 28-C.Gorla	46	12	87	35
Lodi	Codogno (LO)	42	11	142	39
Milano	Milano-v. Castrovillari 20- C. Baggio	39	11	66	35
Lodi	Corneigliano Laudense (LO)	32	11	109	37
Lodi	San Fiorano (LO)	< 7.7		< 25	
Lodi	Terranova dei Passerini (LO) - A	< 7.7		81	35
Lodi	Corno Giovine (LO)	< 7.7		65	34
Lodi	Terranova dei Passerini (LO) - B	< 7.7		104	36
Lodi	Santo Stefano Lodigiano (LO)	< 7.7		73	35

The uncertainty associated with the activity concentration has been calculated according to the appropriate rules of uncertainty propagation to give a combined standard uncertainty [15]. The expanded uncertainty was obtained by multiplying the combined standard uncertainty by the coverage factor $k=2$.

As far as alpha activity is concerned, higher values were found in Milano district waters (mean value: 107 ± 21 mBq/kg); values measured in Lodi district are lower (mean value: 16 ± 5 mBq/kg) except for the sample collected in Lodi town. Actually, Lodi town is the northernmost sampling site among Lodi district ones, which in general lie in the same geographic area as Pavia, Cremona and Mantova; lower radioactivity concentrations of southern Lombardia waters are therefore confirmed.

Gross beta mean concentrations of Milano and Lodi districts are very similar (Milano district mean value: 121 ± 14 ; Lodi district mean value: 86 ± 13). Gross beta activity is not strictly correlated to gross alpha one, as can be seen in Table V. The correlation does not improve even as ^{40}K

contribution is subtracted.

3.2 Fresh waters survey

In 2000 some concern arose in people about possible contamination by depleted uranium (DU) of Garda lake. Actually some unused bombs had been thrown in Garda lake during Kosovo conflict; lack of information about the real nature of weapons increased worries in population. Garda is the biggest Italian lake. It is a famous and crowded bathing site and its waters are used for drinking purposes as well.

Waters normally contain uranium; the mean concentration of ^{238}U ranges from 1 to 90 mBq/L [16]. Observed values of natural uranium isotopes ratio in water vary widely; $^{234}\text{U}/^{238}\text{U}$ is not necessarily close to 1, as expected in geologically undisturbed samples, as a consequence of selective chemical-physical effects (different leaching rate of rocks due to alpha recoil) that take place in waters aquifers [17]; the actual $^{234}\text{U}/^{238}\text{U}$ ratio is often higher than 1 (up to 10) [18]. On the contrary, $^{235}\text{U}/^{238}\text{U}$ activity ratio is reported to be relatively constant (about 0.045).

In the case of DU, the concentration of ^{234}U and ^{235}U is lower than expected in natural uranium. The depletion level found to date in DU ammunition is defined as 0.2% ^{235}U by weight. If DU is mixed with natural uranium in varying proportions, the mass ratio as well as the activity ratio will vary accordingly. Since in waters the ^{234}U activity concentration is usually greater than ^{238}U one, the DU contribution can be easily masked if $^{234}\text{U}/^{238}\text{U}$ ratio is used as checking parameter.

TABLE VI. WEIGHT COMPOSITION AND SPECIFIC ACTIVITY OF NATURAL AND DEPLETED URANIUM

	Isotopes	Natural Uranium	Depleted Uranium
Composition by weight	^{238}U	99.2745%	99.7990%
	^{235}U	0.7200%	0.2000%
	^{234}U	0.0054%	0.0010%
	$^{235}\text{U}/^{238}\text{U}$	0.00725	0.0020
	$^{234}\text{U}/^{238}\text{U}$	5.54 E-5	1.00 E-5
Specific activity	^{238}U (Bq/mg)	12.36	12.38
	^{235}U (Bq/mg)	0.58	0.16
	^{234}U (Bq/mg)	11.56	2.29
	$^{235}\text{U}/^{238}\text{U}$	0.047	0.013
	$^{234}\text{U}/^{238}\text{U}$	0.935	0.185

In order to check the presence of DU, both $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ activity ratios can be used. $^{234}\text{U}/^{238}\text{U}$ ratio can be determined with high precision by alpha spectrometry, due to higher sensitivity of this method for these isotopes. $^{235}\text{U}/^{238}\text{U}$ ratio measurement is more accurate if mass-spectrometric techniques rather than alpha pulse-height analysis are used [19].

8 drinking water and 9 bathing water samples were collected in different Garda lake places; total uranium and $^{234}\text{U}/^{238}\text{U}$ ratio were determined as previously described. LSC alpha spectrometry was preferred to semiconductor alpha spectrometry on electrodeposited samples because of its readiness. Measurement results are reported in Table VII.

TAB.VII – TOTAL URANIUM AND $^{234}\text{U}/^{238}\text{U}$ RATIO IN GARDA LAKE SAMPLES

Towns	(N/S)	Total Uranium (mBq/kg)	±	$^{234}\text{U}/^{238}\text{U}$	±
Lake bath water samples					
Limone camping Nanzel		23.4	2.9	1.09	0.13
Tremosine loc. Campione		28.3	3.4	0.99	0.10
Gargnano - porto		21.8	2.7	1.20	0.14
Toscolano loc. Lungolago		23.2	3.2	1.11	0.14
Salò - cimitero		23.7	2.9	1.26	0.15
Moniga - porto		24.8	3.0	1.14	0.13
Desenzano loc. Rivoltella		24.6	3.0	1.14	0.13
Desenzano loc. Rivoltella		22.3	2.8	1.20	0.15
Sirmione camping Sirmione		23.1	2.8	1.05	0.13
Lake drinking water samples					
Limone loc. Singol		38.8	4.8	1.30	0.15
Gargnano loc. Muslone		40.7	4.8	1.14	0.10
S.Felice loc. Porticcioli		24.4	3.0	1.02	0.12
Manerba loc. Pisenze		21.8	2.8	0.96	0.12
Manerba - vill.tur. S.Giorgio		20.1	2.6	0.98	0.13
Moniga loc. Pescatrice		24.1	3.0	1.00	0.13
Desenzano - cabina vecchia		23.8	3.0	1.11	0.16
Desenzano - cabina nuova		22.3	2.8	1.31	0.17

^{238}U concentration ranged from 10 to 20 mBq/kg, as expected in natural samples. $^{234}\text{U}/^{238}\text{U}$ ratio was never significantly less than 1, as should be in samples heavily contaminated by DU.

4. CONCLUSIONS

Liquid scintillation has proven to be a quick, versatile and accurate tool for radiometric investigation. Gross alpha and beta, uranium and radium isotopes activity can be measured with quick and simple procedures; method sensitivity can be tailored to assure compliance to reference levels, both in normal and in emergency situations. Small differences in sample chemical properties (e.g. pH value, amount of dissolved oxygen etc.) can modify scintillation yields and, as a consequence, measurement outcomes. However, if suitable validation criteria are properly defined in order to maintain control of relevant parameters (e.g. quenching value, chemiluminescence etc.), reliable results can be obtained. Moreover, reduced equipment requirements and relative readiness of radiochemical procedures make LSC an attractive technique which can be applied also by laboratories lacking specific radiochemistry facilities and experience.

Our emergency procedure allows analyzing more than 130 samples per day, with far better sensitivities (actually 1/10) than maximum radioactive contamination levels set by European Council Regulation 2218/89. As gross alpha derived levels are lower than usual ^{222}Rn content of most waters, special care must be taken in removing it. Furthermore, a preliminary study of waters content of natural radionuclides is strongly suggested. In order to avoid both false-negative and markedly false-positive results, decision limits on sample gross counts must be properly set, and a preliminary study of instrumental background behavior is required.

With regard to the natural radionuclides content of waters, preliminary results on Lombardia tap waters show the existence of critical areas where gross alpha activity content exceeds WHO proposed values. High values are usually due to uranium isotopes and the indicative dose reference value of 0.1 mSv/y proposed by Council Directive 98/83/EC was never exceeded. Nevertheless previous works [20] showed that, in specific areas, a relevant dose contribution is due to radium isotopes, whose radiotoxicity is higher than uranium one. A more detailed monitoring program in the whole Lombardia area is in progress, in order to deepen knowledge about drinking waters radioactive content.

Total uranium content of waters can be measured by LSC coupled to selective extraction. If a proper sample preparation procedure is applied, alpha peaks resolution is good enough to allow measurement of $^{234}\text{U}/^{238}\text{U}$ ratio. However it should be pointed out that the effectiveness of alpha spectrometric methods in checking DU contamination of waters is greatly reduced by the well-known variability of natural $^{234}\text{U}/^{238}\text{U}$ ratio; a comparison of uranium isotopes ratios in non polluted and potentially polluted samples could increase actual method sensitivity. Such shortcomings are generally avoided as $^{235}\text{U}/^{238}\text{U}$ ratio is considered, since its value in water samples is supposed to be relatively constant.

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