

Development of a prototype of monitor for alpha and beta radiation in water using new silicone-based contamination-safe detectors

Marcello Lunardon^{1,*}, Paolo Sartori¹, Pierino De Felice² and Luca Stevanato¹

¹Dept. of Physics and Astronomy, University of Padova and INFN, Italy

²National Institute of Ionizing Radiation Metrology, ENEA, Casaccia - Rome, Italy

(*) marcello.lunardon@pd.infn.it

Abstract — We present here the main results of an experimental activity aimed at the realization of a prototype of monitor for alpha and beta radioactivity in water exploiting a novel type of contamination-safe scintillation detector developed by our research group.

Due to the short path-length of alpha and beta particles in water and the low detection limits needed to be compliant with the international legislations in matter of radiation safety for water, the detectors to be used for such a kind of instruments should have in general large area, very low intrinsic background and avoid any kind of window between the monitored water and the active volume of the detector. Even an extremely low contamination of the surface can therefore destroy the detector performance, while protecting the detector with a layer of passive material will reduce the detection efficiency, in particular for alpha particles, and the passive layer can get contaminated itself, making necessary its substitution and representing an important limitation to the realization of a radioactivity monitor that should work continuously for years.

The novel detectors are large-area silicone-based scintillators developed and produced in our laboratories. The technology we propose is a significant step forward in the direction of the realization of radioactivity monitors for water with high sensitivity and reasonable costs, to be used to improve security and quality of the water distributed to European and worldwide citizens.

The detection performance for alpha and beta particles was first tested in air with standard sources, showing results very close to similar detectors commercially available. Later a number of tests were carried out in the ENEA-INMRI laboratories with the aim to characterize the contamination and decontamination properties. Initial activity of each detector foil was checked by low background radioactivity measurements, then the detectors were immersed for fixed times and constant procedure in a variety of radioactive reference liquid solutions with different radionuclides in different chemical forms. After rinsing with distilled water the detector foils were again measured for residual radioactivity adsorbed on the foils surface.

After this preliminary campaign of contamination measurements carried out on small size samples, several large area detectors were realized and used to build a small

demonstrator device for continuous monitoring of the radioactivity in water. The monitor was tested with distilled water (blank) and radioactive aqueous solutions, demonstrating the possibility to realize a new generation of radiation monitors for water with high sensitivity and with the possibility to easily manage the contamination issues.

Keywords — radioactivity in water, windowless plastic scintillation detector, decontamination.

I. INTRODUCTION

In recent history we have been witnessing several important accidents and disasters that led to a large spread of radioactive material in water. Let's remember, as an example, the recent accident at Fukushima's Daiichi reactor following the devastating tsunami in Japan (2011), or the large release of radioactive liquids and solid wastes in the environment at Church Rock in New Mexico (1979), or again the contamination events in the Ontario Lake in the last decade (2009 and 2011 the last ones).

Such events, together with the increasing terroristic threat of possible attacks involving RN materials, has pushed the interest of international community in monitors for radioactivity in water (MRW) intended for human consumption, directly (drinking water) or indirectly (water for crops irrigation, wasted water that can impact on the environment, etc...).

Currently water radioactivity screening procedures are based on periodic samplings followed by laboratory analyses. It's a well-established procedure, but has several deep limitations on the possibility of performing a continuous real-time monitoring, due to the significant time and cost needed to complete a single analysis that should be replicated continuously many and many times. For this reason a number of alternative water monitoring systems based on different technologies are being implemented and are facing the market, most of them taking advantage of the recent advances on scintillation detectors technology. There are a few commercially available MRW for continuous monitoring based on scintillation detectors. They usually declare medium-high Minimum Detection Activities (MDA) between several hundreds of Bq/L down to several tens of Bq/L for reference elements like Cs-137, K-40, Sr-90 and U-238 or Po-210, two

order of magnitude or more larger than the WHO Guidelines detection limits. See as an example the NEX-GEN-SSS and NEX-BETA-ABG systems [1]. Typically no clear information is provided about effects of contamination in the sensors.

Nevertheless several key aspects need still to be further improved, before this technology can become the reference for MRWs. Among them, the problem of contamination of sensors in contact with water to be analyzed is definitely one of the most significant. For this reason many commercial MRW are based on detection of the gamma radiation emitted by contaminants, that is more penetrating and allows protecting the gamma sensor with thick and solid shielding (typically metallic). But gamma detection is not adequate to detect all possible radioactive contaminants in water, e.g. pure beta emitters like Sr-90 (see e.g. the SARA Water system [2]). This kind of devices does not cover properly all possible RN contaminants in water and therefore they are more often used in dedicated applications, as an example the measure of Cs-137 in sea water (see e.g. [3]).

Current radioactivity limits in legislations all around the world refer, in fact, to “gross alpha and beta activities” as first level of screening (see e.g. [4]) and direct alpha and beta radiation detection in water is therefore recommended. Detecting such low activities (1 Bq/L or less) of beta and, even more, of alpha radiation in water with scintillators requires large detection areas, since the mean free path of these particles in water is short (a few tens of microns for alphas). Consequently, even very low levels of contamination per unit of area can destroy the monitor performance. On the other hand, the need of large detection areas makes economically impractical the use of existing robust but expensive scintillators like YAP:Ce crystals.

II. DESCRIPTION OF THE RESEARCH PROGRAM

The main objective of the research activity described in the work is the development of a novel detector for alpha-beta detection in water, which can overcome the limitations of the existing devices as reported above.

This activity is as a follow-up of the EU project TAWARA_RT (FP7-SEC-2012-1, Grant n. 312713), where our research group developed a high-sensitivity monitor for radioactivity in water intended for human consumption [5]. The core of such system, the Real Time Monitor, used a number of large area commercial scintillation phosphor EJ-444 as sensors for alpha and beta detection [6].

The TAWARA_RT system, after being extensively tested and calibrated at the INMRI laboratories of ENEA in Casaccia (Rome), was finally installed and operated for the demonstration campaign at the North Water Treatment Plant of the Warsaw Waterwork Company (MPWiK). Despite its notable results in terms of sensitivity and overall features for water radioactivity monitoring, which make it still a state-of-the-art instrument in this context, the characterization campaign showed several aspects that could be improved, the main one being the effect of surface contamination of the radiation detectors, in terms of both

deterioration of the sensitivity and possibility to efficiently clean-up the system to recover the original performance.

After the end of this project we continued the research on this topic by focusing on the problem of the detector contamination on the surface directly exposed to water with a radioactive content.

A very promising solution was identified in the use of a novel category of scintillation detectors, consisting in a large area phosphor made of ZnS crystal powder embedded in a matrix of active silicone-based scintillator [7]. The silicone physical properties, in particular its hydrophobicity, chemical resistance and mechanical robustness to water exposure, make it particularly interesting for long-term use in water. Surface can be further functionalized in order to achieve a higher level of robustness, making it contamination-safe when exposed to aqueous radioactive solutions.

The basic material of the new detector we are proposing is a silicone-based scintillation material, namely phenyl-polysiloxane (PPS), non-toxic, non-dangerous, easy to be manufactured and handled, working in a wide range of temperatures (-100, +250 C), much wider than in case of common plastic scintillators. A number of possible surface functionalization (e.g. silylation processes) can be applied in order to maximize its resistance against RN contaminants. These detectors can be easily shaped in thin foils (~ 1 mm) with large active areas, of the order of 20 cm x 20 cm or more. Efficient alpha-beta discrimination can be obtained by pulse shape analysis techniques applied to signals.

The particular surface properties described above make this silicone-based detector also a good sensor for RMW operating with raw water from rivers, lakes or sea.

The expected features of this novel detector are:

- good detection efficiency for alpha and beta radiation
- high hydrophobicity, chemical resistance and long-term stability of the surface
- negligible contamination level after exposition to radioactive aqueous solutions
- possibility to clean up the surface from possible residual contaminations using chemical cleaning agents without damaging the detector
- low production cost

After realizing and characterizing the new detectors, a simple single-module radioactivity monitor was built, with the aim of demonstrate the usability of this technology to make a new generation of contamination-safe high-sensitivity WRM, better than the state-of-art instruments.

III. CONTAMINATION TESTS ON SMALL AREA DETECTORS

Many small samples of the new silicone-based detectors have been produced at the chemical labs of the Department of Physics and Astronomy of the Padova University (UNIPD).

They have first optically and mechanically characterized and then tested with alpha (Po-210) and beta (Sr/Y-90) sources in air. Finally they have been exposed to different aqueous radioactive solutions at ENEA-INMRI and the final contamination has been evaluated.

A. Production and test of small samples at UNIPD

The production starts by mixing liquid silicone (polydimethylsiloxane Gelest DMS-V21) with the cross-linking agent (polydiphenyl-co-dimethylsiloxane Gelest PDV-2331) and the scintillation dopants (2,5-diphenyl oxazole + Lumogen F Violet 570) [7,8].

A ZnS:Ag scintillating powder (EJ-600 by Eljen Technology) is added to the silicone and the compound is poured on the mold to have a uniform layer 1.0 - 1.2 mm thick.

A powder sedimentation of about 12h is used to create an active bottom layer about 50 μm thick with 60%wt of ZnS:Ag.

The silicone is finally cross-linked in oven at 70 °C for 1h to create a solid elastomeric slab.

A surface functionalization with nanometric fluorinated silane film is created by vapor phase deposition on several samples. Other samples were made using passive PDMS silicone (only alpha detection capability).

The small bottom layer is the "alpha active layer" where alpha particles coming from radioactive decays are stopped transferring most of their energy to the ZnS:Ag crystals that produce the typical delayed light flash. Beta particles, on the contrary, typically loose their energy in a much longer path inside the active silicone body, producing the typical prompt flash of the phoswich detector.

The final result is shown on Fig. 1 : on the left a cross-section at 40x optical transmission microscope showing the 50 μm alpha active layer and the silicone beta active body. On the right a picture of a typical 5 cm x 5 cm detector sample.

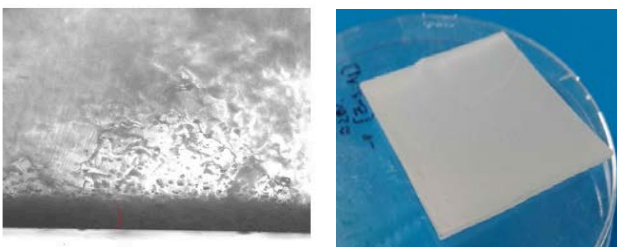


Fig. 1. Left panel: a cross-section at 40x optical transmission microscope showing the 50 μm alpha active layer and the silicone beta active body. (right panel: a picture of a typical 5 cm x 5 cm detector sample.

The samples have been tested as radioactivity detectors using standard alpha (Po-210) and beta (Sr/Y-90) sources in air. The silicone detector was placed on a planar wavelength-shifting light guide (EJ-280) inside a light-proof box. The scintillation light was collected by two PMTs Hamamatsu R3550A 1" diameter acquired in coincidence using a CAEN DT5725B digitizer.

Alpha and beta identification was achieved by standard pulse shape discrimination technique. The alpha and beta spectra were compared to equivalent spectra taken using commercial reference phoswich detector EJ-444/EJ-440 by Eljen Technology. An example of raw alpha and beta spectra are shown in Fig. 2.

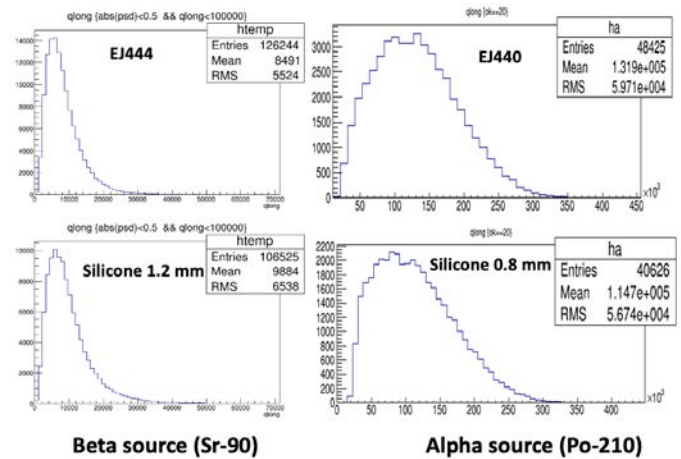


Fig. 2. Example of raw alpha (on the right) and beta (on the left) spectra taken with the reference EJ-444/440 detectors and with the new silicone-based detectors.

A measured efficiency of 80% to 85% relative to EJ-444 detector was measured for the new silicone-based detectors. The corresponding light output amplitude was very similar. For alpha particles, a relative efficiency between 85% to 90% was found, with a slightly lower light output (90% relative to EJ-440).

B. Contamination tests at ENEA-INMRI

Many detectors were produced at UNIPD and moved to the ENEA-INMRI labs in order to test the contamination properties.

Several bunches of 8 sample pairs were hooked to a dedicated fork-like support (Fig. XX, left panel). Each support hosted detectors with different features: new silicone detectors with or without surface silanization, made with scintillating silicone or passive silicone and reference EJ-440 detectors. To be noticed that the external surface of the EJ-444 detectors is the same of EJ-440, changing only the lower plastic support.

The supports were immersed in the aqueous radioactive solutions by means of a moving arm of a dip-coater (Fig. 3, right panel).



Fig. 3. set of samples in the fork (left) and immersion in the radioactive aqueous solutions. See text for details.

The contamination was obtained therefore by immersion and motion inside the aqueous solution, to simulate the flowing of the water inside the real instrument.

Cs-137 and Co-60 solutions with specific activities of about 1, 10 and 100 kBq/L were used. The bath time was varied from 30 min to 15 h.

After contamination, the samples were rinsed with distilled water, dried in air and measured with the certified HPGe gamma spectrometers available at INMRI in order to quantify the residual activity.

Finally we tested several decontamination procedures to further reduce the residual contamination:

1. immersion in a detergent solution of CONTRAD 2000 for 30 min;
2. immersion in an acid solution of HCl 0.5M for 30 min;
3. immersion in CONTRAD 2000 for 30 min + rubbing with a soft towel;
4. immersion in a solution of HCl 1.5M for 30 min.

Steps 1+2 are labelled with "soft cleaning" in the following, while 3+4 are labelled as "strong cleaning". The first procedure was thought as possible cleaning of a sealed device with only a short temporary stop in the monitoring, while the second would require a deeper maintenance intervention.

The main results are summarized in Fig. 4, where the residual contamination of Cs-137 is shown as a function of the specific activity for different samples.

During a first test run we found that the residual contamination saturated after a few minutes, no significant differences were found between shortest and longest immersion times. Furthermore an almost linear increase of with the specific activity used, at least in the considered activity range.

The reference samples (EJ-440) showed the largest residual contamination (magenta points). Moreover, due to the structure of the outer active layer, no cleaning procedure after contamination, either "soft" or "strong", could be used.

The new silicone-based samples, without cleaning procedure, showed in general a contamination level about 10 times lower than the reference samples (blue points). A further reduction of contamination of about a factor 2 was observed for samples with surface functionalization (red points).

A second test run was performed with only large specific activity solutions. In this run we first evaluated the samples with no cleaning procedure, obtaining results similar to the first run (light blue points), then we tried the cleaning procedure.

After the "soft cleaning" the residual contamination was reduced of about one order of magnitude (violet points). The "strong cleaning" reduced further the contamination below the minimum detectable activity of the gamma spectrometer, about three order of magnitude lower than what measured with the reference detectors.

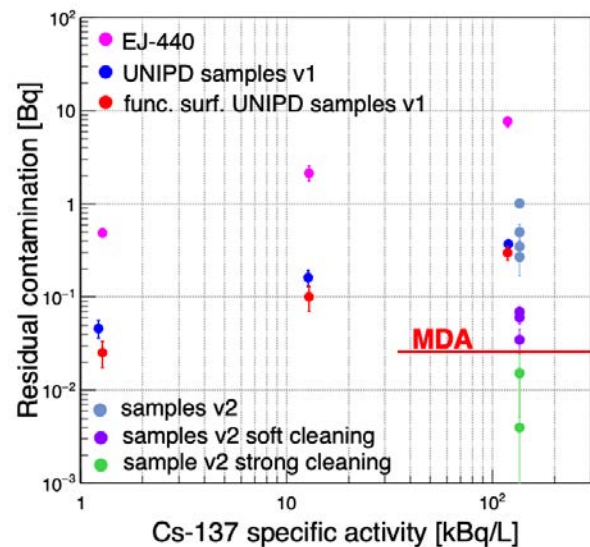


Fig. 4. Residual contamination as a function of the specific activity for different samples in different configurations. See text for details.

IV. DEMONSTRATOR MONITOR DEVICE WITH LARGE AREA DETECTORS

A. Large area detector production and test

Several large-area 20 cm x 20 cm alpha-beta detectors were produced at UNIPD. The production procedure was the same described above for small samples. Only one difference was introduced in order to improve the sedimentation of the ZnS:Ag powder that was initially found not enough homogeneous: a high static electrical field (several kV/cm) was used to push the powder toward the bottom taking advantage of the small electrostatic charge of the powder observed during manipulation. The thickness of the alpha active layer was finally found consistent with the small samples over the whole area.

The homogeneity of the detection efficiency was measured using standard alpha (Po-210) and beta (Sr/Y-90) sources in air. In Fig. 5 we show the detection efficiency relative to a small-size EJ-444 reference detector for a large area detector for alpha (left panel) and beta (right panel) particles. The experimental setup was the same used for the efficiency measurements of the small detectors described above. The efficiency is slightly higher in the upper rows where the PMTs were placed, allowing therefore for a better light collection. This effect was seen also in the homogeneity tests of the TAWARA_RTM device [9], where EJ-444 detectors were used. Considering the efficiency values at the same distance from the PMTs, the spread of the values is limited to a few percent.

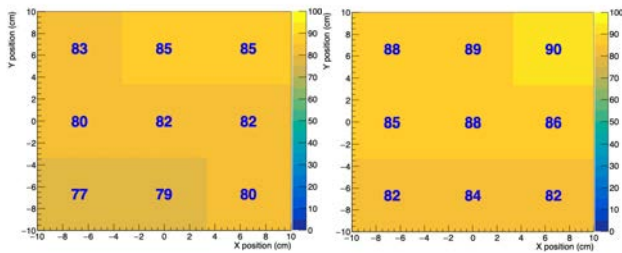


Fig. 5. Detection efficiency relative to a small-size EJ-444 reference detector for a large area silicone-based detector for alpha (left panel) and beta (right panel) particles. Numbers are percentages.

B. Demonstrator device design and realization

After validating the functioning of the new large-area detectors, two of them were mounted on a demonstrator device to show the possibility to realize an alpha-beta monitor system for radioactivity in water with very low intrinsic contamination and decontamination capability.

The system is composed by a wavelength shifting (WLS) light guide EJ-280 of size 21 cm x 21 cm mounted inside a water-proof INOX chamber (Fig. 6, left panel). On the top and the bottom of the WLS two large area detectors are placed (Fig. 6, right panel). After mounting and sealing an active area of about 19 cm x 19 cm was left in each side, for a total of about 2 x 350 cm².

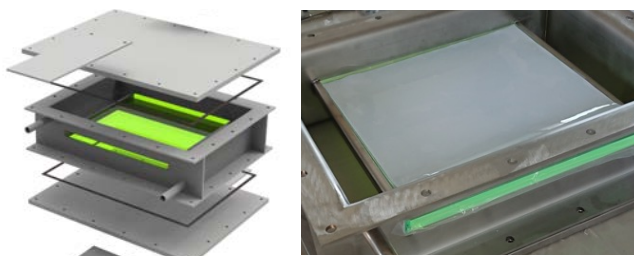


Fig. 6. Design of the demonstrator chamber (left panel) and a picture of the silicone-based detectors placed on the WLS during the assembly phase (right panel). See text for details.

The scintillating light was collected on one side of the WLS by means of two PMTs ET 9266 2" manufactured by Scionix. Electric signals were acquired in coincidence by a CAEN DT5725B digitizer. The full waveforms were acquired on a PC and processed in real time in order to discriminate alpha, beta and residual background signals and display the counting rates.

C. Demonstrator characterization: blank

The demonstrator was tested at UNIPD using demineralized water to characterize the blank and using NORM to evaluate the detection performances. Unfortunately, due to logistic problems related to the post-Covid period, at the moment of writing the calibration tests and finale contamination tests with aqueous solutions of standard radioactive isotopes (like Cs-137) could not be performed.

The blank test was realized with demineralized water by measuring the alpha and beta rates for long periods. In Fig. 7

we show a typical output of a 5 days measuring run.

The observed average beta rate was about 10 counts per second, in line with what was measured in Padova with the TAWARA_RTM detectors (between 6 to 18 cps). The rate was quite stable, except for a small non stochastic day-night fluctuation due probably to temperature, varying of about 5-6 degrees between night and day. In fact, the known effect of temperature on the PMTs was not compensated at the time of writing.

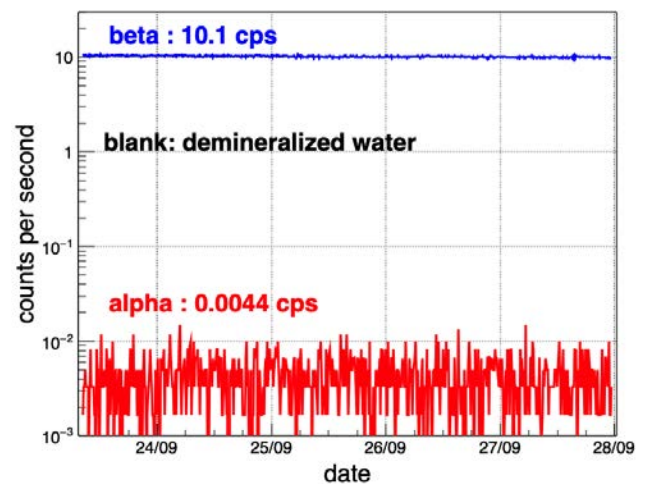


Fig. 7. Differential (a) and integral probability of interaction as a function of angle of incidence. Note that “Fig.” is abbreviated. There is a period after the figure number, followed by two spaces.

The observed alpha rate was about 0.004 counts per second. Again, this value is consistent with what measured in the past for the TAWARA_RTM detectors (between 0.003 and 0.008 cps). In this case the temperature effect is negligible and the distribution of counts in 10 min is reasonably poissonian, as expected. We show in Fig. 8 the frequency plot together with the poissonian fit.

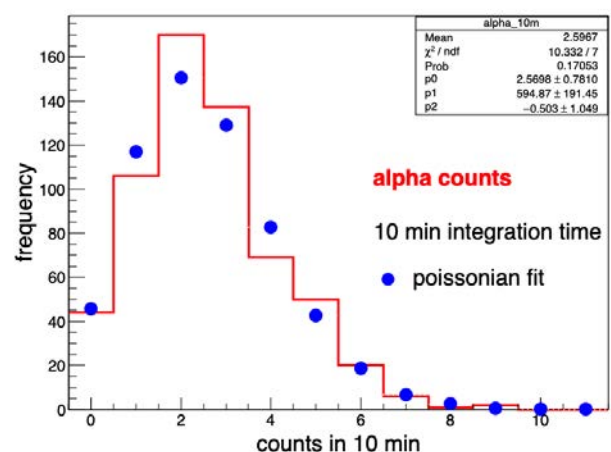


Fig. 8. Frequency plot of the alpha counts in 10 minutes together with the poissonian fit. The experimental distribution follows reasonably the expected behaviour.

D. Demonstrator characterization: test with NORM

Finally the detection efficiency was tested using NORM. In particular for the beta efficiency an aqueous solution containing

K-40 was used. The plot of Fig. 9 shows the increment of the beta rate following the insertion of KCl inside the water circuit. The final specific activity of the solution was about 200 Bq/L.

The measured rate increment was about 2.5 counts per second. This number can be directly compared to the efficiency measured and certified at ENEA-INMRI for the TAWARA_RTM units [10]. In that case, a calibration coefficients of 0.1 to 0.15 Kg⁻¹ were measured for the three units when K-40 is used. Each unit were composed of 8 modules with active area of 2 x 400 cm² each. By rescaling for the number of modules and for the active area, an expected rate increment between 2.2 and 3.3 counts per second with 200 Bq/L of K-40 can be calculated. The measured number fits well with the calculated range of expectation.

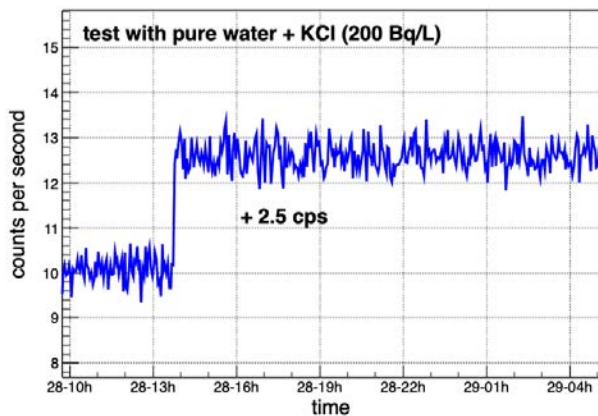


Fig. 9. Beta counts rate as a function of time for the beta efficiency test. The step of +2.5 cps corresponds to the injection of 200 Bq/L of K-40 in the water circuit.

The alpha efficiency was verified only qualitatively by measuring the Radon melted in the Padova tap water. The Padova tap water comes from underground and contains a small amount of Radon, of the order of 5 to 10 Bq/L [11]. This number can vary during the years for natural reasons and, even more important, it depends strongly on the way the water is treated before and during the measurement, therefore it has to be taken only as an indicative value.

Radon was observed and measured during the tests of the TAWARA_RTM detectors. The typical measured values (maximum value before the Radon decay) were ranging from about 0.2 to 0.3 counts per second per module.

In this case we measured a corresponding maximum value of about 0.7 counts per second [Fig. 10]. This value, even if a direct comparison is not possible, is much larger than the one measured with the TAWARA_RTM detectors and suggests the possibility that, as we expect, the alpha efficiency of these detectors is higher due to the absence of passive protection layers on the surface of the detectors.

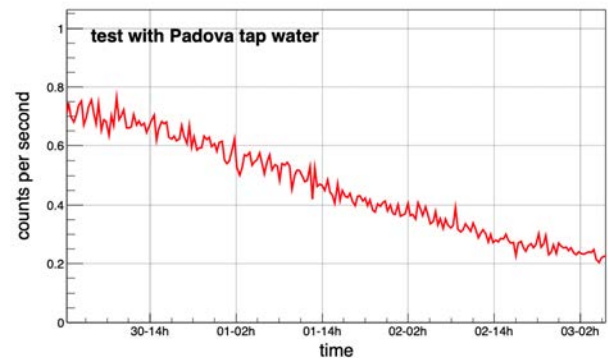


Fig. 10. Alpha rate as a function of time for a run with Padova tap water. The alpha counts are due to the Radon contained in the tap water, coming from the underground aquifer.

V. CONCLUSIONS

In this work we showed the results of a research program aimed at develop and characterized a new type of phoswich detectors for alpha and beta radioactivity in water.

These detectors, thanks to their silicone-based bulk composition, are demonstrated to have lower residual contamination than analogue commonly used commercial detectors. Moreover, thanks to their improved mechanical and chemical resistance, they can undergo simple and effective decontamination procedures that can reduce further the residual contamination up to two order of magnitude.

These new detectors can be used to build a new generation of monitors for alpha and beta radioactivity in water. A simple single-module demonstrator has been built and tested. At the moment of writing, even if the foreseen experimental characterization is not fully completed, it is showing encouraging results.

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