Radiochemical Sensor for Continuous and Remote Liquid Effluents Monitoring - 8223

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ABSTRACT

On-line radioactivity monitoring in liquid effluents is an increasing need according to the
international regulations at present. Classical activity determination procedures include the
sequence of sampling, chemical treatment, measurement and data treatment. These steps are
man-power consuming, generate a great amount of waste and introduce an important delay
between the potential pollution event and its detection and quantification.

To overcome these limitations, we have developed a radiochemical sensor for liquid effluents
capable of sending information about the specific activity and volume of a contamination
episode to a remote position, on line and continuously. The capabilities of the sensor developed
here allow detecting and quantifying contamination pulses of alpha, beta and gamma emitters of
different volumes and activity levels included in a continuous stream.

Sensor receptor includes two detection systems, one addressed to determine alpha, beta and
gamma events and the other to detect sample gamma emissions. Detailed sensor structure will be
shown at the conference because patent is in process at this moment. Detection efficiencies (%) obtained in the alpha-beta-gamma system for the range of contamination volumes considered (2-
300 ml) are: 1.6 - 3.2%, for Pu-240; 22.2 - 58.4%, for Sr-90/Y-90 and 8.8 - 17.7%, for Cs-134. In
the gamma system, values for Cs-134 detection range from 0.6% to 1.3%.

Prediction errors obtained show that sensor is capable to detect Sr-90/Y-90 contamination pulses
of at least 2 ml and 3 Bq/ml with a relative error lower of 10% in activity and 60% in volume.
When contamination pulse increases up to 7 ml, relative errors decrease to 5% for both
magnitudes. For Pu-240 and Cs-134, when contamination pulses are of at least 7 ml and 300
Bq/ml, the relative errors obtained in determinations performed in the alpha-beta-gamma system
are lower than 10% in activity and 20% in volume. The same errors are obtained in the gamma
system for Cs-134 when contamination pulses are higher than 7 ml and activities up to 1300
Bq/ml.

INTRODUCTION

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Since the second half of the twentieth century, many nuclear activities have been developed in the different compartments of the earth [1-3]. Nuclear weapons and nuclear reactors have been the two most important industries; locally, medical and research activities have also introduced important amounts of different radionuclides into the environment [4]. At present, the decommissioning of nuclear installations, together with increased ecological awareness among the population, governments, and international institutions, has led to an increase in the control of these activities on the ecosystems and therefore on the number of measurements necessary for their implementation [5-8].

Moreover, radiation protection plans include the activity determination of many radionuclides in different matrices. These determinations usually follow the classical sequence of sampling, chemical treatment, preparation, measurement and data treatment. These steps require human effort, generate waste, and introduce an important delay between the moment when the compartment is sampled and the moment when the isotope activities are known. Attempts have been made to accelerate this process by establishing air radioactivity controls at some specific sites or worldwide [9-12].

To overcome these inherent limitations of the analytical process, sensors are being developed for many routine applications. In the field of radioactivity, the most important advance is the use of area monitors for gamma emitters [13-14].

The aim of the present paper is to evaluate the behaviour of a prototype of a radiochemical sensor capable of on-time, remote and continuous quantification of the activity of alpha, beta and beta-gamma emitters in liquid effluents.

A plastic scintillator was chosen in order to build up the receptor on the basis of the mechanical properties of this material, its wide sensitivity to the different types of particles and radiations and its ability to operate without consuming any reagent to produce the signal [15-18].

This article summarises the content included in the references [19-20].

EXPERIMENTAL

Reagents And Solutions

All regents used were of analytical or scintillation grade.

Sr-90/Y-90, Cs-134 and Pu-240 active stocks solutions were used for the preparation of active solutions. All the active solutions were prepared by diluting a weighed amount of standard solution in a weighed amount of the specific medium previously prepared with inactive distilled water.
A peristaltic pump Gilson Miniplus 3 with eight channels was used to pump solutions into the sensor. The tubing used was PVC purple-purple pump tubes 2.06 mm i.d. and 50 cm long. A 1414 Liquid Scintillation detector (EGG&Wallac) with logarithmic amplification and a 1024-channel analyser was used. The detector was modified by EGG&Wallac to adapt it to the sensor. SenCont software was designed to control the 1414 detector and manage the files generated. This software enables acquisition time control with high accuracy and extreme reduction of detector dead time.

**Sensor Description**

The sensor is composed of two parts, the receptor and the transductor. The receptor is divided in two parts, the alpha-beta part and the gamma part, which are made of plastic scintillator. The transductor is composed of electronic units that convert the optical signals into electrical pulses and classifies them according to their origin, shape and energy. The spectrum obtained is finally stored for further data treatment. SenCont software commands the transductor and thus the entire measurement process.

**Sensor Operation**

The analysed effluent is pumped into the sensor where the signal is produced. No signal will be produced in the gamma detection part of the receptor as a consequence of the disintegration of an alpha or a beta emitter. However a disintegration of a gamma emitter will produce signal in both parts of the receptor. Finally, any cosmic ray that reaches the sensor will interact with both the gamma and the alpha-beta detection parts of the receptor, obtaining a signal in each. Then, the signal coming from the alpha-beta detection part of the receptor includes information about the alpha, beta and gamma emitters present in the liquid effluent plus the cosmic background, whereas the signal coming from the gamma detection part of the receptor contains information about the gamma emitters and the cosmic background.

**Procedure**

Simulated effluent was introduced into the sensor via a peristaltic pump. The flow was determined in each measurement by determining the volume pumped over a certain period of time. Normal flow was around 0.5 ml/min.

Background was established by measuring for five minutes a continuous flow of the corresponding carrier solution.

Punctual contaminations were done by pumping a known volume of an active solution into the sensor. Once the active solution had been loaded, a carrier solution was pumped into the sensor until the initial conditions were reached. During this period, successive spectra were captured every ten seconds. Initial conditions were reached when five consecutive 10-second measurements did not differ statistically from the previous background value. After this process, a new background measurement was made. All operations were carried out without allowing the entrance of air into the sensor.
A continuous contamination scenario was simulated by continuous pumping of an active solution and taking a measurements of 120 minutes.

The sensor was calibrated for each isotope (Sr-90/Y-90, Pu-240 and Cs-134 in the alpha-beta detection part of the receptor and Cs-134 in the gamma detection part of the receptor) by introducing punctual contamination pulses of increasing volumes from 0.2ml to 20ml and continuous contamination measurements (assimilated to a 60 ml pulse), Figure 1. Evaluation of the calibration curves was performed by measuring a set of nine unknown punctual contaminations (three activity levels and three contamination volumes) for Sr-90/Y-90, Pu-240 and Cs-134 in the alpha-beta detection part of the receptor and a set of five unknown pulses of Cs-134 in gamma detection part of the receptor.

**Data Treatment**

The spectrum collected in each measurement was smoothed using a Savitzky-Golay algorithm. It is possible to generate a signal profile for punctual contamination by plotting the counts registered (Bq) every 10 seconds versus the volume of effluent pumped through the sensor, from the moment when the pulse is introduced to the time when the experiment was ended. Two main parameters can be deduced from the signal profile: Maximum counting rate and (B-A) parameter. Maximum counting rate was obtained by averaging all the values obtained between the maximum count value and this value minus four times its theoretical standard deviation. (B-A) parameter was calculated by measuring the difference between the volume values corresponding to the two inflection points of the signal profile. These values were obtained by applying the second derivate to the signal profile ($\delta^2 \text{Bq}/\delta V^2 = 0$).

Detection efficiency for the optimum window (O.W.) was calculated as the ratio between the net signal, maximum counting rate minus background value, and the specific activity (Bq/ml) of the standard solution pumped. The O.W. corresponds to the range of the spectra with best Figure of
Merit (FM = E$^2$/B, where E is the detection efficiency and B the background). Detection efficiency calibration was done for each radionuclide by fitting the detection efficiencies versus the (B-A) values for a series of punctual contamination experiment and the continuous contamination experiment. Contamination volume calibration was also done for each radionuclide, by modelling the relationship between the volume of contamination pumped and the value of (B-A) parameter.

Activity determination of an unknown punctual contamination pulse was done by registering its signal profile and calculating the maximum counting rate and the (B-A) parameter. From these data, the specific activity (Bq/ml) was determined by using the net signal and the detection efficiency calibration curve, whereas the volume of the contamination, and therefore the total activity of the contamination (Bq), was calculated by using the specific activity and the contamination volume calibration curve.

Detection limits (Bq/ml) were calculated according to the Spanish Consejo de Seguridad Nuclear (CSN) criterion for control of liquid effluents of nuclear power plants:

\[
DL = 2s(B)/E
\]

Where s(B) is the experimental standard deviation of the background values registered in the calibration procedure and (E) is the detection efficiency of the scenario considered, a punctual contamination of 0.2ml or a continuous contamination.

SAFETY CONSIDERATIONS

All experimental procedures were performed in accordance with the regulations of the Spanish Nuclear Authorities (Consejo de Seguridad Nacional) and the University of Barcelona.

RESULTS AND DISCUSSION

Characterisation Of Signal

Alpha-Beta detection part of the receptor

The distribution of signals as a function of the type and energy of the radionuclide for the alpha-beta detection part of the receptor is shown in Figure 2. The order found is related to the penetration power of the different particles; first the high energy beta emitters, Sr-90/Y-90, and then the medium energy beta emitters and the high energy alpha emitters, Cs-134 and Pu-240.

The evolution of the signal versus the volume of the effluent for different contamination pulses shows a delay of 4-5 ml between the moment when contamination pulse is pumped into the sensor and when it is detected. After this point, the detection efficiency increases linearly since it achieves a maximum value which remains constant whatever the detector is full of the active solution. Finally, when the contamination pulse ends, the liquid effluent cleans the detector and the signal registered decreases quickly until the initial values are achieved.
Fig. 2. Spectra of Sr-90/Y-90, Pu-240, and Cs-134, in the alpha-beta receptor, and Cs-134, in the gamma receptor, for a contamination pulse of 20 ml at the effluent volume corresponding to the maxima signals.

Gamma detection part of the receptor

The spectrum of Cs-134 in the gamma detection part of the receptor is shown in Figure 2. With regard to the spectrum obtained at the alpha-beta detection part of the receptor for this radionuclide, the position of the peak is located at slightly lower energies and the detection efficiency is clearly lower. This behaviour can be attributed to changes in geometry for the system sample-detector.

It can be seen that in the gamma receptor the variation of the detection efficiency versus the volume pumped into the sensor is more pronounced than in the alpha-beta receptor.

The variations in the signal detected as a consequence of changes in the volume of the contamination pulse show detection efficiency increasing and decreasing faster in the gamma than in the alpha-beta detection part of the receptor. For any contamination volume, the radionuclide is observed in the gamma detector just 1 ml after the introduction of the pulse in the stream, whereas this signal is not detected in the alpha-beta system until 4-5 ml later.

Background in alpha-beta and gamma detection parts of the receptor
Spectra of background registered at the gamma and alpha-beta detection parts of the receptor spread approximately over the same range of energies but the former does so with a slightly higher intensity. This fact could be related to the different size of both detectors. On the other hand, the coincidence spectrum of both systems shows a distribution similar to that obtained for each receptor (0.365 Bq). If we subtract this value to the alpha-beta detection part of the receptor background we obtain the reduction expected for background when the two detectors of the sensor operate in coincidence with a double transducer system (0.457 Bq).

**Activity Determination**

The sensor’s ability to quantify radionuclides in liquid effluents was evaluated by determining the specific activity and the volume of the contamination pulse of several active solutions. For this purpose, the two detection parts of the systems were calibrated and then applied to the quantification of spiked solutions. Sr-90/Y-90, Cs-134 and Pu-240 were analyzed in the alpha-beta detection part of the receptor, whereas the radionuclide quantified in the gamma detection part of the receptor was Cs-134.

**Sr-90/Y-90 in the Alpha-beta detection part of the receptor**

Calibration of the alpha-beta detection part of the receptor was performed by introducing a series of contamination pulses, between 0.2 to 20 ml and an infinite volume (included as 60 ml), in a continuous stream of the liquid effluent. For each case, the maxima signal and the (B-A) parameter were obtained from the profile of total signal versus the volume of liquid effluent. By using this information and the corresponding background spectra, the net signals and the detection efficiencies at the optimum window (1:189) were calculated for each pulse and the two calibration models were built: detection efficiency versus (B-A) and volume of contamination versus (B-A). Calibration of the volume of contamination pulse versus (B-A) parameter shows a linear relationship with higher dispersion at volumes below 3 ml.

Different scenarios can be considered in the application of these models: when the contamination pulse is very small (<< 5 ml), intermediate volumes (5-15 ml) and continuous contamination episode (> 15 ml). For very small contamination pulses, the detection efficiency can be as low as 5-10% and there is a good deal of uncertainty regarding the volume of the contamination. Also, in the continuous episode, detection efficiency is high and constant, around 116%, and the contamination volume can be clearly established. In these two cases, detection limits can vary from 2.06 Bq/ml for a contamination pulse of 0.2 ml to 9.78 x 10-2 Bq/ml for a continuous contamination situation.

The quantification capability of the sensor was evaluated at three activity levels and three contamination volumes, Table 1. Relative errors obtained in the specific activity determination are mainly caused by the uncertainty associated with the determination of the (B-A) parameter and, therefore, of the detection efficiency in the optimum window for low contamination pulses. This behaviour could be expected whenever the contamination volume was smaller than 3-5 ml. Relative errors are also related to the activity level but, if the contamination pulse threshold of 5 ml is overcome, the specific activity can be determined with relative errors lower than 6% (10% for low activity level).
Similar discussion holds true for the results achieved in the determination of the volume of the pulse contamination, Table 1. Thus, for contamination pulses of less than 3-5 ml, the relative errors rose to 65%, whereas when this volume increased, the amount of the contamination pulse could be determined with relative errors lower than 8%.

These results indicate that contamination episodes of Sr-90/Y-90 in liquid effluents can be quantified in activity and volume whenever the pulse is not extremely small (< 5ml) and, even in these cases, the values determined could be considered a very good approximation to evaluate the importance of the contamination.

Pu-240 in the Alpha-beta detection part of the receptor

The behaviour found for Pu-240 is very similar to that already described for Sr-90/Y-90. Calibration was done following the same procedure and as in the case of Sr-90/Y-90, the detection efficiency in the optimum window (1:161) increases, as does the (B-A) parameter, to achieve a stationary value. In any case, the detection efficiency values for Pu-240 are very low, probably due to the short pathway of alpha particles.

The relationship between the volume of the contamination pulse and the (B-A) parameter is linear, as it was for Sr-90/Y-90, with an important scattering for volumes lower than 3-5 ml.

Again three different situations can be established for a contamination episode. First, for very small contamination pulses (<5 ml), there is considerable uncertainty in the determination of the value of (B-A) parameter and, therefore, in the detection efficiency and in the volume of contamination. Additionally, the values of detection efficiency obtained are lower than 2.5%. The second situation corresponds to contamination volumes between 5 and 15 ml. In this case, efficiency increases up to 3.5% and the (B-A) parameter is better defined. Finally, for continuous contamination episodes, the detection efficiency can be considered to remain constant (around this same 3.5%).

The detection limits calculated for the extreme situations of volume of contamination are 67.42 Bq/ml, for pulses of 0.2 ml, and 2.68 Bq/ml for continuous contamination situations.

Several test samples of different volumes and activity levels were analysed, Table 1. Unlike the Sr-90/Y-90 results, relative errors obtained for Pu-240 determination depend on both volume of contamination and activity level. It is clear that for low contamination volumes, e.g., 2 ml, the problems in finding out the value of the (B-A) parameter introduce an important error in the detection efficiency of the optimum window and, therefore, in the calculated activity value. For higher volumes, 7 ml, the (B-A) can be better established but the relative errors in the activity are up to 30%. Probably in this case the main problem comes from the low value of the detection efficiency for the alpha emitters. When the contamination volume is higher (12 ml) the determination of the activity is better established with relative errors of less than 10%.
**TABLE I.** Results obtained in the specific activity and volume of contamination quantification for different radionuclides. Values correspond to the optimum windows.

<table>
<thead>
<tr>
<th></th>
<th>Low activity level</th>
<th>Medium activity level</th>
<th>High activity level</th>
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</thead>
<tbody>
<tr>
<td><strong>Sr-90/Y-90</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(alpha-beta detection part of the receptor)</td>
<td>Pulse V. (ml)</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Activity Error (%)</td>
<td>-4.02</td>
<td>2.80</td>
<td>-9.38</td>
</tr>
<tr>
<td>Pulse V. Error (%)</td>
<td>61.52</td>
<td>-5.82</td>
<td>7.53</td>
</tr>
<tr>
<td><strong>Pu-240</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(alpha-beta detection part of the receptor)</td>
<td>Pulse V. (ml)</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>Activity Error (%)</td>
<td>26.37</td>
<td>29.70</td>
<td>-8.98</td>
</tr>
<tr>
<td>Pulse V. Error (%)</td>
<td>37.05</td>
<td>-23.35</td>
<td>-18.01</td>
</tr>
<tr>
<td><strong>Cs-134</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(alpha-beta detection part of the receptor)</td>
<td>Pulse V. (ml)</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>Activity Error (%)</td>
<td>42.81</td>
<td>1.87</td>
<td>4.12</td>
</tr>
<tr>
<td>Pulse V. Error (%)</td>
<td>19.85</td>
<td>-2.85</td>
<td>-5.51</td>
</tr>
<tr>
<td><strong>Cs-134</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(gamma detection part of the receptor)</td>
<td>Pulse V. (ml)</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>Activity Error (%)</td>
<td>-26.82</td>
<td>0.44</td>
<td>15.52</td>
</tr>
<tr>
<td>Pulse V. Error (%)</td>
<td>115.88</td>
<td>-1.21</td>
<td>-6.35</td>
</tr>
</tbody>
</table>
The same behaviour can be found in the determination of the volume of contamination. For very small pulses, relative errors are up to 38%; for 7 ml pulses and low and medium activity levels relative errors are up to 24% and for volumes of 12 ml the values decrease to a maximum of 18%. The best result is obtained for 12 ml and high activity level: 13%.

These values allow the quantification of contamination episodes of Pu-240 in liquid effluents with relative errors of less than 13% except for very small pulses that can also be determined but with higher errors.

Cs-134 in the Alpha-beta detection part of the receptor

Calibration and quantification of Cs-134 solutions in the alpha-beta detection part of the receptor were done as in the two previous cases.

The relationships of detection efficiency at the optimum window (1:202) and volume of contamination versus the (B-A) parameter are similar to those described for Sr-90/Y-90 and Pu-240. The difference, in this case, is that the stationary situation for detection efficiency is achieved for (B-A) values around 10 ml instead of 20 ml probably due to the gamma component of this radionuclide.

Calibration of contamination volume versus (B-A) shows the same problems pointed out in the two previous radionuclides: the important scattering in (B-A) determination for volumes of less than 3-5 ml.

This fact allows us to establish, in this case as well, three situations in the analysis of a contamination pulse: small pulses (<5 ml), with detection efficiency lower than 15%; large contamination volumes (> 10ml), with detection efficiency constant around 20%, and the intermediate situations (5-10 ml), with intermediate efficiencies. The limits of detection for the extreme volumes are 16.22 Bq/ml for 0.2 ml and 0.78 Bq/ ml for continuous contamination.

The results obtained in the quantification of the activity and the volumes of contamination episodes are shown in Table 1. The most important relative errors in the activity determination are found when the volume of the contamination pulse is very small (2 ml). In this case, relative errors can be up to 50%. Again, the origin of this problem could be related to the difficulties in determining (B-A) values in addition to the low values of detection efficiency for these short episodes. For larger contamination volumes at any activity level, the relative errors obtained are always less than 10%.

Similar behaviour can be observed in the determination of the volume of the contamination pulse. For very short pulses (2ml), the relative errors can be as high as 40%, whereas when the volume is larger the errors decrease to maximum of 10%.

These results show the capability of the alpha-beta receptor to quantify the activity and the volume of any contamination episode of Cs-134 but also of Sr-90/Y-90 and Pu-240 in liquid effluents with acceptable relative errors whenever the volume considered is not very small (< 5ml). For these cases, detection of the contamination is achieved and quantification errors are higher.
Cs-134 in the gamma detection part of the receptor

The characteristic of beta and gamma emitter of the Cs-134 radionuclide allows its detection in the gamma detection part of the receptor.

Calibration and quantification of this isotope was done, in this case, by following the same procedure as in the alpha-beta detection part of the receptor. The relationship between detection efficiency at the optimum window (13:81) and volume of contamination versus (B-A) parameter follow the same pattern already described for the previous isotopes. Extreme values of detection efficiency for short and continuous contamination are 0.04% and 1.3 %. These values are very low and imply detection limits of 114 Bq/ml, for pulses of 0.2 ml, and 2.95 Bq/ml for continuous contamination.

The capability of the gamma detection part of the receptor was evaluated by quantifying spiked contamination pulses of 7 and 12 ml. Relative errors obtained in activity and volume determinations are less than 15% and 7 % respectively (Table 1). The already described limitation related to the (B-A) values for short contamination pulses is the factor responsible for the relative error obtained for activity, 25%, and volume, 115%, quantification in a 2 ml pulse. On the contrary, very good results are achieved for a pulse of 12 ml and high activity level: 7%, for activity, and 3 % for volume.

In spite of the low detection efficiency, these values show the capability of the gamma receptor to quantify contamination pulses of Cs-134 whenever the volume of the contamination is higher than 5 ml.

CONCLUSIONS

The radiochemical sensor developed can be applied to the determination of alpha, beta, and beta-gamma radionuclides included in liquid effluents.

Specific activity and volume of a contamination pulse can be simultaneously established following the profile of the continuous signal detected.

Relative errors in the activity and volume quantification of Sr-90/Y-90 and Cs-134 in the alpha-beta receptor are always lower than 10% for contamination pulses higher than 3-5 ml. For the alpha emitter Pu-240, the relative errors obtained are, in general, less than 15%. Cs-134 has also been quantified in the gamma receptor with similar values.

These results illustrate the capability and flexibility of the sensor designed to detect and determine successfully on-line, remotely, and continuously the presence of different types of radionuclides in a liquid stream for contamination pulses higher than 5ml and specific activities up to 1 Bq/ ml.

The minimum volume and detection limits will improve with new designs adapted to specific problems.

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