

1 **TITLE PAGE**

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43 **EVALUATION OF SYNTHESIS CONDITIONS FOR PLASTIC SCINTILLATION FOILS**
44 **USED TO MEASURE ALPHA- AND BETA-EMITTING RADIONUCLIDES**

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54 **1. ABSTRACT**

55 Plastic scintillation foils of polystyrene and polycarbonate with a thickness between 45 and 200 µm,
56 have been produced using the solvent evaporation method. PSfoils presented a reproducible
57 thickness (10-20%). PSfoils were characterized by the measurement of ³⁶Cl or ²⁴¹Am. For ³⁶Cl
58 spectrum is located at medium energies since not all energy is deposited in the scintillator and not
59 all betas interact with the foils. For ²⁴¹Am the efficiency values are very high and spectrum is a
60 sharp peak located at high energies. ²²²Rn absorption (L_D and K) and desorption capacities of the
61 PSfoils have been also evaluated.

62

63 **2. INTRODUCTION**

64 There is general concern about radioactivity widespread as a consequence of different nuclear
65 activities. Those activities are mainly related to energy production, research, medical applications
66 and waste management. The variety of scenarios in which radioactivity can be generated or released
67 has led to this heightened concern and consequently to an increase in the analysis required to
68 monitor its distribution. Therefore, there is also a demand for simpler, quicker and cheaper
69 analytical protocols that can determine alpha and beta radiation under field conditions. Such
70 protocols have to overcome, at least partially, the limitations that are imposed when samples have to
71 be transported to the laboratory and subjected to the successive steps involved in dissolution,
72 separation and measurement. Those steps introduce an important delay between sampling and the
73 relevant information becoming available, and require significant amounts of resources in terms of
74 human labour, reagents and dealing with the waste produced [1].

75 Plastic scintillators (PS) are a good option to explore in this situation because they are solids and
76 sensitive to alpha and beta emissions. The use of PS as a tool for the measurement of radioactive
77 particles was discovered in the 1950s [2, 3], at the same time as that of other types of organic
78 scintillators [4]. Since then, many studies have been performed with the aim of increasing our

79 understanding of their interaction with the different radioactive particles (gamma rays, x rays, beta
80 particles, alpha particles, neutrinos, etc.), as well as to define their scintillation mechanism and to
81 develop applications based on them [5, 6]. PS have several advantages over other means of
82 detection of radioactivity: they are cheap, they can be prepared in different shapes and sizes, and
83 they have low toxicity. Several research activities are currently in progress focused on the
84 preparation of new formulations of PS that are tailor made for different applications [7]. These new
85 formulations are oriented towards the production of innovative PS shapes, the use of novel
86 monomers and the inclusion of additives to enhance the detection of particles or improve the
87 scintillation signals obtained. The new scintillators are designed for applications such as the
88 detection of neutrons [8] or dosimetry [9, 10], and to be used as veto detectors for cosmic and
89 gamma rays, in the analysis of alpha- and beta-emitting radionuclides [11][12][13], or in
90 scintillation proximity assay [14], among other practices.

91 One of the shapes that PS can be prepared as is foils: sheets just a few tens or hundreds of
92 micrometres thick (PSfoils). This form is especially convenient to detect alpha- and beta-emitting
93 radionuclides because, in spite of the minimal amount of PS involved, the nature of such particles
94 produces an efficient interaction. This format constitutes an interesting approach to overcome the
95 limitations mentioned above associated with the analysis of alpha and beta radionuclides in the
96 laboratory by alpha spectrometry and liquid scintillation, respectively [15]. Moreover, PSfoils
97 represent a new tool that can be used in the design of analysis protocols that are capable of fast
98 and/or field determinations of alpha and beta emitters.

99 Preparation of PS in the form of foils is described in the bibliography, through polymerization, by
100 cutting thin slices off a block of PS and by solvent evaporation [16][17]. Previous work of ours with
101 PS microspheres [18] suggests that solvent evaporation is a simple and cheap method to prepare PS
102 materials that could be used in the preparation of PSfoils. Thus, PSfoils could then be used directly
103 or as a platform for selective strategies, such as those employing PSresins [19], to produce selective
104 scintillating dipsticks, for fast analysis of liquid solutions; or as scintillating wipes, for screening
105 analysis of solid contaminated surfaces [20]. Another interesting potential application of PSfoils is
106 related to the determination of ^{222}Rn in field or laboratory conditions by using polycarbonate or
107 polystyrene. The usage of polycarbonate foils as ^{222}Rn samplers combined with liquid scintillation
108 counting is shown to be very useful for ^{222}Rn measurements [21]. There is, however, significant
109 potential for improvement of the usage of polymer materials for ^{222}Rn measurements, namely in
110 creating scintillating polymers which absorb and concentrate ^{222}Rn from the environment. Such
111 studies have been performed previously with PS in format of microspheres with promising results,
112 which are not totally understood [22].

113 The objective of the current research is therefore to establish a synthesis procedure for PSfoils and
114 to evaluate the influence of each variable on their morphology and capacity to detect alpha- and
115 beta-emitting radionuclides. The variables considered are related to the composition and conditions
116 of synthesis when the solvent evaporation method is applied.

117

118 3. EXPERIMENTAL

119

120 3.1. Reagents and materials

121 Polystyrene (PS_SA) (molecular weight: 260,000 g mol⁻¹) was purchased from Acros Organics
122 (Geel, Belgium). Makrofol DE polycarbonate (PC_MAKD) was obtained from Bayer AG
123 (Leverkusen, Germany). 2'5-Diphenyloxazol (PPO) (scintillation quality), dichloromethane,
124 toluene and ethyl acetate (liquid chromatography solvent, 99.9% purity) were purchased from
125 Merck (Darmstadt, Germany). 2'6-Diisopropyl-naphthalene (DIN) (synthesis quality) was supplied
126 by TCI (Zwijndrecht, Belgium). 1'4-Bis-(5-phenyloxazol-2-yl) benzene (POPOP) (scintillation
127 quality) was supplied by the Montedison Group, Chimica Division (Milan, Italy).

128 A toluene-based home-made liquid scintillation (LS) cocktail was used for the measurement of the
129 ²²²Rn activity absorbed in the foils. The composition of the cocktail is: 10 g of PPO, 1 g of Bis-
130 MSB in 1 L of toluene. All components are from SigmaAldrich, scintillation grade.

131 The stock solutions used were: ³⁶Cl active stock solution of 0.571(7) kBq g⁻¹, which was prepared
132 from a standard that contained 38.40(48) kBq g⁻¹ of ³⁶Cl (from CERCA/LEA (Pierrelate cedex,
133 France)) in a water solution at a concentration of 65 µg L⁻¹ of NaCl; and ²⁴¹Am solution (Am³⁺) of
134 185(2) Bq g⁻¹ prepared from a standard of 924(9) kBq g⁻¹ supplied by GE-Healthcare-Amersham
135 International (Buckinghamshire, England) in 0.5 M HCl and deionized water.

136 3.2. Equipment

137 The radioactive samples were determined using a 1220 QUANTULUS liquid scintillation
138 spectrometer (Perkin Elmer, Whaltman, USA) equipped with logarithmic amplification, a
139 multichannel analyser (4096 channels distributed between four segments of 1024 channels each),
140 pulse shape discrimination and background reduction through an active guard detector.

141 Scanning electron microscopy (SEM) images were obtained using a "JSM-7100F Field Emission"
142 scanning electron microscope at the Scientific and Technological Centres of the University of
143 Barcelona (CCiTUB). The samples were anchored using double-sided adhesive tape and coated with
144 carbon using a sputter coater.

145 The measurements of ²²²Rn absorbed in the PSfoils were performed with a Rackbeta1219 LS
146 spectrometer (Wallac, Finland). The measurements of the reference radon-in-air concentrations
147 during the exposure of the PSfoils are performed with an AlphaGuard RnTn Pro radon monitor
148 (Saphymo, Germany).

149 An FT-IR Nicolet IN10 MX (Thermo Fisher Scientific, Waltham, MA, USA) at the CCiTUB was
150 used for the infrared spectroscopy mapping measurements. The spectrum range available with this
151 equipment is 4000-715 cm⁻¹ with a spectral resolution of 4 cm⁻¹. An area of 2.5 mm was mapped with
152 a sampling rate of 25 micrometres per second. The OMNIC Picta software (Thermo Scientific,
153 Waltman, MA, USA) was used to treat the spectra and generate the images.

154 The PSfoil thickness was determined with an MDC-25SX micrometer (Mitutoyo, Kanagawa, Japan)

155

156 **3.3. Procedures**

157 **3.3.1. Preparation of PSfoils**

158 PSfoils were prepared using the solvent evaporation method. A solution composed of a certain
159 amount of the polymer, diisopropylnaphthalene (20% m/m of the polymer), PPO (2% m/m of the
160 polymer), and POPOP (0.05% m/m of the polymer) in an organic solvent was poured into a glass
161 Petri dish of 12 cm diameter containing 9 pieces of glass (5 cm in length, 0.52 cm in width and 0.18
162 cm in height). Once the solvent evaporated, the PSfoils deposited on the surface of the pieces of
163 glass were recovered using water.

164 Five different types of PSfoils were prepared: only polystyrene (100/0 PS/PC), only polycarbonate
165 (0/100 PS/PC) and mixtures of polystyrene and polycarbonate (75/25 PS/PC, 50/50 PS/PC and
166 25/75 PS/PC). In all cases proportions of polystyrene and polycarbonate are in mass.

167 Three different solvents were used: dichloromethane, ethyl acetate and toluene.

168 Five different concentrations (m/m %) of polystyrene in dichloromethane were tested: 1.5%, 2.25%,
169 3%, 3.75% and 4.45%.

170 The effect of the amount of polymer solution poured into the Petri dish was also tested. The
171 amounts studied were: 30 g, 34 g, 40 g, 45 g, 50 g and 60 g.

172 Three replicate procedures were performed for each set of preparation conditions (i.e., a maximum
173 of 27 PSfoils, 3 Petri dishes and 9 glass pieces in each Petri dish, were obtained).

174 **3.3.2. Radiometric Characterization**

175 Samples for radiometric characterization were prepared by adding 10 microlitres of the corresponding
176 radioactive solution at three equidistant positions on the surface of the PSfoil. The solution was added
177 with the help of a 100 microlitre micropipette and the PSfoil was weighed before and after the addition
178 of the 30 microlitres of radioactive solution to determine the exact amount added. After addition of
179 the solution, the PSfoils were dried in an oven at 40°C overnight to ensure evaporation of the solution.
180 Finally, each PSfoil was placed in a 20 mL polyethylene vial (from PerkinElmer, Waltham, MA,
181 USA) and measured. The activity added to the PSfoils was around 15 Bq for ³⁶Cl and 11 Bq for ²⁴¹Am.

182 Five samples were prepared for each radionuclide, ³⁶Cl and ²⁴¹Am, and type of PSfoil. Three of the
183 samples were prepared using PSfoils from the same Petri dish and two more were prepared using one
184 PSfoil from each of the other two Petri dishes. Three blank samples were also prepared for each type
185 of PSfoil, each one from a different Petri dish, containing double-deionized water instead of the
186 radioactive solution.

187 Each sample was analyzed in the Quantulus detector for 10 min in the pulse shape analysis (PSA)
188 configuration using the 'low' coincident-bias option, and at PSA values of: 1, 30, 60, 90, 120, 150

189 and 180. PSA is a parameter of the Quantulus detector that can vary from 1 to 250 (at unity
 190 intervals). The user defines the PSA value before counting and then the alpha/beta discrimination is
 191 performed through the comparison between this value and the ratio between the total area of the
 192 pulse to the area of the tail of the pulse. Shorter events are classified as beta (in the first half of the
 193 first MCA) and longer ones as alpha (in the second half of the first MCA). As a result, two spectra
 194 (i.e., a beta spectrum and an alpha spectrum) are obtained. In addition, the spectrum produced by
 195 the Compton electrons produced by the external standard gamma source (^{152}Eu) was obtained after
 196 10 min of measuring when PSA was 1. In all cases, the measurement vials were stored in the dark
 197 for at least 2 h before counting.

198 From the results obtained, three parameters were calculated: the detection efficiency; the quenching
 199 parameter, SQP(E); and misclassification. Detection efficiency corresponds to the mean value of the
 200 ratio between the net count rate measured at each PSA and the activity added to the PSfoil. SQP(E)
 201 was calculated by the detector and corresponds to the end-point channel that limits 99.75% of the
 202 total counts of the spectrum generated when the sample is irradiated by the external gamma-ray
 203 source: ^{152}Eu . Misclassification corresponds to the percentage of pulses not correctly classified as
 204 beta for ^{36}Cl and alpha for ^{241}Am . In the case of beta-emitting radionuclides (i.e. ^{36}Cl), it is
 205 calculated as the ratio between the net count rate in the alpha spectrum and sum of net count rate in
 206 the beta and the alpha spectra; whereas for alpha-emitting radionuclides (i.e. ^{241}Am), it is calculated
 207 as the ratio between the net count rate in the beta spectrum and sum of net count rate in the beta and
 208 the alpha spectra.

209 3.3.3 Radon absorption characterization

210 The radon (^{222}Rn) absorption in thin polymer foils can be described by the one-dimensional diffusion
 211 equation, taking into account the radioactive decay [23]:

$$212 \quad \frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \lambda c \quad (1)$$

213 where $c(x,t)$ is the ^{222}Rn atom concentration, D is the diffusion coefficient of ^{222}Rn atoms in the
 214 polymer and λ is the ^{222}Rn decay constant. If we consider a PSfoil exposed to ^{222}Rn containing air for
 215 exposure time t_s and then left to desorb in radon-free air for desorption time t_d , the ^{222}Rn activity in
 216 the foils is given by the solution of Eq. 1 [23]:

$$217 \quad A(t_s, t_d) = \frac{8KV\lambda L_D^2 A_{V0}}{L^2} \sum_{k=0}^{\infty} \frac{(e^{-\lambda^* t_s} - e^{-\lambda_{2k+1} t_s})}{\lambda_{2k+1} - \lambda^*} e^{-\lambda_{2k+1} t_d} \quad (2)$$

218 where V and L are the volume and the thickness of the foil, $\lambda_{2k+1} = \lambda \left(1 + \left(\frac{(2k+1)\pi L_D}{L} \right)^2 \right)$. If the

219 exposure was to constant radon activity concentration then A_{V0} is the ^{222}Rn activity concentration in
 220 the air and $\lambda^* = 0$. If the foil was exposed to ^{222}Rn concentration decaying with the radon half-life
 221 then A_{V0} is the ^{222}Rn activity concentration in the beginning of the exposure and $\lambda^* = \lambda$. The

222 partition coefficient K (or solubility) in Eq. (2) is defined as the ratio of the inside
223 ^{222}Rn concentration at the surface of the polymer [23] :

$$224 \quad K = \frac{c_{in}}{c_{out}} \quad (3)$$

225 The diffusion length L_D gives the mean distance travelled by the ^{222}Rn atoms in the material before
226 their decay. It is defined as [23]:

$$227 \quad L_D = \sqrt{\frac{D}{\lambda}} \quad (4)$$

228 The diffusion length (L_D) and the partition coefficient (K) are the two physical parameters which fully
229 characterize the radon absorption properties of a given polymer foil. That is why we have performed
230 dedicated experiments in order to determine the L_D and K of the newly synthesized PSfoils. The L_D
231 and K determination was performed according to the methodology described in [23]. This
232 methodology requires exposure of the PSfoils to known radon activity concentration and follow up
233 of the activity in the foils during desorption in radon-free air. An advantageous feature of the
234 experiments performed in this work is the usage of LS counting together with dissolution of the foils
235 in the LS cocktail in order to determine the ^{222}Rn activity in each foil. This type of measurement
236 allows precise timing (the end of the desorption is the moment when a foil is placed in the cocktail)
237 and accurate determination of the ^{222}Rn activity in the vials (see [21] for details).

238 The experimental procedure is as follows: a set containing several same PSfoils of each kind was
239 exposed to reference ^{222}Rn -in-air concentration for $t_s=95.72\text{h}$. During the exposure, the ^{222}Rn
240 activity in the air decreased with the ^{222}Rn half-life. The initial ^{222}Rn activity in the air was $A_{V0}=$
241 $1.604(87)\text{ MBq/m}^3$ and was measured with reference radon monitor AlphaGuard 2000 RnTnPro.
242 After the exposure the foils are left to desorb in radon-free air and periodically in different moments
243 a foil is placed in high performance glass vials, fully filled with home-made toluene-based LS
244 cocktail. The vial is closed tightly and shaken by hand for few minutes while the foil is dissolved in
245 the cocktail. The samples were measured on the RackBeta 1219 LS spectrometer 5 hours after their
246 closing, in order to achieve secular equilibrium between ^{222}Rn and its short-lived progeny. The L_D
247 and K are then determined from the desorption curves according to the methodology described in
248 [23].

249 4. RESULTS

250 The results presented in this section show the influence of polymer composition, the amount of
251 polymer and the solvent on the morphology and radiometric capacities of PSfoils obtained by the
252 solvent evaporation method.

253 4.1. Influence of synthesis conditions on PSfoil morphology

254

255 4.1.1. Effect of composition: transparency and porosity

256 PSfoils with five different polystyrene/polycarbonate compositions (100/0; 75/25; 50/50; 25/75 and
257 0/100 w/w %) were prepared using the evaporation/deposition method. The PSfoils made of
258 polystyrene (100/0 w/w %) were always transparent with no visual differences between the side of
259 the foils in contact with the air and the side in contact with the glass (Figure 1). In contrast, the
260 PSfoils composed of polycarbonate (0/100 w/w %), or mixtures of polystyrene and polycarbonate,
261 were opaque to a greater or lesser degree, but still there was no visual difference between the side of
262 the foil in contact with the air and the side in contact with the glass.

263 SEM images obtained (Figure 1) show that only the 100/0 PS/PC PSfoil presents a smooth surface
264 on the side of the PSfoil that was in contact with the air. All the other foils present cavities to a
265 greater (75/25 proportion) or lesser extent (50/50 proportion). In all cases, the side of the PSfoils
266 which was in contact with the glass pieces had a smooth surface, although some holes and small
267 pores are observed in the 75/25 and 0/100 proportion PSfoils.

268 It can be concluded that opacity or transparency is related to the presence of pores in the surface of
269 the PSfoils. The formation of pores can be attributed to the condensation of microdrops of water
270 during evaporation of the solvent and to the immiscibility of the components. When the solvent is
271 evaporated, there is a reduction of the temperature at the liquid/air interface that can cause the
272 condensation of water vapour in the form of very small droplets. When the polymer is still soft the
273 presence of such microdrops may modify the final structure of the solid surface. This behaviour is
274 enhanced by ambient humidity and also by the polarity of the polymer, as in the case of
275 polycarbonate. In the case of pure polystyrene, pores are only formed under conditions of very high
276 humidity.

277 Regarding the effect of polymer immiscibility, Figure 2 shows the infrared mapping of the PSfoils
278 containing 50/50 % w/w proportions of polystyrene and polycarbonate, at two characteristic bands:
279 1425-1475 cm^{-1} for polystyrene (caused by the aromatic C-C bonds stretching vibration); and 1740-
280 1800 cm^{-1} for polycarbonate (caused by the C=O stretching vibration). It can be observed that the
281 PSfoils are in fact a heterogeneous mixture of the two polymers, where polystyrene is in the form of
282 spherical agglomerations. The modification of the PS/PC proportion led to different equilibrium
283 states, which probably also affect the formation of different sized pores in the surface of the foil.

284 4.1.2. Effect of the amount of polymer: thickness

285 The thickness of the foils can be modified either by increasing the amount of solution added to the
286 Petri dish or by increasing the concentration of polymer in the solution.

287 PSfoils formed by deposition of 30 to 60 g of the polymer solution were prepared for the five
288 different polymer compositions. The values of thickness obtained are presented in Figure 3. It can be
289 seen how the thickness of the PSfoil increases with the amount of polymer solution and also
290 depends on the composition of the foil. Pure PSfoils are the thinnest; whereas mixtures are thicker.
291 This could be attributed to the porous surface of the PSfoils made from a mixture of polymers.

292 Regarding the variability it varies between 0 and 20%, it does not depend on the polymer
293 composition and decreases when the amount of solution increases (from 19% to 13%).

294 The effect of polymer concentration was evaluated for polystyrene PSfoils (Table 1). The thickness
295 increases with the increase in the concentration of polymer, and PSfoils between 40 and 100 μm
296 thick can be produced successfully. With regard to the thickness variability, it decreases with
297 increasing concentration of polymer solution (lower than 10% for PSfoils of 100 μm).

298 Our results demonstrate that control of the PSfoil thickness between 50 and 100 μm can be
299 achieved through the amount of polymer solution deposited.

300 4.1.3. Effect of solvent: density (packaging)

301 Three solvents with different polarities and boiling points were used to prepare the polymer
302 solutions: dichloromethane (boiling point: 39.6 $^{\circ}\text{C}$; logP: 1.5), ethyl acetate (boiling point: 77.1 $^{\circ}\text{C}$;
303 logP: 0.7) and toluene (boiling point: 110.6 $^{\circ}\text{C}$; logP: 2.7). Comparison was restricted to polystyrene
304 PSfoils, since the polycarbonate Markrofol D was not soluble in ethyl acetate.

305 The PSfoils made in toluene were thin; whereas those with ethyl acetate were the thickest (Table 2).
306 In spite of the uncertainty associated with determination of thickness, the differences between
307 toluene and the other two solvents are significant. Observation of the PSfoil surfaces via SEM does
308 not reveal significant differences between the foils, which are smooth in all cases. Since the PSfoils
309 were prepared by adding the same amount of polymer, we can conclude that the solvent has an
310 effect on the polymer packing during the formation of the polymer and thus the resultant polymers
311 present different densities.

312 4.2. Influence of synthesis conditions on the radiometric capacities of PSfoils.

313

314 A beta emitter (^{36}Cl) and an alpha emitter (^{241}Am) were used to perform the radiometric
315 characterization of the PSfoils. The influence of the synthesis conditions is discussed in terms of
316 their effects on spectra and detection efficiencies.

317

318 4.2.1. Effect of composition.

319 Figure 4 shows the spectra obtained when ^{36}Cl and ^{241}Am were measured with the PSfoils made of
320 polystyrene, polycarbonate and mixtures of the two. PSfoils made of polystyrene present a peak at
321 the 700-800 channels in the case of ^{241}Am and a band with the maximum at channel 400 in the case
322 of ^{36}Cl . When the amount of polycarbonate was increased, the maximum of the ^{36}Cl band shifted to
323 channel 300, and a second peak appeared at lower energies (the 600-700 channels) in the case of
324 ^{241}Am . From these results, we can conclude that polycarbonate is a worse scintillating polymer than
325 polystyrene, probably due to the chemical quenching caused by the ester moiety of the former
326 structure.

327 Moreover, the different behaviour observed for ^{241}Am and ^{36}Cl also confirms the heterogeneity of
328 the foils in terms of composition. On one hand, the beta particles from ^{36}Cl with a range greater than
329 the thickness of the foil, interact with both the polystyrene and polycarbonate irrespective where the
330 disintegration takes place. Therefore, all the beta particles emitted by ^{36}Cl interact with polystyrene
331 and polycarbonate, and the spectrum moves to lower energies as the amount of polycarbonate
332 increases.

333 On the other hand, the alpha particles from ^{241}Am , with a range of around 40 micrometres, mostly
334 interact with the polymer in the surroundings of where the particle is emitted. As consequence,
335 alpha particles can interact with polystyrene or polycarbonate or both, resulting in two peaks: one
336 for each polymer, and a band that links the two signals as a consequence of the intermediate
337 situations. The intensity of each peak depends, in this case, on the polymer proportions.

338 Apart from the peaks at high energies, there are also bands at low energies in both cases. For ^{36}Cl ,
339 the band at low energies (100-250 channels) could be attributed to those beta particles that have
340 interact very little with the polymer, due to their angle of emission and to the Cerenkov radiation
341 from those beta particles emitted in the opposite direction to that of the polymer. In the case of
342 ^{241}Am , several factors can cause the bands at 100-200 and 300-400 channels: gamma rays that are
343 detected when alpha particles are not detected; air luminescence caused by alpha particles; and
344 scintillation of the walls of the polyethylene vials.

345 Regarding the detection efficiencies (Table 3), unlike the behaviour observed in the spectra, there is
346 no clear correlation between detection efficiency and the proportion of polycarbonate. This could be
347 attributed to the fact that both radionuclides are energetic enough to produce a signal in all
348 circumstances but also to variability on sample preparation, which could also contribute to this lack
349 of trend. In this scenario, all ^{36}Cl values seem equivalent, around 70%, which corresponds to the
350 sum of the scintillating signal of beta particles emitted in the direction of the foil and the Cerenkov
351 signals from those emitted in the opposite direction. The only slightly lower value is that for 100%
352 polystyrene, which corresponds to the only PSfoil that is smooth with less room from active
353 residue. ^{241}Am detection efficiencies were higher, probably because to the alpha particles detected
354 by scintillation we have to add the gamma radiation detected in non-coincidence, the scintillation by
355 the polyethylene walls and air luminescence.

356

357

4.2.2. Effect of the amount of polymer.

358 Figure 5 shows the spectra obtained when PSfoils of different thickness are used in the
359 measurement of alpha- and beta-emitting radionuclides. It can be seen that for ^{36}Cl measurements,
360 the increase on the thickness causes a shift of the spectrum to higher energies, since more
361 scintillating material interacts with the beta particles emitted by ^{36}Cl , which were capable of
362 crossing all the PSfoils. This behaviour was not observed for ^{241}Am , since the alpha particles
363 emitted in the direction of the foil were almost all stopped in the PSfoils and only slight broadening
364 of the spectrum is observed for the three thinnest PSfoils. The values of detection efficiency (Table

365 4) do not follow any tendency and the differences observed can be attributed to the variability in
366 sample preparation and measurement.

367 **4.2.3. Effect of the solvent**

368 The last variable we evaluated was the solvent used for the preparation of the foils. The ^{36}Cl spectra
369 follow the same tendency as that shown previously, with a shift of the spectra to lower energies
370 correlated with the decrease in thickness. In the case of ^{241}Am , again it is observed that the thinnest
371 PSfoils (i.e. toluene) present a broader peak than the thicker ones (i.e. ethyl acetate). Regarding the
372 detection efficiency values, these are of the same order as those obtained previously: 50%-65% for
373 ^{36}Cl and around 90% for ^{241}Am , with no significant differences between solvents. Taking into
374 account that some of the solvents can cause quenching, these results suggest that the solvents are
375 effectively removed during the evaporation process.

376 **4.3. Sandwich PSfoil configuration**

377 The measurements reported so far correspond to the use of a single PSfoil, and this configuration
378 leads to a certain proportion of the beta or alpha particles emitted not interacting with the
379 scintillator. In order to overcome this drawback, we tested a new configuration consisting of two
380 PSfoils, coupled face to face, with the radionuclide in between (sandwich). To assure that the
381 PSfoils were firmly attached, hot air was applied to the sandwich until a compact foil was obtained.

382 Figure 6 shows the spectra of the coupled PSfoils, compared to those obtained using only one foil.
383 It can be seen that in the case of ^{36}Cl , the band at low energies generated by the Cerenkov emission
384 disappears and the spectrum moves to higher energies, since more photons are detected for each
385 disintegration. In the case of ^{241}Am , the situation is similar and the peaks at low energies disappear;
386 furthermore, all the signals appear at higher energies in a single peak. In a similar fashion, the
387 detection efficiency increases in both cases to values close to 100%, 95(4) for ^{36}Cl and 100(5) for
388 ^{241}Am , which indicates that all the particles interact with the PSfoils and are detected.

389 **4.4. Potential applications.**

390 PSfoils have been developed as a new tool for use in analytical protocols that require fewer
391 resources and could be applied under field conditions. Two potential applications are: the analysis
392 of contaminated surfaces and the detection of ^{222}Rn .

393 **4.4.1. Analysis of contaminated surfaces**

394 One of the potential uses of PSfoils is as technique for the direct analysis of solid surfaces
395 contaminated with radionuclides. In this scenario, the capacity to discriminate between alpha- and
396 beta-emitting radionuclides is of paramount importance to define a simple and economic screening
397 methodology or to take advantage of the very low background of the alpha spectrum. Figure 7
398 shows the alpha/beta misclassification obtained using one PSfoil and coupled PSfoils.

399 It can be seen that the misclassification of beta particles is slightly greater when coupled foils are
400 used, this is probably because the pulses are longer in time since more photons are produced.
401 However, misclassification of alpha particles is greatly reduced when two foils are used, probably
402 because all the low-energy signals that were previously classified as beta are more energetic in this
403 configuration and their pulse shows a longer duration. Therefore, the crossing point of the alpha and
404 beta misclassification curves shifts from 50 to 100 PSA units; and misclassification was reduced
405 from 35% to 15%, which is a value similar to that found in liquid scintillation. This
406 misclassification rate could also be improved to values lower than 5% if a proper selection of the
407 regions of interest is performed.

408 4.4.2. ^{222}Rn determination

409 The determined partition coefficients (K) and diffusion lengths (L_D) for PS foils of different PS/PC
410 compositions are shown in Tables 5 and 6, respectively. The results in Table 5 show that there is no
411 significant difference between the partition coefficients of PS foils made of 100% polystyrene and
412 100% polycarbonate. If we compare the partition coefficient for PS foils made of 100% Makrofol DE
413 polycarbonate determined in this work $K=11.7(28)$ to the partition coefficient of Makrofol DE
414 polycarbonate grains of which the foils were produced $K=26.2(25)$ [21], we observe more than two
415 times difference. This implies that the partition coefficient depends not only on the material content,
416 but also on the way the polymer was produced. This result is similar to what was obtained previously
417 with plastic scintillating microspheres (PSm) [22] and implies that the way of production of the
418 polymer is of paramount importance for the partition coefficient. The results for the partition
419 coefficient of foils with mixed polystyrene/polycarbonate content seem to be lower than the others,
420 but, as noted above, these have bubbles in their volume and these bubbles may cause bias in the
421 determined K values.

422 The inhomogeneity of the foils with mixed PS/PC content prevented us from determining the ^{222}Rn
423 diffusion lengths in them. Strictly speaking, in the determination of L_D by the solution of the diffusion
424 equation (Eq. 2) it is assumed that the material of the slab is homogeneous. This is clearly violated in
425 the case of the foils with mixed content (see Figure 2) and consequently Eq. 2 cannot be applied in
426 this case. Thus, the L_D is determined only for the PS foils made of 100% PS or 100% PC. The
427 corresponding values are: $L_D=259(61)$ μm for 100% polystyrene foils and : $L_D=51(17)$ μm for 100%
428 polycarbonate foils. The diffusion length of the PC foil determined here $51(17)$ μm is the same
429 (within the estimated uncertainties) with the one determined previously for Makrofol DE
430 polycarbonates $52.1(10)$ μm [21]. This implies that the diffusion length L_D (and respectively the
431 diffusion coefficient, D) depends mainly on the material content and is much less dependent on the
432 way of production of the polymer, compared to the solubility K .

433 The PS foils synthesized in this work provide some advantageous features for ^{222}Rn measurements.
434 The small thickness (of the order of few tens micrometers) combined with the different diffusion
435 lengths of the foils according to their material (PS or PC), result in very different time responses to
436 the changes in the ambient ^{222}Rn concentrations. Thus it is possible to develop PS foils with pre-

437 defined (or required) time response. To illustrate this functionality, Figure 8 shows the dynamics of
438 ^{222}Rn sorption and desorption in polystyrene and polycarbonate PSfoils with dimensions 5cm x 0.5
439 cm x 70 μm , when these are exposed to constant ^{222}Rn -in-air concentration (1 Bq/m³) and
440 afterwards left to desorb in radon-free air. The absorbed activity is calculated from Eq. 2 using the
441 K and L_D values from Tables 5 and 6. Figure 8 shows that the PSfoils made of PS have much faster
442 response to the change of the external ^{222}Rn concentration compared to the PC foils. The
443 polystyrene foils need approximately 4h to equilibrate with the ambient ^{222}Rn concentration, while
444 the PC foils need more than 100h. The desorption is also very different. The polystyrene foils
445 release the ^{222}Rn absorbed in them for about 2.5 h, while the PC foils need about 100 h to desorb. It
446 is evident that the PSfoils of polystyrene provide very fast time response, while the polycarbonate
447 foils provide slow response and these differences are due to the different ^{222}Rn diffusion lengths in
448 the foils.

449

450 5. CONCLUSIONS

451 Here we have successfully developed a method to produce PSfoils based on solvent evaporation of
452 a solution of a polymer over glass pieces. The method provides PSfoils of thickness between 40 and
453 120 micrometres, depending on the following preparation parameters: amount of polymer solution
454 and polymer concentration. The variability in the thickness is around 20% for the thinnest and just
455 10% for the thickest.

456 We prepared PSfoils of polystyrene, polycarbonate and mixtures of the two. Polystyrene PSfoils
457 present a smooth surface, whereas PSfoils containing polycarbonate present pores in the surface.
458 Polystyrene and polycarbonate are not miscible and when the solvent is removed, the polymers
459 become separated in the final solid material.

460 From the point of view of radioactivity measurements, polycarbonate and polystyrene present
461 different scintillation properties and signals due to polycarbonate producing less energy due to a
462 quenching effect caused by the ester functional group of its structure.

463

464 For beta emitters, the signals registered (around 60% of the disintegrations) are a sum of the
465 scintillating signals of the particles emitted in the direction of the foil and the Cerenkov signals of
466 the particles emitted in the other directions. For alpha emitters, the signals registered (around 85%)
467 are a sum of the scintillating signals of those alpha and gamma particles emitted in the direction of
468 the foil, together with the air luminescence and wall scintillation signals of the particles emitted in
469 the other directions.

470

471 When the alpha and the beta particles are placed between coupled foils (in a sandwich
472 configuration) almost all the particles are detected and in all cases due to a scintillation process with
473 the foils. This leads to a simplification of the spectra shape and an improvement in the alpha/beta
474 discrimination capacities of the scintillators which is then comparable to that of liquid scintillators.

475

476 The study of the ^{222}Rn absorption properties of the developed PSfoils shows that they all concentrate
477 ^{222}Rn from the air at their surface, as for all cases $K > 1$. It appears that the ^{222}Rn solubility (K) in the
478 material of the foils does not depend too much on their composition (PS/PC content) and rather
479 depends on the way of production of the foils. The diffusion length L_D depends strongly on the
480 material composition of the foils and is around 5 times higher for the polystyrene foils compared to
481 the polycarbonate ones. The PSfoils can be used for ^{222}Rn measurements and provide an interesting
482 functionality – based on their material composition and thickness their timing response to the change
483 of the ambient ^{222}Rn concentration can be tuned – from very fast response (2-3 hours) to a very slow
484 response (2-3 days).

485

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492 7. REFERENCES

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546

547 **8. FIGURE CAPTIONS**

548 **Figure 1:** Example of PSfoils we prepared **and** SEM images of the PSfoils made of 100/0, 50/50
549 and 0/100 polystyrene and polycarbonate proportions. Side in contact with the air.

550 **Figure 2:** IR mapping of PSfoils made of 50/50 polystyrene/polycarbonate. Optical image and
551 characteristic polystyrene ($1425\text{-}1475\text{ cm}^{-1}$) and polycarbonate ($1740\text{-}1800\text{ cm}^{-1}$) bands.

552 **Figure 3:** Thickness of the PSfoils prepared with variable amounts of polymer solution in
553 dichloromethane. The polymer solutions contain different proportions of polystyrene and
554 polycarbonate as indicated.

555 **Figure 4:** ^{36}Cl and ^{241}Am normalized detection efficiency spectra for PSfoils made of different
556 proportions of polystyrene and polycarbonate (50 g of polymer solution in dichloromethane)

557 **Figure 5:** ^{36}Cl and ^{241}Am normalized detection efficiency spectra of the PSfoils made using
558 different concentrations of polymer solution in dichloromethane (40 g of polymer solution 100/0
559 polystyrene/polycarbonate)

560 **Figure 6:** ^{36}Cl and ^{241}Am normalized count rate spectra for one PSfoil and two PSfoils stuck
561 together (50 g of 100/01 polystyrene/polycarbonate solution in dichloromethane)

562 **Figure 7:** Pulse shape discrimination of ^{36}Cl and ^{241}Am with one PSfoil and two PSfoils stuck
563 together (50 g of 100/01 polystyrene/polycarbonate solution in dichloromethane)

564 **Figure 8:** Dynamics of the ^{222}Rn sorption and desorption processes in 70 μm thick PSfoils made of
565 PS_SA polystyrene (a) and PC_MAKD polycarbonate (b).

566