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Simple on-line monitoring of α- and β-emitters by solid scintillation counting

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Abstract

We prepared a solid scintillation cell by vortexing a molten plastic scintillator at 195°C through a heat-resistant plastic tube. The cell was adapted to commercially available counting equipment and used for on-line monitoring and tested with high-level waste components such as Sr/Y-90, Ru/Rh-106, Sb-125, Cs-134, Pm-147, U-233, Am-241 and Cm-244. We obtained perfectly linear calibration curves and determined the detection limits to be in the range of 0.5–70 Bq per sample or 1–40 Bq ml^{-1} for β-emitters and 50 Bq per sample or 35 Bq ml^{-1} for α-emitters. The α-detection limits can be reduced to 10 Bq ml^{-1} by setting energy windows. Due to the minimal pressure loss and lack of scintillation contaminants in the cell effluent, the cell can be employed for monitoring processes on an analytical as well as on a technical scale. Although the detector was originally designed for gross α- and β-counting, even high-energetic β-emission can be partially suppressed by choosing the appropriate energy range and varying the cell geometry. © 1998 Elsevier Science S.A.

Keywords: On-line; Solid scintillation counting; α- and β-emitter

1. Introduction

Within the framework of our studies on actinide partitioning, we have identified an urgent need for an on-line detection of α- and β-emitters in order to characterise our process solutions and to monitor our separation processes. Commercial detection systems for such purposes are based on scintillation counting adding either an excess of a liquid scintillator to the flowing solution (LSC) [1] or pumping the solution through a fixed bed of solid scintillator (SSC) particles (e.g. CaF_2 [2] or Y_3SiO_4. [3]). On-line LSC is susceptible to chemical and colour quenching due to the unfavourable ratio of scintillator to solution to be measured (3–4:1) and, in addition, it yields an unusual waste which is difficult to dispose of. In on-line SSC, the scintillator particles cause a significant pressure build-up and large memory effects are often observed depending on the medium used [4]. These negative effects are acceptable or partly avoidable in analytical grade separation monitoring [5]. The waste volumes are small, the medium can be kept constant and, thus, the quenching effects corrected. Safe high-pressure equipment is available (HPLC) and memory effects are avoided by choosing an adequate eluent. It is, however, obvious that these effects strongly impede the employment of the above procedures for technical grade separations with predefined starting parameters.

When we developed the monitoring system for a treatment process for analytical wastes containing Pu [4], we overcame the above problems by designing a cylindrical cell [6] with Perspex™ windows at the top and bottom covered on the inside surface by the thermoplastic scintillator Meltlilex™ [7]. This material melts at ≈60°C, keeps its scintillation properties up to 120°C and can thus be easily shaped on transparent or translucent plastic materials. The solution to be measured was pumped through nozzles into the cell interior and left the cell through another set of nozzles placed at the opposite cell wall. The detector operates without pressure build-up, shows no significant memory effects and has only a slightly delayed response due to temporary dead zones within the cell. The cell is, however, susceptible to plugging and the scintillator has a limited lifetime. After exhaustion, the cell has to be replaced as a whole, when used in areas with restricted access, as it appears impossible to replace the windows contaminant-free under remote conditions.

In this paper, we introduce an even simpler and cheaper version of the cell which can be manufactured under routine laboratory conditions without sophisticated equip-

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ment. It is easily adapted to commercial scintillation counting equipment and its replacement does not constitute a significant cost factor.

2. Experimental

We carried out our experimental work within the framework of investigations on high-level radioactive waste partitioning. Therefore, in our detector tests we focused on transuranium isotopes and special long-lived fission products and used components of a commercial HPLC and a custom-made front chromatography separation unit.

2.1. Chemicals and equipment

The radioactive isotopes were obtained from Isotopendienst, Waldegg, Germany. The Sr/Y-90 couple was separated using a routine ion chromatographic method. We calibrated our dilute solutions with the LSC TriCarb 1900 CA, Packard Instrument Company, Meriden, CT, USA.

For the tests, the detector was adapted to the radioactivity monitor LB 506 C/1 from EG and G Berthold (Bad Wildungen, Germany) and operated in two modes with reference to the chromatographic techniques employed in our institute:

- *the dynamic mode*, as used for elution chromatography, feeding a 20 μl sample into the HPLC delivery system S1020 (Sykam GmbH, Gilching, Germany) and flushing the sample loop with an eluent; in this mode we used a detector cell with a volume of 0.41 cm^3, a surface of 12.3 cm^2 and a residence time of 24 s;
- *the stationary mode*, as used for front chromatography, by permanently conveying the radioactive feed solution through the detector by a peristaltic pump (Verder GmbH, Haan, Germany).

Chemicals were procured from Merck, Darmstadt, Germany in p.a. quality. For the detector adaptation, we used stainless steel fittings from the Swagelok Companies (B.E.S.T, Bornheim, Germany).

2.2. Preparation of the detector

As raw materials, we used the plastic scintillator Meltilex$^{\text{TM}}$, a product of Wallac, Turku, Finland, and transparent PFA (perfluoroalkoxy) tubes from Dupont, USA, supplied by B.E.S.T., Bornheim, Germany. According to the manufacturer [7], Meltilex$^{\text{TM}}$ consists of a low molecular weight aromatic polymer and an ethylene vinyl acetate copolymer together with paraffin. The fluors PPO (diphenyl oxazole) and MSB (methyl styryl benzene) are dissolved at 100°C in the mixture. At room temperature, the product is solid ($S=0.96$ g cm^{-3} and translucent and is available in thin foils (100×200×0.5 mm). The PFA tubes used were of different sizes (outer diameter × wall thickness (mm): 8×1.5, 6×1, 6×1.5, 3.175 ≙ 1/8‘)×0.8).

We cut the scintillator foil into thin stripes and placed the stripes into the PFA tube. Then, by means of a fan we blew hot air (85°C $\leq T \leq$ 195°C) through a nozzle into the filled tube. The Meltilex$^{\text{TM}}$ melted and the liquid was vortexed by the air stream through the tube forming a thin liquid layer at the tube walls. When the entire inner tube surface was covered with the liquid, we continued blowing hot air into both ends of the tube, alternately, thus homogenising the Meltilex$^{\text{TM}}$ layer. Finally, we cooled the tube down at room temperature [8]. Tubes with an inner diameter >3 mm could be coated without further support for the melting process, smaller tubes were additionally heated in a water bath at boiling temperature, as the hot air throughput was too small to achieve a homogeneous scintillator layer. We determined the mass of the scintillator coating by weighing and controlled the layer thickness by blowing out excess Meltilex$^{\text{TM}}$ and repeating the coating process. We replaced the commercial detector cell of the LB 506 (Berthold, Wildbad, Germany) and mounted the coated tube on the cover plate with bulkhead unions without further modification to the detector chamber. In the left-hand part of Fig. 1, the components of the detector cell, the raw materials Meltilex$^{\text{TM}}$ and PFA tube and the mounted cell already adapted to the LB 506 counter are shown. The right-hand part shows the cross sections of several coated tubes. The photographs were taken under UV light.

3. Results and discussion

In our tests, we investigated the preparation parameters, the energy dependency of the count rate for α- and β-emitters, the detector efficiency and sensitivity, the low-level detection limits for α- and β-emitters in pure solutions and for α-emitters in the presence of β-emitters and possible ways for at least partially discriminating β- from α-detection.

3.1. Preparation parameters

We identified two significant preparation parameters, the tube length and the coating temperature. With the simple equipment we deliberately imposed on the preparation procedure, we determined the maximum coatable tube length as 40 cm for 1/8 in. tubes. The length of tubes with larger outer diameters was limited to 20 cm by the detector chamber geometry.

We coated tubes at 85°C and 195°C (fan temperature) keeping the other preparation parameters constant. We could not discover any significant differences in the count yield. We concluded that the scintillator does not decay if briefly exposed to temperatures above the stability limit of

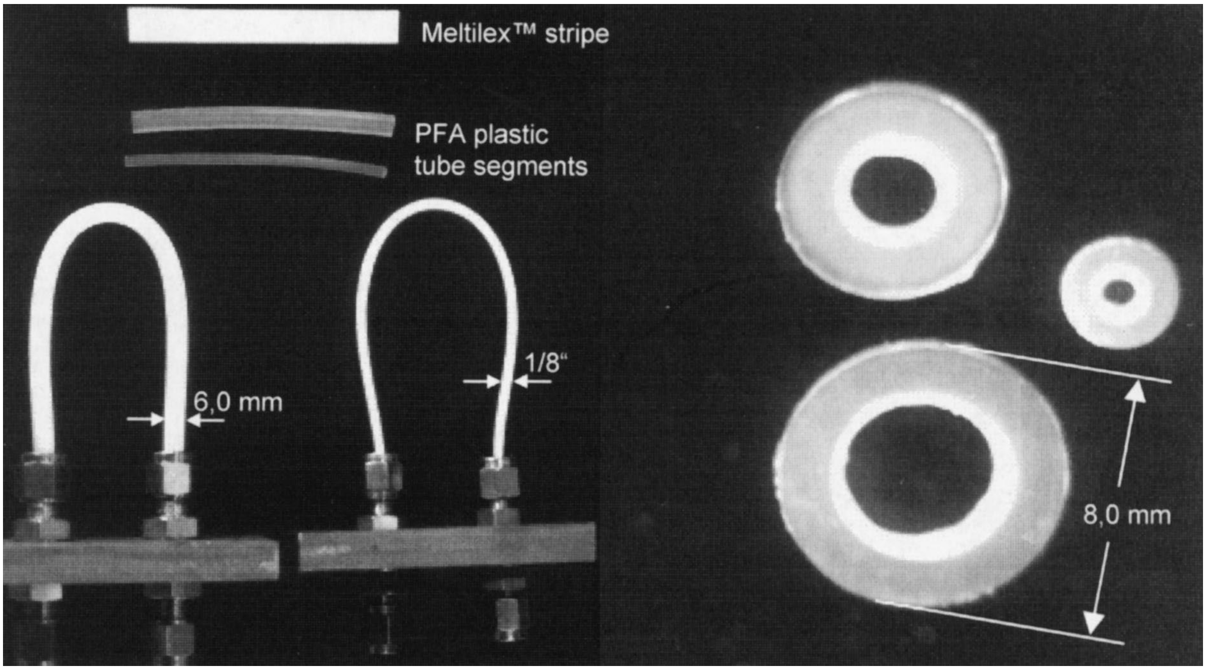

Fig. 1. Components of the detector cell; left: raw materials, coated tubes and mounted cells, right: coated tube cross sections.

120°C as stated by the manufacturer [7]. We therefore established the high-temperature procedure, since in this way we obtained smoother scintillator surfaces.

We determined the coating homogeneity by cutting a coated tube into small segments of equal length and weighing the segments. We noted differences between individual segments in the same order of magnitude as those of corresponding uncoated tube segments, and we inferred that the coating was sufficiently homogeneous over the whole tube length.

3.2. α- and β-energy distribution

We acquired the energy spectra of the selected fission product (Sr/Y-90, Ru/Rh-106, Sb-125, Cs-134, Pm-147) and actinide (U-233, Am-241, Cm-244) isotopes in the stationary measurement mode. The four results are depicted in Fig. 2 normalised to a specific activity of 5000 Bq ml^{-1}. The measurement cell used had a volume of 2.3 cm^3 and a scintillator surface of 19.3 cm^2. We found the expected strong dependency of the count rate on the β-energy for the fission products. The spectrum shows a slight decrease at low energies (up to 200 keV) and a precipitous one beyond that level. The α-spectra decrease more strongly at low energies and form a plateau between 100 and 300 keV. At higher energies, the α count rates exceed those of low-energy β-emitters such as Sb-125 and Pm-147. The overall α count rate, however, is orders of magnitude lower than that of high-β-energy emitters due to the absorption within the medium.

3.3. Calibration curves

We calibrated various detectors in the dynamic and in the stationary mode. In either case, we obtained straight lines with a correlation coefficient of >0.999 for the individual isotopes, regardless of whether we used the full energy range or arbitrarily set an energy window. Fig. 3 shows the calibration curves for individual α- and β-emitters over the entire energy range acquired in the dynamic mode.

In Fig. 4, we adapted a single calibration curve to the α-emitters. The measurements were carried out in the stationary mode with a 2.34 cm^3/21.7 cm^2 cell using the energy region between 100 and 300 keV. According to Fig. 2, α-emitters have an almost identical count rate in this region. In a first approximation, all the measured values fit the straight line sufficiently (correlation coefficient = 0.991); if more accurate measurements are required, individual calibration is also recommended for α-emitting isotopes.

3.4. Efficiencies and detection limits

We obtained the detector efficiency in the dynamic mode (ε_{dyn}) using Eq. (1) and in the stationary mode (ε_{stat} using Eq. (2).

$$\varepsilon_{dyn} = \frac{\text{net counts}}{A*rt} \quad \text{with: } A = \text{ activity [Bq]} \qquad (1)$$

rt = Residence time [5]

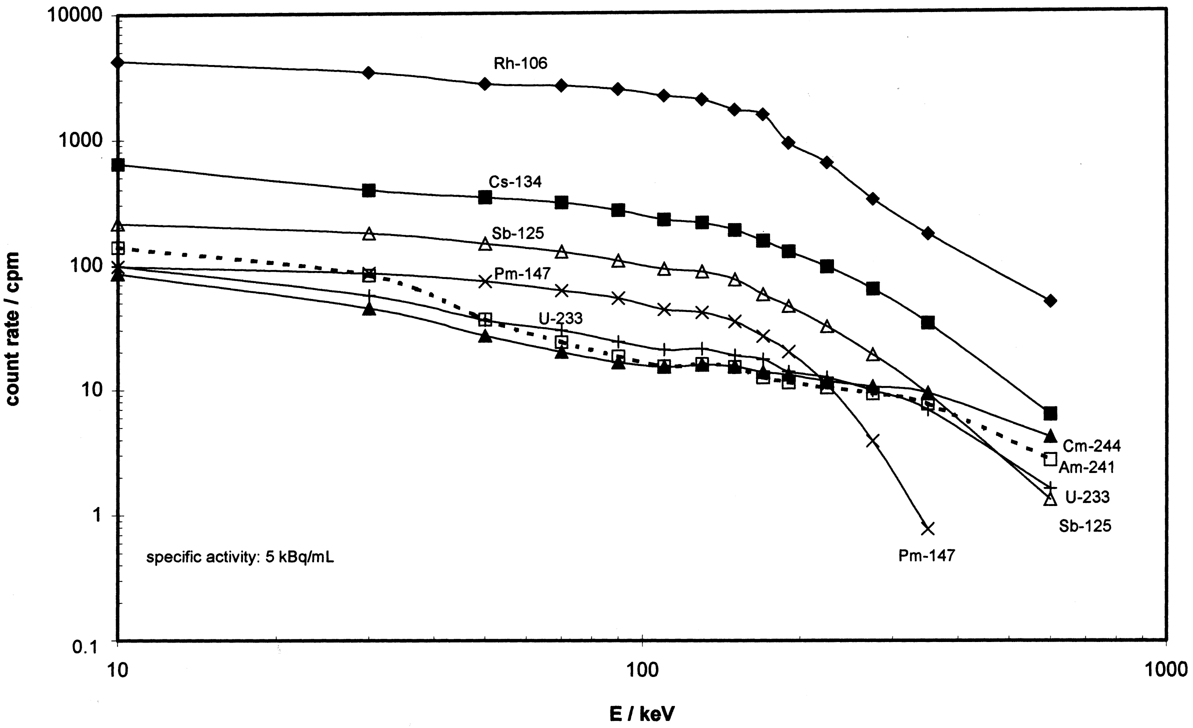

Fig. 2. Energy spectra of α- and β-emitters.

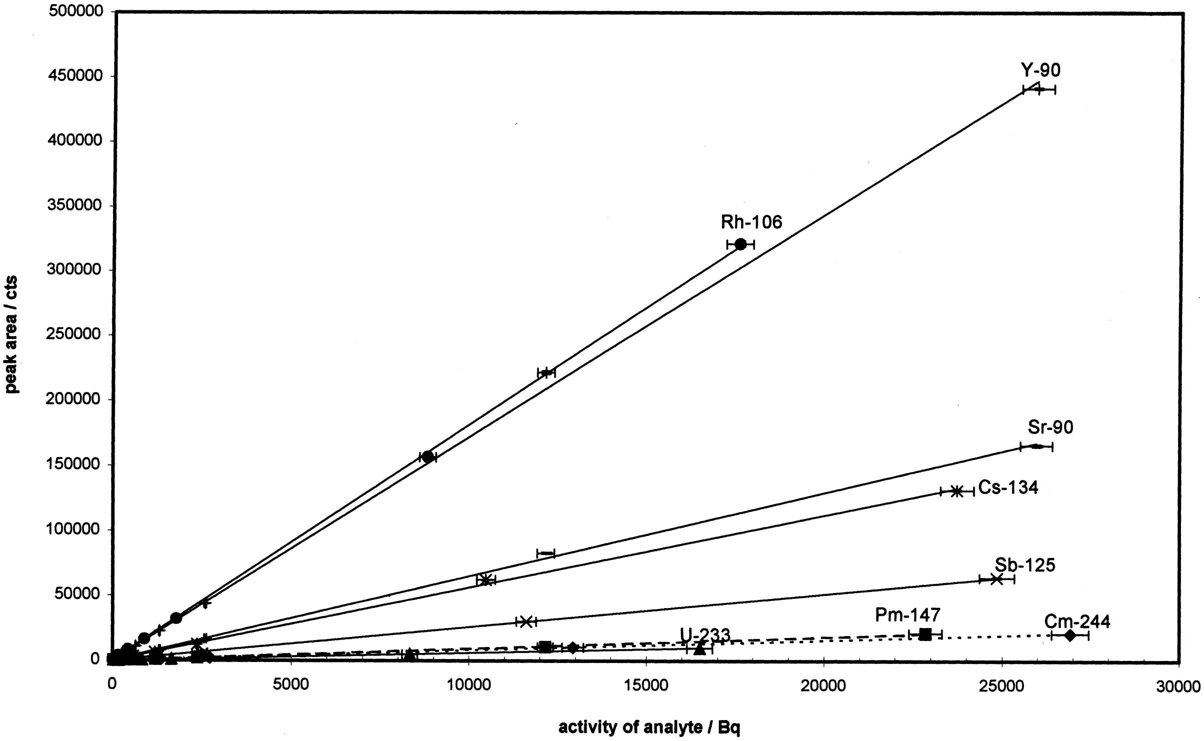

Fig. 3. Calibration curves for individual α- and β-emitters (full energy range).

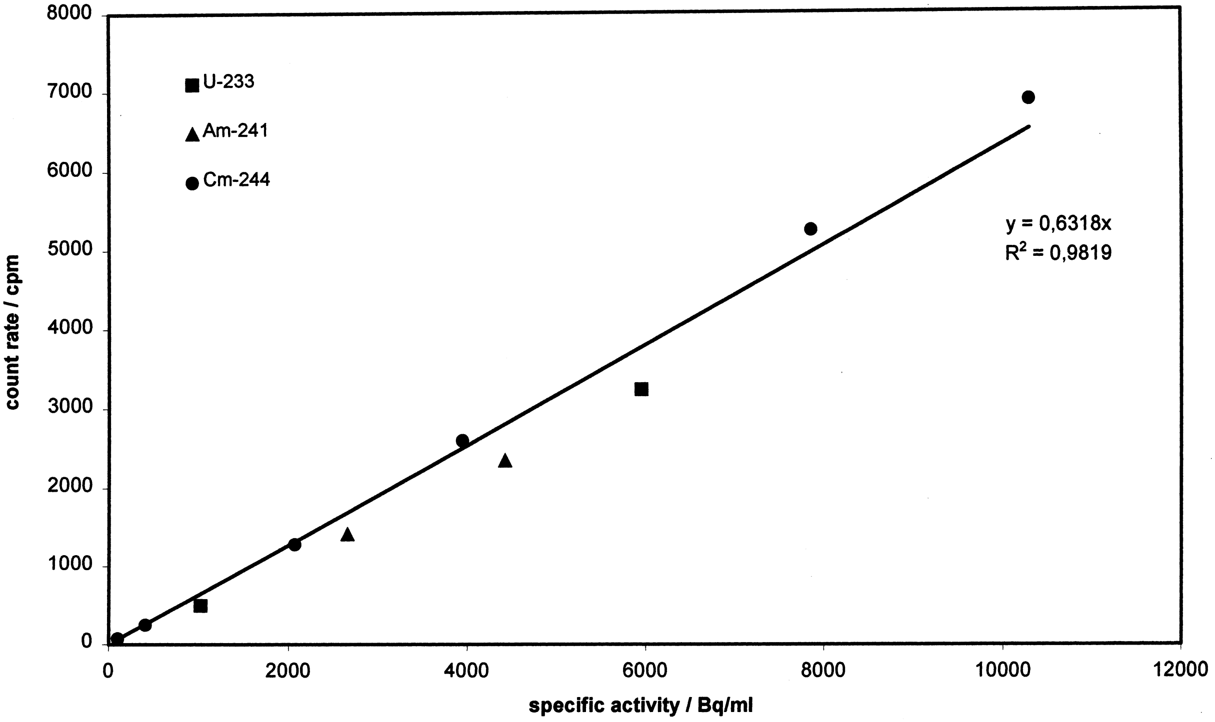

Fig. 4. Calibration curve for α-emitters.

$$\varepsilon_{\text{stat}} = \frac{\text{net count rate}}{A^{*}_{\text{spec}} V_{\text{cell}}} \qquad (2)$$

A_{spec} = specific activity [Bq ml^{-1}]

V_{cell} = cell volume [ml]

We compiled the results of our measurements in the dynamic mode in Fig. 5. At low energies, the β-efficiency shows a steep increase and assimilates to a maximum value for high-energetic β-emitters as Y-90 and Rh-106. The α-energies do not fit into the curve, due to their poor energy–light conversion and their short free mean path λ. Assuming $\lambda \approx 50$ μm for α-particles in aqueous solutions and a conversion factor of ≈0.1, we assessed the α-efficiency to be in the range of Sr-90. By comparing the results with those acquired in the stationary mode (Table 1), we found great differences for α- and low-energetic β-emitters, e.g. Cm-244 and Pm-147, which almost disappeared for high-energetic β-emitters like Rh-106. We ascribe this effect to absorption in the solution, since we used a detector with a 1.3 mm inner diameter for the dynamic and a 4.7 mm diameter for the stationary measurements.

In Table 1, we also listed the detection limits determined in the dynamic and the stationary mode. These two sets of values should, however, not be compared, as the reference value is the minimum activity per injected sample for the dynamic mode and the minimum specific activity per conveyed feed solution for the stationary mode. The values of Table 1 refer to the full energy range. Setting energy windows, the detection limits of β-emitters deteriorate much more than those of α-emitters which benefit from their almost constant count rate over a wide energy range as can be seen in Fig. 2. As the background drops strongly at higher energies (>100 keV), the a detection limits improve. Using a 2.34 cm^3/21.7 cm^2 cell in the stationary mode we determined the detection limit for Cm-244 over the full energy range to be 23 Bq ml^{-1} (different from Table 1). By setting the energy window to 0.1–1 MeV, we obtained 8 Bq ml^{-1} and in the range 0.1−0.3 MeV, we found 8.9 Bq ml^{-1}.

3.5. *α/β-discrimination*

In principle, the detector responds with a higher count rate to β-emitters above 0.3 MeV than to α-emitters. This appears to be insignificant in combination with elution chromatography, as an isolation of the nuclides to be measured is carried out on the column. In front chromatography, however, only a partitioning takes place (e.g. a partitioning of α-emitters from other waste components), and all the unretained isotopes run through the column and contribute to the total detector signal.

We have identified two ways to at least improve the unfavourable α/β-count rate:

(1) by setting appropriate energy windows and (2) by reducing the cell diameter ϕ_{cell}.

We summarised the results of these two possibilities in Table 2 using Cm-244 as α- and Rh-106 as β-emitters. The

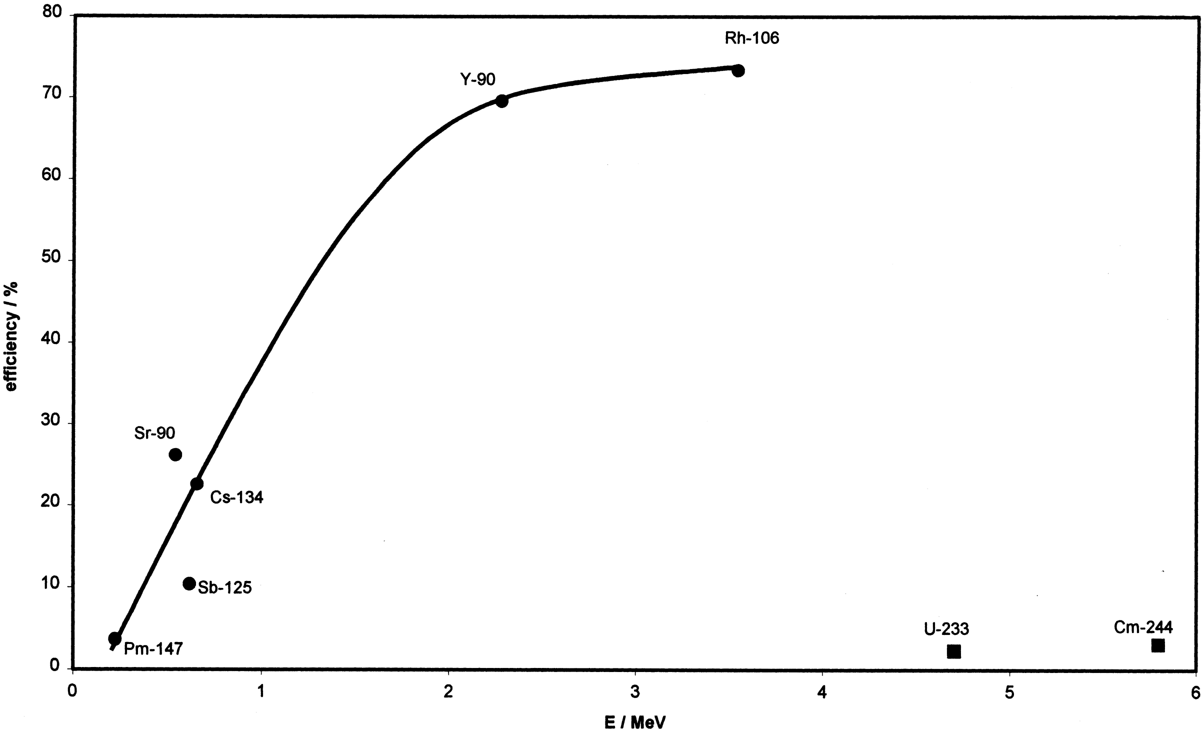

Fig. 5. Efficiency of α- and β-emitters.

Table 1
Efficiencies and detection limits

Nuclide	Energy (MeV)	Dyn.efficiency (%)	Stat. efficiency (%)	Dyn. detection limit (Bq)	Stat. detection limit (Bq ml^{-1})
Pm-147	0.225	3.6	1.6	70.9±1.3	29
Sr-90	0.546	26.1		3.4±0.6	
Sb-125	0.621	10.3	3.7	21.6±0.6	12
Cs-134	0.658	22.6	10	4.2±0.8	4.5
Y-90	2.279	69.6		1.4±0.2	
Rh-106	3.54	73.4	78	1.4±0.3	0.6
U-233	4.70	2.3	1.2	53.8±3.7	38
Am-241	5.41		1.4		33
Cm-244	5.80	3.1	1.2	45.5±7.8	38

nuclide values are normalised to 1 Bq ml^{-1}. By applying both measures, a significant amount of even the high-energetic β-emission can be suppressed.

Table 2
Ratio of count rates Cm-244/Rh-106 for different energy windows

energy range→	full range	100–300 keV	100–1000 keV
ϕ_{cell}	Ratio of count rates Cm-244(α)/Rh-106(β)		
[cm]	[-]	[-]	[-]
0.43	0.015	0.022	0.020
0.38	0.018	0.025	0.033
0.27	0.024	0.066	0.075
0.12	0.048	0.083	0.110

4. Conclusions

We designed and manufactured a simple solid scintillation cell which can be built employing ordinary laboratory equipment. The cell is made by vortexing the melted scintillation material (Meltilex$^{\text{TM}}$) through a transparent heat-resistant plastic tube. After cooling, the scintillator adheres tightly to the inner tube surface forming a homogeneous thin layer. The tube can be readily adapted by easy means to commercially available radioactivity counters and used in an on-line mode. After coating, the scintillator maintains its advantageous properties, it is insoluble in water and most organic solvents, and resistant to oxidizing and reducing agents. Originally, the detector was designed for technical scale flow monitoring, as it does not show memory effects nor pollute the detector effluents with scintillator components and the pressure build-up in a separation unit by the detector is negligible. The efficiency and detection limits are quite satisfactory for technical scale separations. In addition, we showed that monitoring of analytical scale separation processes such as the HPLC appears to be feasible. In principle, the detector monitors gross α- and β-disintegration. We could, however, fade out a significant part of the β-emission by choosing the appropriate detector geometry and by setting energy windows. The effect may even be improved with tubes of a diameter below 0.05 cm. Such tubes have already been prepared, but not yet tested. For gross α-counting, we recommend setting the energy region to 100–300 keV, despite slightly lower efficiency and reduced β-suppression. In that region we obtain a better agreement of the results among different detector cells. The full energy range should be used for gross β-counting and determination of individual isotopes. Further studies will focus on the long-term use of the detector for monitoring technical scale separations including its resistance against radiolytic decomposition and chemical attack.

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