Surface degradation of laminated metal ^{226}Ra foils used in school sealed sources in the UK

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Abstract

In the few years leading up to this research, CLEAPSS noticed a small but steadily increasing number of calls from UK schools regarding a red-brown discolouration on the surface of the foil of their radium source. There were no reports of this type of discolouration on foils of other radionuclides. CLEAPSS and the University of Liverpool collaborated to investigate the nature and cause of this discolouration and the likelihood that the foils were becoming unsafe. The evidence indicates that the discolouration is principally caused by some combination of silicon, sulfur and possibly lead from within the foil diffusing into the face layer. There is no indication currently that the face layers are fragmenting on these foils, but the longer-term integrity of the discoloured foils now becomes questionable. Given the age of the foils and the radiotoxicity of radium, the recommendation from this research is that discoloured foils should be taken out of service and disposed of.

Introduction

Small sealed sources are commonly used in UK secondary schools for science teaching. The sources became widely available in the early 1960s. The common design of the sources is known as the cup-style. See figure 1. This comprises a radioactive laminated metal foil, (except for the ^{60}Co source which is not a foil, but a small pellet of cobalt metal) typically 185 kBq, mounted in a small recessed holder. The radionuclides that have been used in the foils are ^{226}Ra, ^{241}Am, ^{239}Pu and ^{90}Sr, although radium and plutonium foils were discontinued several decades ago. The last catalogue entry for radium cup-style sources in the UK from school-science equipment suppliers was in 1998.

Figure 1. Photograph of a recently-purchased cup-style source.

In the past few years, CLEAPSS noticed a small but steadily increasing number of calls from schools regarding a red-brown discolouration on the surface of the foil of their radium sources. The reports came from schools mainly when they had carried out the periodic leak-test and inspection of sealed sources, a requirement of the Ionising Radiations Regulations 2017; the inspection includes an indirect visual inspection of the foil surface which is usually done with a mirror. There were no reports of this type of discolouration with foils of other radionuclides. CLEAPSS and the University of Liverpool collaborated to investigate the nature and cause of this discolouration and the likelihood that the foils were becoming unsafe.

This change in the foil surface looks to be a relatively sudden transition. The surface appeared for decades to be highly-reflective, just as it was when new. Then, in just a few years, it changed from a highly-reflective to a dull surface with a red-brown cast, seen now. See figure 2.

Figure 2. The front of a radium foil cup-style source (R01) showing the dull red-brown foil surface. In this example, the colour is mottled. (The foil is behind the mesh.)

Source design.

The design had to meet a specification set by the then government Department of Education and Science (currently the Department for Education) in the 1960s (Dance 1967). The cup-style sources currently sold by UK science equipment suppliers still conform to this original specification. The cup-style design has been detailed by Whitcher *et al.* (2014), but for convenience, the salient points are repeated here. As can be seen in figures 1 and 2, the holder is a metal cylinder that is recessed, external diameter roughly 15 mm, internal diameter a little over 10 mm and recessed by 5 mm. The foil is a 10 mm disc held in place by a circlip, and sometimes adhesive too. The front of the cup is protected by a wire mesh held in place by an interference-fit cap. The rear has a spigot so the cup can be manipulated with forceps.

Fabrication of the radium foil

The foils were originally manufactured by the Atomic Energy Authority Radiochemical Centre, Amersham. This became Amersham International plc, and through various transitions, renamed as Amersham plc up to 2004, covering the period when radium foil cup-style sources were available to schools. The evidence from the packing notes supplied by Amersham with the sources is that the foil design did not change significantly over the decades. The same overall process was used to fabricate the ^{226}Ra and ^{241}Am foils (Amersham 1991).

The radium used to fabricate the foil was in the form of radium sulfate. It was widely used in manufacturing radium sealed sources because it is insoluble in water, has no water of hydration, and is not hygroscopic. (Radium, an alkaline earth metal, is very reactive, consequently unsuitable in metal form for fabricating foil sources.) The radium sulfate was first mixed with gold powder. Once mixed, the gold and radium sulfate was sintered at 800 °C to form a small briquette. The briquette was then partially encased with silver on the sides and base. The Amersham note also described a gold interface, a layer of gold beneath the sintered radium sulfate and gold, but it is not clear if this was added at the sintering or encasement stage. A gold layer (or less commonly for radium sources, a gold-palladium alloy layer) was hot-forged on the top of the briquette to seal in the radium sulfate. The fully-encased briquette was cold-rolled repeatedly to form a laminated foil, about 0.15 – 0.2 mm thick. The foil has two distinct side edges of silver, formed from the silver part of the encasement. See figure 3.
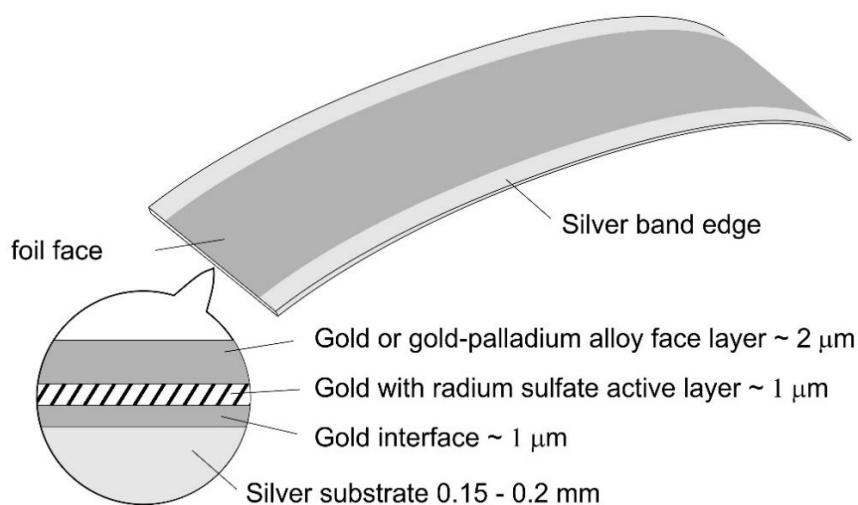

Figure 3. Diagram (not to scale) showing the construction of a laminated radium foil.

The face layer thickness is a balance between being thick enough to protect the active layer, and thin enough so the energy of the emergent alpha radiation is adequate for the intended practical work.

Discs of diameter 10 mm were stamped from the foil. Each disc contained about 5 μg of radium in the active layer, giving a nominal activity of 5 μCi, i.e. 185 kBq, although the activity variation among the radium discs was about 50% either way (Lucas 1966). The width of the rolled foils was reported as 20 mm (NEA 1977). However, the width of some rolled foils was less, around 10 mm, because one of the authors has observed some stamped discs with two silver edges. The stamping was designed to cold-weld the edge of the disc so that the active layer was sealed within the inactive metal layers. The National Radiological Protection Board (NRPB, now Chemical, Radiation and Environmental Hazards within the UK Health Security Agency) carried out foil integrity tests on plutonium and radium foils (Williams 1974). The tests included wipe tests directly from the side and face surface of two new radium disc foils. The wipes had very small but detectable activity, mainly from the disc side. The highest was 46 Bq (1230 pCi). The wipe directly from the face surface was very small, 5 Bq (125 pCi). Williams concluded that, for radium foils, the stamping did not completely seal the active material between the layers. The activity was probably from radium and the decay chain, but this was not stated in the NRPB report. The [222]Rn outgassing could also be contributing to the surface contamination, with a fraction of the decay chain products plating-out on the foil surface.

Radium sealed foil source as a teaching source

Radium has several marked limitations as a foil source for secondary science teaching. It has a branching decay chain, but the principal chain comprises eight radionuclides before reaching stable ^{206}Pb. Only 0.04% of the decays branch from the principal decay chain from ^{226}Ra to ^{206}Pb. See figure 4
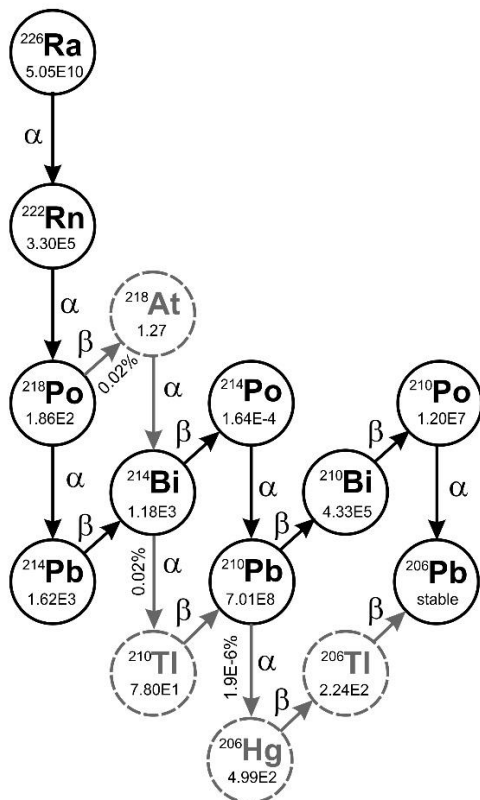

Figure 4. ^{226}Ra and its decay chain. The principal radionuclides in the chain are shown in solid black circles. The half-lives are given in seconds. The main gamma emitters in the chain are ^{214}Pb and ^{214}Bi. (Data from the National Nuclear Data Center, Brookhaven National Laboratory.)

Owing to the growth of the decay chain, within a few months, 185 kBq of initially pure ^{226}Ra will reach a total activity of over 1.2 MBq. Radium and its decay chain is a prolific emitter of alpha and beta particles, gamma and x-ray photons, and conversion electrons, so the source is of limited use in demonstrating the characteristics of a particular emission unless the detector is insensitive to all but that type of emission. Radium also poses a problem for leak-testing; it decays to ^{222}Rn which has a half-life of 3.82 days. In the time before decay, the radon can diffuse through the foil face layer. This happens significantly in about 30% of radium foil sources (Whitcher 2009) to the extent that the subsequent radionuclides of ^{222}Rn plate-out on nearby surfaces and cause low but measurable contamination. It is difficult for a school to distinguish the contamination from ^{222}Rn outgassing from ^{226}Ra contamination caused by a loss of seal integrity.

Hypotheses on the cause of the discolouration

The initial suspicion was that the discolouration was being caused by external contact with a corrosive agent, for example, hydrochloric acid from a leaking protactinium generator, or the adhesive that was used to hold the foil in place. These ideas were quickly discounted because there was no evidence that the discoloured foils in this study had ever been in contact with corrosive

chemicals, particularly source R03 which had been stored at CLEAPSS for decades. The discolouration was also observed in foils that were retained by a circlip only, therefore eliminating foil adhesive as the cause. An electrochemical reaction between the dissimilar metals was also highly unlikely because the discolouration was not observed on americium or strontium foils. Consequently, this research focused on the following two hypotheses for the discolouration.

1. Significant radium compound migrating into the face layer.
2. Other material in the active layer, including material from chemical changes caused by newly-formed radioactive atoms, migrating into the face layer.

Methods and results

Selection of radium sources for investigation

Four sources were selected, three that showed discolouration and one that appeared in good condition with a shiny gold surface. CLEAPSS contacted two schools where the photographs showed the foils were held by circlip only, rather than circlip and adhesive. This meant the foils could be removed from the source holders for further investigation. CLEAPSS holds cup-style sources for training courses and legacy research. One of the sources had begun to show discolouration, and in the short time it was taken out of service, the discolouration had increased noticeably on subsequent inspection. The foil in this source was retained by circlip and adhesive. The radium source R04 was in good condition; it was from a set of sources donated by a school that was permanently closing and had no further need of them.

The date of manufacture was uncertain for three of the sources, but an estimate could be made from the style of the lead-pot wooden box container used for storing the source and the style of labelling on it.

Source identifier	Date purchased	Foil retention	Front face material (from face colour)	Discolouration
R01	estimated 1960s	circlip	gold	heavy
R02	school stated 1962	circlip	gold-palladium	noticeable
R03	estimated 1970s	circlip & adhesive	gold	noticeable
R04	estimated 1970s	circlip	gold	none observed

Table 1. All sources were nominally 185 kBq. The foil of source R01 had a silver band to one side of the foil face layer. There was no observable discolouration of the silver band. The foil of source R02 was of interest because, unusually, it had a gold-palladium face layer.

The four sources were leak-tested by the dry wipe method, wiping the cup-style source holder, not the foil directly, using cellulose filter paper. Using a ZP1481 GM detector and a count of 100 seconds, there was no detectable activity on the wipes.

Alpha energy spectra

If the discolouration is caused by significant radium sulfate migrating through the face layer, this would be indicated by the alpha energy spectrum of the foil. Alpha radiation loses energy as it passes through the face gold layer and causes a spread of energy. This is termed energy straggling; the thicker the layer, the more the straggling. Radium and its decay chain comprise five radionuclides that decay predominantly by alpha radiation (with consequent secondary emissions

such as gamma photons and x-ray photons). Of these five, [214]Po has the highest alpha energy of 7.687 MeV. See table 2

Radionuclide	Principal alpha energy / MeV
[226]Ra	4.784
[222]Rn	5.489
[218]Po	6.003
[214]Po	7.687
[210]Po	5.304

Table 2. The decay chain radionuclides that decay predominantly by alpha radiation.

The alpha spectra of the foils were analysed using a Canberra 7401VR alpha spectrometer with an 8k multi-channel analyser. The analysis was done with the foils in their cup holder. The spectra were very similar. Figure 5 shows the spectra of foils R03 and R04. Foil R03 was discoloured, foil R04 was not.
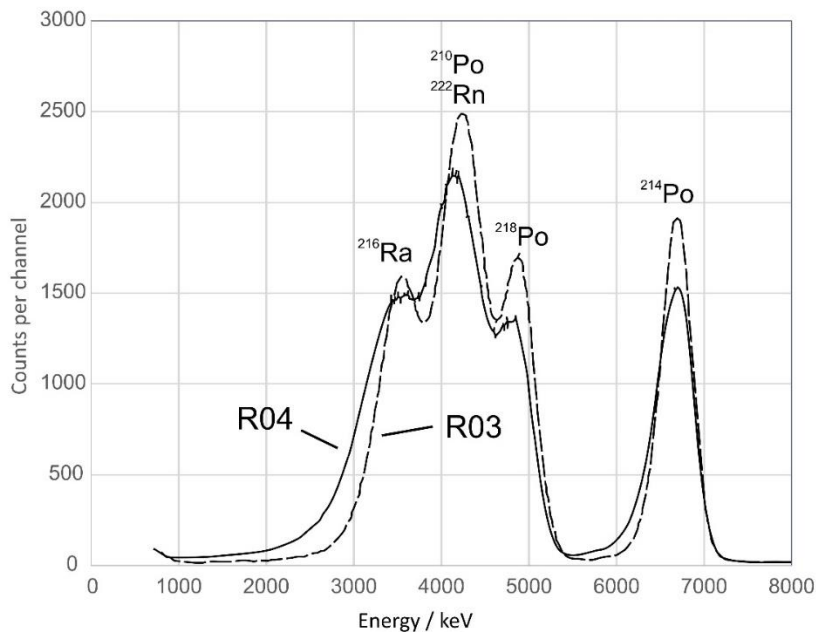

Figure 5. Alpha energy spectrum for [226]Ra foils R03 (dashed line) was a discoloured foil, and foil R04 (solid line) was not discoloured.

To estimate the foil layer thicknesses and compare them to the Amersham specification, the energy straggling was simulated with SRIM (Ziegler *et al.* 2010), software version 2013. The radium was modelled as normally distributed through the thickness of the active layer in a direction normal to the face layer. The simulation comprised 5E4 simulated emissions and assumed the [226]Ra decay chain was in secular equilibrium. The results were scaled to give the same total counts from the alpha spectrometry. A good fit by the simulation was achieved using a face layer of 1.25 µm and an active layer of 3 µm. See figure 6.
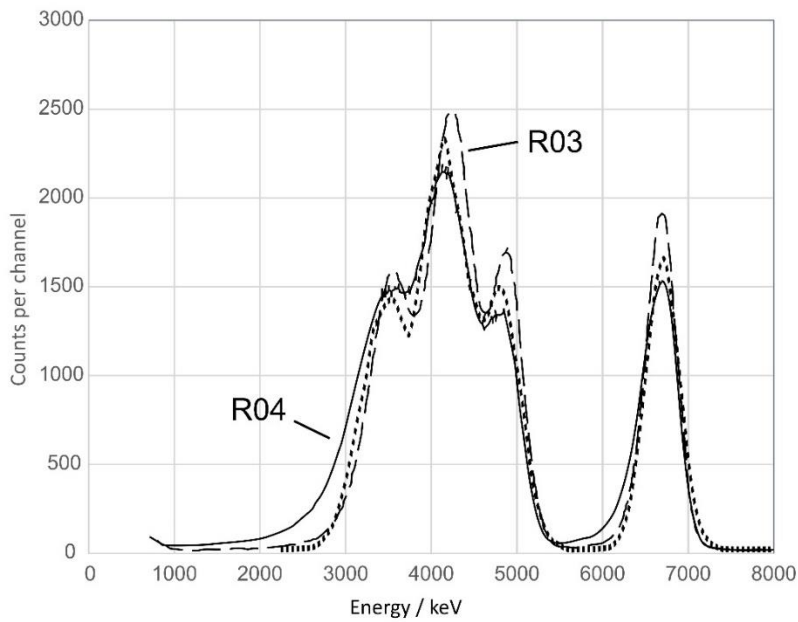
Figure 6. Monte Carlo simulation of the alpha particle energy straggling through the foil compared to the measured alpha energy straggling of foils R03 (dashed line) and foil R04 (solid line). The simulation result, shown by the fine-dotted line, shows the straggling of ^{226}Ra and its decay chain, normally distributed in a 3 µm active layer and faced with 1.25 µm gold.

The alpha spectrum for foil R01 was different from the others. It showed much greater straggling, indicating that either the active layer was thicker when manufactured, or there has been a net movement of the radium deeper into the foil. Again, the energy straggling was simulated with SRIM (Ziegler *et al.* 2010), software version 2013. The radium was modelled as before. A reasonable fit by the simulation was achieved using a face layer of 1.5 µm and an active layer of 9 µm. See figure 7.
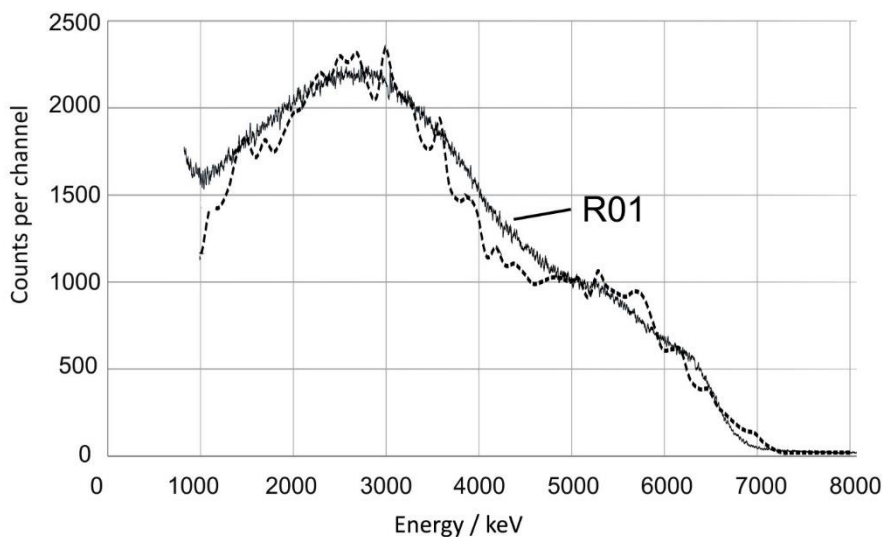

Figure 7. Monte Carlo simulation of the alpha particle energy straggling through the foil compared to the measured alpha energy straggling of foil R01 (solid line) and the simulation result, shown by the fine-dashed lined

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The face layer of foil R01 is within the manufacturer's specification, but not the active layer. This will not affect the integrity of the foil seal, but there will be increased alpha energy straggling. This will not unduly affect the performance of the source for science practical work owing to the high alpha energy of the ^{214}Po.

From the data, for all the foils, no alpha emission was detected, above the noise level of the multi-channel analyser, from the face layer beyond about 7.3 MeV. These data show the face layers are within specification for thickness with no faults such as fissures or pitting, otherwise there would have been a detection of alpha emissions at 7.687 MeV.

Gamma spectrometry of the foils

The spectra of the photon emission from the foils were analysed with an HPGe detector connected to an Ortec ASPec-927 16k multi-channel analyser. This was calibrated first with a 74 kBq ^{152}Eu calibration source. The gamma spectrum of each foil was as expected, showing the peaks for the ^{226}Ra and the decay chain. From the spectra, there was no evidence of any other radionuclides. See figure 8 which gives an example from foil R03.
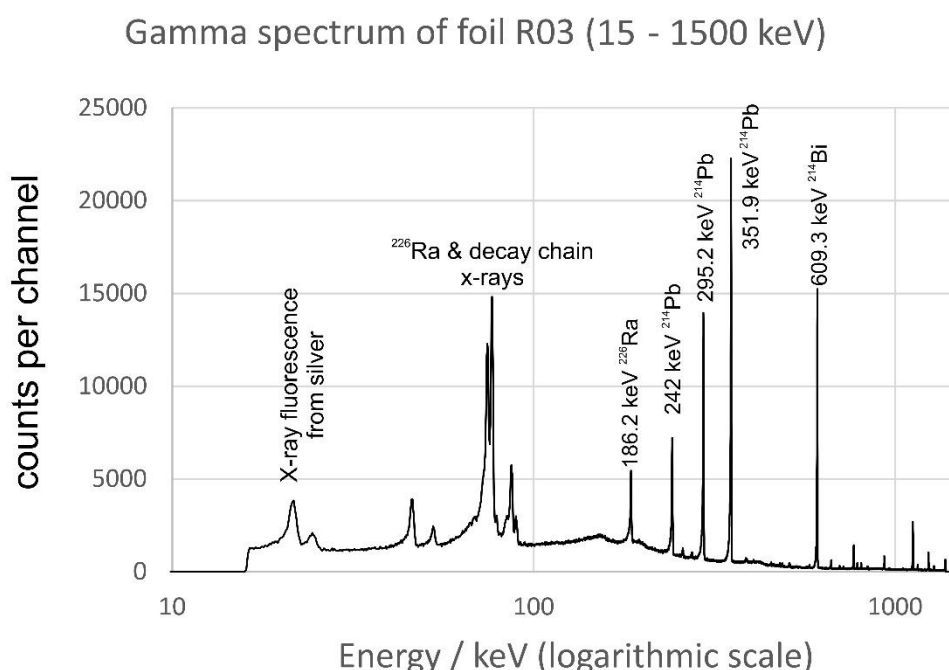

Figure 8. Gamma spectrum of R03 foil in its cup-style holder. The other foils gave near-identical shaped spectra.

Analysis of removable material from the foil surface

The alpha spectral data and the gamma spectral data do not provide evidence for non-radioactive materials in the face layer. Direct surface analysis by x-ray fluorescence (XRF) of the foil face layer does, but it would be hampered by the relatively high radiation field from the radium and decay chain in the active layer. However, a wipe could be used to remove unfixed materials causing or contributing to the surface discolouring, which could then be analysed using XRF, but the amount of material removed by the wipe will be small.

To access the foil surfaces, the wire meshes of the cup-style sources R01, R02 and R03 were removed by carefully cutting a slot down the interference fit caps and releasing the caps and mesh. This was done working over a plastic tray. The caps appeared to be plated copper from the colour of the metal as it was cut. The cutting caused a small amount of metal debris which was carefully removed by gently tapping the holder onto paper. The circlips of sources R01 and R02 were easily removed. The foil of R03 was held in place by both circlip and adhesive. The adhesive gave way with a small amount of careful easing of the circlip. The adhesive was easily removed but it is possible that but traces of the adhesive remained on the foil. During this procedure, additional precautions were taken owing to the radiation field, particularly from the beta emissions that can give appreciable dose rates, around a few mSv/h, at 10 cm from the foil. The foils were manipulated from behind a beta shield, using long curved forceps. The foils were photographed, see figure 9. The rear of foils R01 and R02 had a distinct gold-tinted band. It appears that gold has diffused through the silver, but why this is restricted to a band across the centre is not clear.
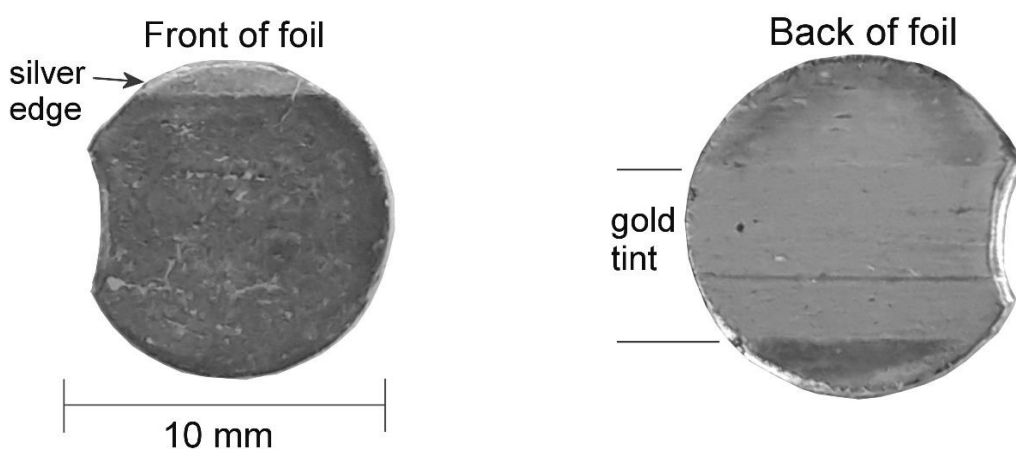

Figure 9. Photographs of the radium foil R01 that has been removed from its cup holder. The photograph on the left shows the front face. It is red-brown discoloured gold, with a silver band that comes from the edge of the rolled foil when it was stamped out. The red-brown discolouring covers all of the gold face but not the silver. The photograph of the back shows the silver is tarnished a little, and there is a distinct gold-tinted band across the centre. The disc is misshapen during manufacture because it was mis-stamped from the rolled foil strip. While not common, the mis-stamping is not rare because it has been seen several times by one of the authors.

Surface wipes were taken directly from the foil top faces. The wipes were Whatman No 42 low-ash quantitative filter papers, 42.5 mm diameter, taken from a new, sealed box of filter papers. The forceps jaws had additional filter paper fixed to them to minimise contamination from the forceps, such as fragments of metal, when holding the wipe. When the foil surfaces were wiped, there was no easily removable material from the surface of the discoloured foils; the wipes had to be pressed quite firmly to obtain a faint light-brown streak. This was surprising because visually, the foil surfaces appeared to have a layer of easily-removable material. The streaks on the filter paper from the wipes of foils R01 and R02 were weakly radioactive when checked with a Mini Instruments 900E contamination monitor. The wipe of foil R03 was fainter than R01 and R02. It did not show a count rate above background. The wipes were placed in small sealable plastic bags for gamma spectral analysis. This was undertaken using a Canberra BEGE 2825 with Canberra LYNX 8k multi-channel analyser. This detector covers a broad energy range of 3 keV to 3 MeV with a high resolution (0.70 keV full-width half-maximum at 122 keV). Long counting periods, around 90

hours, were used owing to the very low activity of the wipes. The background spectrum was taken over 24 hours and scaled to the same count time used for the wipes. The region of interest was the x-ray region and the gamma photon energies up to about 400 keV which is sufficient to identify radium and the decay chain. See figure 10. The spectra of wipes of foils R01 and R02 were identical in peak profile. The count rate from the wipe of foil R02 was nearly three times that from the wipe of foil R01. As suspected, there was no discernible gamma emission from the wipe of foil R03 above background.

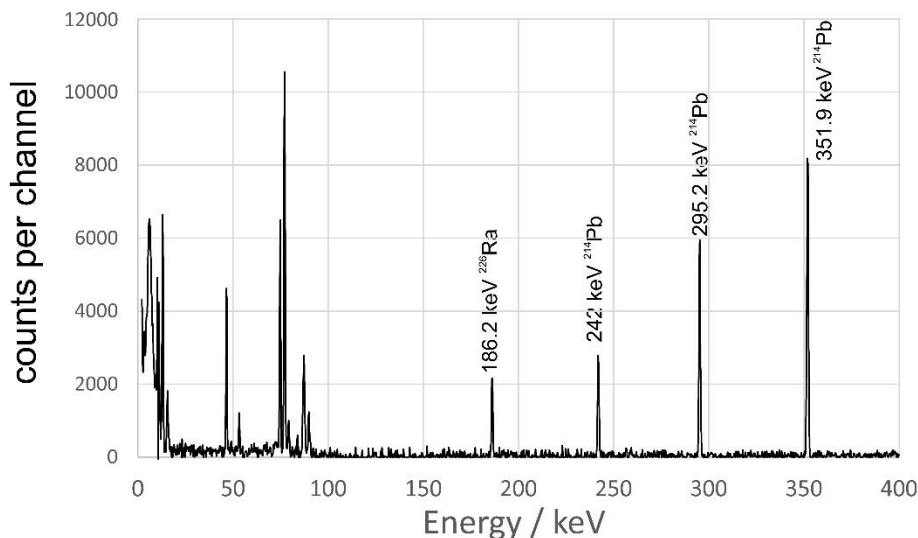Gamma spectrum of a wipe from foil R02, background subtracted (Count time 333800 s, RoI 3 - 400 keV)

Figure 10. The gamma spectrum of the wipe of foil R02, minus background, region of interest 3 – 400 keV.

The gamma spectrum of the wipe of foil R01 showed similar spectra but higher counts per channel over the same time. The net full-energy photopeak counts (wipe counts less background) detected from the significant gamma-emitting radionuclides were used to estimate the activity of each on the wipe. See table 3. The net full-energy photopeak counts were determined using Excel and graphically estimating the peak edges. Owing to the high-resolution of the Canberra BEGE 2825, the peak edges were well-defined. The calibration software Labsocs (Laboratory Sourceless Calibration Software) (Mirion Technologies Inc 2022) was used to determine the absolute detector efficiencies for the energies of interest.

Radionuclide	Energy of peak / keV	Estimated activity / Bq		
		Wipe of foil R01	Wipe of foil R02	Wipe of foil R03
^{226}Ra	186.211	7.3	3.2	< LoD
^{214}Pb	241.99	6.5	2.8	< LoD
^{214}Bi	609.321	4.8	2.4	< LoD
^{210}Pb	46.539	5.9	2.8	< LoD

Table 3. The estimation of radionuclide activity on the wipes. (<LoD = below limit of detection)

The activity of the wipe is given by $A = \frac{N_p}{e \times L \times p}$ where A is the activity in Bq, N_p is the net full-energy photopeak count, e is the full-energy photopeak absolute efficiency for the position of the wipe to the detector, L is the live time of the detection system, and p is the probability of the emission per decay. From this, the ^{226}Ra activities on the wipes of foils R01 and R02 were estimated as 7.3 Bq and 3.2 Bq respectively. The uncertainty of the estimated activities, which arises mainly from the error bounds of the efficiency determination, is no more than 0.8 Bq for the wipe of foil R01, and 0.4 Bq for the wipe of foil R02. These surface wipe activities correspond with the findings of Williams (1974).

X-ray fluorescence (XRF) analysis

An initial XRF analysis was carried out using a hand-held Niton XL3t, an energy dispersive spectrometer. The soil sample test mode was used, and 8 mm sample measurement areas. The sample time was 200 seconds. The soil mode uses Compton normalisation which is suitable for detecting elements likely to be less than 1% of the sample, by mass, which is the case with the material on the wipes. While it is suitable for initially characterising the elemental content of the material picked up on the wipe, there are several limitations to this approach. The Niton XL3t, although an advanced XRF spectrometer, will not have good accuracy for quantifying trace levels of elements (McIntosh *et al.* 2016), particularly low atomic number elements (Z < 18) where the intensity of fluorescence is poor. The Niton XRF concentration results were treated as relative because the concentration values were calibrated for a soil matrix, not filter paper. (The soil test mode assumes a soil matrix of about 1.8 g cm^{-3}, but the material under analysis is a smear on filter paper.)

The wipe material becomes an important consideration because trace impurities could give false positives. The Whatman No 42 filter paper specifications (GE Healthcare Life Sciences 2019) are favourable in that the typical trace element impurities do not include radium, lead, sulfur, gold, silver or palladium, elements relevant to this research. The typical trace element impurities in the filter paper exceeding 0.5 µg g^{-1} in concentration are, in µg g^{-1}, aluminium 2.5, calcium 8.3, chromium 1.5, copper 2, iron 12, magnesium 4, potassium 2.3, silicon 6.2, sodium 16.8, and zinc 64.5. However, there was no data on the distribution, i.e. the degree to which the impurity likely to be unevenly distributed through the paper, causing localised points at higher concentration.

Three readings were taken for each wipe. An XRF analysis was also carried out on several unused wipe filters, i.e. blanks, from the same packet. See figure 11. The vertical scale is logarithmic otherwise the low quantity detected elements would not show on the graph.
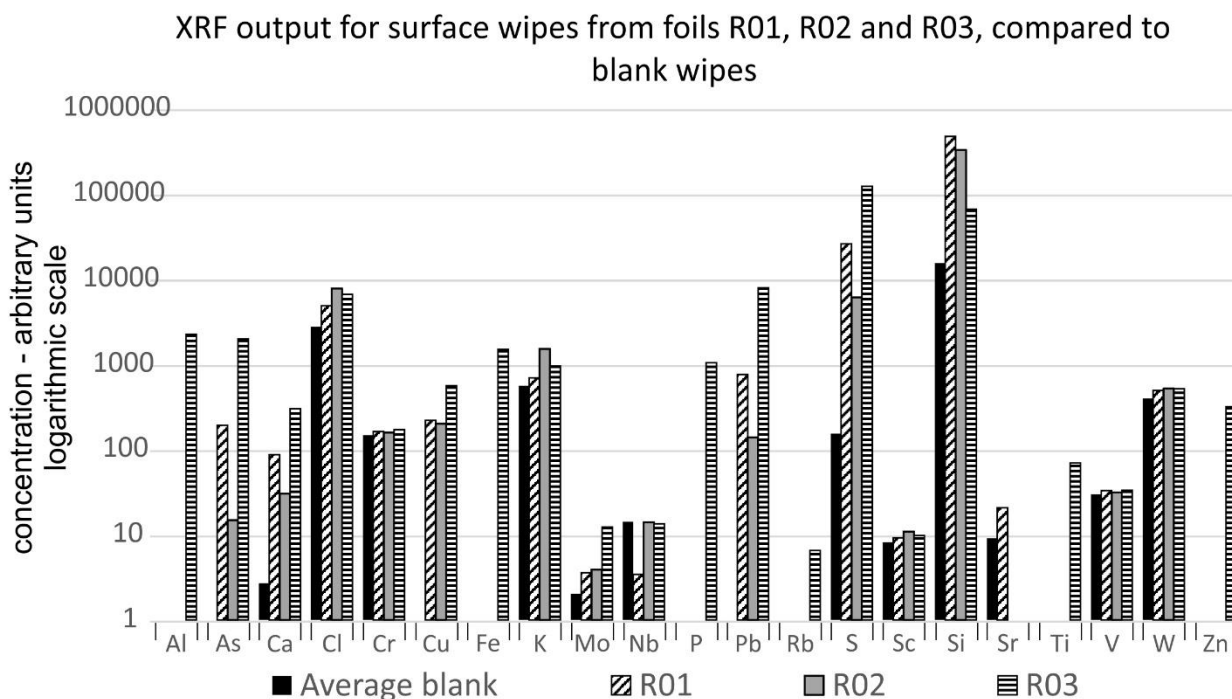
Figure 11. The concentration (arbitrary units) was the average of the three readings for each wipe. Note that the Y-axis is a logarithmic scale.

As an initial assessment, the energy-dispersive XRF showed that silicon and sulfur were the most prominent of the detected elements above the blank levels. The XRF data suggested traces of lead, calcium and copper, but at these low levels these could be false positives from impurities in the filter paper. (McIntosh *et al.* (2016) found that the Niton XL3t reports copper trace values with a positive bias.) The calcium detection was mainly on the wipe from foil R03. There was no gold, silver or palladium detected on the wipes. The concentration of elements such as chlorine, potassium and tungsten were not significantly above the levels in the blank filters. The R03 wipe low-level outliers could be from traces of adhesive, or localised impurities in the filter paper. The detection of arsenic could be a false positive, coming from the lead L3-M4 and L3-M5 transitions; it is a known problem with energy dispersive XRF. Another anomaly was the significant concentration of silicon on the blank wipes, more than would be expected from the manufacturer's specification of filter paper impurities.

The lead picked up by the wipes could be from contamination by lead (II) carbonate hydroxide, which often forms on the lead pots stored in wooden boxes, typical of the storage containers for cup-style sources. Following the analysis of the first wipe of foil R01, the foil was carefully swabbed with an ethanol-dampened filter paper to remove any loose material. There was no observable change to the foil surface, and no observable material on the swab; the discolouration appeared impregnated in the face layer and was not removed by ethanol. When dry, the foil was dry-wiped again with a fresh filter paper. As before, firm pressure had to be applied to obtain a noticeable streak on the filter. XRF analysis was undertaken on this, again with the Niton XL3t. The results showed that the silicon and sulfur, still present and in roughly the same proportions as in the first wipe. It also showed trace levels of lead. See figure 12. This confirmed that lead from the storage pot was not contributing to the trace level detected by the Niton XRF.
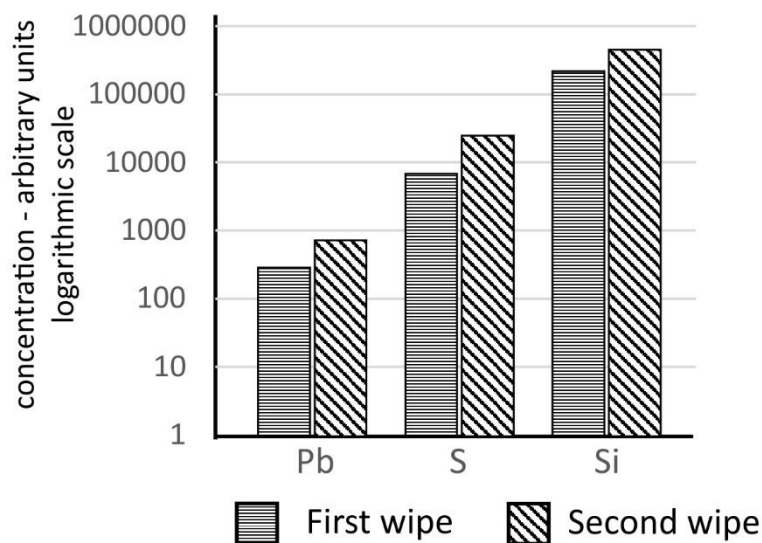
Figure 12. Comparison of Niton XL3t XRF results of two wipes of foil R01, the second taken after gently swabbing the foil face with an ethanol-dampened filter paper.

XRF analysis of radioactive samples brings an additional problem; the x-ray peaks from radioactive decays can affect the analysis. Energy-dispersive XRF instruments are particularly affected by this phenomenon (Worley 2008). However, the wipe of foil R03 showed no detectable activity and the XRF did show the same elevated levels of silicon and sulfur, and again with possible trace levels of lead.

To corroborate the presence of silicon and sulfur on the foils, and the suspected lead, calcium and copper at trace levels, the same wipes were analysed using a Rigaku Supermini200, high-power benchtop wavelength-dispersive XRF spectrometer, using Rigaku's SQX analysis software. The Rigaku x-ray power is 200 W, so the photon emission from radioactive decay will be much smaller in comparison. The Rigaku instrument has suitable light element sensitivity for detecting the elements of interest.

The Rigaku SQX results confirmed the relatively high levels of silicon on all the wipes. Sulfur and lead were also detected on all the wipes but at lower concentrations than silicon. The concentration levels reported are shown in table 4. Several blanks were tested and the highest concentration reported.

Wipe reference	silicon	Sulfur	lead
R01	0.524	0.0112	0.0003
R02	0.364	0.0146	0.0003
R03	0.0246	0.0040	0.0041
Blank	0.0000	0.0004	0.0000
Limit of detection	0.0033	0.00006	0.00003

Table 4. The Rigaku SQX results of the percentage concentration of the elements on the wipes compared with the mass of the filter paper. (The streak on the wipe from R03 was fainter compared with R01 and R02.)

From the Rigaku measurements, calcium was detected only on the wipe from R03, and only just above the limit of detection of 0.0023%. It could not be confidently distinguished from a localised filter paper impurity or possibly adhesive trace. Arsenic and copper were not detected on any of the wipes. These look to be false positives from the Niton XRF. In line with the Niton XRF data, chlorine was also detected, about the same as the levels detected in the blanks at around 0.009%.

Discussion

External environmental conditions are not causing the discolouration. No discolouration has been observed in americium and strontium foil sources (which have the same method of foil fabrication) stored for decades alongside radium sources in the same store. For sources R01 and R02, the schools confirmed that their radioactives store contained only sealed sources, there were no protactinium generators or other devices that had corrosive components. Similarly, source R03 at CLEAPSS is stored in a secure cabinet with other sealed sources and no items that cause corrosive fumes.

The gamma spectra show trace levels of radium on the wipes of foils R01 and R02 are commensurate with the levels found on new foils by the NRPB, and not an indication of the foil seal failing. The XRF data indicate that none of the gold or palladium in the face layer is loose, indicating that the face layers are not fragmenting and coming away from the active layers. This finding is supported by the alpha energy spectra.

The wavelength-dispersive XRF data consistently and positively detected silicon, sulfur and lead on the wipes, silicon being the predominant element. This raises the question of the origin of these elements in the metal foil top layer. The components in the fabrication of the foil were not just radium sulfate, gold, silver and palladium. Owing to the high specific activity of radium sulfate, only microgram amounts would have been needed to fabricate a foil and this would have made it impractical to mix it, in pure form, into the gold powder. Radium sulfate was commonly supplied with a relatively inert filler, for example, barium sulfate, to make the specific activity of the material much less (Van Roosenbeek 1968). Other fillers were also used, such as magnesium oxide (Pawlicki *et al.* 2016).

Silicon contaminant

This was unexpected. There is nothing about the use of silicon compounds in the literature relating to the fabrication of radium foils. Literature on the fabrication process and materials is scarce, and the exact details could have been restricted through commercial sensitivity. The silicon could be a component of the radium filler, possibly silica powder because of its stability, and in conjunction with barium sulfate. Equally, the silicon could be from a component introduced in the fabrication process, either at the sintering stage, or less likely, in the hot-forging of the face layer. If silicon is within the active layer, the smaller atomic mass would mean a faster diffusion rate compared with the heavy metals such as lead and radium, and it would more readily diffuse into the face layer.

Sulfur contaminant

The sulfur on all the wipes is a lower concentration compared with silicon. The XRF data do not indicate the form of sulfur, whether it is elemental or in a compound. There is no evidence to support that the bulk of the sulfur detected is from the compound radium sulfate. If the detection of sulfur from the wipe was mostly due to radium sulfate compound, the Rigaku XRF data should show both radium and sulfur, with a higher concentration of radium since it has a molar mass roughly seven times that of sulfur. But this is not so. An obvious candidate for the source of sulfur

is the dissociation of radium sulfate when the radium decays to ^{222}Rn. Radon, an inert gas, would no longer be ionically bound in RaSO$_4$. The recoil energy of the newly-formed atom would remove it from its lattice position and leave an orphaned sulfate anion. The orphaned anion is in a matrix of gold, possibly acting as an anode. In the electrolysis of molten salts, sulfate ions can be directly reduced to sulfur in an inert atmosphere (Kumar *et al.* 2018), so a parallel mechanism in the solid-state is feasible. Elemental sulfur would then diffuse into the face layer. However, a flaw in this argument is the quantity of elemental sulfur that could be released this way. The fractional change of ^{226}Ra by radioactive decay in a period t is $1 - e^{\lambda t}$ (where λ is the radioactive decay constant for ^{226}Ra). Taking 60 years as the time from the refinement of the original radium in the foil, this gives a fractional change of 0.0257 in radium. The nominal activity of the radium was 185 kBq, i.e. 5 μg in mass. If 0.0257 of this has decayed, it would amount to a corresponding 15 ng of sulfur from the changed RaSO$_4$. It is unlikely such a small quantity would noticeably change the colour of the gold face, or be detected on a wipe by XRF since a wipe would only remove a fraction of this amount. However, if the radium was supplied as (Ra, Ba)SO$_4$, it would provide a greater quantity of sulfur in the active layer. In (Ra, Ba)SO$_4$, formed by co-precipitation, the radium migrates into the lattice of the barium sulfate until isomorphous crystals are formed (Kirby 1964). The crystal structure will be in a relatively intense radiation field that could disrupt it. Kirby reports that in the case of radium bromide sealed in a glass tube, there is a chemical decomposition by this mechanism, evident from the detectable liberation of bromine. Unfortunately, there is no foreseeable technique using the radium foils to confirm this phenomenon with (Ra Ba)SO$_4$. There is no straightforward non-destructive method of retrieving the active material from the foil for further analysis. It is sintered into gold and it would require dissolving the foil in an aggressive acid such as aqua regia. This would disrupt the characteristics of the material being investigated.

Lead contaminant

Contamination from the lead storage pot has been eliminated as an origin. The lead within the active layer will comprise three isotopes of lead: ^{214}Pb, ^{210}Pb and ^{206}Pb. The activity of ^{210}Pb on the wipe was very low, a few becquerels, not an indication of gross migration into the face layer. Assuming the foil was fabricated 60 years ago with newly prepared radium sulfate, and the original activity was 185 kBq, the quantities by mass of the decay chain would be as shown in table 5. The half-life of each decay radionuclides up to and including ^{214}Po are many orders of magnitude less than ^{226}Ra, so the activities of these can be taken as the same as the ^{226}Ra. The activity of ^{210}Pb and the three subsequent decay radionuclides were calculated from the Bateman equations (Bateman 1910) by treating ^{214}Po as the parent radionuclide but with the same initial activity and same radioactive decay constant as ^{226}Ra since it will be in equilibrium with it within a few months from new. The Bateman equation is: $N_n(t) = N_1(0) \left\{ \prod_{i=1}^{n-1} \lambda_i \right\} \left\{ \sum_{i=1}^{n} C_i e^{-\lambda_i t} \right\}$ where $C_i = \prod_{j=1}^{n} (\lambda_j - \lambda_i)^{-1}$ for $j \neq i$, $N_n(t)$ is the number of atoms at time t of the radionuclide at position n in the decay chain and $N_1(0)$ is the initial number of atoms at the head of the decay chain. λ_i is the decay constant of the ith radionuclide in the decay chain. The consequent activity, $A_n(t)$, of each decay radionuclide at time t, at position n in the decay chain, will be $A_n(t) = \lambda_n N_n(t)$ with a mass m, in grams, of $m = \frac{N_n(t) \times m_a}{L}$ where m_a is the relative atomic mass of the radionuclide and L is the Avogadro constant. The mass of stable ^{206}Pb from the decay chain was calculated by using the Bateman equation and treating ^{206}Pb as a radionuclide with a decay constant of zero. The small fraction of decays that are outside of the main decay chain is ignored.

Radionuclide	Half-life seconds	Activity kBq	Mass g

^{226}Ra	5.049E+10	180.2	4.923E-06
^{222}Rn	3.302E+05	180.2	3.165E-11
^{218}Po	1.858E+02	180.2	1.749E-14
^{214}Pb	1.62E+03	180.2	1.500E-13
^{214}Bi	1.183E+03	180.2	1.093E-13
^{214}Po	1.636E-04	180.2	1.512E-20
^{210}Pb	7.037E+08	153.7	5.443E-08
^{210}Bi	4.330E+05	153.7	3.349E-11
^{210}Po	1.196E+07	153.2	9.219E-10
^{206}Pb	Infinite	0	6.395E-08

Table 5. ^{226}Ra, originally 185 kBq, and decay chain showing the activity and masses of each radionuclide in the chain after 60 years.

In terms of mass, the significant lead isotopes are ^{210}Pb and ^{206}Pb. After 60 years, there will be a total of about 130 ng of lead. The mass of the source face layer is about 3 mg. If all the lead migrated into the face layer, and none of it was lost through outgassing of ^{222}Rn, it would comprise about 5% of the face layer material. However, it is unlikely all of the lead would have diffused into the face layer, the activity of ^{210}Pb picked up on the wipe was so small, but it could feasibly be contributing to the change in it.

Conclusion

There is no evidence that the discolouration has come from external conditions such as exposure to corrosive chemicals, and no evidence to support that it is caused by radium sulfate moving into the face layer. Foil R03 was noticeably discoloured yet no activity was detected on the wipe. The balance of evidence indicates that the discolouration is principally caused by some combination, through diffusion, of silicon and sulfur from within the foil into the face layer. Lead could be contributing to the discolouring. The silicon was unexpected; the XRF data are convincing evidence of its presence, but how it was introduced in the fabrication of the foil, and why, remains unknown to the authors. A probable explanation is a relatively inert filler used to reduce the specific activity of the radium sulfate powder. But equally, it could have been a component of the sintering process. If so, this warrants further research because it could be a factor in the longer-term safety of foils of other radionuclides.

The gold and gold-palladium face layers of the radium foils tested in this research have not altered to the extent that the metal is directly removable by wipes with filter paper. Nor are the discoloured surfaces releasing active material into the environment – the wipes had to be pressed quite firmly to remove material, an event that should not happen in the normal use of the source. The foils would pass a wipe test based on the international standard ISO 9978:2020, which sets a fail at more than 200 Bq picked up on the wipe. Of the foils tested, there is no evidence that the discoloured face layers are fragmenting, but it cannot be assumed that the foil integrity will remain. The face layer is an important part of the foil seal. Since the discoloured foils are no longer meeting the original design, the longer-term integrity now becomes questionable. Bearing in mind the age of the foils, the radiotoxicity of radium, and that it is not possible with typical school equipment to distinguish the contamination from ^{222}Rn outgassing from ^{226}Ra contamination caused by a loss of seal integrity, a radium source found to have a discoloured foil surface should be taken out of service and disposed of, in line with the current legal controls on radioactive waste.

Advice for educational establishments.

The foil face layer should be visually inspected indirectly and carefully at least annually, e.g. when the source is being leak-tested. If it shows any sign of discolouration, the source should be taken out of service and disposed of, regardless of whether it passed a leak test. If the radium source was used as an alpha emitter for demonstrating spark counters and ionisation chambers, it can be replaced with an [241]Am foil cup source. However, if it was used as a source that emitted alpha, beta and gamma radiation, there is no cup-style source substitute. A thoriated TIG welding rod can be used, but the activity is much lower, roughly 3 kBq.

Acknowledgements

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