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► To cite this version:

Philippe Cassette, Franck Notari, Marie-Christine Lépy, Candice Caplan, Sylvie Pierre, et al.. Residual radioactivity of treated green diamonds. *Applied Radiation and Isotopes*, 2017, 126, pp.66 - 72. 10.1016/j.apradiso.2017.01.026 . hal-01623125

HAL Id: hal-01623125

<https://hal.science/hal-01623125>

Submitted on 12 Jan 2023

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Residual radioactivity of treated green diamonds

Philippe Cassette^{1*}, Franck Notari², Marie-Christine Lépy¹, Candice Caplan², Sylvie Pierre¹, Thomas Hainschwang³, Emmanuel Fritsch⁴

¹ CEA, LIST, Laboratoire National Henri Becquerel (LNE-LNHB), Gif-sur-Yvette, France

² GGTL Laboratories, Geneva, Switzerland

³ GGTL Laboratories, Balzers, Liechtenstein

⁴ Institut des Matériaux Jean Rouxel, Université de Nantes, France

*Corresponding author: philippe.cassette@cea.fr

Abstract

Treated green diamonds can show residual radioactivity, generally due to immersion in radium salts. We report various activity measurements on two radioactive diamonds. The activity was characterized by alpha and gamma ray spectrometry, and the radon emanation was measured by alpha counting of a frozen source. Even when no residual radium contamination can be identified, a measurable alpha and high-energy beta emission could be detected. The potential health impact of radioactive diamonds and their status with regards to the regulatory policy for radioactive products are discussed.

Highlights:

- Treated green diamonds can show residual radioactivity, generally due to immersion in radium salts.
- Various activity measurements on two radioactive diamonds are reported.
- Activity characterized by alpha and gamma ray spectrometry and radon emanation measured by alpha counting of a frozen source.
- Potential health impact of radioactive diamonds and their status with regards to the regulatory policy for radioactive products are discussed.

Keywords: treated diamond, radioactive gemstones, ²²⁶Ra, ²¹⁰Pb, ²¹⁰Po

Introduction

In 2013, the GGTL Laboratories Switzerland received three green diamonds set in ring and earrings for gemmological characterization. After analysis, it turned out that the colour of these diamonds was due to irradiation and that one of them appeared to be radioactive. This was not the first time that GGTL Laboratories Switzerland was faced with irradiated gemstones, and this shows that the traffic of radioactive diamond is still an actual problem. Previous measurements of these radioactive samples were undertaken by gamma-ray spectrometry (Asbaugh, 1992), and alpha-ray measurements were also performed on five radioactive samples. Some high radioactivity levels were recorded, with a maximum of about

20 kBq for one specimen. From this it was concluded that these stones had been treated with radioactive salts, probably RaBr_2 , to change their colour.

GGTL Laboratories Switzerland contacted LNHb, the National Metrology Institute of France for radioactivity units, in order to precisely characterize the activity and properties of two treated green diamonds.

Historical background

Treated green diamonds have frequently been mentioned in the gemmological literature. Today, these stones are typically treated with fast electrons generated by electron accelerators or with neutrons in nuclear reactors (Collins, 1982). Decades before these techniques were available, the method used to turn diamonds to green involved direct contact of diamonds with radioactive salts of radium bromide or with radon gas (Crookes, 1904, 1914) and later using americium oxide (Reinitz and Johnson, 1994).

Sir Crookes was the first to discover radiations effects on the colour of diamond: he treated diamond crystals by contact with radium salts and observed that then they turned to green after few months. He donated one of these crystals to the British Museum in London in 1914. The sample exhibits an almost uniform green surface coloration simulating a green body color and it is still radioactive.

The technique consisting in irradiating diamonds with radioactive substances like radium or americium salts was quickly abandoned since diamonds treated with these radioactive elements exhibit long-lasting residual radioactivity which make them unwearable.

Materials and methods

Although several radioactive green diamonds, ranging from 0.11 to 12.86 carats (ct), were analyzed at GGTL Laboratories Switzerland, this paper will focus on two specimens: a small 0.5 ct dark-green diamond (Figure 1) and an over 7 ct pale-green diamond initially set in a ring (Figure 2).

Initial gemmology characterization and routine testing for radioactivity was performed with a Geiger-Müller counter. More detailed radioactivity measurements were performed at Laboratoire National Henri Becquerel, CEA Saclay in France, with a high-purity germanium detector (HPGe), an alpha spectrometer and an absolute radon measurement instrument, based on alpha counting in a defined geometry on a cold spot at 80 K.

Gemmological optical testing

The green colour of the diamonds is apparently distributed on the surface or penetrating only into the subsurface (few tens of μm) of the diamonds. Magnification revealed the presence of irradiation stains (Fig. 3) on the surface. These green marks showed strongly irregular and coma-shape associations in contrast to the normally relatively round regular shape (usually with more blurred outline) of the natural green spots (Fig. 4) found at the surface of many rough diamonds (Koivula, 2000). Sometimes, the green stains coalesce to form a continuous green surface coloration called a “green skin”.

Until about 25 years ago, the presence of green stains usually situated on the girdle or pavilion of polished diamonds, was considered as an indicator of natural irradiation and there are also examples of near-colourless rough and cut diamonds with natural green stains. However, Crookes' diamond octahedra and the faceted examples examined here remind us that green spots and skins can be generated by artificial alpha irradiation of rough and polished diamond surfaces as well. Faceted diamonds are the main targets for radium salt exposures and show green stains on the facets of crown and pavilion.

Fourier-transform infrared and near-infrared absorption spectroscopy

All tested diamonds are of type IaAB (with nitrogen impurities aggregates), which is an unusual type for natural green diamonds, which are usually of type IIa (without detectable nitrogen or boron, by infrared spectroscopy). The infrared spectra were not characteristic of irradiated diamonds (Fig. 5). The absence of consistent irradiation criterion (H1a) is a consequence of the small thickness of the irradiated zone, due to the small path length of alpha particles in condensed matter.

Visible and near infrared spectroscopy

The Vis-NIR spectrum of the 0.5 ct diamond (Fig. 6, red trace) recorded at 77 K indicates an irradiation at ambient temperature, as no nitrogen-vacancy centres indicating annealing were detected. The spectrum mainly consists of a strong absorption band in the 750 to 510 nm region. This wide absorption band induces the green colour. Besides the GR1 system with its zero phonon line (ZPL) in the 740.9 to 744.4 nm range, only the 3H absorption is apparent in the spectrum, with a distinct ZPL at 503.4 nm, and a vibration sideband at 491 nm. Both absorption systems are superimposed on a general absorption continuously rising from about 950 nm to the ultraviolet region, which induces a yellowish colour component.

Preliminary radioactivity measurement

For the 0.5 ct diamond, the apparent radioactivity measured with the Geiger-Müller counter revealed a high value in the direction of the pavilion for an analysed surface of approximately 1.5 mm^2 at a distance of about 6 mm from the detector. Despite the arbitrary readings of a GM counter, this activity is exceptional considering the small size of the sample. This apparent activity is one order of magnitude greater than the activity of all observed gems at GGTL Laboratories Switzerland. This is why this stone deserved a more precise activity measurement and also a measurement of its radon emanation.

Gamma ray spectrometry

The 0.5 ct diamond was placed in a polymer container and measured with an HPGe detector at LNHB, in its calibration position, i.e. at a distance of 10 cm from the detector window. The spectrum recorded during an acquisition time of 20 000 s is presented in Figure 7.

The observed peaks can be related to the gamma ray emission of ^{226}Ra and the radionuclides of its decay chain (Figure 8, Table des radionucléides 2008).

The activity was deduced from the net peak areas of the gamma lines of ^{226}Ra , ^{214}Po and ^{214}Bi , using the efficiency calibration curve obtained with standard point sources. The activities are presented in Table 1.

The 7 ct diamond was measured with an HPGe detector, the table placed on a PET foil support at a distance of 1 cm from the entrance window of the detector (Figure 9).

The spectrum was recorded during 250 000 s (Figure 10) and the main gamma lines can be attributed to ^{210}Pb , ^{226}Ra , ^{214}Pb and ^{214}Bi .

The activity of each radionuclide was determined using the efficiency calibration curve obtained with standard point sources and a geometry transfer calculation. The values obtained are presented in Table 2.

Radon emanation measurement

The decay product of ^{222}Rn is an alpha-emitting radionuclide, decaying through alpha and beta short half-life transitions towards ^{210}Pb , a 22.2 years half-life beta-emitting radionuclide. In a confined ^{226}Ra source, a secular equilibrium is expected between ^{226}Ra and its daughters until ^{214}Po , but with a coefficient depending on the emanation coefficient of the radium source. For these diamond sources, the value of this emanation coefficient can be deduced from the activity of radium and the activity of radon and daughters at equilibrium. This coefficient can give some information on the nature of the radium deposition: if it is present at the surface, a high emanation coefficient can be expected, but this coefficient should be much lower if the radium is implanted in the carbon lattice or deeply included in some cracks of the crystal.

To measure the radon emanation we placed the diamond in a closed stainless-steel container, and pumped on it in order to eliminate the initial radon concentration. Then the container was isolated to allow the ingrowth of radon. The theoretical evolution of the radon activity with time is given by equation (1),

$$A_{Rn}(t) = A_{Ra} \cdot f \cdot (1 - \exp(-\frac{\ln 2 \cdot t}{T_{1/2Rn}})) \quad (1)$$

where $A_{Rn}(t)$ is the radon activity at a delay t after the beginning of the accumulation, A_{Ra} is the radium activity, f is the emanation factor and $T_{1/2Rn}$ is the ^{222}Rn half-life (3.82 d).

In this experiment, the radon activity was measured after 65.85 hours of accumulation, using the primary ^{222}Rn measurement system at LNHB. The measurement method, described in (Picolo, 1996) is based on the condensation of radon on a surface maintained at 80 K by a cryogenic system, and then measured by alpha defined solid angle method. The measured activity was 1.15 (12) kBq. Using equation (1) we can deduce that the emanation factor is about 0.17. This shows that a non-negligible part of the radium contamination is present at the surface of the crystal or in cracks in contact with the surface, and thus that this diamond is a non-negligible source of radon.

Alpha spectrometry

The 0.5 ct diamond was not measured by alpha spectrometry because its radon emanation was likely to cause a ^{210}Pb contamination of LNHB alpha detectors, with an anticipated increase of ^{210}Po background counting rate over time.

The 7 ct diamond was measured by alpha spectrometry using an implanted silicon detector (PIPS) in defined solid angle geometry. Two measurements were undertaken: one with the culet of the gem towards the PIPS and another with the table of the diamond towards the detector. The experimental setup is presented in Figure 11. The energy scale was previously determined with a multi-alpha standard source and the spectrometer background was recorded before and after the diamond measurement.

An example of the alpha spectrum recorded during 230 000 s, with the culet towards the detector, is presented in Figure 12, and the observed alpha peaks are identified in Table 3. The main peak corresponds to the energy of ^{210}Po and the others peaks are those of ^{226}Ra , ^{222}Rn and its short-lived solid progenies. From Figure 12, it appears that there is no equilibrium between ^{226}Ra and ^{210}Po and that the resolution of the ^{210}Po peak is lower than the one of the ^{222}Rn and its progenies. This suggests that the radium, radon and short-lived progenies are trapped at the surface of the gem but ^{210}Po is implanted in the crystal.

The detection solid angle was evaluated by an analytical calculation, and the activity of the pavilion is detailed in Table 3. The activity of ^{210}Po is two orders of magnitude higher than the one of radium, which is approximately 1.5 times the activity of radon and its progenies. This is coherent with the presence of radium at the surface of the crystal, with a slight emanation of radon. The ^{210}Po peak position was about 27 keV lower than the expected value for an ideally thin source. It must be observed that the activities determined by alpha

spectrometry are coherent with the ones obtained by gamma spectrometry (Table 2), except for ^{226}Rn , where the value measured by gamma spectrometry is almost eight times higher than the one measured by alpha spectrometry. One possible explanation can be related to the inhomogeneous distribution of the radium contamination on the crystal.

A similar measurement was undertaken with the table of the diamond facing the detector. The global alpha spectrum is similar to the previous one but with an activity about 30 % lower.

The ^{210}Po peak shift is approximately 13 keV, a value approximately two times less than the one obtained with the culet facing the detector. This can be the result of the measurement geometry, as the alpha particles path length inside the carbon lattice is lower when the particles arise from a flat surface, but, more probably, the explanation is related to the fact that it was known that the table of this diamond has been reprocessed after its irradiation.

A specific ^{210}Po high resolution source was made by spontaneous deposit of polonium on a silver disk, and measured in order to give information to experimentally determine the implantation thickness of ^{210}Po in the diamond lattice: the source was first measured to determine the peak centroid and then, a new measurement was undertaken by placing a 1.5 μm thick polyethylene terephthalate (PET, Mylar) foil between the source and the detector. The peak shift observed in our experimental conditions was 95 keV, to be compared with the values of 27 keV and 13 keV previously mentioned for the 7 ct diamond. Assuming a linear dependence between the peak shift and the absorber thickness, the observed peak shifts correspond to approximately 300 nm and 150 nm of PET absorber for the culet and table respectively. The transfer from PET ($\text{C}_{10}\text{H}_8\text{O}_4$) to diamond can be evaluated from the relative absorption cross sections calculated by the SRIM software (SRIM, 2013).

Discussion

There are two causes for residual radioactivity in diamonds treated with RaBr_2 salts: surface and crack contamination and implantation of radon solid daughters in the crystal lattice by nucleus recoil energy.

The former phenomenon is enhanced by the presence of defects and irregularities at the surface of the crystal, and is only observable because of the huge activity of the radium salts used for the treatment.

The latter phenomenon is well known in the case of solid material in contact with high radon activity (Ross et al., 2002). The decay chain of radon includes three alpha decays: ^{222}Rn , ^{218}Po and ^{214}Po (Figure 8). In each alpha decay, the energy and momentum of the alpha transition is shared between the alpha particle and the recoil nucleus. For these transitions, the energies of the recoil nuclei are a few hundreds of keV, and these energies are large enough to implant the recoil nucleus inside the crystal lattice. The implanted atom then decays and eventually creates an atom of ^{210}Po . This latter radionuclide decays through ^{210}Bi , a short half-life high-energy beta emitter, which in turn decays to ^{210}Po , a 168-days half-life alpha radionuclide. After about two years, the ^{210}Po is in secular equilibrium with ^{210}Pb and the ^{210}Pb progeny induces a high-energy beta and alpha emissions, which easily escape from the crystal and can be observed. This phenomenon is dominant in the case of the 7 ct diamond, as the ^{210}Po alpha peak is much higher than the other peaks from the ^{226}Ra decay chain.

The legislation relative to the detention of such radioactive diamonds is somewhat unclear, depending on the country considered, but it can be assessed that the detention of a radium source of activity lower than 37 kBq does not require any specific authorization. Nevertheless, the exemption level for the transportation of ^{226}Ra and ^{210}Pb is 10 kBq, according to the international transportation rules (ADR). This means that the transportation of the 0.5 ct diamond would require the special procedure of an excepted radioactive source.

The evaluation of the risk associated with these diamonds could be made by comparing the dose transferred to the skin to the legal limits. According to the international regulations, the irradiation dose limits for the skin is 50 mSv over 1 year for the public. The dose rate induced by a ^{226}Ra point source (in secular equilibrium with its radioactive daughters) in contact with the skin is 3.4 $\mu\text{Sv/h}$ per Bq of ^{226}Ra (Delacroix *et al.*, 2004). This dose is mostly due to the beta emission of the decay products of this radionuclide, as the alpha radiation is absorbed by the epithelial layer and thus, does not contribute to the irradiation of the skin. For the 0.5 ct diamond considered in this study, this corresponds to a dose rate of about 60 mSv/h at the contact of the skin. This means that the irradiation dose limit is reached in about one hour, if this diamond is placed in contact with the skin. The effective dose reached if the diamond is mounted on a ring or necklace is more difficult to assess but we can assume that the dose rate will be of the same order of magnitude. This means that wearing this diamond will induce a real radioactive risk, not mentioning the risk of contamination by radium and radon.

For the 7 ct diamond, the main contribution to the irradiation is ^{210}Bi , radioactive daughter of ^{210}Pb emitting high-energy beta particles. From (Delacroix *et al.*, 2004), the skin dose rate for a point source in contact with the skin is 1 $\mu\text{Sv/h}$ per Bq of ^{210}Pb (in secular equilibrium with ^{210}Bi and ^{210}Po). This corresponds to an exposition dose rate of 27 $\mu\text{Sv/h}$. In this case the assumption of a point source for the dose rate calculation is quite crude, as this gemstone cannot be considered as punctual. Nevertheless, we can assume that this gives a conservative value of the dose rate, from which we can conclude that this diamond is not likely to present a real irradiation risk, even if it is permanently in contact with the skin, which is an unlikely situation considering the size of the stone. Nevertheless, for the sake of precaution, it is always advisable to avoid unnecessary irradiation (ALARA principle), and thus it cannot be recommended to wear such a radioactive jewel.

As previously mentioned, the 0.5 ct diamond is also a significant source of radon. This radioactive noble gas is, according to WHO, the second cause of lung cancer in the world after tobacco. As an indication, the action level recommended by the WHO is an activity concentration of 100 Bq of radon per m^3 of air in living areas. The radon emanation of the 0.5 ct diamond in confined area could be an issue, even if it is difficult to assess it in a realistic way.

Conclusions

We observed that some treated diamonds could exhibit radioactivity levels, which are not compatible with their release in the public and thus forbid their use in jewelry. The presence of residual radium salts at the surface of the crystal also suggests that it could also be a source of contamination. For diamonds with much smaller radium contamination, the beta emission of ^{210}Bi and the alpha emission of ^{210}Po could nevertheless be a non-negligible irradiation source. As the implanted radionuclides are very close to the surface, recutting the stone could be an option but this process would involve the machining of radioactive substances, which could present severe health hazards especially because one of the radionuclide of concern is ^{210}Po .

Because the presence of stains is not an absolute proof of the natural or artificial origin of the green colour, the discrimination relies only on radioactivity measurement, with sensitive measurement systems. Such systems are obviously not common in professional jewelry industry and thus, cooperation of the jewelry industry with specialized activity measurement laboratories is necessary to evaluate the activity of some gemstones in order to maintain a good protection level for the consumers.

The health problem associated with these treated diamonds is to be replaced in the context of the ubiquitously available radium sources, which can be found for example in old clocks, watches and fluorescent panels. Nevertheless, this must not minimize the problem of contamination and irradiation by treated diamonds, especially because, these gemstone are generally mounted on jewels and thus in close contact with the human skin. A simple dose calculation shows that wearing the 0.5 ct diamond, even during a short period, is likely to engage a skin irradiation overpassing the legal limit.

Even though treated, radioactive diamonds are very rare in the market, it is advisable to be cautious when handling yellowish green, green and greenish blue to apparently black (very dark green or green-blue) diamonds.

Coloured stones arriving on the market without a certificate from a recognized laboratory may thus not only be irradiated but sometimes even radioactive, depending on the process used to modify their colour. It must be pointed out that the residual radioactivity of treated diamonds will not completely disappear at the scale of a human life and the age of such gemstone is not an indicator of its innocuity.

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Tables captions

Table 1: gamma ray spectrometry of the 0.5 ct diamond

Table 2: gamma ray spectrometry of the 7 ct diamond

Table 3: alpha spectrometry of the 7 ct diamond

Figures captions

Figure 1: Photography of the 0.5 ct diamond

Figure 2: Photography of the 7 ct diamond mounted on a ring

Figure 3: Irregular, coma-shaped dark green stains on the polished surface of the 0.5 ct diamond. The red arrow points to a fracture containing residual radium salts. Micrograph F. Notari

Figure 4: Surface of alpha-treated green diamonds. **a**: stains on the table, **b**: stains on pavilion facets, **c**: an irregular stain on the pavilion, **d**: image contrast revealed stains of different morphologies, diameters and contrast. Micrographs F. Notari

Figure 5: Infrared spectrum showing a very weak H1a absorption at 1450 cm^{-1}

Figure 6: Visible and near infrared spectrum of the 0.5 ct diamond (red trace) compared to another alpha-irradiated diamond (blue trace), an electron irradiated diamond (green trace) and a naturally diamond (black trace), recorded at 77 K

Figure 7: gamma ray spectrum of the 0.5 ct diamond

Figure 8: ^{226}Rn decay chain (www.nucleide.org)

Figure 9: view of the 7 ct diamond in the HPGe gamma detection system

Figure 10: gamma ray spectrum of the 7 ct diamond

Figure 11: view of the 7 ct diamond in the alpha detector

Figure 12: alpha spectrum of the 7 ct diamond, culet towards the detector

Energy, keV	Radionuclide	Activity, kBq	Standard uncertainty, kBq
186.14	²²⁶ Ra	17.59	0.23
351.93	²¹⁴ Pb	15.03	0.17
609.31	²¹⁴ Bi	15.00	0.17

Table 1

Energy, keV	Radionuclide	Activity, Bq	Standard uncertainty, Bq
186.14	²²⁶ Ra	1.71	0.09
351.93	²¹⁴ Pb	0.15	0.01
609.31	²¹⁴ Bi	0.15	0.01
46.45	²¹⁰ Pb	27.4	0.6

Table 2

Radionuclide	Energy of the alpha particle (MeV)	Activity, Bq
²²⁶ Ra	4784	0.22
²¹⁰ Po	5300	24.55
²²² Rn	5489	0.16
²¹⁸ Po	6002	0.15
²¹⁴ Po	7686	0.13

Table 3



Fig 1



Fig 2

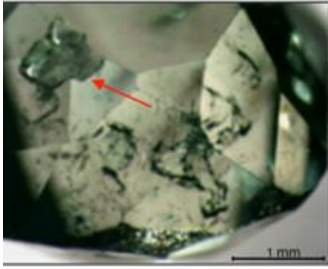


Fig 3

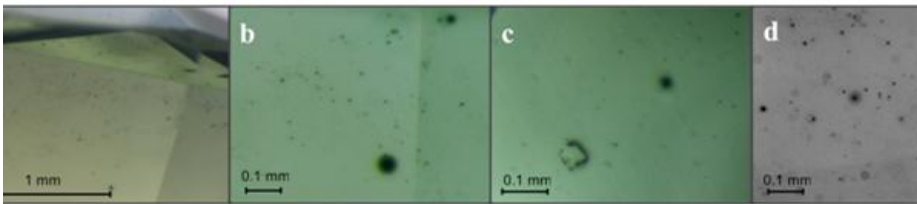


Fig 4

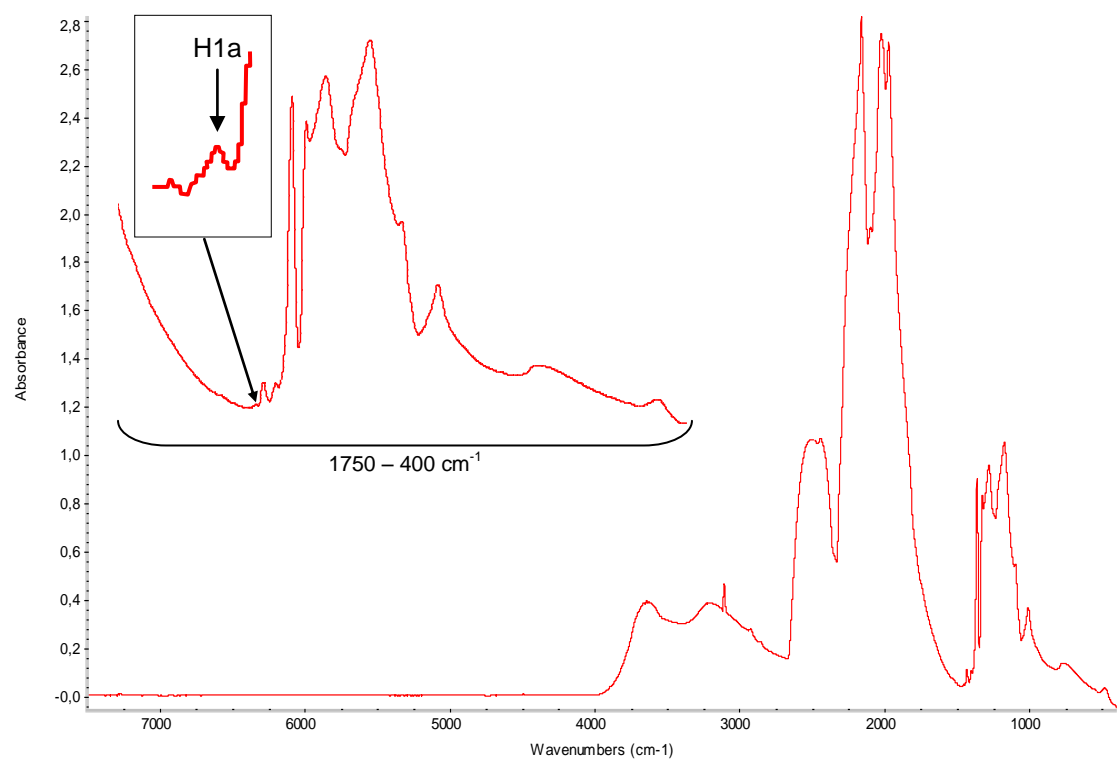


Fig 5

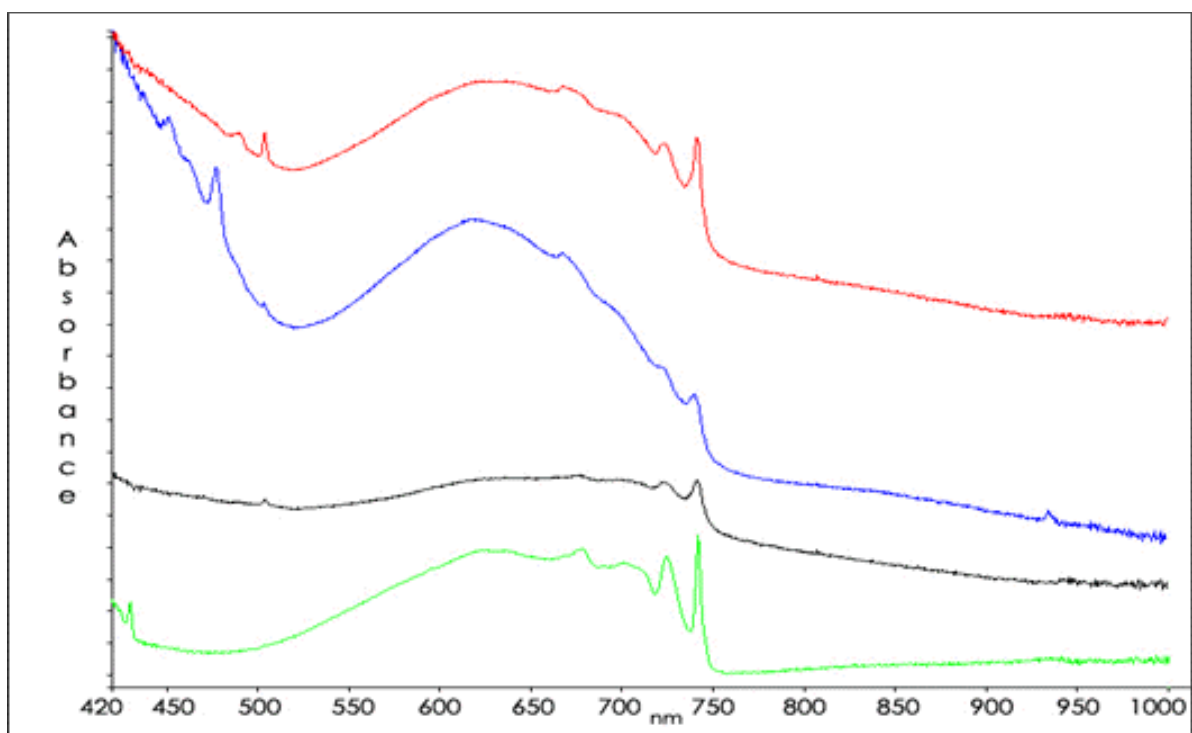


Fig 6

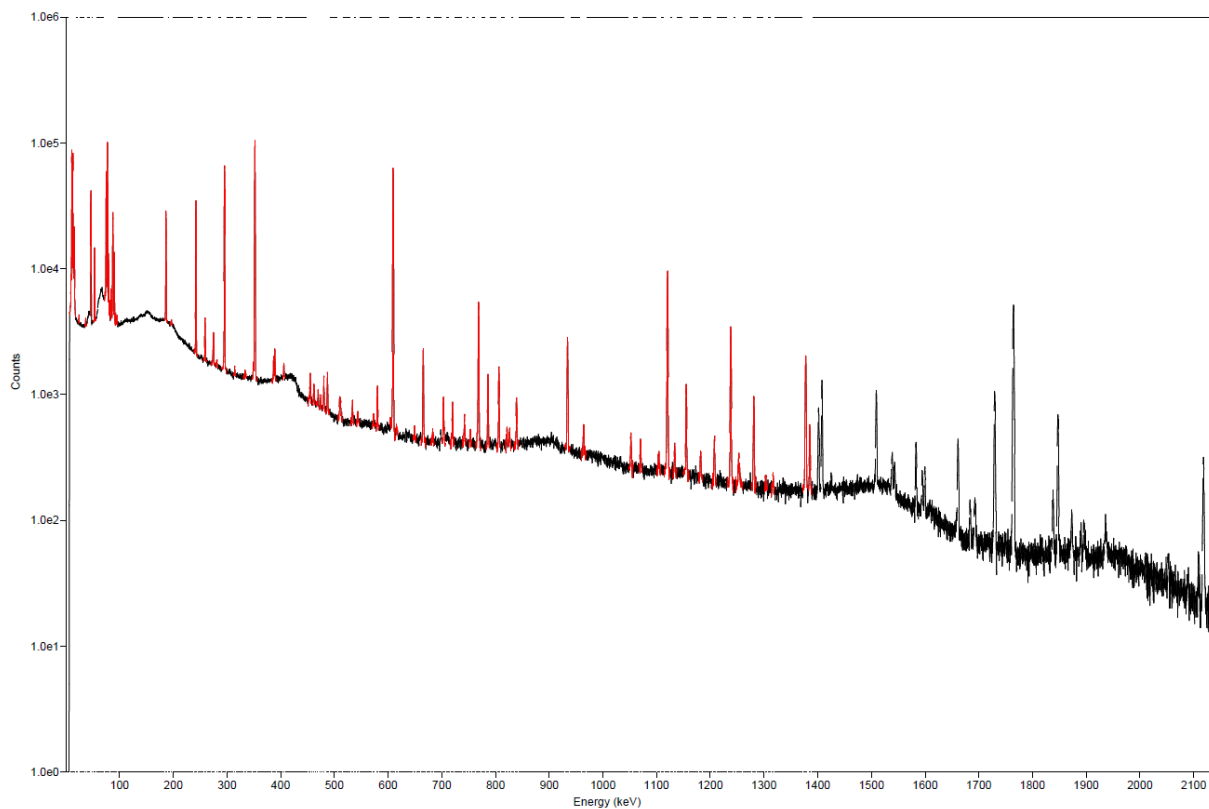


Fig 7

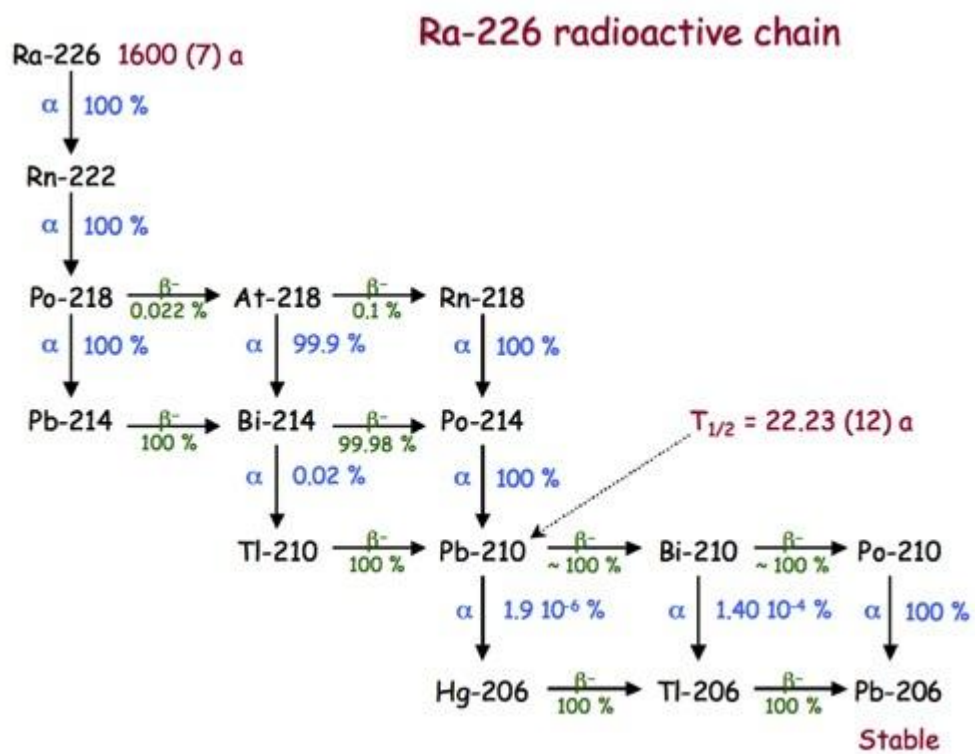


Fig 8

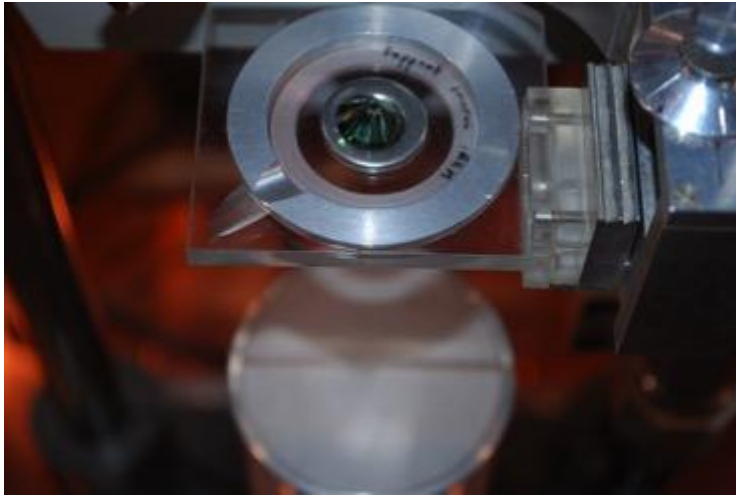


Fig 9

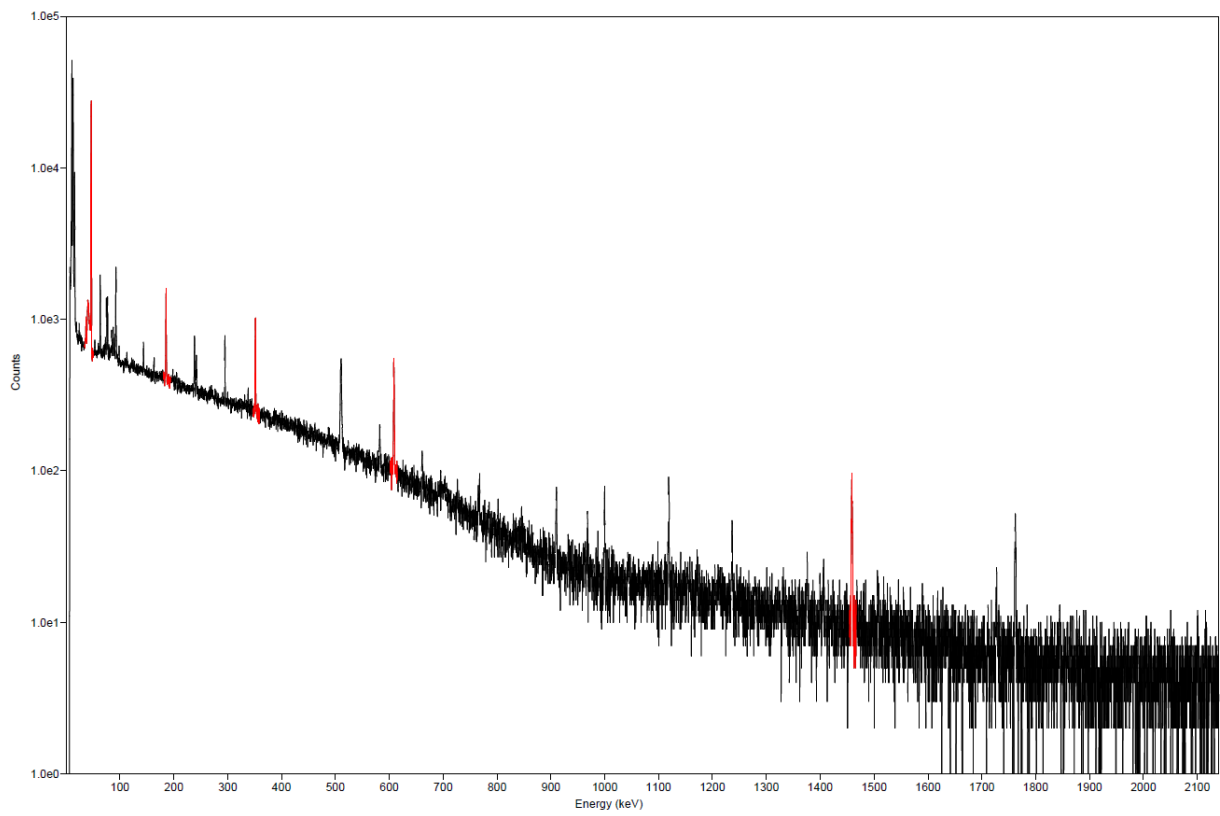


Fig 10



Fig 11

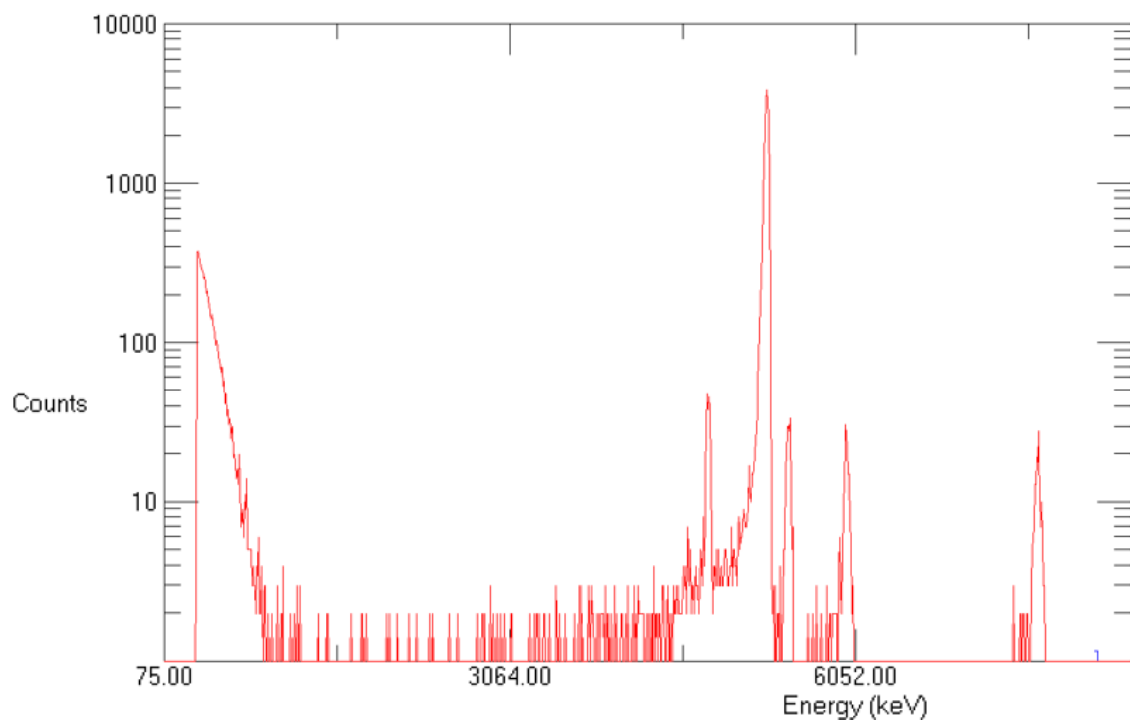


Fig 12