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Do pyrotechnics contain radium?

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Abstract

Many pyrotechnic devices contain barium nitrate which is used as an oxidizer and colouring agent primarily for green-coloured fireworks. Similarly, strontium nitrate is used for red-coloured pyrotechnic effects. Due to their chemical similarities to radium, barium and strontium ores can accumulate radium, causing a remarkable activity in these minerals. Radium in such contaminated raw materials can be processed together with the barium or strontium, unless extensive purification of the ores was undertaken. For example, the utilization of 'radiobarite' for the production of pyrotechnic ingredients can therefore cause atmospheric pollution with radium aerosols when the firework is displayed, resulting in negative health effects upon inhalation of these aerosols. In this study, we investigated the occurrence of gamma-photon-emitting radionuclides in several pyrotechnic devices. The highest specific activities were due to K-40 (up to 20 Bq g^{-1} , average value 14 Bq g^{-1}). Radium-226 activities were in the range of $16\text{--}260 \text{ mBq g}^{-1}$ (average value 81 mBq g^{-1}). Since no uranium was found in any of the samples, indeed, a slight enrichment of Ra-226 in coloured pyrotechnics can be observed. Radioactive impurities stemming from the Th-232 decay chain were found in many samples as well. In the course of novel developments aiming at the 'greening' of pyrotechnics, the potential radioactive hazard should be considered as well.

Keywords: fireworks, inhalation, natural radioactivity, ^{238}U decay chain, ^{226}Ra , ^{228}Ra

1. Introduction

Fireworks are probably the application of chemistry with the best resonance with the general public. Nonetheless, fireworks are increasingly raising environmental concerns. Although the problem of pollution caused by fireworks (and other civil and military pyrotechnic applications) had been identified many years ago [1, 2], the number of environmental studies focusing on this problem has dramatically increased quite recently, e.g. [3–11]. Also the search for environmentally benign pyrotechnic formulations exhibits a rapidly expanding scientific field and has not hit its peak yet [5].

Pyrotechnics are thermodynamically metastable mixtures which consist of at least two basic constituents: the reductant/fuel (e.g. magnesium, aluminium, magnalium alloy, sulfur, charcoal, red phosphorus, etc) and the oxidizer (alkali metal or alkaline earth metal nitrates, perchlorates, chromates, metal oxides, etc). Several additives may find application in pyrotechnics in order to obtain a certain intended effect (e.g. colouring agents, propellants, smoke or sound generators,

etc). Colours in pyrotechnics are obtained by the addition of compounds of elements with the desired flame colour. For red light, strontium nitrate is used; barium nitrate for green light; sodium oxalate or cryolite (Na_3AlF_6) for yellow; and any copper/chlorine system (compounds or mixtures) for blue (see table 1 for some typical compositions of pyrotechnics). During combustion, very short-lived and unstable compounds, such as the monochlorides of alkaline earth metals (SrCl , BaCl) are formed, which emit light in the desired spectra [5, 12, 13]. The formation of the monochlorides thus depends on the presence of a chlorine source. If no chlorine donor is added to a pyrotechnic formulation, barium nitrate causes combustion under the emission of almost white light. This is the reason why barium nitrate is not only used as an oxidizer in green or greenish flares (with a chlorine donor, which is typically PVC powder) but also for white and yellow flares (without a chlorine donor), as shown in table 1. In the presence of chlorine, barium nitrate acts as a combined pyrotechnic oxidizer and colouring agent.

Table 1. Some typical barium nitrate-or strontium nitrate-containing pyrotechnic compositions (data taken from [5, 12, 27]). Values in wt%.

Ingredient	Mk 117 green navy flare	Mk 118 yellow navy flare	Turquoise formulation	Chartreuse formulation	White formulation	Mk 124 red navy flare	Red highway flare
Barium nitrate	22.5	20.0	75	75	55	—	—
Strontium nitrate	—	—	—	—	—	34.7	74
Magnesium	21.0	30.3	—	—	—	24.4	—
Potassium perchlorate	32.5	21.0	—	—	—	20.5	6
Sodium nitrate	—	—	—	5	—	—	—
Potassium nitrate	—	—	—	—	25	—	—
PVC	12.0	—	5	10	—	11.4	—
Sodium oxalate	—	19.8	—	—	—	—	—
Copper powder	7.0	—	—	—	—	—	—
Asphaltum	—	3.9	—	—	—	9.0	—
Sulfur	—	—	10	10	20	—	10
Cuprous chloride	—	—	10	—	—	—	—
Binder	5.0	5.0	—	—	—	—	10

From an environmental and toxicological point of view, the formation of barium-rich aerosols following the display of a firework is a problem. The inhalation of barium-rich aerosols has adverse effects on the lungs and heart and causes muscle cramps [14, 15]. In cases of fireworks and pyrotechnics, barium compounds are set free in the form of mostly water-soluble and thus bioavailable compounds: BaO, Ba(OH)₂, BaCl₂ and undecomposed Ba(NO₃)₂. The raw material of barium compounds is generally barium sulfate (barite). In 2006, approximately 8 million tons barite have been produced by mining worldwide [16]. Only a very minor percentage is used in pyrotechnics. The major amount of barium sulfate is used as a pigment (*Blanc fixe*), or as a filler for paper, paint, varnish, rubber, etc. This mineral is also used as a constituent of heavy concrete for the shielding of ionizing radiation.

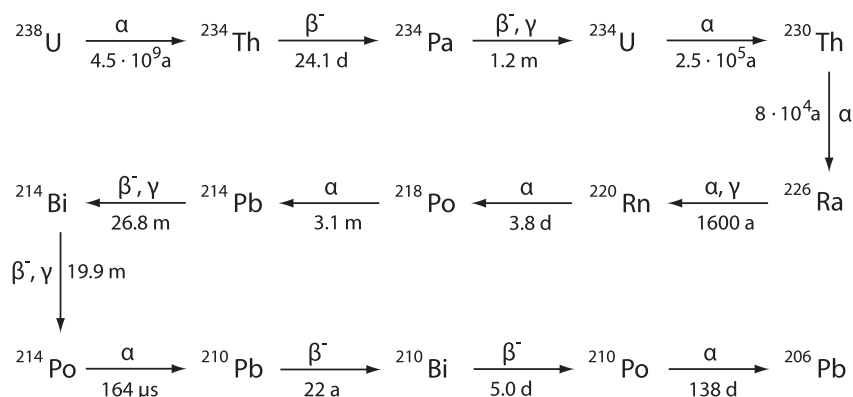
To the authors' knowledge, the potential hazard of fireworks due to liberated radionuclides has never been the subject of investigation in the scientific literature before. The radioactive alkaline earth metal radium has very similar chemical properties to barium (and also strontium), as they occur in the same group of the periodic table. This similarity is used, for example, in the preconcentration of radium from water by coprecipitation with barium in the form of Ba(Ra)SO₄. Natural sequestering leads to the formation of so-called radiobarite minerals. These minerals accumulate all naturally occurring radium isotopes, in particular the ²³⁸U decay chain member ²²⁶Ra (half-life $T_{1/2} = 1600$ a) and the ²³²Th decay chain member ²²⁸Ra ($T_{1/2} = 5.76$ a). However, the potential accumulation of ²²⁶Ra is of higher environmental significance than ²²⁸Ra, because the latter is simply too short-lived to be extremely accumulated in barium (or strontium) deposits. If young enough, these minerals and ores have remarkable ²²⁶Ra activities. On geological timescales, however, ²²⁶Ra has a relatively short half-life. If radiobarite minerals, therefore, are older than 10–20 ka and isolated from any further radium supply, they slowly lose their radioactive properties. The radiobarite-rich sludges and scalings at oil-field-production sites investigated by Zielinski *et al* [17], have ²²⁶Ra activities in the range between 3 and 130 Bq g⁻¹, with one sample as active as 4.9 kBq g⁻¹. In their study, the ²²⁸Ra activities have been found to be always lower than the ²²⁶Ra values. Radiobarite ores in the

Ohře Rift (Bohemian Massif) have activities between 0.02 and 7.80 Bq g⁻¹ [18]. The scales and tailings in Polish hard coal mining sites were reported to contain radiobarites with activities in the range of 40–100 Bq g⁻¹ for ²²⁶Ra and 27–62 Bq g⁻¹ for ²²⁸Ra (barium-rich Rontok scale), and 5.3–6.4 Bq g⁻¹ for ²²⁶Ra and 6.4–8.5 Bq g⁻¹ for ²²⁸Ra (barium-poor Bojszowy tailings), respectively [19]. The ambient γ -dose rates are strongly elevated with more than 1 μ Sv h⁻¹ at both sites.

Previous studies [20, 21] have investigated the trace element content of pyrotechnics and their poisoning potential. From an economic point of view, it is clear that raw materials for the production of fireworks are usually not purified beyond the grade which is necessary for the intended effects. This explains why the fireworks investigated in those studies contained significant traces of heavy metals which do not have a pyrotechnic function. The utilization of radium-rich barium and strontium ores would, therefore, involve the risk that radium might be processed together with barium and strontium into the final product. The display of such radium-containing pyrotechnics would set the radioactive material free in the form of easily inhalable aerosols. The incorporation of α -emitting radionuclides (such as ²²⁶Ra) is a major health threat in human radiation protection. The ingestion or inhalation of α -emitters should thus be avoided under all circumstances. In order to examine this potential hazard, we applied radioanalytical methods to investigate the radioactivity of pyrotechnics purchasable in Austria.

2. Materials and methods

Fourteen samples of pyrotechnic devices (sky rockets, shell-type rockets, volcanoes) have been investigated with γ -spectrometry in this study (see table 2). The samples were weighed and filled into cylindrical polyethylene (PE) containers (comparable filling level). In principle, for the quantification of the ²²⁶Ra activity, two methods are possible: the 186 keV γ -photon emitted by the nuclide itself can be measured. Alternatively, the γ -photons of its decay products ²¹⁴Pb and ²¹⁴Bi can be measured, as they are in equilibrium with ²²⁶Ra after three or four weeks (due to the short half-lives of ²¹⁴Pb and ²¹⁴Bi as well as the intermediate ²²⁶Ra-daughter



Scheme 1. Simplified decay scheme of the ^{238}U decay chain, including only the major decay route, and showing the decay types and half-lives of the nuclides. For γ -radiation, only nuclides are marked if significant for our measurement set-up. For exact nuclear data, see table 3.

Table 2. Samples investigated in this study.

Sample code	Sample name	Pyrotechnics type	Potential radium carrier
R1	Weco green glamour	Sky rocket	Barium
R2	Weco green glamour	Sky rocket	Barium
R3	Weco green flower	Sky rocket	Barium
R4	Weco red glamour	Sky rocket	Strontium
R5	Weco red glamour	Sky rocket	Strontium
R6	Weco red flower	Sky rocket	Strontium
R7	Weco pink flower	Sky rocket	Strontium
R8	Weco yellow flower	Sky rocket	Barium
R9	Weco white glamour	Sky rocket	Barium
R10	Wolm Pyrostar Kugelblitz	Shell-type rocket	Barium and/or strontium
R11	Wolm Pyrostar Kugelblitz	Shell-type rocket	Barium and/or strontium
R12	Wolm Pyrostar Kugelblitz	Shell-type rocket	Barium and/or strontium
R13	Weco Riesen Flimmer-Vulkan	Volcano	Barium and/or strontium
R14	Weco Fegefeuer	Volcano	Barium and/or strontium

nuclides ^{222}Rn and ^{218}Po , respectively), see scheme 1. Since radon is known to diffuse through many materials (sample vials), causing a loss of activity, the latter method appears to be the less reliable for our analytical purposes.

When the 186 keV γ peak of ^{226}Ra is used, the possible interference of ^{235}U , which also emits γ photons in this energy region, has to be considered. However, since we can assume that uranium in environmental samples must be present in its natural isotopic ratio, a γ spectrum showing a ^{235}U peak should also show the γ peaks of the short-lived ^{238}U granddaughter ^{234}Pa (with several γ photons at 1001, 743, 786 keV, etc), as shown in scheme 1. Since we did not detect any ^{234}Pa in our samples (detection limit approx. 20 mBq g⁻¹), the uranium content in pyrotechnics can be regarded as negligible. Consequently, any radium in the sample cannot be due to a contamination with uranium minerals being in equilibrium with the daughter ^{226}Ra . Rather, it must be a significant enrichment of radium itself in one of the raw materials.

Gamma-spectrometry was performed on the novel low-level counting facility of the Atominstitut, consisting of a 226 cm³ HPGe detector (Canberra™, detector model GC5020; 2.0 keV resolution at the 1332 keV ^{60}Co peak; 52.8% relative efficiency), connected to a PC-based multi-channel analyser with preloaded filter. The measurement position of the sample was fixed at a distance of approximately 11 cm on top

of the detector. The new detector system is characterized by only approximately one-tenth of the background of the other γ detectors of the radiochemistry group in the same institute. This is due to the improved shielding of the detector by the ORTEC™ HBLBS1 shielding (solid-cast virgin lead with steel casing, total weight 1134 kg). For calibration of the detector’s efficiency for ^{226}Ra , 50 μl of QCY48 (Amersham® Ltd) solution in hydrochloric acidic solution (comparable bulk density) was used. The measurement times of the pyrotechnics were at least 1 week, or longer, until no significant improvement of the counting error of the most interesting peaks could be yielded by a—reasonably—longer measurement time. The standard solution was measured for 328 000 s. A background spectrum was recorded (1 816 000 s) and considered for the evaluation of the γ spectra of the pyrotechnics. For quantification, the γ photons with characteristic energies were used as listed in table 3. All nuclear data in this paper are taken from the National Nuclear Data Center [22].

3. Results and discussion

The results of the γ spectrometry are shown in table 4.

The main activity in pyrotechnics is due to ^{40}K (up to 20 Bq g⁻¹, mean value 14 Bq g⁻¹). The presence of ^{40}K

Table 3. Nuclear data of the radionuclides measured by γ spectrometry.

	^{40}K	^{212}Pb	^{214}Pb	^{214}Pb	^{226}Ra	^{228}Ac
Half-life	1.248×10^9 a	10.64 h	26.8 m	19.9 m	1600 a	6.15 h
Principal γ -photon energy (keV)	1460.822	238.632	351.932	609.320	186.211	911.204
γ -photon yield (%)	10.66	43.6	35.60	45.49	3.59	25.8
Decay chain member	—	^{232}Th	^{238}U	^{238}U	^{238}U	^{232}Th

Table 4. Results of the γ -spectrometric measurement of commercially available pyrotechnics. Specific activities are given in mBq g^{-1} , except for ^{40}K (Bq g^{-1}). Errors are due to counting statistics and the efficiency curve error and are given in % relative. ‘n.d.’ stands for ‘not determined’.

Sample (colour)	^{40}K		^{212}Pb		^{214}Bi		^{214}Pb		^{226}Ra		$^{228}\text{Ac}^a$	
	(Bq g^{-1})	Error	(mBq g^{-1})	Error	(mBq g^{-1})	Error	(mBq g^{-1})	Error	(mBq g^{-1})	Error	(mBq g^{-1})	Error
R1 (green)	11.6	1.6	35	9.2	77	13	79	2.1	110	7.0	29	21
R2 (green)	11.8	1.7	32	4.3	48	3.4	54	8.5	87	43	32	9.2
R3 (green)	17.5	1.7	33	12	48	5.1	41	5.4	16	30	37	14
R4 (red)	12.4	1.7	n.d.		46	3.8	48	3.7	97	12	51	7.0
R5 (red)	11.8	1.7	48	3.5	48	11	41	13	92	63	43	8.1
R6 (red)	17.5	1.8	n.d.		36	17	40	5.2	<50		38	13
R7 (pink)	15.8	1.7	48	18	39	5.5	45	5.1	120	47	41	40
R8 (yellow)	12.9	1.8	45	15	54	12	55	13	120	21	37	38
R9 (white)	11.3	1.8	32	4.6	49	3.6	50	3.5	73	14	20	16
R10 (multi-coloured)	15.9	1.7	11	34	28	20	22	18	<40		12	74
R11 (multi-coloured)	14.0	1.7	150	2.1	110	2.5	120	2.5	260	6.7	120	4.0
R12 (multi-coloured)	11.4	1.7	18	13	67	4.4	66	12	120	15	<25	
R13 (multi-coloured)	19.3	1.7	25	23	26	4.8	21	5.4	42	69	18	16
R14 (multi-coloured)	9.23	1.7	3.9	46	11	5.4	9	23	<20		<10	

^a In such environmental samples, ^{228}Ac is in secular radioactive equilibrium with its longer-lived mother nuclide ^{228}Ra (a poor γ emitter). The ^{228}Ac activities thus correspond directly to the ^{228}Ra activities.

in the mixtures can easily be explained by the application of oxidizing potassium salts (nitrate, perchlorate) in pyrotechnics. Black powder, for example, consists of some 75% of potassium nitrate; the increased ^{40}K activity, therefore, did not come as a surprise.

Much more noteworthy is the presence of ^{226}Ra (and/or its daughter nuclides ^{214}Pb and ^{214}Bi , respectively) in almost all pyrotechnics investigated. According to the hypothesis of this study, ^{226}Ra in the samples must be the result of the utilization of slightly active radiobarite ores for the production of the pyrotechnic raw material barium nitrate. As stated in the introduction, the use of barium salts in pyrotechnics is not restricted to green luminescent formulations, as it may be applied as an oxidizer with ‘neutral colour’, if no chlorine donor is added to the mixture. Accordingly, this explains one of the highest specific radium activities (120 mBq g^{-1}) in sample R8—a rocket with a yellow effect.

The highest specific ^{226}Ra activity was 260 mBq g^{-1} (sample R11), whereas only in three samples was the detection limit not exceeded. The average value of all 14 samples was 81 mBq g^{-1} . Pyrotechnics thus exhibit a specific radium activity that is approximately one order of magnitude lower than the lowest active radiobarite sample investigated by Zielinski *et al* [17]. The specific radium activities of our samples, however, correspond to those found in the radiobarites of the Ohře Rift (Bohemian Massif). Some pyrotechnic samples exceeded the lowest active samples from the Ohře Rift (0.02 to 7.80 Bq g^{-1} radium) [18].

We could also find similar levels of ^{226}Ra activity in red luminescent pyrotechnics, where we actually expected much

lower activities due to the less obvious chemical similarities of strontium (red colourant) and radium. However, it seems that both alkaline earth ore deposits, strontium and barium, respectively, similarly accumulate radium from the geological environment.

Comparing the ^{214}Pb activities to the respective ^{214}Bi activities shows very good agreement. This observation comes as expected, because the short-lived nuclide ^{214}Bi must be in radioactive equilibrium with its mother ^{214}Pb . Since the principal γ photons of both nuclides have their energy in different regions of the spectrum (352 keV for ^{214}Pb and 609 keV for ^{214}Bi), this observation leads to the conclusion that our simplified approach of ‘comparable bulk densities’ of samples and QCY48 standard solution is a valid approach for these measurements. If the γ -photon self-absorption properties of sample and standard were significantly different, this would have led to a deviation in the evaluation of γ photons with different energies (and thus different detector efficiencies). Some occasionally higher deviations are due to higher counting errors.

The activities of ^{214}Pb and ^{214}Bi were in the same range (at least in the same order of magnitude) as the ^{226}Ra activities. Remarkably, the ^{226}Ra activities were a little higher than the activities of the daughter nuclides in most cases. This must be, indeed, due to the leaking from the PE sample container.

In contrast to uranium, ^{232}Th and its progeny appeared to be common impurities in pyrotechnics. Since the members of the ^{232}Th decay chain are generally characterized by much shorter half-lives, the thorium decay chain reaches its radioactive equilibrium within only a few decades [23]. The

presence of ^{228}Ra (and its short-lived daughter nuclide ^{228}Ac) in pyrotechnics, therefore, can hardly be the result of a natural, selective incorporation of ^{228}Ra into the barium or strontium ore. Radium-228 ($T_{1/2} = 5.75$ a), without a supply from the mother nuclide ^{232}Th , would decay completely after a few decades.

The specific activities of ^{228}Ac and ^{212}Pb correlate to a high degree, although, as with the ^{238}U chain, a gaseous decay product lies in between, namely ^{220}Rn . In this specific case, however, we believe that the much shorter half-life of the noble gas ^{220}Rn ($T_{1/2} = 55.6$ s) does not allow a significant diffusion through the PE container. Consequently, ^{220}Rn and all its decay products are trapped in the container and measured without any losses.

According to the Swiss Administration [24], 1700 tons of pyrotechnics are annually consumed in Switzerland. We can safely assume that these numbers compare to Austria as well. Assuming an average radium content in pyrotechnics of $81 \text{ mBq } ^{226}\text{Ra g}^{-1}$ and $14 \text{ Bq } ^{40}\text{K g}^{-1}$, these numbers will correspond to an annual emission of $138 \text{ MBq } ^{226}\text{Ra}$ and $23.8 \text{ GBq } ^{40}\text{K year}^{-1}$ from pyrotechnics only (in countries like Switzerland or Austria).

4. Conclusions

Pyrotechnics do contain radium—not extreme activities but certainly enough to be detected in our new low-level γ spectrometer. The ^{226}Ra activities are in the range of $16\text{--}260 \text{ mBq g}^{-1}$ and must be due to the selective incorporation of radium into the barium and strontium ore body, as no traces of the mother nuclide (^{238}U and its early daughters) could be found.

In contrast to this, ^{232}Th and its decay chain members (like ^{228}Ra) probably is present in the form of thorium-containing minerals, which are an impurity in the raw materials of pyrotechnics. Due to its much shorter half-life, ^{228}Ra is unlikely to accumulate significantly in the ore body of an alkaline earth metal deposit. This hypothesis is further supported by the very weak or non-existing correlation of the activity concentrations of the two radium isotopes.

Although the radium activities were relatively low, we believe that this potential hazard should be considered as well in the development of environmentally friendly pyrotechnics [5]. The incidental utilization of highly active radiobarite ores as pyrotechnic raw materials would probably exhibit a greater health hazard than the toxicity of the poisonous pyrotechnic constituents (heavy metals, perchlorate) [5]. In particular, when applied as indoor pyrotechnics, the health aspects of pyrotechnic devices should be taken seriously with respect to air pollution by toxic and radioactive substances. This finding justifies the efforts that are currently being undertaken in the search for barium-free pyrotechnics [25]. One possible method to remove radium from the radiobarite ore, however, could be to set it under reducing conditions which causes the complete mobilization of radium from the barite [26].

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