Sparklers as a nanohazard: size distribution measurements of the nanoparticles released from sparklers

Maja Remškar · Gašper Tavčar · Srečo D. Škapin

Abstract Sparklers, sometimes called Bengal lights, are widely used for the celebration of a variety of events due to their esthetic and entertaining effects. They are especially popular with children. While their associated safety measures deal with rules regarding possible burns to the skin or eyes, the strong emission of nanoparticles during the combustion of sparklers is usually both ignored and unregulated. Here, we report on the high concentrations of nanoparticles released during the indoor combustion of sparklers. Large proportions of the metals making up the sparking material are released into the atmosphere. Information based on chemical analyses of pristine and burned sparklers is compared to the relevant data relating to the released nanoparticles. Their small size and the presence of barium suggest that the use of sparklers as a children's entertainment should be reconsidered.

Keywords Air pollution · Sparklers · Size distribution measurements · Barium · Nanoparticles · Pyrotechnics

Introduction

Sparklers are pyrotechnic materials that after ignition undergo highly exothermic chemical reactions that produce light, either on the surface of the sparkler or, more frequently, as flying sparks. Such pyrotechnic materials are classified as "explosives" for the purposes of transportation (Regulatory guidelines for the shipping and transporting of fireworks 2012), regulated at occupation sites by the OSHA standards (Occupational Safety and Health Standards—OSHA 29 CFR 1910), and in trade (Directive of the European Parliament 2007). According to the EU Directive on pyrotechnics, sparklers are classified as category-1 fireworks (the least hazardous of four categories). Although the latter document came into partial force recently, i.e., on 4 July 2010, the release of nanoparticles (NPs) during combustion is not mentioned. Sparklers are normally used without any precautionary measures for the protection of the respiratory system with respect to the inhalation of the produced gasses and the released nanoparticles. The chemical composition of sparklers is made up of a metallic component, an oxidizing component, a combustible binder, and a fuel component (McManus et al. 1975). A chemical analysis of the ambient air collected during the Indian festival Diwali, at which crackers and sparkles are used to express happiness, has revealed metal pollution in the air that is higher than reported at industrial sites (Kulshrestha et al. 2004). Only two reports were found on measuring the release of nanoparticles from sparklers (called Bengal lights). The scanning mobility particle sizer (SMPS) used for the monitoring in the first report (Klouda et al. 2012) was situated 12 m from the area where the Bengal light was gradually ignited. The size of the particles (pt) was found to be greater than 100 nm, while the total concentration did not exceed 16,000 pt/cm^3. The second report (Betha and Balasubramanian 2013) described the overall concentrations of three types of sparklers burned inside a small experimental chamber with a volume of 0.125 m^3.

Several standards regulate the air quality with regard to the pollution with particulate matter (PM) of size below 10 μm (PM10) or 2.5 μm (PM2.5). The limit values are expressed in mass concentration units and regardless to the source of pollution. European Commission has set the limit values for environment: 50 μg/m^3 for PM10, 24-h averaging period, and the target value of 20 μg/m^3 for PM2.5, considering 1-year averaging period, which is entering in force in 2015 (Directive 2008/50/EC). The limit values of US National Ambient Air Quality Standards (NAAQS) for indoor pollution are higher for PM10 (150 μg/m3), 24-h period, and lower for PM2.5

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(15 µg/m3), 1-year averaging period. The US OSHA has set the limits for indoor air contaminants depending on chemical composition of the pollutants (OSHA Standard PART 1910). The limit values for air pollution with nanoparticles expressed in the size distribution metric are not set yet.

The motivation for our research was to discover to what extent the sparklers pollute the air with nanoparticles under the more realistic conditions of domestic indoor use. A laboratory was chosen for the simulation of a room in an apartment with a window and a door. Forced ventilation was implemented by opening the door and the window simultaneously. The air pollution was monitored at distances inside a circle with a diameter of a few meters centered on the burning sparklers. Sparklers on general sale to the public were chosen for the investigation. Here, we report on the high concentrations of nanoparticles released during the burning of these sparklers, their chemical composition, agglomeration, and the dynamics of their removal from the local atmosphere.

Experimental

The so-called "Magic Sparklers" with a length of 23 cm were produced in the People's Republic of China and imported by Art in Heaven Betrayers GmbH, Germany. The sparklers were burned in a laboratory with a volume of 33 m^3. The forced air exchange was produced by ventilation through an open door and a window. The size distribution of the nanoparticles was obtained in two steps: the nanoparticles were first selected with respect to size using a Differential Mobility Analyzer-DMA (TSI, Model 3080) and then counted using a water-based Condensation Particle Counter (TSI, Model 3785 UWCPC). The particles with sizes between 14.1 and 700 nm were detected in subsequent 5-min size scans. Any coarse water droplets were removed with a Diffusion Dryer (TSI, Model 3062). Simultaneously, a cascade, low-pressure impactor (DLPI-Dekati), which classifies airborne particles into 13 size fractions from 30 nm to 10 µm, was used to collect the nanoparticles for morphology and chemical analysis. The particles were collected on aluminum foils (Dekati, CF-300) covered with APIEZON L grease. The pristine and combusted sparklers as well as the material collected at different stages of the impactor were coated with an amorphous carbon layer and studied with a scanning electron microscope (FE-SEM, Supra 35 VP, Carl Zeiss). The X-ray diffraction (XRD) was performed at room temperature with a D4 Endeavor diffractometer (Bruker AXS) using a quartz mono-chromator Cu-Kα1 radiation source (λ=0.5406 nm) and a Sol-X energy-dispersive detector. The 2θ angular range was from 10° to 70° with a step size of 0.02° and a collection time of 3 s. The elemental analysis of these materials was performed by X-ray energy-dispersive analysis (EDS) inside the SEM and by chemical decomposition analysis. The presence

of the different elements was determined using different analytical methods: barium was determined using a gravimetric method; aluminum was determined by atomic absorption spectroscopy (AAS); and the concentration of iron was determined by complexometric titration. The amounts of carbon, hydrogen, and nitrogen were determined from an elemental analysis on an Elementar vario EL cube.

Results

Size-selective counting of the nanoparticles released during the burning of the sparklers

The numerical and the total concentrations of the particles released during the burning of the sparklers are presented in Fig. 1. The SMPS instrument inlet was positioned at a height of 0.9 m above the floor, while the center of the burning wand was at a height of 147 cm. The temperature in the room was 32±0.5 °C and the relative humidity was 36±1 %. A gas lighter was used for the ignition of the sparklers. The preliminary use of a match was found to increase the total concentration of nanoparticles in the air to 10 times that of the background level (i.e., 2,000 pt/cm^3). The released nanoparticles were smaller than 60 nm. This undesirable pollution is represented in Fig. 1 as a relatively small peak positioned on the left-hand side of the spectra. The selected gas lighter did not release any nanoparticles above the detection limit. The size distribution measurements were performed in a closed room at three distances from the burning sparkler: 65 cm (position A), 1.5 m (position B), and 3 m (position C). The shortest distance was selected to simulate the air pollution affecting a child who handles a sparkler, the second one as the pollution affecting an adult next to the child, and the third distance was the greatest distance available inside the room and which simulates the lower limit of the pollution. The room was ventilated for 10 min before each lighting of the sparklers in order to recover the background level of air pollution. Each sparkler was lit at the beginning of a 30-min-long monitoring period. The numerical concentration of particles released during the combustion of the sparklers (Fig. 1a) is shown in the form of an image that reveals two size maxima, i.e., around 100 nm and at 14.1 nm, which was the lower limit of the size detection. The selected numerical concentrations for both sizes of NPs are shown in Fig. 1b. The majority of the particles were inside the size range of 70–200 nm, although the numerical concentration of the smallest NPs was also high. Each combustion event increased the total concentration of particles in the atmosphere by at least 150 times with respect to the background level (Fig. 1c). The maximum concentration of larger particles matched the ends of the combustion events. A short (5′) time delay in the concentration peak maxima was detected for the smallest NPs. The decrease in the total
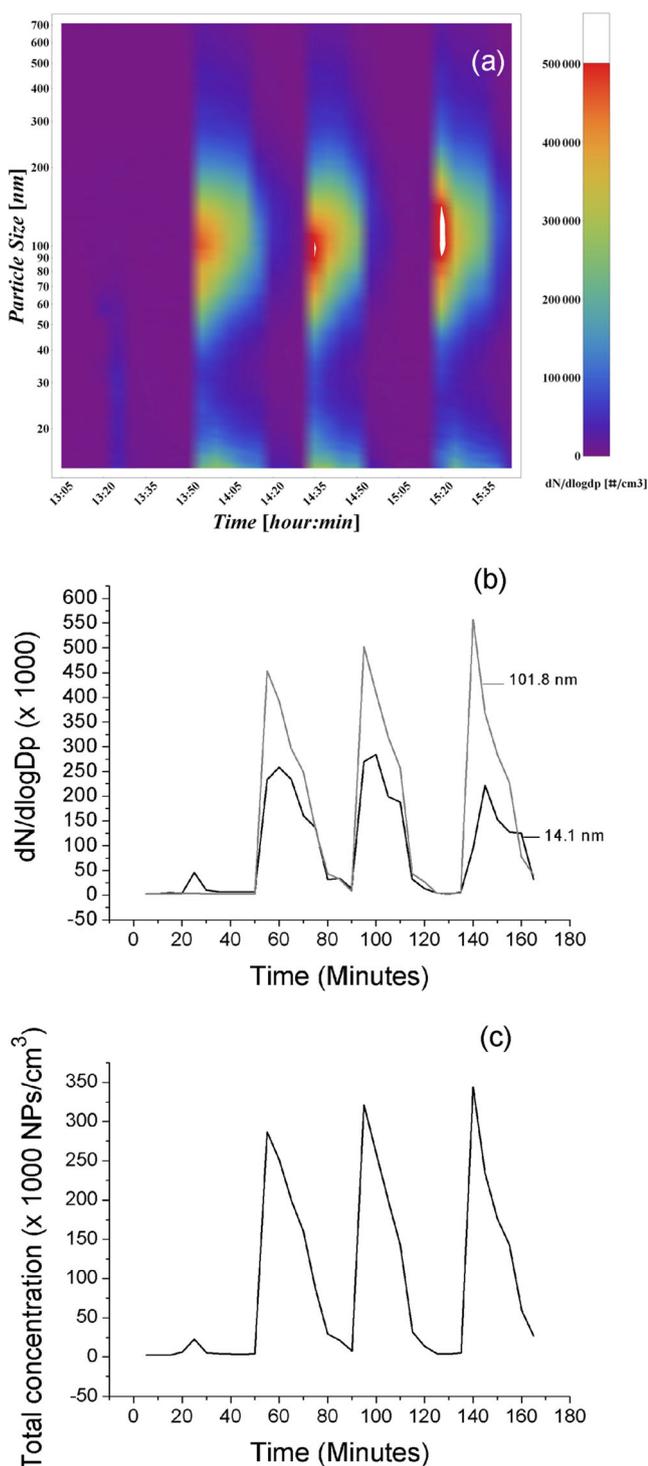
Fig. 1 Numerical concentrations of nanoparticles released from the Magic Sparklers: **a** an image representation (maximum color scale bar: 500,000 #/cm³), **b** the numerical concentration for the smallest nanoparticles (14.1 nm) and for the most frequent particles (101.8 nm), and **c** the total concentration of all particles with sizes between 14 and 700 nm. The *weak peak* on the left-hand side of the spectra is caused by the combustion of a match

concentration with a rate of 11,000 pt/min in the first 20 min after combustion is attributed to the agglomeration and/or

sedimentation of the particles inside the closed room. The ventilation involving the simultaneous opening of the door and window resulted in a faster air clearance rate of 13,000 pt/min. This clearance was equally effective for both the selected sizes of particles.

The spectra measured every 5 min after the combustion of a single sparkler are presented in Fig. 2 for all three distances from the sparklers: A, B, and C. Four measurements were performed at each position prior to the laboratory being ventilated. The positions of the centers of the dominant peaks in the size distribution spectra, together with the corresponding values of the FWHM (full width at half maximum) for the selected measuring periods, are presented in Table 1.

The spectrum measured at position A (0.65 m) during and immediately after the combustion event (time 0) shows two strong maxima, i.e., at 75 and 100 nm, and a weak peak between 22 and 29 nm, which was only visible in the first size scan (Fig. 2a). The intensity of the peak centered at 75 nm decreased with time, but it was still clearly visible after the fourth size scan, 15 min after the ignition (15′). The peak centered at 100 nm, which dominated the spectrum, was shifted toward 130 nm, thereby indicating an agglomeration process. The next three measuring sequences show the evolution of the size distribution of the particles during the ventilation. The dominant peak position initially shifted to smaller values (97 nm) (spectrum, 20′), indicating that the larger NPs were more efficiently removed from the room, while the measurement taken 5 min later (spectrum 25′) showed that the smaller NPs were removed, and the spectrum at 30′ is considered to be the same as a typical background spectrum.

The spectra measured at position B, i.e., 1.5 m away from the burning sparkler, presented in Fig. 2b, show qualitatively similar size distributions of the NPs, albeit with some small peculiarities: (a) the peak that was centered at 75 nm in position A is shifted slightly to 72 nm in the spectra for position B and (b) its intensity is lower, indicating that a larger fraction of NPs is agglomerated, and because this peak is less intense, the spectra show a slightly narrower size distribution of the NPs (Table 1). The peak intensities decreased with time in an asymmetrical way, with a more rapid decrease being typical for smaller NPs. Like in the previous spectra, the agglomeration and/or redistribution of smaller NPs is faster.

Spectra measured for position C, i.e., 3 m away from the burning sparkler, show a shift of the central peak position to 130 nm and a considerably extended size distribution function with respect to the series A and B (Fig. 2c). Although the presence of small NPs is clearly visible as shoulder peaks at approximately 30 and 70 nm, the majority of the particles are larger, indicating a successful agglomeration during the movement of the NPs over this relatively short distance. The time evolution of the peak shape is more symmetrical with regard to the size of the NPs. This confirms that the agglomeration process is finished, and the decrease in the number distribution
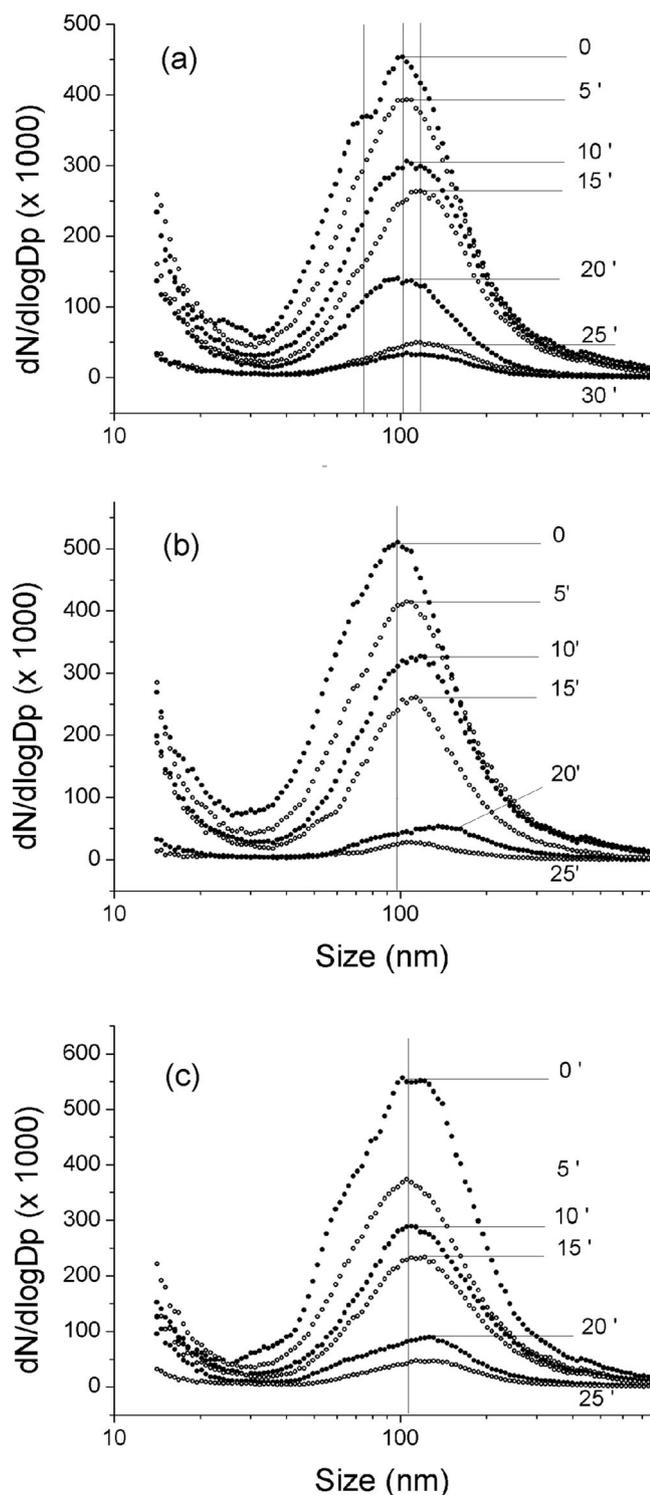
Fig. 2 Time evolution of the size distribution of the particles released during the combustion of three sparklers measured at three distances between the sparklers and the SMPS inlet: **a** 0.65 m (position A), **b** 1.5 m (position B), and **c** 3 m (position C). The *vertical lines* are drawn as position markers. Ventilation took place after the fourth measurement in each series (labeled with 15′)

Table 1 The time shifts of the centers of the dominant peaks in the size distribution spectra of the particles with the corresponding values of FWHM (full width at half maximum) measured at three distances from the sparklers

Peak center (nm) FWHM (nm) Distance	Time (min)			
	0′	5′	10′	15′
A (0.65 m)	111	118	138	184
	114	118	128	124
B (1.5 m)	107	119	126	119
	110	118	123	98
C (3 m)	130	120	129	131
	159	122	127	130

Chemical, structural, and morphological investigation

The elemental composition of a pristine sparkler in mass percentages was as follows: Ba, 36.6 %; Al, 6.1 %; Fe, 17.0 %; C, 6.96 %; H, 0.5 %; and N, 5.75 %. The rest of the material consisted of oxygen coming mostly from the metal oxides, NO_3^- and CO_3^{2-} groups. Tests for the presence of chlorate, sulfur, and molybdenum were negative, despite a variety of chemical analysis methods being used. The mass of the pristine sparkler was 7.2 g, and the mass of the metal holder was 2.7 g. The relevant composition of the burned sparkler was as follows: Ba, 40.8 %; Al, 7.8 %; and Fe, 20.9 %. Based on the subtraction of the mass of the metal holder, the mass of the sparkler measured before and after the combustion was reduced by 30 %.

The X-ray diffraction measurements were made on the sparklers before (Fig. 3a) and after the combustion (Fig. 3b). The material before combustion consisted of a mixture of $Ba(NO_3)_2$ (PDF no. 04-0773), elemental iron (PDF no. 06-0696), elemental aluminum (PDF no. 04-0787), and traces of calcite ($CaCO_3$). The material remaining on the sparkler holder after the combustion consisted of the following crystalline phases: $BaAl_2O_4$ (PDF no. 17-0306), $BaFe_2O_4$ (PDF no. 44-0897), and $Ba_3Al_2O_6$ (PDF no. 25-0075).

The results from the X-ray powder diffraction are in good agreement with the results obtained from the chemical analysis. A pristine sparkler consisted of $Ba(NO_3)_2$, metal Al and Fe, and an organic binder, while the mixed metal oxides are solid products of the combustion.

Scanning electron microscopy (SEM) images of the particles collected at stages 1 and 3 of the impactor are shown in Fig. 4. The smallest nanoparticles from stage 1, presented in the Fig. 4a, were smaller than 100 nm, while the spherical particles from stage 3 (Fig. 4b) were 140 to 360 nm in size, with an average value of 210 nm. Using the window EDS analysis performed at 15 keV, carbon, iron, aluminum, potassium, sodium, sulfur, and oxygen were detected in the NPs collected at both stages (Fig. 4c) and the presence of barium

indicates only the redistribution of the particles in all the available space.
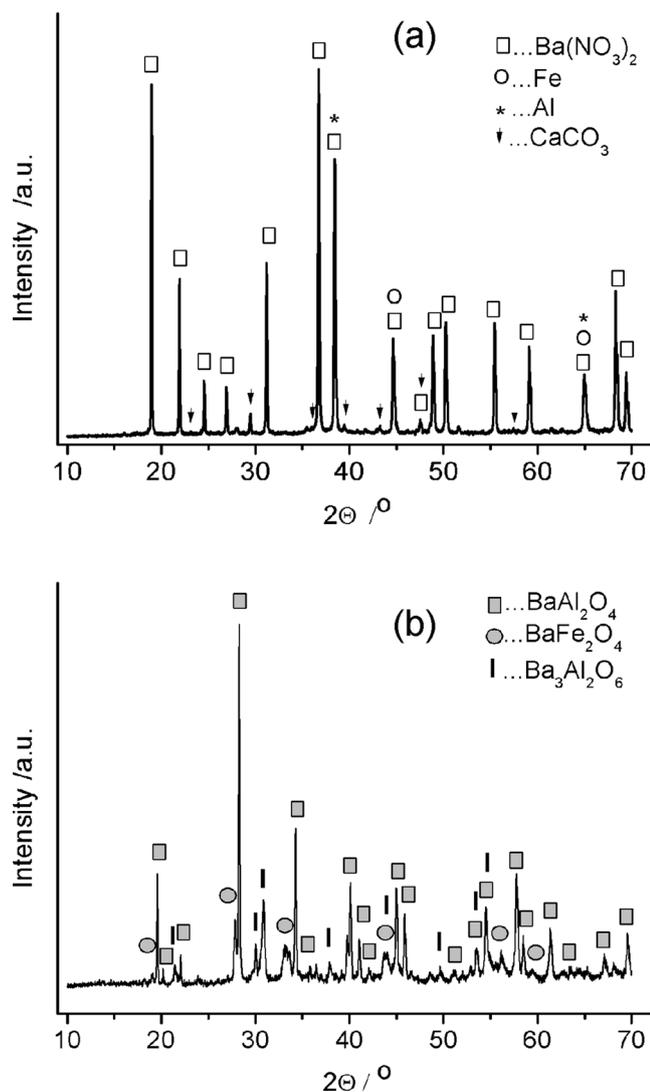
Fig. 3 The XRD spectra taken from the pristine (a) and burned (b) sparklers

was confirmed in the spherical particles collected at stage 3 (Fig. 4d). The sulfur could have originated from the APIEZON L grease, while the other identified elements belong to the collected nanoparticles.

Discussion

Recent air pollution concerns due to the widespread use of sparklers, sometimes also called glow sticks, sparkling wands, Bengal lights, etc., have led to discussions regarding the safe use of these products, which are classified as the least hazardous of all pyrotechnic materials. Currently, the recommendations for the safe use of sparklers warn against possible skin burns, the vicinity of some flammable materials, and the inhalation of the smoke. Other precautionary measures for

the protection of a person's respiratory system against the inhalation of the produced gasses and nanoparticles are not referred to. These sparklers are mostly used for the entertainment of children, who are the most vulnerable population group with regard to air pollution.

According to our studies, which simulated the realistic indoor use of sparklers, we can conclude that the sparklers cause a large increase in the total concentration of NPs in the atmosphere, up to 150 times. Very high concentrations were found in the range of several hundred thousand nanoparticles per cubic centimeter, with the vast majority of them being smaller than 100 nm. These numbers are comparable with those obtained from measurements made on welding, shooting, modern diesel cars, or from non-heated, classic diesel engines (Klouda et al. 2012). The removal of NPs from the atmosphere depends on their size, the degree of agglomeration, the available volume, and the ventilation conditions. Typical NPs with a size of around 100 nm were removed from the air with a time constant of 11,500 pt/min. The monitoring showed that the nanoparticles released from the sparklers remained airborne for several hours inside the closed room.

The chemical composition of the sparklers and especially of the released nanoparticles have shown the presence of elements and compounds that are not normally found in rural air. Their impact on lungs and the possible translocation inside the human body are not known. Although the released gasses were not measured in this study, a large amount of barium in the sparklers (around 40 wt%) and the eventual formation of a gas phase of barium oxide (BaO) represent an additional potential health problem. The temperatures of the sparklers during combustion exceeded 1,000 °C, which is more than sufficient for the formation of barium oxide.

The most likely chemical reactions between the inorganic, nongaseous components during the combustion are

$$4Ba(NO_3)_2 + 4Al + O_2 \rightarrow BaAl_2O_4 + Ba_3Al_2O_6 + 8NO_2$$

$$Ba(NO_3)_2 + 2Fe + O_2 \rightarrow BaFe_2O_4 \rightarrow BaFe_2O_4 + 2NO_2$$

The experimentally obtained 30 % mass reduction of the sparklers can be explained by the release of barium, aluminum, and iron and other elements from the sparkler into the local atmosphere. The relative mass losses of all three metals were as follows: 21.3 % of barium, 13.9 % of iron, and 10.5 % of aluminum. By transforming these numbers into mass units, we can calculate that during the combustion of a single sparkler, approximately 107 mg of iron, 29 mg of aluminum, and 348 mg of barium were released into the local atmosphere. The presence of all three elements in the released nanoparticles was indeed confirmed with EDS analyses in the SEM studies.

Fig. 4 SEM micrographs of the nanoparticles collected at stage 1 (**a**) and stage 3 (**b**) with the corresponding EDS spectra (**c, d**)
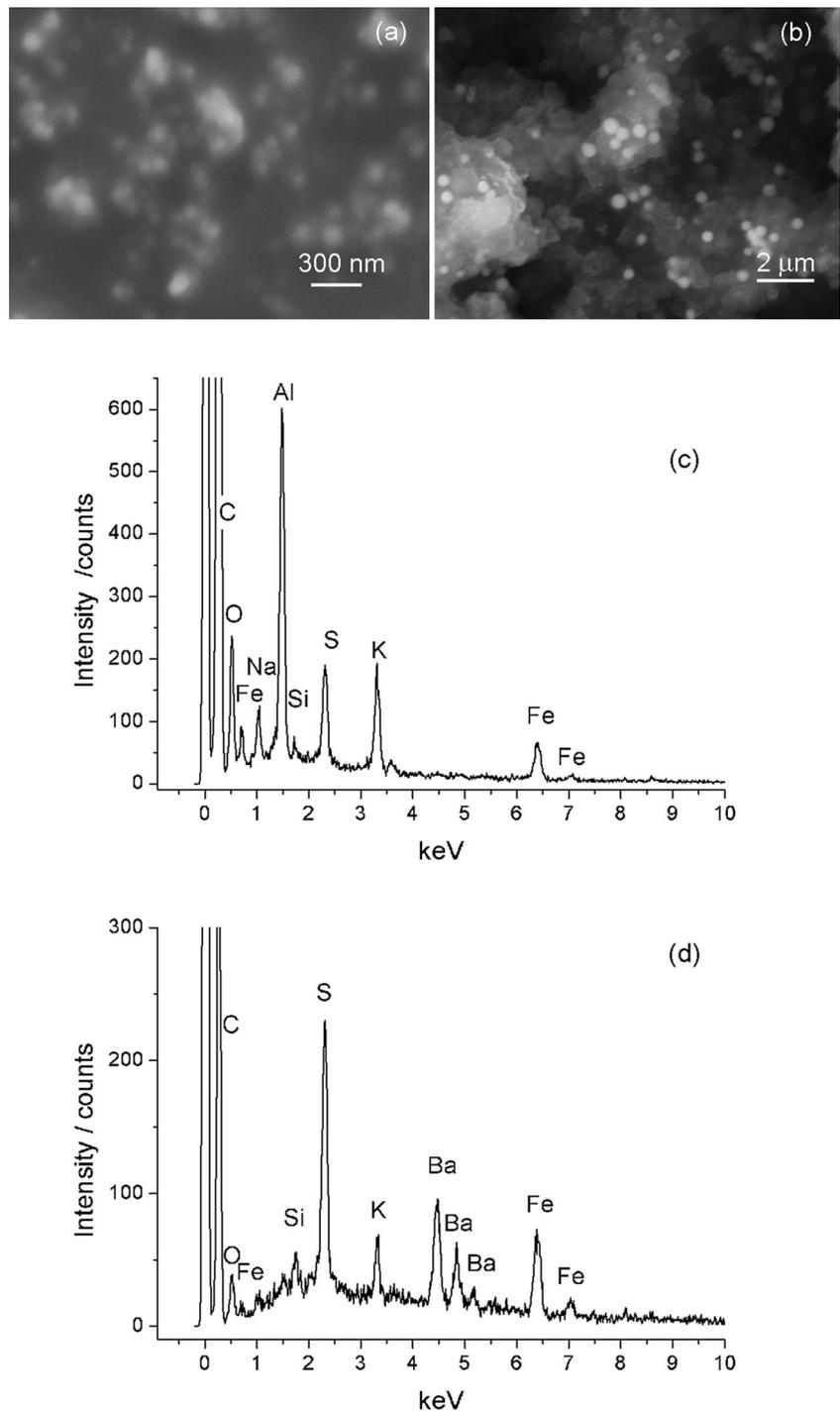
Regarding health concerns, it is important to note that BaO is extremely hazardous in the case of ingestion and hazardous in the case of eye contact (corrosive) and of inhalation (lung corrosive) (MSDS 9923002). Barium has been identified in ecosystems/workplaces that are associated with the high-incidence clustering of multiple sclerosis and other neurode-generative diseases (Purdey 2004). Barium nanoparticles have also been identified in fibrous tissue blood clots in patients with blood disorders (Gatti et al. 2004). The OSHA limit for indoor air contaminants for barium compounds is only 0.5 mg/m^3. Considering the mass of barium released into the local atmosphere, this limit was exceeded for at least 20 times by the use of only one sparkler. It is reasonable to believe that the released Al and Fe are oxidized during the combustion of the sparklers, although the completeness of this oxidation is not known. The oxidation of Al is size-dependent, with a

higher combustion efficiency being observed for nanosized particles (Azhagurajan and Selvakumar 2014). The inhalation of Fe oxides may cause irritation of the upper respiratory tract as well as affecting the blood (I-MSDS0002), while the inhalation of finely divided Al_2O_3 dust may cause coughing, the production of mucous, and shortness of breath (A-MSDS0004).

Conclusions

The numerical concentrations of nanoparticles released during the combustion of sparklers were measured using a scanning mobility particle sizer in simulated conditions representing a child holding a sparkler, its parents standing close by, with the door and window of the room being closed. The sparklers, which consisted of $Ba(NO_3)_2$, elemental Fe, and elemental Al, burned to produce $BaAl_2O_4$, $BaAl_2O_6$, and $BaFe_2O_4$ and emitted nanoparticles that contained Ba, Fe, Al, Na, K, C, and O. The combustion of a single sparkler increased the concentration of NPs in a cubic centimeter of air by at least 150 times. More than 10 % of the metals from the sparklers were released into the local atmosphere. The majority of these released particles were around 100 nm in size, but a substantial amount of them were found to be smaller than 20 nm in diameter. The closest position of the inlet to the sparkler (simulating a child's position) is the most hazardous because of the lowest degree of agglomeration of the nanoparticles. The NPs remained in the atmosphere for several hours. Due to the small size and the chemical composition of the released NPs, and according to the published data on health hazards resulting from their inhalation, the use of sparklers as a children's entertainment should be reconsidered. As safety measures, we recommend an efficient protection of the respiratory systems of all people, particularly of children, who are present at indoor use of sparklers. The sparklers should not be used for decoration of food because of likely pollution of food with nanoparticles. The location where the sparklers have been combusted should be ventilated immediately after the combustion event. An outdoor use of the sparklers of the current chemical composition is also not recommended due to unnecessary pollution of air with toxic substances. The development of less-hazardous pyrotechnics should be encouraged.

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