

Good practice report

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The production of less harmful and less toxic sparklers in an experiment for school students

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Abstract: In this article, a new and simple way of producing sparklers is presented as a school experiment. These sparklers are more environmentally friendly and less health threatening than sparklers produced with existing preparation methods. The problem of conventional sparklers is the toxicity of barium nitrate, which is used as the oxidizer. The substitution of this oxidizer with strontium nitrate and also the reduction of the weight proportion makes the new mixture less dangerous and less toxic. Various tests for the categorization of high-energetic materials show that the newly developed sparklers are not classified as explosives. Furthermore, the tests demonstrate that the newly developed sparklers are not as dangerous as commercial sparklers. Due to their lower health risk, these new sparklers are well suited for use in school education. In addition, expenditure for this experiment is low and integrating it into the upper secondary level curriculum is easy. Sparklers are an impressive example of redox reactions from everyday life. The experiment is a best-practice application for chemistry education, incorporating current results of chemistry research.

Keywords: green chemistry; redox reaction; school student experiment; sparkler.

Introduction

The exact date of the invention of the first sparkler is not known. However, it is known that the sparkler in its present form was invented by Franz Jacob Welter more than 100 years ago. In 1908, he received the patent for his “method for producing a spark-emitting light stick” from the Imperial Patent Office in Hamburg, Germany (Welter, 1907). The exact chemical composition of the first sparkler is not recorded in this patent.

Since their invention, sparklers have captivated people with their fascinating sparks. In addition to the use of sparklers at Christmas time and on New Year’s Eve, there are various other uses in everyday life. For example, sparklers are used to decorate food at birthday celebrations or wedding parties. However, due to their chemical compounds, sparklers can be hazardous to health (Helmenstine, 2018). Normal sparklers use barium nitrate as the oxidizer. Therefore, the ingestion of the sparkler’s combustion products, because the dust from the sparkler drips down onto the food, and the inhalation of the smoke from the sparkler can be harmful to health. Up until now, an experimental procedure for producing safer sparklers has not been discussed or examined.

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For this reason, the goal of the cooperation between different research groups was to develop less health-threatening and more environmentally compatible sparklers. To achieve this goal, barium nitrate was replaced with the safer and less toxic oxidizer strontium nitrate and the weight proportion of the oxidizer was reduced. Because strontium nitrate has a higher solubility in water than barium nitrate, the new sparkler mixture is easier to roll by hand than sparklers with barium nitrate.

Due to the ease of preparation and the very close burning behavior in comparison to commercial sparklers, the production of the new sparklers is well suited as an experiment for school students at the upper secondary level. In addition, several professional state-of-the-art sensitivity tests proved that the new sparklers are safe to manufacture and to use. The new sparklers have already found their way into our science laboratory for school students, where school students produce them several times a week.

General information

Sparklers consist of five main components (Keeney, Walters, & Cornelius, 1995):

- Oxidizer: an oxygen source for the oxidation of the metals
- Iron: to generate the sparks of the sparkler
- Aluminum and magnesium: as powder or dust to accelerate the reaction
- Binder: flour, starch, dextrin, or a similar chemical become a binder when mixed with water and thus hold the composition together
- Wire: iron, copper, or steel wire as carrier material

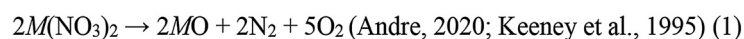
In addition, there are usually also other components, such as coal or sugar, in order to ensure uniform reactions with good spark patterns. Borax can be added so that the products of the sparkler remain attached to the steel wire during combustion (Bast, 2013). These components are not discussed in this article because they are not used in the sparkler mixture presented here.

To develop the barium nitrate-free sparklers, several experimental instructions from various sources on using barium nitrate as an oxidizer were studied (Helmenstine, 2015; Keeney et al., 1995). However, the spark pattern produced by all of the sparkler mixtures tested was much smaller than the spark pattern produced by commercial sparklers. In reaction to this, many correction loops were necessary until a perfect spark pattern could be obtained while considering all of the safety aspects. In general, it can be assumed that the combustion of sparklers produces a large number of different reaction products (Martin & Vries, 2004). In the following, only the reactions that school students must know in order to understand how sparklers work are listed.

Oxidizer

In conventional sparklers, the cheap oxidizer barium nitrate is used. Barium nitrate is toxic (LD50 oral, rat: 355 mg/kg) (NCBI, 2020a) and problematic for the environment. Strontium nitrate with an LD50 value (oral, rat) of 2750 mg/kg (NCBI, 2020b) is toxicologically and ecologically less harmful. For this reason, strontium nitrate is used as the oxidizer for the sparkler mixture presented here. Another important aspect of replacing barium nitrate with strontium nitrate is that the sparkler mixture with strontium nitrate is much less sticky because strontium nitrate has a higher solubility in water than barium nitrate (NCBI, 2020a, 2020b). This makes it easier to manually shape the mixture into the form of a sparkler.

In addition to the reactions with the two metals described below, the thermolysis of the oxidizer when the sparkler is burned can be assumed as:



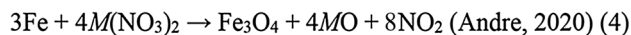
“M” in this and all the following reaction equations is representative of a divalent metal cation, such as Ba^{2+} or Sr^{2+} .

Iron

The iron powder in the sparkler mixture produces the sparks by being oxidized with the oxygen of the air to magnetite (Fe_3O_4), which was verified by X-ray powder diffraction. This oxidation produces the typical sparks of a sparkler, which are warm white to yellow in color. The size of the iron particles and their carbon content are essential for their appearance. In order to achieve a good spark pattern, a powder mixture of 44–149 μm (–100 mesh to +325 mesh) is recommended. In order to obtain the typical branching of the sparks, which can be recognized in pictures as asterisks, a carbon proportion of 1–2% is necessary (Shimizu, 2010). The reaction equation for the oxidation of iron powder with the oxygen of the air is:



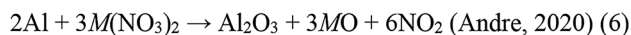
Furthermore, the iron powder reacts with the oxidizer. This happens in the mixture and is not recognizable as flying sparks. Two reactions are described in the literature:



Aluminum

The oxidation of elemental aluminum releases large amounts of energy (Jennings-White & Kosanke, 1995). Aluminum-free sparklers only glow and do not have any flying sparks. Due to the large amount of energy released during the oxidation of aluminum, its proportion in the production of a safe sparkler should be as low as possible. Aluminum dust has a larger surface area than aluminum powder and it therefore reacts faster. Because of this, by using aluminum dust instead of aluminum powder, an aluminum proportion of only 5.7% in the mixture is enough to produce a good spark pattern.

Furthermore, sparklers with aluminum dust create a more homogeneous spark pattern than sparklers with aluminum powder. In addition, the use of aluminum dust does not create large hot sparks, which could be easily recognized by their cool white color. The best particle size for the aluminum dust is flaky particles that are smaller than 45 μm (–325 mesh). Several reactions of aluminum with the oxidizer are described in the literature, for example:



Magnesium

The third metal commonly used in sparklers is magnesium (Keeney et al., 1995). Similar to aluminum, it increases the temperature of the sparkler’s flame. If magnesium meets water, hydrogen is formed. The water of wet salts such as nitrates can already cause potentially dangerous reactions with magnesium and hydrogen (Jennings-White & Kosanke, 1995). To avoid this risk in the manufacture and disposal of the sparklers, no

magnesium powder is used in this mixture. In the newly developed sparklers, the aluminum dust is sufficient to create a good spark pattern.

Binder

In commercial sparklers, dextrin is used as the binder (Bast, 2013). However, dextrin is not suitable for producing a tough mass that can be rolled to form sparklers. It is more suitable for the preparation of a sticky mass into which the wire is dipped in the industrial production of sparklers. Therefore, food starch, cold-water-soluble starch, glue, and flour were tested for the production of the new sparklers, and cold-water-soluble starch turned out to be the most suitable. On the one hand, cold-water-soluble starch has good adhesive force and, on the other hand, it requires only a small amount of water (six drops or 0.3 mL) in the sparkler mixture for a sparkler with 1.75 g of combustible material, which means that it can dry quickly. Thus, the sparklers are ready for use after only 2 h in the drying oven. This is an important aspect if the sparklers are to be produced in a school laboratory within one day.

An important aspect that must be considered when adding binders is their influence on the burning behavior. All of the binders tested, including the cold-water-soluble starch, inhibited the reaction and the spark patterns of the sparklers.

Wire

For the production of a sparkler, a carrier is needed. Commercially available sparklers use a copper-coated steel wire. The copper ensures that the heat is conducted along the wire of the sparkler, so that the sparkler burns well. The sparkler mixture presented here contains enough energy to burn well on a steel wire without a copper coating. The optimal steel wire diameter is 0.8 mm for sparklers with the mixture given below.

Experimental procedure

The production of the sparklers takes about 45 min but the drying time (at least 2 h in the drying oven or 24 h in the air) and the time required to burn the sparklers must also be scheduled (Figure 1).

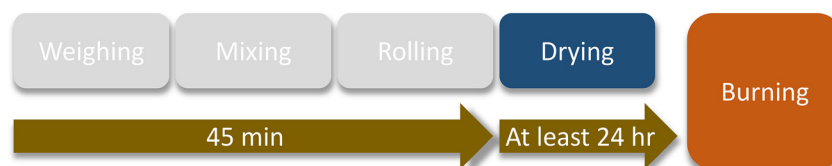


Figure 1: Experimental procedure of making sparklers.

Materials

Strontium nitrate, iron powder, and cold-water-soluble starch can be purchased from standard chemical suppliers, for example, Acros Organics. A degree of purity of 99% of the strontium nitrate is enough; the degree of purity of the iron powder should be about 98%. A higher degree of purity is not recommended for the iron powder; if a higher degree of purity is used, the sparkler does not show the typical spark pattern for which the contained carbon is responsible. Aluminum dust or rather flakes that have a particle size smaller than 45 μm can be bought from a pyrotechnics supplier, for example, Skylighter (Skylighter, 2020). Normal aluminum

powder is not fine enough to create a good spark pattern. Furthermore, one steel wire that is 0.8 mm thick, a spatula, two 50 mL beakers, a 1.0 mL syringe, a drying oven, and a precision scale are needed.

Making the sparklers

For the production of one sparkler, the following chemicals in the following quantities are required:

- 0.85 g strontium nitrate
- 0.10 g aluminum flakes (–325 mesh)
- 0.60 g iron powder (98%, –100 + 325 mesh)
- 0.20 g cold-water-soluble starch

These chemicals are mixed in a dry state until a homogeneous powder is formed. After the addition of water in the following step, it is important to work quickly to form the sparkler, because the sparkler mixture begins to harden after 3 min. Five to six drops of distilled water (about 0.3 mL) are added to the chemical mixture and the mixture is kneaded with a spatula until a sticky mass is formed to a single lump (Figure 2). This lump should have the same consistency as the clay or dough that children use for modeling. After this, protective gloves should be worn to roll the mixture to a cylindrical shape. An approximately 25 cm-long steel wire is pressed into the cylindrical shape (Figure 3) and then covered up again with the mixture. The sparkler is then rolled by hand (Figure 4). It is important to ensure that the sparklers are formed as uniformly as possible (Figure 5), to ensure the best possible burning behavior and spark pattern.

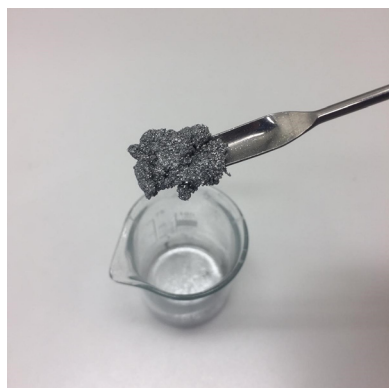


Figure 2: The lump of mixture used to make the sparkler.

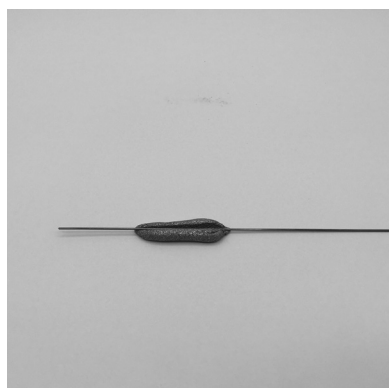


Figure 3: The wire is pressed into the rolled-out mixture.

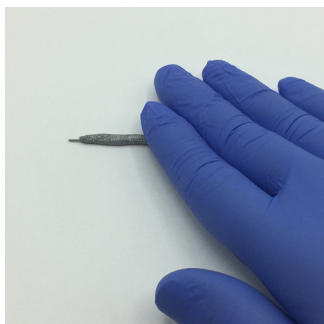


Figure 4: The sparkler is formed by rolling the mixture by hand.

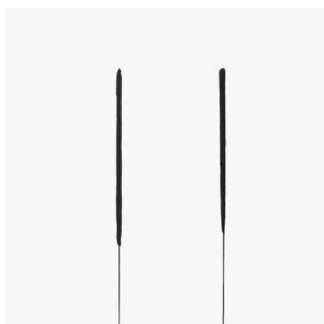


Figure 5: A self-made sparkler (left) and a bought sparkler (right).

After rolling, the sparkler is placed vertically in a clay pot filled with sand and is dried either for 24 h in the air or for 2 h at 70 °C in a drying oven. It is recommended to dry the sparklers for 24 h in the air, because drying in the oven leads to small cracks in the sparklers because of the fast drying process. However, these cracks do not affect the spark pattern of the sparklers.

Burning the sparkler

Due to the emission of gas during the burning of the sparklers, the sparklers should only be burned in fume hoods or outside. After the sparkler is lit at the top, it burns down with a spark pattern similar to that of commercial sparklers (Figure 6). The sparklers should be burned in a noncombustible pot filled with sand and placed on a large, nonflammable surface. Because of the risk of hot drops and sparks, the burning sparklers must not be held in the hand. Leftover educts and unburnt sparkler mixtures should be dissolved in water and disposed of in a container for metal salt solutions. Burnt sparklers can be disposed of in a container for solids.



Figure 6: Spark pattern of a self-made sparkler (left) and a bought sparkler (right).

Safety benefits of the school experiment

Because the strong oxidizer strontium nitrate is used in the sparkler mixture, together with the combustible substances iron powder and aluminum dust, the sparkler mixture is formally categorized as an explosive substance. In order to assess the hazardous potential of the newly developed sparklers, the Berthelot-Rot value B_R of the mixture was calculated and the final mixture was exposed to mechanical and thermal stress and also to electrostatic pulses. The Berthelot-Rot value B_R of the mixture with a density of 2.19 g cm^{-3} , which is the highest theoretical density, was calculated to be 2180 kJ m^{-3} , which is lower than the value of the Oppauer salt used for comparison, which was calculated to be 3434 kJ m^{-3} (density = 1.74 g cm^{-3}) (Sućeška, 2018). Thus, the mixture can be considered to be relatively safe with respect to accidental explosions (Klapötke, 2019). In the impact sensitivity test (using the BAM drop hammer with a load of 40 J), the friction sensitivity test (load of 353 N), the steel-sleeve test (a nozzle plate with a hole of 2 mm in diameter), and the ESD test (electrical impulse of 1.5 J), the newly developed sparkler mixture could not be stimulated to react or explode. This shows that the mixture is not a hazardous, explosive substance (Figure 7) (Klapötke, 2019). In contrast to the self-made sparklers, some commercially available sparklers reacted so strongly to thermal stress that they did not pass the steel-sleeve test (Figure 8).



Figure 7: Clockwise from top: Impact sensitivity test, friction sensitivity test, steel-sleeve test, and ESD test.



Figure 8: Left: Although the steel sleeve used in the steel-sleeve test with the self-made sparklers is deformed at the bottom, the test can still be considered negative. Right: The steel sleeve of a steel-sleeve test used for the bought sparklers was blown up into seven parts. Thus, the steel-sleeve test was not passed.

Thus, the appropriate production and burning of the new sparkler mixture described above can be classified as safe. Nonetheless, the regulations of the respective country for conducting experiments with energetic materials at schools and in experiments for school students must be observed. For example, in Germany, school students in the fifth grade, around the age of 11, are allowed to produce these sparklers (KMK, 2019).

School use

Every school student knows sparklers and, therefore, they are a good example from the school student's everyday life for redox reactions. To understand the chemical processes behind the experiment, students should be familiar with the basics of redox chemistry. The idea of the transfer of oxygen from the initial class is sufficient. Astonishingly, pyrotechnics is rarely used in chemistry education although the topic could attract students' interest (Sjøberg & Schreiner, 2010) and it provides many links to the chemistry curriculum. Oxidizers and redox reactions can be found in all chemistry curricula worldwide (ACS, 2018; Department for Education of England, 2015) and the experiment can be used as a simple school student experiment to demonstrate these topics from chemistry education. Depending on the grade, a teaching unit on this topic can be used to deal with various parts of the redox theory in more detail with the school students.

The experiment is particularly suitable for intensifying the topics of oxidizing agents and oxidation of metals and for changing the concept of the transfer of oxygen to the idea of redox reactions as electron transitions. Furthermore, pyrotechnics in general and sparklers in particular can also be found in some curricula. A use at upper secondary level to illustrate the principles of green chemistry is also conceivable, since the substitution of a substance with a less harmful and less toxic alternative can be easily understood by the school students. In the sense of "minds-on chemistry" there is also the opportunity to discuss the possibilities and contributions of chemistry to environmental protection.

Students' experience and comments

The experiment was presented on several conferences, seminars and chemistry teacher-training courses on the topic of modern materials. As a result, the experiment has already been used in regular chemistry classes. It was reported that the school students could easily produce the sparklers and that this lesson content of sparklers will be repeated with other students. In addition, a short form of the instructions for the experiment will be published in the new edition of the Bavarian collection of experiments for chemistry education, "Chemistry – but safe", which will be available in spring 2021.

Although the experiment was designed for school students in the eighth grade, who are mostly over the age of 14, it can also be carried out by younger school students. In our school student laboratory, more than 40 school students in the fifth grade, around the age of 11, and more than 600 school students over the age of 14 successfully produced the newly developed sparklers. In addition to the production of sparklers, the school student laboratory program contains four further stations that can be worked on by the school students. In surveys at the end of the days spent in the school laboratory, the station for making sparklers is always the most popular station among the school students, as these exemplary comments from the school students show:

"It's a nice example from everyday life and an exciting chemical topic."

"I liked the combination of theory combined with practical work."

"The experiments helped me to understand how to make sparklers and what chemical processes are behind a sparkler."

"I liked being able to manufacture my own sparkler."

"Discussing the aspect of the environmental problems of pyrotechnics was exiting."

With this experiment, the topic of redox chemistry can be intensified using an interest-promoting (Sjøberg & Schreiner, 2010) everyday chemical product. Additionally, school students get an insight into the toxicological and environmental problems of commercial sparklers. Students are encouraged to reflect critically on the daily

use of chemical products and, at the same time, they are shown that chemical research may reduce environmental problems.

For example, in our student laboratory, supervisors were often asked by school students why these new sparklers are not available in shops yet. The students said that this would be much more reasonable because they are much better for health and the environment. After the experiment, other students came to the conclusion that, in the future, they would like to do without New Year's Eve fireworks for the sake of the environment. These suggestions and comments show that the students may have changed their opinions and attitudes. The majority of students who conducted the experiment in our science laboratory for school students stated that the experiment increased their interest in the topics of pyrotechnics and redox chemistry in particular, as well as in chemistry in general.

Teachers receive an instructional guide to assist them in carrying out this experiment with school students. With this guide, it is possible to produce these new, fully functional sparklers in a simple, cost-effective, and safe manner. Furthermore, this simple experiment with such a popular object from the field of pyrotechnics is also fun for school students. The future development of this experiment could involve the further scientific development of a sparkler that uses an ecologically safe oxidizer such as potassium nitrate.

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