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Pyrotechnics Lab Experiences with Critical Raw Materials

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General Introduction

This toolkit will give the students the opportunity to study pyrotechnics reactions, as well as the exploration of the colour production in every chemical reaction dedicated to visual spectacles such as fireworks or magic shows.

The targeted audience are students from 14 to 18 years old, as it is advisable to have some physicochemical background.

Pyrotechnics is the science and craft of using materials capable of experiencing self-contained and self-sustaining exothermic chemical reactions to produce heat, light, gas, smoke and/or sound. The most important feature of this lab experience is the production of colour. It can be generated by two phenomena: luminescence and incandescence. The pyrotechnic field can be applied in fireworks, maritime and automotive industry, mining, agriculture, animal husbandry, signalling and location.

In this toolkit, students will learn how to apply basic chemicals knowledge to produce visual effects with specific salts (some of them critical raw materials) through a combustion. Essentially, a specific amount of salt is solved in methanol and ignited.

Key words:

Combustion, incandescence, luminescence, pyrotechnics

Extended background information

HISTORICAL INTRODUCTION

Pyrotechnics are all devices prepared for specific chemical reactions that produce different effects, used, among other applications, in fireworks displays.

Gunpowder may be considered the first pyrotechnic. It was discovered in China, according to plenty of different historical studies. A famous legend narrates that a chef discovered gunpowder when he cooked together sulphide, saltpetre, and coal (all elements used in cooking during the time) giving rise to a mixture that, when contacted an ignition environment, made clear its explosive characteristics. However, the most accepted hypothesis states that during the VII century a monk named Li Tang, from the city of Liu Yang, created the first explosive mixture called black powder, and due to this discovery, every April 8th in China Li Tang is offered tributes.

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After its discovery, gunpowder was developed in China and introduced into pyrotechnic phenomena, first for social events, and later for war purposes. Gunpowder arrived in Europe around the XIII century, via the Silk Road. In the Old Continent, people from countries such as Italy, especially in Florence, pioneered the fireworks industry since the XV century. The spectacularism of the fireworks reached its maximum splendour in the XIX century, highlighting its wide range of colours.

However, over time, gunpowder lost its importance in the field of warfare, as nowadays, there are other substances with greater explosive power.

SCIENCE OF PYROTECHNICS

Pyrotechnics take place due to chemical reactions that occur inside the pyrotechnic devices. In most cases, they give rise to the following effects: flames, smoke and sparks. In certain pyrotechnic devices, there are also controlled explosive reactions that trigger another typical effect, the explosion.

Pyrotechnics are based on the chemical reactions of reduction and oxidation (redox reactions) produced between oxygen and fuels. A redox reaction consists of a chemical reaction in which there is an exchange of electrons. One substance loses electrons and is oxidized (in this case, fuel) and another substance gains electrons and is reduced (oxygen). For this reaction to take place, it requires four elements that are known as the tetrahedron of fire.

Fire Tetrahedron

- Fuel (reducing agent): a flammable mixture that makes up the pyrotechnic device. They represent the combustion fuel and react with the oxygen released by oxidants, producing enormous amounts of gas at elevated temperatures. Among the most common reducing agents used in pyrotechnics are sulphur (S) and carbon (C), which react with oxygen to form sulphur dioxide (SO_2) and carbon dioxide (CO_2). These two elements, together with potassium nitrate, normally give rise to black powder, by using them in the appropriate percentages.

- Oxidizer (oxidizing agent): Usually oxygen. The oxidizing agents are the elements responsible for generating the oxygen necessary to produce the combustion reaction of the pyrotechnic mixture. They are metallic salts that are composed of anions with a metal cation. The main distinct types of oxidants that are known are the following: chlorates (ClO_3^-), nitrates (NO_3^-), and perchlorates (ClO_4^-). It is typical for these anions to pre-form a salt with potassium (K^+).

- Heat: Fuel activation energy. The agents responsible for providing the heat are called activation agents. In other words, they produce the ignition in pyrotechnic devices, responsible for providing the heat and activation energy necessary for the reaction to begin its course, and thus be able to achieve the desired effects with each type of artifice.

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- Chain reaction: the process that allows the progress of the mixture-fuel reaction.

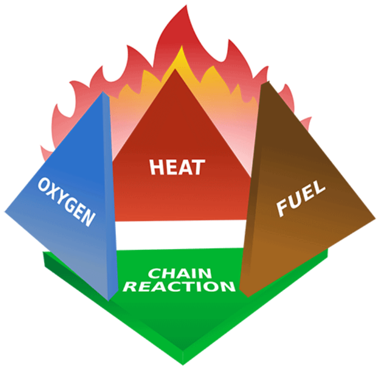

Figure 1. Fire tetrahedron

Types of reactions

In the reduction and oxidation reactions, several levels are differentiated depending on the energy released and the speed of the reaction.

1. Combustion: it is a reaction that produces the emission of light (flame) and heat. The reaction rate is not remarkably high.
2. Deflagration: The reaction rate is exceedingly high, although with values below the speed of sound, less than 300 m/s.
3. Detonation: It is a reaction with a supersonic propagation speed, greater than 300 m/s of sound, and able to reach in the case of high detonation to 9000 m/s.

The last two levels of oxidation are called explosions because a large amount of gas is released at high pressure in a very short time lapse and the energy released is transmitted by a shock wave.

Additional Components

Apart from these basic substances of pyrotechnic compositions, other complements that modify the characteristics of combustion are added to the mixtures.

1. Catalyst substances: those capable of accelerating or slowing down the reaction depending on the type of element. These can trigger an explosion by generating an increase in the speed of the reaction.
2. Binding substances: they give the pyrotechnic composition a strong cohesion, which consolidates the mixture of stability during storage. In addition, it increases the resistance to any type of solvent. Dextrin or gum arabic are the most common ones.
3. Decorative substances:
    - Sound and whistling effects: the first of them is caused by the release of gas at high pressure very fast, and whose compositions are usually formed with perchlorate and chlorate. The latter is achieved with compositions formed by benzoates or

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salicylates, or even with compositions of black powder (potassium nitrate, C and S). It is sealed by a plug with a nozzle that, while expelling the gases, is the culprit of the emission of the whistling effect.

- Visual effects: salts and metallic elements are the elements which, at a specific reaction temperature, will give rise to effects as striking as those that will be appreciated in lab practice. Depending on the element(s) added to the combustion reaction, a specific colour can be obtained. These elements must be used free of impurities since this could spoil the final colourful effect with parasitic emissions.

Table 1. Emission colour chart

COLOUR	CHEMICAL ELEMENT
Yellow	Sodium salts ($Na_2C_2O_4$, $NaNO_3$…)
Red	Strontium salts ($SrCO_3$, $Sr(NO_3)_2$…)
Blue	Copper salts or oxide (CuO, CuCl…)
Green	Barium salts ($BaCl_2$, $Ba(NO_3)_2$…)
White	Magnesium and Aluminium salts or alloys (Al, Mg)
Gold	Iron (Fe)
Violet	Strontium and Copper mixture of salts ($SrCO_3$, $CuCO_3$…)
Orange	Calcium salts ($CaCO_3$, $CaCl_2$…)
Silver	Titanium (Ti)

VISUAL PHENOMENA

The two phenomena that produce impressive visual effects in pyrotechnics are incandescence and luminescence.

- Incandescence: generation of coloured light due to the heat energy from the elements subjected to the reaction. When the emitting body reaches a certain temperature, it emits radiation that, within the visible spectrum and an adequate wavelength, gives rise to the emission of light of the desired colour. It starts with the red colour from the infrared range, and as the temperature rises, it adopts more yellowish colours, until it reaches white. This phenomenon only achieves warm colours. The rationale behind this is when the white colour is obtained due to the high temperatures, the compound starts disintegrating.

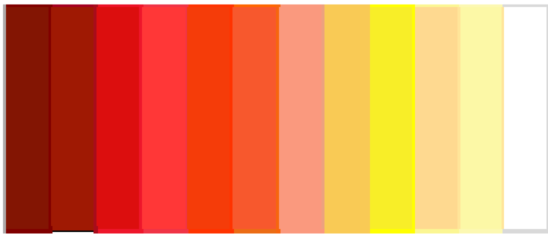

Figure 2. Incandescence visible spectrum

- Luminescence: A chemical process by which the electrons of heat-producing metal cations are excited by receiving a large amount of energy. These electrons reach a higher energy level. Since they are not stable at that energy level, they return to their ground state, emitting energy in the form of photons with a colour spectrum characteristic of each element called the emission spectrum. The larger the energy jump, the cooler the colours emitted. The phenomenon can emit coloured light at both high and low temperatures, thus achieving all the colours of the visible spectrum depending on the wavelength of the emitted radiation.

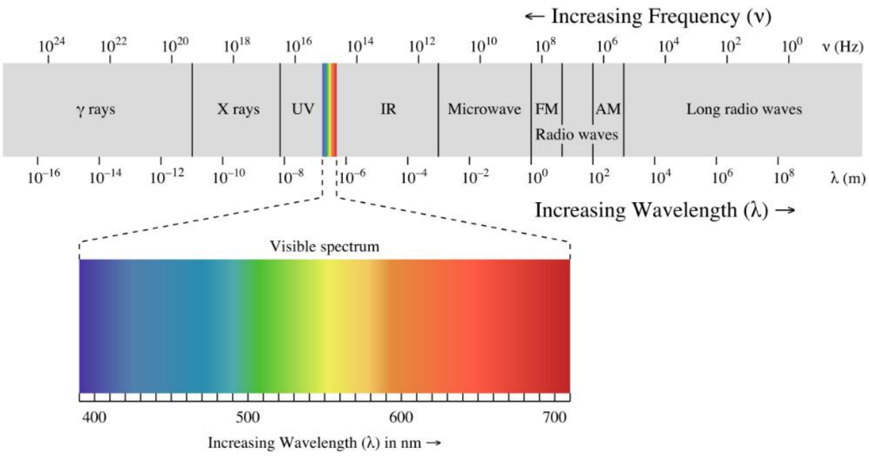

Figure 3. Luminescence visible spectrum

RELATIONSHIP WITH CRITICAL RAW MATERIALS

Raw materials are essential to produce a wide range of everyday products and services. Accelerating cycles of technological innovation and rapid growth in emerging economies have led to an increased global demand for certain metals and minerals. Ensuring access to a stable supply of many raw materials has become a major challenge for national and regional economies that have limited production. The European Union (EU) depends on the import of many of these minerals and metals needed by industry, including many of the critical raw materials. In 2008 the European Commission launched the "European Raw Materials Initiative" which consisted of:

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- Ensure a fair and sustainable supply of raw materials from international markets.
- Promote sustainable supply within the EU.
- Promote the efficient use of resources and promote recycling.

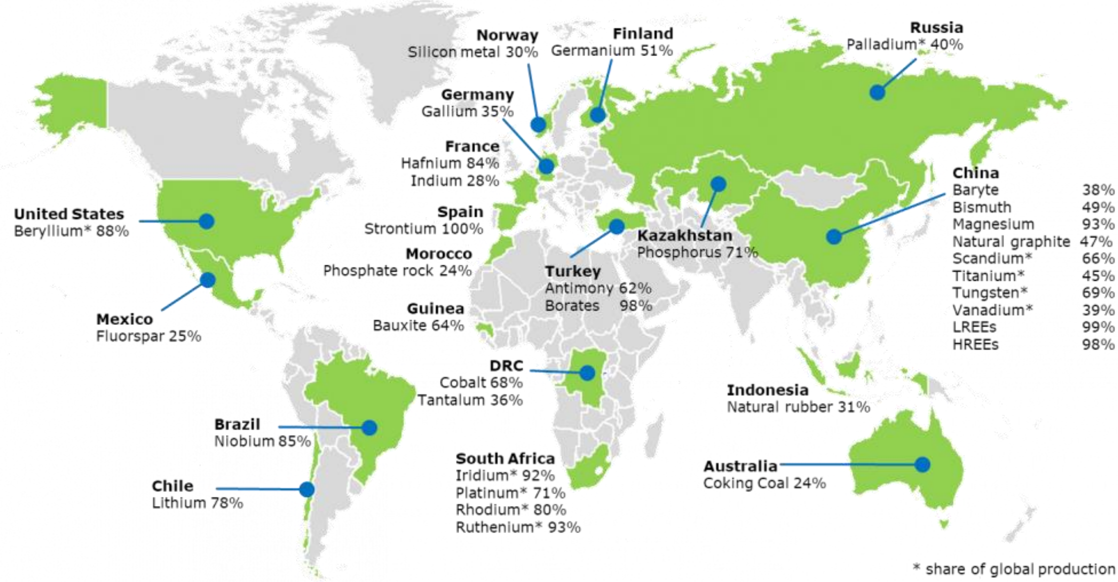

Figure 4. Critical Raw Material production.

The critical raw materials used in pyrotechnics are mainly titanium, strontium, barium, phosphorus, aluminium and magnesium, which are mainly used for visual purposes. In this practice, instead of using these elements and pyrotechnics, due to safety reasons, a combustion with methanol and metallic salts will be performed. Some of the salts used also contain critical raw materials such as lithium and boron.

- Strontium nitrate in addition to pyrotechnics, is used for railway signalling and tracer bullet formulas. Strontium hydroxide builds several organic acids soaps and fats of stable structure, resistant to oxidation and decomposition in a wide range of temperatures. The main minerals are celestite ($SrSO_4$) and strontianite ($SrCO_3$). Spain is the country with the highest production of this mineral and has the largest strontium mine.
- Barium compounds are obtained from mining and by conversion of two barium ores. Barite, or barium sulphate, is the main mineral and contains 65.79 % barium oxide. It is used for pyrotechnics, oil and gas industries, paint, bricks, tiles, glass and rubber.
- Lithium is the lightest solid metal. It has a high thermal conductivity, high specific heat and very low density. The main uses of lithium are glass and ceramic production, lubricating greases, cement production, rechargeable batteries, Al-Li alloys, improving strength and making lighter and pharmaceutical products. The main producers are Chile and China.
- Boron is a non-metallic element. Enhance chemical, thermal and water resistant. It is an essential macronutrient for plant growth, crop yield and seed development. Also, enhance stain removal and bleaching. The main uses are glass insulation (fire glass), on frits and

ceramics, fertilizers and detergents. It is mainly produced in Turkey, United Estates and Chile.

Learning Outcomes

By the end of the lesson, the students will be able to know:

- Fire tetrahedron of combustion.
- Combustion (redox) and pyrotechnics reactions.
- Luminescence and incandescence concepts and colours generation.

Key Competence European Framework

Literacy competence
S1. Ability to understand and interpret concepts, feelings, facts or opinions in oral and written form.
S2. Ability to express concepts, feelings, facts or opinion in written and oral form.
Multilingual competence
S1. Ability to understand and interpret concepts, feelings, facts or opinions in oral and written form.
S2. Ability to express concepts, feelings, facts or opinion in oral and written form.
S5. Knowledge of vocabulary, grammar and language.
S7. Ability to use technical language accordingly to the field of work.
Mathematical competence and competence in science, technology and engineering
S3. Ability to model mathematically a situation from the real world and to transfer mathematical expertise to non mathematical contexts.
S5. Capacity for quantitative thinking.
S6. Ability to extract qualitative information from quantitative data.
S8. Ability to design experimental and observational studies and analyse data resulting from them.
Digital competence
S4. Ability to use and handle technological tools and machines.
Personal, social and learning to learn competence
S3. Ability to gain process and assimilate new knowledge, skills and qualification required for career goals.
Citizen competence
S3. Ability to work effectively and collaborate with other team members.

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Entrepreneurship competence
S1. Awareness of local, national, European culture heritage and their place in the world.
Cultural awareness and expression competence
S3. Ability to plan and manage tasks

United Nations' Sustainable Development Goals

The Sustainable Development Goals are the blueprint to achieve a better and more sustainable future for all. They address the global challenges we face, including those related to poverty, inequality, climate change, environmental degradation, peace and justice. *Goals linked to this activity:*

	1, 2 Enable access to basic services		10 Equal access to global expertise
	3 Safe medical devices		11 Sustainable urbanization
✓	4 Access to education		12 Responsible consumption and production
	5 Less hardship, more opportunities		13 Strengthen resilience, reduce disaster impact
	6 Safe and affordable water		14 Reduce marine pollution
	7 Energy – the golden thread		15 Sustainable use of terrestrial ecosystems
	8 Safety of workers and economic growth		16 Promote peaceful and inclusive societies
✓	9 Resilient infrastructure and sustainable industrialization		17 Better access to technology and innovation

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Contents – Theoretical principles

A pyrotechnical reaction can be defined as a chemical reaction of combustion, deflagration or detonation in which principally fuel and oxygen are consumed producing heat, light, sound and residual elements.

Pyrotechnic principles will be explained using black gunpowder as example. However, due to the high risk of deflagration that causes extremely high temperatures, during the lab experience, different salts dissolved in methanol will be used instead (see lab procedure) to illustrate the generation of the different colours.

Black gunpowder is normally made up of potassium nitrate (75 %), coal (15 %) and sulphur (10 %).

$$10\ KNO_3 + 3\ S + 8\ C \rightarrow 2\ K_2CO_3 + 3\ K_2SO_4 + 6CO_2 + 5\ N_2$$

In order to achieve the light phenomenon, strontium or barium salts are added.

Strontium

This element is usually used to obtain the red colour in pyrotechnic reactions. The visual effect is achieved with the phenomenon of luminescence. The energy required to achieve this phenomenon is obtained thanks to the succession of exothermic chemical reactions. The first step is a metal vaporization when it reaches the right temperature. It is made up of strontium carbonate and nitrate.

$$SrCO_3 + heat \rightarrow SrO(g) + CO_2$$

$$2\ Sr(NO_3)_2 + heat \rightarrow 2\ SrO(g) + 2\ N_2 + 5\ O_2$$

Taking advantage of this strontium oxide and the resulting water vapor or hydrochloric acid (depends on the oxidizing/fuel reaction), the colour-producing substance is formed.

$$SrO(g) + HCl \rightarrow SrCl(g) + OH$$

$$SrO(g) + H_2O \rightarrow SrOH(g) + OH$$

Again, it is thanks to the heat released from the oxidant/fuel reaction that the colour-producing substance absorbs that energy, passing into a state of excitation, which leads it to ascend the energy level:

$$SrCl(g) + heat \rightarrow SrCl(g)^*$$

$$SrOH(g) + heat \rightarrow SrOH(g)^*$$

Where * represents the excitation of the electron

Finally, after excitation, the electron is in a state of unstable energy and releases excess energy until it returns to its ground state in the form of a luminous photon, expressed as follows:

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$$SrCl(g)^* \rightarrow SrCl(g) + \text{red light photon}$$

$$SrOH(g)^* \rightarrow SrOH(g) + \text{red light photon}$$

Barium

This element is usually used to obtain the green colour in pyrotechnic reactions. The visual effect is achieved with the phenomenon of luminescence. The energy required to achieve this phenomenon is obtained thanks to the succession of exothermic chemical reactions. Following the same steps as Strontium:

Vaporization: It is made up of barium carbonate and nitrate.

$$BaCO_3 + \text{heat} \rightarrow BaO(g) + CO_2$$

$$2\ Ba(NO_3)_2 + \text{heat} \rightarrow 2\ BaO(g) + 2\ N_2 + 5\ O_2$$

Formation of colour-producing substances:

$$BaO(g) + HCl \rightarrow BaCl(g) + OH$$

$$BaO(g) + H_2O \rightarrow BaOH(g) + OH$$

After absorbing the heat-producing substance that comes from the oxidant/fuel reaction and undergoing excitation, de-excitation occurs where the photon of green luminous light is released.

$$BaCl(g)^* \rightarrow BaCl(g) + \text{photon with green light}$$

$$BaOH(g)^* \rightarrow BaOH(g) + \text{photon with green light}$$

Lab Procedure/Activity

The previous theorical activity described in the chapter "Theorical contents" cannot be carried on a school laboratory because of the complexity of working with gunpowder, the equipment required and the high risk of deflagration.

For this reason, the laboratory procedure will consist only in a more controlled combustion of solutions. The main difference between strontium/barium gunpowder and the proposed combustion solutions is that the heat required for gunpowder is much higher. Pyrotechnic mixtures (gunpowder) cause deflagration, while methanol solutions generate a combustion.

Methanol (CH_3OH) takes relevance for the lab experience because its flame does not emit colour. This useful characteristic helps to watch clearly the colour produced by certain elements.

The activity is divided into two parts. The first consists of measuring and dissolving each salt into methanol. The salts used are:

- Boric acid (H_3BO_3) to produce a green colour.
- Potassium hydroxide (KOH) to produce a pink colour.
- Copper chloride ($CuCl_2$) to produce a blue, but firstly has green tones.
- Lithium chloride (LiCl) to produce a magenta colour.
- Sodium bicarbonate ($NaHCO_3$) to produce an orange colour.

In the second part, the solution fills an aluminium container and is ignited.

As we explained before, the elements that truly produce the colour are Boron, Potassium, Copper, Lithium, and Sodium due to their emission spectrum.

Module – Luminescence colour effect

Learning Pathway

Step 1 (10 minutes) – Teachers start the activity by telling the historical introduction. Then, give a short reminder about combustion reactions and explain how the importance of critical raw materials and their relation to pyrotechnics (explained in background information).

Step 2 (10 minutes) – Students read the 'Introduction' of the Student's Card.

Step 3 (5 minutes) – Students watch the pyrotechnic video: www.youtube.com/watch?v=-0YyhiBy86k

Step 4 (45 minutes) – Students complete the experiment following the 'Lab Procedure' of Student's Card.

Step 5 (10 minutes) – Students complete the 'Questions' of the Student's Card (on their own or answer a Kahoot).

Step 6 (10 minutes) – Results analysis and discussion of the answers.

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Evaluation

The activity could be evaluated with a lab report or by qualifying student’s answers to ‘Questions’ on Student’s Card or Kahoot.

The link to the Kahoot is:

https://create.kahoot.it/share/pyrothecnic-s-toolkit/95110f2d-24df-403e-93b6-2bfaf0fea4af

The second option can be done by collecting the students’ answers before discussing them (that means doing step 6 when the teacher has already collected the answers instead of right after the experiment), or by asking students to give their answer papers to a classmate and discussing the correct answers altogether. In this way, every student will be checking someone else’s answers. The teacher must collect the papers after that so he can note down the marks.

Description of Student’s Cards

Student’s Card – Luminescence colour effect

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