Teachers' Card

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General Introduction

This toolkit is based on experimental activities and helps teachers in increasing students' understanding of recycling metals, water pollution and the relevance of a circular economy. Moreover, it allows studying the behavior of the coordination compounds.

The target of students is from 11 to 19 years old, because it is possible to divide the activities in two steps:

- Synthesis reaction of Prussian Blue. It's more difficult and the teacher must work in a chemistry lab. It is for students 16 years old or above.
- Water filtration. It uses the Prussian Blue compound for capturing metal's ions from water. It's easier, so suitable also to younger students (from 11 yrs), and the teacher can work also in the classroom.

Prussian Blue is one of the first synthetic pigments ever created. It's thanks to its particular structure it can interact with CRMs ions in order to capture them.
Prussian Blue can be synthesized in a laboratory or it can be purchased, therefore the synthesis is proposed to student over 16, while for younger students we only proceed with recovery of metals from the water.

Key words:

Sustainability, Recovery, Coordination compounds, Critical Raw Materials, Adsorption

Extended background information

What are Critical Raw materials?

Critical Raw Materials (CRMs) are those raw materials which are economically and strategically important for the European economy, but have a high-risk associated with their supply. These materials are not only 'critical' for key industry sectors and future applications, but also for the sustainable functioning of the European economy, because they are used in environmental technologies, consumer electronics, health, steel-making, defense, space exploration, and aviation.

It is important to note that these materials are not classified as "critical" because these materials are considered scarce, rather because:

1. **they have a significant economic importance for key sectors in the European economy**, such as consumer electronics, environmental technologies, automotive, aerospace, defense, health and steel.

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AND

2. **they have a high-supply risk** due to the very-high import dependence and high level of concentration of set critical raw materials in particular countries and **there is a lack of (viable) substitutes,** due to the very unique and reliable properties of these materials for existing, as well as future applications

Thus, Raw materials are ranked according to the economic importance of the material compared to the risk in accessing the material (the supply risk). If the supply risk is high and the material has high economic importance, then it will be considered a critical raw material for the functioning of the European economy

Key points:

Reasons why a material becomes critical:

- Deposits located in one or very few countries
- Low abundance on Earth's crust
- Problems in extraction and /or work-up
- Lack of alternatives in strategic applications
- Absent or inadequate recycling network

Why CRMs are so important?

- **Link to industry** - non-energy raw materials are linked to all industries across all supply chain stages
- **Modern technology** - technological progress and quality of life rely on access to a growing number of raw materials. For example, a smartphone might contain up to 50 different kinds of metals, all of which contribute to its small size, light weight and functionality.
- **Environment** – raw materials are closely linked to "clean" technologies. They are irreplaceable in solar panels, wind turbines, electric vehicles, and energy-efficient lighting.

Where can we find CRMs?

The EU's industry and economy are reliant on international markets to provide access to many important raw materials since they are produced and supplied by external countries. Although the domestic production of certain critical raw materials exists in the EU, notably hafnium, in most cases the EU is dependent on imports from non-EU countries.

China is the major supplier of critical raw materials, accounting for 70% of their global supply and 62% of their supply to the EU (e.g. rare earth elements, magnesium, antimony, natural graphite, etc.). Brazil (niobium), USA (beryllium and helium), Russia (palladium) and South Africa (iridium, platinum, rhodium and ruthenium) are also important producers of critical raw materials. The risks associated with the concentration of production are in many cases compounded by low substitution and low recycling rates.

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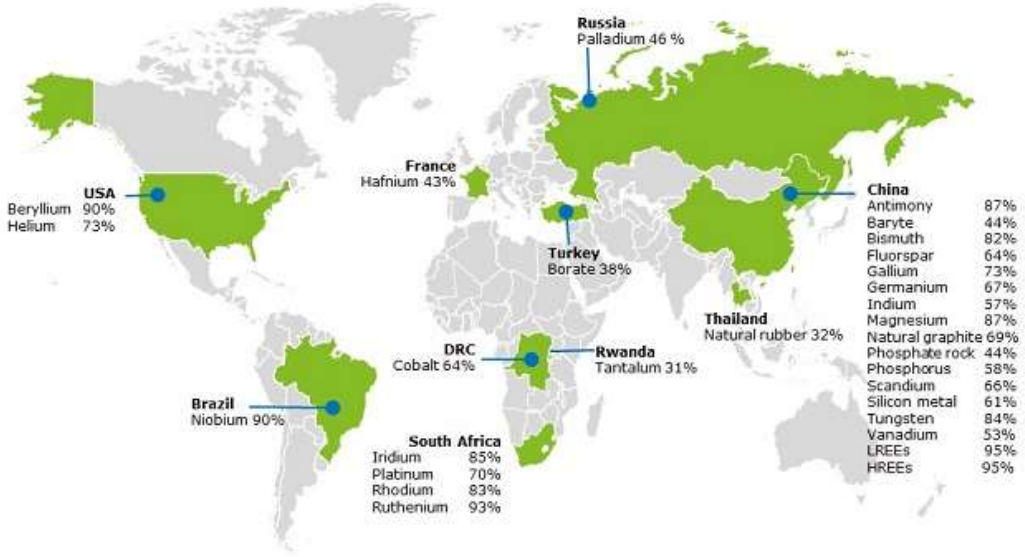
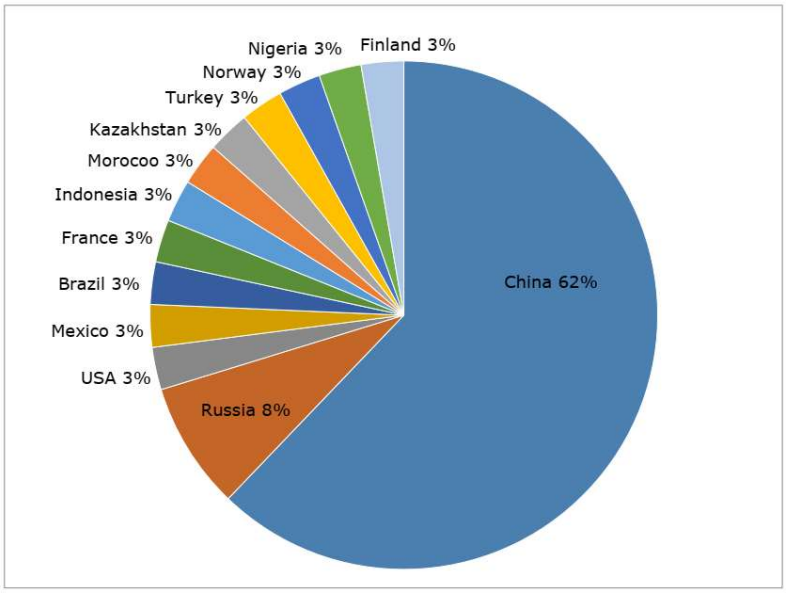
Countries accounting for largest share of global supply of CRMs



Main EU suppliers of CRMs (based on number of CRMs supplied out of 37), average from 2010-2014



***Source*: Deloitte Sustainability et al., *Study on the Review of the List of Critical Raw Materials*, cit., p. 16.**

The list of critical raw materials for the EU of 2017

In 2017, the European Commission published its revised list of Critical Raw Materials.
The new list includes 9 more new materials than the 2014 list: baryte, bismuth, hafnium, helium, natural rubber, phosphorus, scandium, tantalum, vanadium. This brings the number up to 27 raw materials which

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are now considered critical by the Commission. 3 of these are entirely new to the list: bismuth, helium, phosphorus. The other 17 critical raw materials are included in the CRM table below. For the first time, individual assessment results are available for the 3 grouped metals: HREEs (heavy rare earth elements), LREEs (light rare earth elements), and PGMs (platinum group metals).
All raw materials, even when not classed as critical, are important for the EU economy.

2017 CRMs					
Antimony	**Cobalt**	**Hafnium**	**Natural rubber**	**Silicon metal**	**HREEs***
Baryte	**Coking coal**	**Helium**	**Niobium**	**Tantalum**	**LREEs***
Beryllium	**Fluorspar**	**Indium**	**Phosphate rock**	**Tungsten**	**PGMs***
Bismuth	**Gallium**	**Magnesium**	**Phosphorus**	**Vanadium**	
Borate	**Germanium**	**Natural graphite**	**Scandium**		

*HREEs = Heavy Rare Earth Elements[1], LREEs = Light Rare Earth Elements[2], PGMs = Platinum Group Metals[3]
1 dysprosium, erbium, europium, gadolinium, holmium, lutetium, terbium, thulium, ytterbium, yttrium;
2 cerium, lanthanum, neodymium, praseodymium, samarium
3 iridium, platinum, palladium, rhodium, ruthenium

Why a list?

The CRM list, as first produced in 2010, has had as benefit to draw the attention of policymakers, stakeholders and others to the importance of certain substances to the European economy. Although this highlighting of relevance is positive, it is not worth the effort if this list is not taken into account in current policymaking and legislation. Efforts need to be made to formalize the position of CRMs in policymaking. CRMs are particularly relevant in the following policy areas: industrial development, in particular high tech industries; international trade; R&D; Environment and Health Legislation.

Learning outcomes

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

- Know the concept of CRMs and their recovery
- Know what a coordination compound is and know how to apply its properties to practical cases
- Choose a synthesis process according to the parameters
- Apply the experimental method and verify its efficiency with different metal ion solutions

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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.
S3. Ability to interpret the world and relate to others.
S4. Ability to interact in an appropriate and creative way in any situation.
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.
S3. Ability to interpret the world and relate to others.
S4. Ability to interact in an appropriate and creative way in any situation.
S5. Knowledge of vocabulary, grammar and language.
S6. Appreciation of cultural diversity.
S7. Ability to use technical language accordingly to the field of work.
Mathematical competence and competence in science, technology and engineering
S1. Ability to use constructed thinking in order to solve a problem in every situation.
S4. Readiness to address new problems from new areas.
S6. Ability to extract qualitative information from quantitative data
S8. Ability to design experimental and observational studies and analyse data resulting from them.
S9. Ability to formulate complex problems of optimisation and decision making and to interpret the solutions in the original contexts of the problems
Digital competence
S2. Basic skills in ICT
Personal, social and learning to learn competence
S1. Ability to pursue and persist in different kinds of learning.
S2. Identifying available opportunities.
S3. Ability to gain process and assimilate new knowledge, skills and qualification required for career goals.
Citizen competence

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S1. Ability to effective interaction with other people
S2. Ability to adapt to the changing situation, being flexible and work under pressure
S3. Ability to work effectively and collaborate with other team members
Entrepreneurship competence
S1. Awareness of local, national, European culture heritage and their place in the world
S2. Basic knowledge of contemporary culture
S3. Understanding of cultural diversity
Cultural awareness and expression competence
S1. Ability to turn idea into action
S2. Creativity/innovation
S3. Ability to plan and manage tasks
S4. Independence, Motivation and Determination

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 NO POVERTY, 2 ZERO HUNGER — Enable access to basic services		10 REDUCED INEQUALITIES — Equal access to global expertise
	3 GOOD HEALTH AND WELL-BEING — Safe medical devices		11 SUSTAINABLE CITIES AND COMMUNITIES — Sustainable urbanization
✓	4 QUALITY EDUCATION — Access to education		12 RESPONSIBLE CONSUMPTION AND PRODUCTION — Responsible consumption and production
	5 GENDER EQUALITY — Less hardship, more opportunities		13 CLIMATE ACTION — Strengthen resilience, reduce disaster impact

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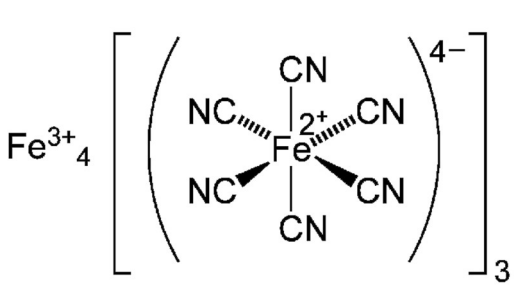
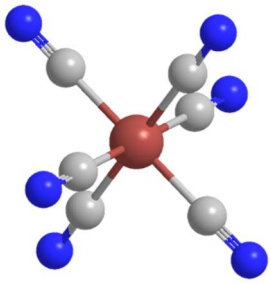
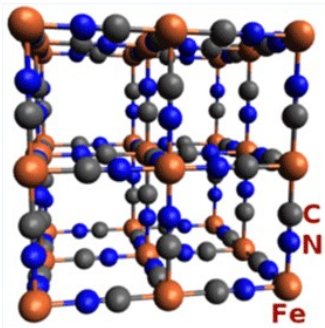
✓	6 CLEAN WATER AND SANITATION — Safe and affordable water	✓	14 LIFE BELOW WATER — Reduce marine pollution
	7 AFFORDABLE AND CLEAN ENERGY — Energy – the golden thread	✓	15 LIFE ON LAND — Sustainable use of terrestrial ecosystems
	8 DECENT WORK AND ECONOMIC GROWTH — Safety of workers and economic growth		16 PEACE, JUSTICE AND STRONG INSTITUTIONS — Promote peaceful and inclusive societies
	9 INDUSTRY, INNOVATION AND INFRASTRUCTURE — Resilient infrastructure and sustainable industrialization	✓	17 PARTNERSHIPS FOR THE GOALS — Better access to technology and innovation

Contents – Theoretical principles

The Prussian Blue (iron hexacyanoferrate: $Fe_4[Fe(CN)_6]_3$) is a metal complex.







The Prussian Blue pigment consists of iron cations, cyanide anions, and water. This complex contains Fe(II) and Fe(III).

As shown in the two upper drawings, the $Fe(CN)_6$ anion in Prussian Blue is octahedral. The bottom drawing shows its unit cell, which has a cubic lattice structure. In addition to having as many as 16

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molecules of water per formula unit, the compound usually contains inorganic impurities, which can affect its color.

The name Prussian Blue originated in the 18th century, when the compound was used to dye the uniform coats for the Prussian army. Over the years, the pigment acquired several other "blue" names, including Berlin, Parisian, and Turnbull's blue. It has been used for centuries in unusually diverse applications. Despite the presence of cyanide groups, the pigment is not toxic to humans.

Prussian blue was first synthesized about 1704 by the reaction of salts of iron in the +2 oxidation state (ferrous salts) with potassium ferrocyanide; modern commercial methods are similar:

$$4FeCl_3 \cdot 6H_2O + 3K_4[Fe(CN)_6] \cdot 3H_2O \rightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$$

Coordination compounds are molecules that pose one or multiple metal centres that are bound to ligands (atoms, ions, or molecules that donate electrons to the metal). These complexes can be neutral or charged. When the complex is charged, it is stabilized by neighbouring counter-ions. A complex ion has a metal ion at its canter with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds and, in some cases, the bonding is actually more complicated than that. The molecules or ions surrounding the central metal ion are called ligands.

In the Prussian Blue, a complex ions is Fe^{2+} and Fe^{3+} and ligands are cyanide ions CN^-.
Crystalline salts containing complex ions include potassium hexacyanoferrate(3−) (potassium ferricyanide), $K_3[Fe(CN)_6]$. The charge on the complex ion is balanced by ions of opposite charge. In the potassium ferricyanide, three positively charged potassium ions, K^+, balance the negative charge on the complex. The oxidation state of the central metal is determined from the charges on the ligands. In hexacyanoferrate (3−), all six cyanide ligands have a charge of –1; thus, the overall charge of –3 dictates that the oxidation state of Fe is +3.
When the solution containing the metal ions passes through the Prussian Blue, Fe 3+ is replaced by the metal ion, forming a more stable complex.

Lab Procedure

The laboratory activity consists of two modules: a first one which is more difficult (for students over 16 years old), and an easier second one (for all students):

1- To Synthesize Prussian Blue
2- Extraction of metal ions from water

For this activity you do not need special instruments, only some reagents. If you intend to do the second activity only, you will need to purchase some Prussian Blue.

Module 1 – Synthesis of Prussian Blue in the lab

Module 2 – Extraction of metal ions from water

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Learning Pathway

Step 1- Time & Activity: 1h: Teachers give a short introduction with a prepared PowerPoint presentation (Introduction to CRMs and theoretical principles)

Step 2 (module 1) – Time & Activity: 45 minutes: Students are divided into groups (preferably the number of students in each group should be 3-4, maximum 5). Each group completes the synthesis of Prussian Blue in order to use it in the second part.

Step 3 (module 2) – Time& Activity: 20 minutes: the teacher assigns to each group the preparation of a solution containing a metal ion with the defined concentration.

Step 4 (module 2) – Time& Activity: 30 minutes: each group prepares the equipment for filtration and tests all the solutions prepared previously, recording its observations.

Step 5 – Time& Activity: 15 minutes: discussion of the results obtained by the various groups.

Step 6 (module 1 and 2) – Time& Activity: 45 minutes: evaluation test. The time spent on the assessment test depends on the number of questions entered.

Evaluation

The suggested evaluation is valid for both modules; it will be up to the teacher to choose which questions to assign based on the modules carried out. Questions can be complemented by other assessment systems.

1. What are CRMs?
2. Why are CRMs so important?
3. Where can we find CRMs?
4. What is a coordinating bond?

   The bond that holds the atoms of the coordination compounds together is called the coordination bond. It occurs between the donor atom of the binding group and the metal atom.

   In general, the binder is a molecule or ion containing a donor atom that has one or more unshared electronic duplicates that can be used to form bonds with the central metal ion.

5. Why are the coordination compounds often colored?

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The color of many coordination compounds comes from the excitation of electrons, which make energy jumps by occupying higher energy empty orbits; this effect is induced by the radiation of the visible. The absorbed energy hν for this transition corresponds to the separation energy. The color observed is the one complementary to the λ of the absorbed light.

6. Explain the different stoichiometric ratio of the two syntheses of Prussian Blue.

   By working with twice as much ferric chloride as the other reagent, the yield of the reaction will be better.

7. Why does paper soaked in hexacyanoferrate become stained when it comes into contact with metal ion solution?

   The metal ion of the solution reacts with the potassium hexacyanoferrate by replacing the potassium with the metal ion, which provides some staining depending on the metal.

8. Why doesn't the paper change color become stained?

   Passing through Prussian Blue the colored solution containing the metal ion becomes colorless as the metal ion has been "captured" by the coordination compound.

9. Is the process more economical from the point of you of material and energy costs?

   The synthesis of Prussian blue has high yields and low costs. This method also makes it possible to remove dangerous dissolved metals from the water.

10. Does the procedure only work with metals?

    The procedure works only with metal ions because they must replace the ferric ion present in the Prussian Blue, and the complex that is formed must also be more stable.

11. What are the adverse effects on the environment?

    The effects on the environment are positive. Of course, the various substances used must not be dispersed but must be collected and disposed of properly.

If you also wish to check the prerequisites, you can introduce an exercise on stoichiometric reaction ratios (optional calculations – student's card 1):

Determine the amount of reagents required to prepare 1 kg of Prussian Blue with the reaction yield determined experimentally.

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Description of Student's Cards

This activity suggests to use the Prussian Blue, also known as iron hexacyanoferrate, to absorb CRM ions from water. This pigment can interact with metals such as Copper, Manganese and others.
Prussian Blue is one of the first synthetic pigments ever created.
Thanks to its particular structure, it can interact with CRM ions in order to capture them. Actually, it is also used in the pharmaceutical sector to soak up dangerous substances such as Cesium and Thallium in infected hosts.

It can be synthesized in a laboratory or it can be purchased, therefore the synthesis is suggested to student over 16, while for younger students we only proceed with the recovery of metals from the water.

List of Students' Cards associated to this toolkit.

Student's Card 1 – Synthesis of Prussian Blue in the lab

Student's Card 2 – Extraction of metal ions from water

Sources

- http://criticalrawmaterials.org
- https://en.wikiversity.org/wiki/Critical_materials
- http://www.iai.it/en/pubblicazioni/europes-dependence-critical-raw-materials
- Report of Legambiente on water conditions in the countries of the European Union on June 2020.

Acknowledgement

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I.S. "A. SOBRERO"