



Good Practice Report

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A lab experiment on metals separation and recovery from waste ink-jet cartridges as a non-formal appealing learning activity for students of secondary schools

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Abstract: Since 2004, the Italian Ministry of Education, University and Research (MIUR), the Conference of Science and Technology Headmasters, and Confindustria, have been promoting the National Plan for Scientific Degrees (PLS) aimed at supporting students in acquiring scientific skills better responding to contemporary society challenges and increasing vocations in basic sciences. This paper describes a successful experience of the University of Cagliari together with selected local secondary schools, in which the *hot* topic of technological waste valorization was selected to create an orientation laboratory for students towards chemistry disciplines. Specifically, students and teachers were guided into the challenging world of e-waste production and treatment through the practical activity of noble metals recovery from real waste ink-jet cartridges. A specific emphasis was placed on fundamental chemical aspects – separation and recovery of metals driven by redox processes favored by a complexing agent – as well as on the chance to play on coordination chemistry to promote a green chemistry approach. The close collaboration between school and university teachers in planning and implementing laboratory activities is the element that characterizes PLS actions and promotes the development and strengthening of relations between secondary school and university courses in science, technology, engineering, and mathematics (STEM).

Keywords: science teaching; recycling; precious metals recovery; redox reactions; electronic waste; non-formal learning

1 Introduction

Waste from electrical and electronic equipment (commonly referred to as WEEE or e-waste) encompasses a wide range of devices, including computers, refrigerators, and mobile phones at the end of their lifespan and consists of a complex blend of materials, both valued and hazardous. The volume of e-waste generated annually worldwide is rapidly increasing, making it one of the fastest-growing and most relevant waste streams. Data from the Global E-Waste Monitor show how in the five years 2014–2019 the total e-waste produced worldwide increased by 44.4–53.6 Mt and the projection for 2030 is estimated to reach 74.7 Mt (Forti et al., 2020). If improperly managed, these materials can lead to significant environmental and health issues (Purchase et al., 2020). To address the growing volume of e-waste, new regulations have been established in the last 20 years worldwide (Shittu et al., 2021). A relevant role is played by the WEEE and the RoHS Directive established by the

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EU (Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE), 2012; *RoHS Directive*, 2022). These regulations aim to contribute to the sustainable production and management of electrical and electronic equipment by addressing environmental and other concerns arising from the escalating number of discarded electronics, by enhancing the collection, treatment, and recycling of e-waste. Furthermore, modern electronics contain valuable and rare resources that can be recycled and reused by appropriate waste management. To achieve these goals, the awareness, information, and education of civil society in recognizing the dangers of an irresponsible disposal of these wastes, as well as the wealth of resources they contain, represent a key factor in addressing the current issues and in turning these wastes to *urban mines* for next generations (Zuo et al., 2019). A relevant role is played by young people's education, whose awareness can stimulate a respectful approach to the environment and good practices in the consumption and management of valued resources. In this framework, here we report a pioneering and noteworthy case study of non-formal learning on this topic conducted by the University of Cagliari in collaboration with a selection of Sardinian secondary schools in the framework of the PLS (National Plan for Scientific Literacy). PLS was established in 2004 and funded by the Italian Ministry of Education (Anzellotti et al., 2014). It is playing a significant role in reshaping the perception and challenging stereotypes related to scientific disciplines. Furthermore, through an experiential approach, it is helping secondary school students make more informed educational choices, fostering professional growth among teachers, and facilitating access to university courses in the scientific field. The specific activity described here aimed to provide upper secondary school students (16–18 years old) with an engaging laboratory experience focused on the fascinating field of technological waste valorization, ultimately fostering their interest in chemistry-related subjects. The project involved students participating in hands-on activities centered around the production and treatment of electronic waste, with a specific focus on the recovery of precious metals from authentic waste inkjet printer cartridges. The increasing interest in noble metals (NMs) arises from their utilization in various cutting-edge technologies such as electronics, automotive, aerospace, and more. Among them, copper and gold are largely used in ink cartridges connections (Deplano et al., 2008; Serpe et al., 2008). An extensive exploitation of limited natural resources, strong economic and political dependence on producing countries (South Africa, Russia, and South America) and an accumulation of waste rich in NM having high economic value and potential toxicity, has been observed in the last decades. Both students and teachers were fully immersed in the intricate realm of e-waste through guided self-assessment exercises for students and training sessions for teachers. It is worthy to note that this activity was proposed and carried out in early 2000s when the awareness of e-waste accumulation and on the critical raw materials shortage was still very low. This immersive experience allowed them to delve into practical applications and techniques related to e-waste, increasing their awareness and sensitivity on this emerging, increasingly critical concern. On the other side, this appealing topic was exploited to recall and reinforce some basic concepts of chemistry, an integral part of the secondary school education syllabus.

2 Methods

The proposed activity involved chemistry teachers and their students, typically enrolled in the last three years of secondary school, wide-spreading among technical institutes and classical and scientific lyceums.

Beforehand, teachers were trained in a 2-h lecture by a colleague accomplished in the field from the University of Cagliari who introduced them to the topic of noble metals recovery from secondary sources, highlighting connections between the specific application and base chemistry concepts behind hydrometallurgical metal recovery processes. The experiment designed for the students was, then, presented to the teachers as a case study of the general topic, to provide insights for introducing the students to the subject and the practical activity.

Later, students, already introduced to the topic by the teachers at school, were hosted in the labs of the University of Cagliari for the practical activity, assisted by expert tutors, and even supported by a poster description (Supplementary Material).

The last part of the traineeship consisted of a guided self-assessment and the production of a group presentation addressed to elaborate concepts and information related to the experience.

3 Implementation

Printer cartridges are a widespread heavily polluting category of e-waste. The global market for ink cartridges was valued at approximately US\$18 billion in 2022 and is expected to increase to around US\$ 34 billion by 2032 (anticipated growth rate of 6.7 %) (Ink-Cartridge Market, s.d.). With around 370 million units sold each year, Europe holds approximately 20.7 % of the global market share. It has been estimated that, on average, nearly every individual residing in the EU purchases, utilizes, and discards one cartridge annually (Ding et al., 2020; LIFE NEW4CARTRIDGES, s.d.). The disposal of printer cartridges falls under the regulations of the EU WEEE Directive (2012/19/EU), which establishes collection schemes allowing consumers to return their WEEE at no cost. However, the rate of cartridge reuse is relatively low, accounting for only around 20 % of the cartridges in circulation. Most of these items are still incinerated or sent to landfills, resulting in significant environmental issues. On the other hand, traditional regeneration processes involve a cleaning phase that consumes substantial amounts of water and chemical solvents.

In the present experience, ink-jet printer cartridges were proposed as potential secondary sources rich in gold and copper.

As an example, in the typology of ink cartridges reported in Figure 1, the metal fraction represents around 0.2 wt%, mainly located inside the resinous strip containing the electrical pads and pathways.

Figure 2 shows the multi-metal layer system that characterizes electrical connections in these devices.

The resinous strip can be easily removed by hand from the cartridge case and represents the richest part of the device in terms of precious metal content. In there, Cu and Au represent about 40 wt% (Serpe et al., 2008). Ink cartridges are worthy to be considered “urban mines”. Indeed, they may contain up to 100 g Au/ton and 2 kg Cu/ton of cartridges (Au 14 kg/ton; Cu 360 kg/ton of strips), comparable to or even higher than the primary sources of these metals [Au mine grades: spanning from 0.5 to 40 g/t, with >1.5 g/t and >8 g/t considered *High Grade* for open pit and underground gold mines, respectively (*How Is Gold Graded In Mining?* | *BullionByPost*, 2023); Cu mine grades: spanning from 4 to 80 kg/t, with a global average grade of 6 kg/t («The Ten Highest-Grade Copper Mines in the World -», 2019)].

The well-known methods applied for noble metal recovery from ores, currently implemented by secondary sources’ treatments, typically involve energy-intensive thermal treatments (pyrometallurgy) and traditional chemical methods (hydrometallurgy) (Cui & Zhang, 2008; Serpe, 2018). Conventional hydrometallurgical processes for noble metals recovery exploit the leaching action of strong and oxidizing acids (i.e. boiling aqua regia) for Au, Pd, Pt; cyanides in alkaline media typically used for Au-mine extraction processes and recovering plants (Tasker et al., 2004). Furthermore, thiosulfate and thiourea in the oxidizing environment have been proposed for Au-mine extraction processes.

These methods exploit the presence of a complexing agent (Cl^- , CN^- or S-donor), which lowers noble metals’ highly positive reduction potential and makes them easier to oxidize.

Based on this consideration, the properties of metals related to their position in the periodic table of elements, some basic principles of coordination chemistry, and the effect of metal complexation in lowering the reduction

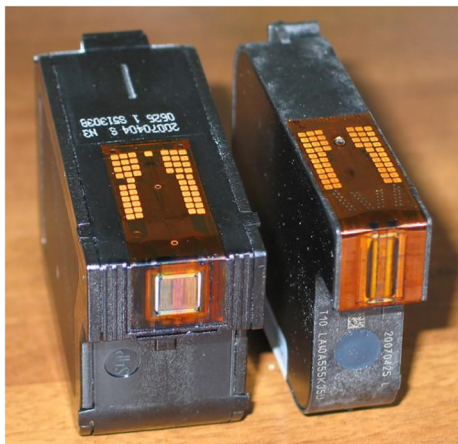


Figure 1: Typology of ink-jet cartridges used for the experiments.

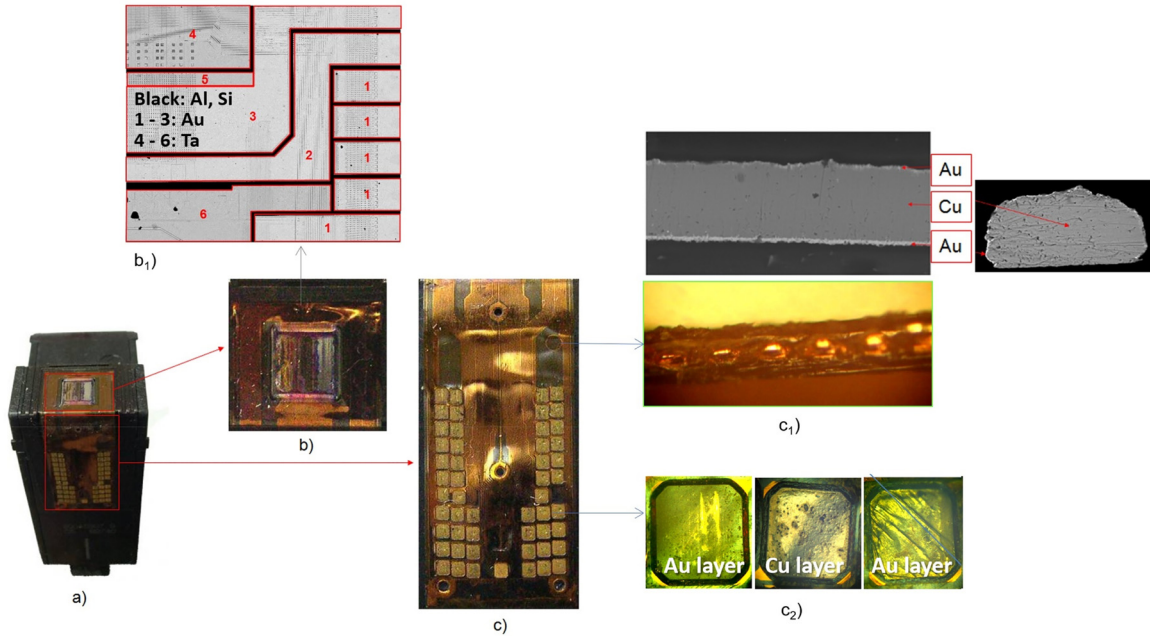


Figure 2: Pictures of (a) the printer cartridge; (b) the chip area; (c) the contacts area. (b₁) Chip back-face composition. (c₁) Optical (below) and scanning electron microscopy combined with energy dispersive spectroscopy (SEM/EDS) (above) characterization of a section of the strip containing Cu-based metal pathways. (c₂) SEM micrographs (and EDS elemental maps) of the layered structure of square contacts.

potential of the species (through the appropriate application of the Nernst Equation) were revisited and reinforced to both teachers and, by them, to students. A summary of the fundamentals of the calculation of the *Normal* (also called *Apparent*) reduction potential, a key parameter in metal leaching, is reported in Box 1. Based on this, it is shown in Table 1 how the complexation with cyanides and chlorides makes gold easily oxidizable by oxygen and nitric acid, respectively.

Box 1. *Effect of the complexation on the metal standard reduction potential.*

The Nernst equation relates the cell potential to the standard potential and the activities (approximated by concentration for diluted solutions) of the electroactive species.

For the general semi-reaction of reduction: $M^{n+} + ne^- \rightleftharpoons M$

the Nernst equation is:

$$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{0.0592}{n} \log \frac{1}{[M^{n+}]}$$

where:

F = Faraday constant (96,485.3 C/mol or sA/mol); E = cell reduction potential (E° , at standard conditions); R = gas constant (8.3145 J/kmol at $T = 298$ K); n = number of electrons transferred in the reaction.

In the presence of competitive equilibria which involve M^{n+} , e.g. complex formation (L = ligand):

$$M^{n+} + xL^{m-} \rightleftharpoons [ML_x]^{n-mx}$$

$$K_{\text{form}}^* = \frac{[ML_x]^{n-mx}}{[M^{n+}][L^{m-}]^x} \rightarrow [M^{n+}] = \frac{[ML_x]^{n-mx}}{K_{\text{form}}^* [L^{m-}]^x}$$

Nernst equation can be written as:

$$E = \frac{E^\circ - \frac{0.0592}{n} \log K_{\text{form}}^*}{E^{\circ'}} - \frac{0.0592}{n} \log \frac{[L^{m-}]^x}{[ML_x]^{n-mx}}$$

$E^{\circ'}$ = apparent standard potential (or normal potential) related to the formation of the complex.

* K_{form}^* is the overall formation constant for the complex.

Table 1: Apparent reduction potentials of Au^{n+}/Au in the presence of cyanide and chloride as complexing agents [references].

Reduction process	E° (V)	$E^{\circ'}$ (V)	Log K_{form}
$\text{Au}^+ + 1e^- \rightarrow \text{Au}$	+1.68	-	-
$[\text{Au}(\text{CN})_2]^- + 1e^- \rightarrow \text{Au} + 2\text{CN}^-$		-0.60	38.3
$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$	+0.40	-	-
$\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$	+1.50	-	-
$[\text{AuCl}_4]^- + 3e^- \rightarrow \text{Au} + 4\text{Cl}^-$		+0.95	28
$\text{NO}_3^- + 4\text{H}^+ + 3e^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	+0.96	-	-

The scheme of the experiment was, then, described to the teachers and explained by the students before approaching the practical lab experience at the University of Cagliari. The scheme of the laboratory experience titled “*Metal Separation and Recovery from Printer Cartridges*”, is reported in Supplementary Material and details procedure description, data analysis and self-assessment questions, as well as needed material and safety information.

With specific reference to the experimental procedure, the experiment was carried out by groups of 5–6 students, and consisted of the following phases:

- Manual detachment of the strip containing the contacts from the ink container of the cartridge;
- Soaking the strip in acetone to clean it of ink residue and dry by air;
- Cutting the strip into small pieces (about 2×2 mm) with scissors and putting them into a 50 cm^3 beaker together with a magnetic bar;
- Adding about 20 cm^3 of NH_3 conc. to the pieces (under fume-hood), then carefully add, under stirring, $1\text{--}2 \text{ cm}^3$ of H_2O_2 (30 wt%) allowing the system to react: the solution turns an intense blue color when the copper leaching goes off;
- Transferring the solution to a 50 cm^3 beaker and adding a Zn chip;
- Adding drop by drop a diluted (approximately 0.5 M) HCl solution until the solution becomes colorless and the precipitation of metallic copper occurs;

At the end of this first leaching step carried out hands-on by students themselves, the tutor made them observe in a participative way how the dissolution of gold can occur using an oxidizing acid such as concentrated (>65 wt%) HNO_3 but only in the presence of an excess of a complexing agent such as Cl^- (from concentrated, 37 %, HCl).

A further discussion at school with classmates and teachers on the outcomes of the whole experience, also exploiting the comprehension questions suggested inside the scheme of the lab experiment, helped to deepen understanding of the subject and supported the writing of a final report by the different working groups.

4 Results and discussion

The described activity was carried out in 2005–2007 by involving 9 secondary schools in the Sardinia region (Italy) as shown in the map of Figure 3.

Figure 4 provides the overview of the 222 students’ distribution among technical institutes and classical and scientific lyceums and gender (male, female). 18 teachers from the different schools actively participated in the project. The schools are located at various distances from the University of Cagliari where the PLS – Chemistry activities were performed. Cagliari is the capital city of the island. The decision to carry out the experiments in Cagliari was taken together with the teachers of the schools aiming to introduce them and their students to the University of Cagliari facilities and exploiting the didactical laboratories that are well equipped for receiving up to 120 students at once. Last but not least taking the opportunity of having young undergraduates as instructors was considered a captivating plus.

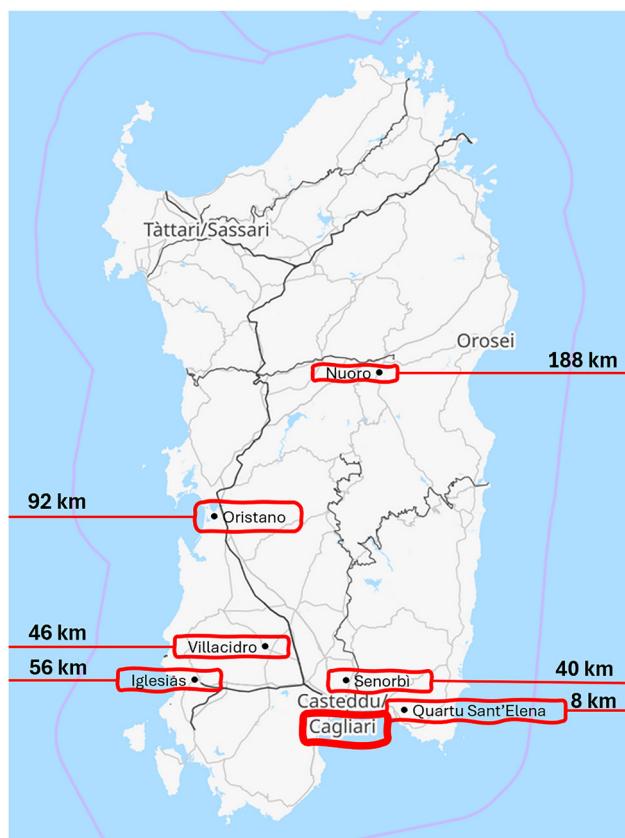


Figure 3: Map of Sardinia that shows the provenience of the schools involved in the PLS – chemistry, and section distance of the schools from the University campus. Adapted by © OpenStreetMap.

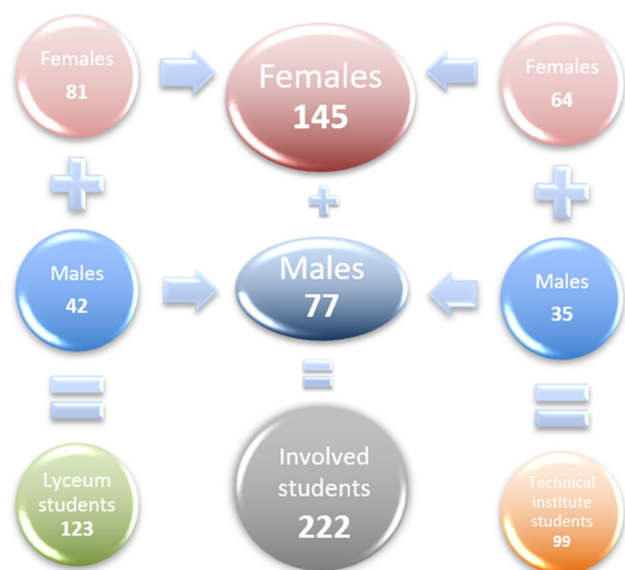


Figure 4: Distribution of students among lyceums and technical institutes and the number of males and females who participated in the project.

By exploiting the challenging case of precious metals recovery from e-waste, and besides the goal to stimulate their awareness and sensitivity towards e-waste concept and value for future generations as secondary sources of critical materials, this activity was performed:

- for training the student in keen observation, reasoning in executing the experiments, and critical thinking on the results, for providing the scientific attitude of mind;
- for encouraging the placement of chemistry in the fifth year of high school;

- to encourage students to keep notebooks, which shall be an accurate record of laboratory experience expressed in concise, clear Italian;
- to encourage students to use reference books in addition to their textbook;
- to help pupils to discover whether they have an aptitude for further study in chemistry;
- to encourage such students to continue their study of science at university.

The teacher was asked throughout the course to stress the general principles involved in the specific activity on the recovery of precious metals from ink-jet printer cartridges studied.

Teachers and students were individually interviewed about their experiences by answering a specific questionnaire at the end of the laboratory activity. Figures 5 and 6 summarize the teachers' and students' feedback. Students' and teachers' questionnaires are provided in the supplementary materials.

Specifically, for teachers:

- their participation in planning activities;
- the involvement and collaboration among the teachers;
- their satisfaction with the location (adequacy of the premises and labs) and the educational material;
- the importance of the contributions of the school teachers in the implementation of the plan;

were investigated and their feedback is summarized in Figure 5a.

Despite the importance attributed by teachers to their involvement in the project, just less than 50 % of them declared to have taken part in the planning activity. This lack of participation was attributed to the non-chemistry

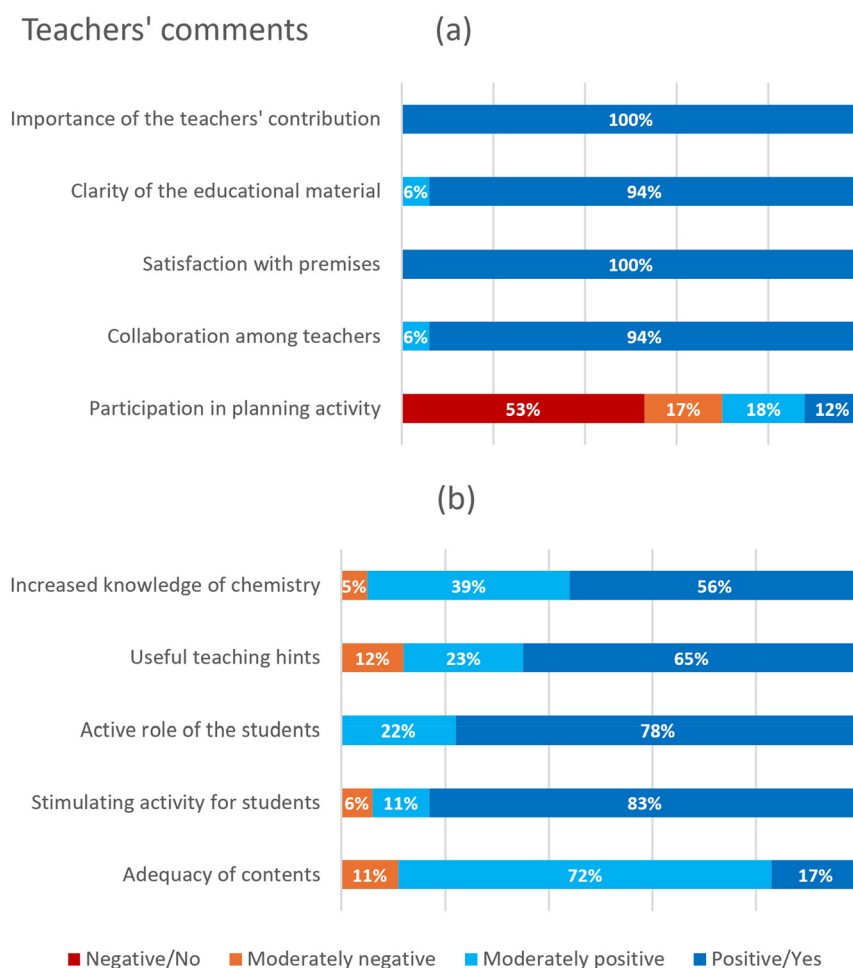


Figure 5: Teachers' final feedback after overall activity. (a) General satisfaction; (b) impact on students' education. Graphs are based on a pool of 18 teachers.

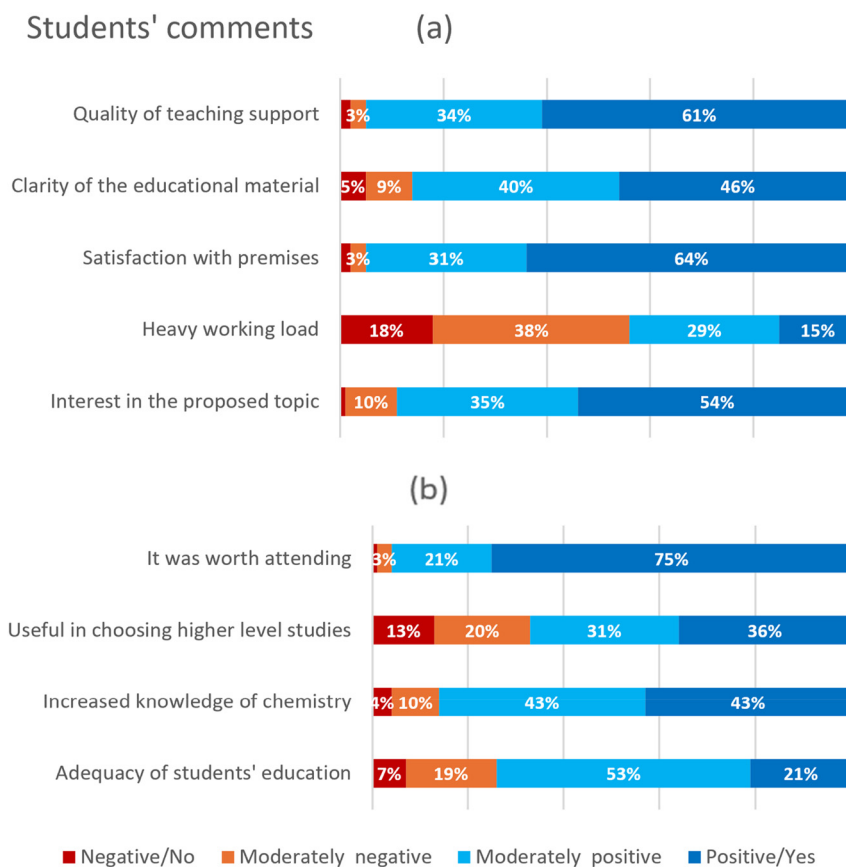


Figure 6: Students' final feedback after the overall activity. (a) General satisfaction; (b) impact on students' chemistry knowledge. Graphs are based on a pool of 222 students.

background of most of them. While, they expressed high satisfaction with the training they received during PLS on this topic, recognized by their institutions as a training and professional development path for teachers. Furthermore, this activity was considered a suitable approach to support developing the critical thinking of their students about green chemistry and circular economy.

On the other hand, teachers were also asked to express their assessment of the proposed activities on the educational impact, which has been here summarized in Figure 5b.

In the following, the opinion of the students about the proposed experimental activities is presented.

Specifically, for students:

- the interest in the proposed topics;
- the working load required for running the experiments and data elaboration;
- the satisfaction with the location (adequacy of the premises and labs) and the educational material;
- the quality of the teaching support provided by young university tutors;

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Among the other comments, it is worth noting that students found the activity very interesting but demanding at the same time. This can be ascribed to the fact that unfortunately secondary school students are often not trained to take part in laboratory activities.

Students were also asked to assess the adequacy of their background to face the proposed challenges, the impact of this experience on their understanding of chemistry concepts as well as on their future educational choices. Finally, they were asked to assess their global satisfaction with the project, as shown in Figure 6b.

Based on the teachers' and students' answers, Table 2 groups the positive feedback on the main specific investigated points.

Table 2: Grouping of teachers' (T) and students' (S) feedback on key points.

Key point	Participant	Question	Feedback rate (%)	
			Moderately positive	Positive/yes
Educational activity towards students	T	– <i>Stimulating activity for the students</i>	11	83
		– <i>Active role of the students</i>	22	78
	S	– <i>Interest in the proposed topic</i>	35	54
		– <i>It was worth attending</i>	21	75
Adequacy of students' background and impact of the activities on students' chemistry knowledge	T	– <i>Adequacy of contents</i>	72	17
		– <i>Increased knowledge of chemistry</i>	39	56
	S	– <i>Adequacy of students' education</i>	53	21
		– <i>Increased knowledge of chemistry</i>	43	43
Rooms, laboratories, and teaching materials	T	– <i>Clarity of the educational material</i>	6	94
		– <i>Satisfaction with premises</i>	–	100
	S	– <i>Clarity of the educational material</i>	40	46
		– <i>Satisfaction with premises</i>	31	64
Teachers involvement	T	– <i>Importance of the teachers' contribution</i>	–	100
		– <i>Collaboration among teachers</i>	6	94

Summarizing, based on the average value of the combination of two feedback categories, “moderately positive” and “positive”, for a specific key point (see Table 2, Figures 5 and 6):

- The educational activity toward students was appreciated 97 % by teachers and 92 % by students
- Both teachers and students pointed out a little concern about students' background (only 17 and 21 % fully positive feedback, respectively) and the impact of the activities on students' chemistry knowledge (relatively low 56 and 43 % fully positive feedback, respectively)
- Rooms, laboratories, and teaching materials were considered suitable by 100 % of teachers and 90 % of students
- Teachers found their involvement satisfactory (100 % appreciation) despite the poor participation in planning activity, and reported receiving useful hints for their teaching activity (88 % appreciation under *Useful teaching hints*).
- Despite the interest in the activity, only 67 % of students considered the overall activity useful in addressing their choice towards scientific higher level studies.

Furthermore, both teachers and students gave particular praise to the young tutors – for their patience, enthusiasm, and preparation.

It is worth noting that the response of the students to the proposed experiment was different depending on their educational background. By appraising students' answers to proposed open questions, it is notable to emphasize that the experiments were considered unsuitable for students with a lack of a sound background in chemistry. More specifically, unexpectedly, students from science-oriented secondary schools expressed more concerns about the chemical knowledge requisites for fully understanding the reactions involved in the recovery of precious metals processes. On the contrary less skilled students coming from human science-oriented high

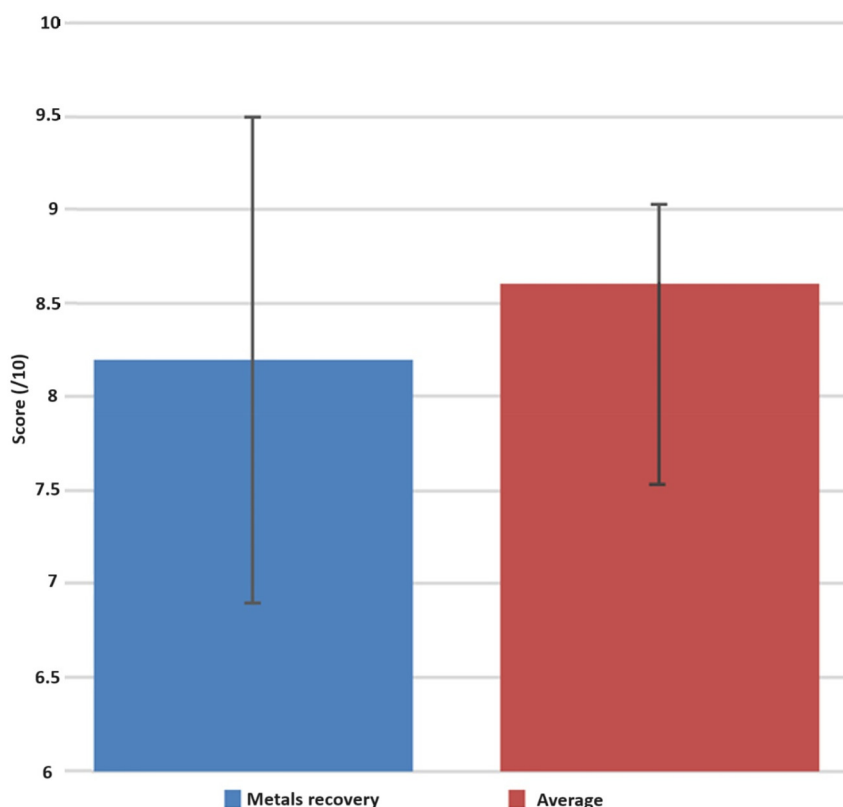


Figure 7: Students' final score (over 10) specifically expressed for the metals recovery experiment (left column) compared with the average score expressed for the set of different experiments carried out (right column). A vertical bar showing the range of students' satisfaction is also reported.

schools were more enthusiastic because they emphasized the relevance of the social and economic perspectives of the metal recovery application. Furthermore, students attending technical high schools were more prone to appreciate the practical activity while lyceum students were more intrigued by the discovery related to the scientific aspects. In any case, the experiments were evaluated as interesting when the students could deepen their understanding of the topic during the course at school. It is also worth noting that the reported assessment is related to the whole project which involved a variety (i.e. 9) of experiments covering different topics. A specific assessment of the metals' recovery experience on a school base, suggests an improvement in the student background preparation would allow a better understanding of the fundamentals behind the experiment. Indeed, as shown in Figure 7, the global satisfaction range towards the experiment is very wide.

5 Conclusions

This paper describes a good practice developed in the context of the Italian PLS – Chemistry at the University of Cagliari and addressed the stimulating topic of precious metals recovery from waste ink cartridges to increase the interest and awareness of secondary school students towards scientific disciplines. It was designed by a synergistic teaching action, involving a specific training for secondary school teachers and their direct involvement in the project activities, as well as lab experiences for students supported by tutoring and educational material appropriately shaped for them. The feedback collected at the end of the project activities highlighted, on one side, the interest and enthusiasm of the pupils and, on the other side, the importance of the tutoring activity, by secondary school teachers as well as by young tutors during the practical activity, in reinforcing and supporting their scientific background to make the most of the carried-out experience. The specific topic, proposed at a time when it was an absolute novelty, garnered attention and appreciation from both teachers and students. Today, it fits perfectly into the topics of interest of the ONU 2030 agenda as well as in the EU and worldwide policies addressing sustainable waste management and a more respectful use of natural resources. In this framework, it

represents a suitable approach to captivate students into the world of circular economy in Hi-Tech manufacturing and to introduce them to the importance of a strong scientific background to face the challenges that will arise from now on in this “hot” field.

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Competing interests: The authors state no conflict of interest.

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Data availability: The raw data can be obtained on request from the corresponding author.

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