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PRECIOUS METALS REFINING

Aurum. The Arezzo Seminar on Precious Metals

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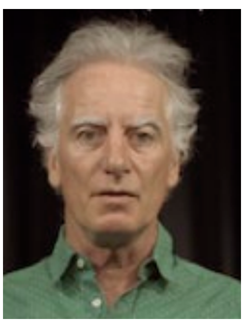

Study Seminar

Precious Metals in the History of Science and Technology

May 7th 2018
Centro Affari e Convegni
via L. Spallanzani 23, Arezzo

9,30 - 10,15 Registration
10,15 - 10,30 Opening session

Goldsmith's art

Chairs: *Carla Martini* and *Marco Fontani*

10,30 - 11,00 **Apprentices and masters – the transmission of ancient goldsmith techniques**
Alessandro Pacini

11,00 - 11,30 **The authenticity of the false**
Daniela Ferro

11,30 - 12,00 **Electrodeposition and innovative characterization of precious metal alloys for the Galvanic and Jewel industry**
Massimo Innocenti

12,00 - 12,40 **Gold and silver: perfection of metals in medieval and early modern alchemy**
Ferdinando Abbri

12,40 - 13,00 **"Antichi Strumenti Orafi" of the Garuti Collection – The Virtual Exhibition**
Francesca Frasca, Isabella Baldini, Adelmo Garuti, Gianlorenzo Calzoni

13,00 - 14,30 Lunch break

14,30 - 15,00 **Do monetary systems rediscover precious metals in the era of 'bitcoins'?**
Roberto Santi

Recovery of precious metals

Chairs: *Marco Panarese* and *Valerio Zanotti*

15,00 - 15,30 **The primary goldfields and their meaning within circular economy**
Paolo Garofalo

15,30 - 16,00 **Gold parting with nitric acid in gold-silver alloys**
Iacopo Ciabatti

16,00 - 16,30 **Hi-Tech waste as "Urban Mines" of precious metals: new sustainable recovery methods**
Angela Serpe

16,30 - 17,00 Closing session

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Carla Martini
University of Bologna

Marco Fontani
University of Florence

Marco Panarese
Project Manager, TCA

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The Arezzo seminar on precious metals

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A GOLDEN STORY

Gold is a valuable bright yellow metal with a resplendent lustre and high density (more than 19 times the weight of an equal volume of water). Due to its inalterability, brilliant appearance and occurrence in the native condition, or elementary state, gold was certainly one of the first metals to attract the attention of men.

It was known, highly valued and widely employed by earliest civilization. In our Peninsula, Etruscan made gold ornaments with great variety of workmanship. Some of them survived over the centuries and appear today as perfect as they were over two thousand years ago.

Under a certain point of view, gold has to be considered the driving force that led to modern chemistry. In fact, the making of gold from other metals, by means of the philosopher's stone, and the discovery of the elixir of eternal life were the chief aims of the alchemists in the Middle Ages. It is reasonably correct to say that advances in early chemistry were a direct outcome of such experiments.

Gold, whose symbol is Au (from Latin, Aurum) has atomic number 79 and atomic weight 196,9665 g/mol. Physically, gold is of chief interest for its remarkable ductility, malleability and resistance to chemicals. Gold can be drawn into extremely fine wire or beaten into the filmiest gold-leaf. With exception of boiling aqua regia, alkali cyanides or free chlorine, gold will not readily combine with other chemicals (neither compounds nor elements).

In every culture, gold was taken as model of wealth. Throughout history, human beings have fought and toiled for this precious and durable metal.

It is estimated that the greater amount of all gold mined from the earth in the last ten millennia could still be accounted for in the bank and government vaults, and in the widely distributed wealth of ornaments, jewellery, technological or clinical artefacts through the world.

No other possession in all time has been so zealously and effectively protected. Silver, gold and their alloy (or artificial mixture) called *electrum* were used for manufacturing ornaments, vessels, weapons, minted for coinage, as well as for inlaying and plating baser transition metals.

The occurrence of gold in nature is quite particular among the other elements. Being thermodynamically stable at ambient conditions and the least chemical active of all metals, gold is generally found in the native or uncombined state. Gold has not only attracted the interest of alchemists: in recent time also, physicists and industrial chemists looked with interest at this peculiar element. Many articles have been written about the presence of gold in sea water. In the last century more than 50 patens have been issued on processes for recovery of gold from sea.

We may mention only two of the most significative episodes: the first one occurred at the turn of the XIX century, when analysts and chemists realised that seawater was filled with gold. Element 79 was just floating out there for being taken. "The trouble was figuring out how to extract this precious metal. For over a century, dreamers, artists, lunatics and well-intentioned inventors have been trying to find a way to pull the trigger on an oceanic gold rush. So far, the search for all those riches proved fruitless. In the early 1920s, the German Nobel Prize winner and sadly renowned chemical-weapons developer, Fritz Haber (1868-1934) sought to refill Germany's post-World War I coffers by developing a process to extract gold from the sea. Haber and his colleagues spent years trying to perfect a profitable extraction method, involving centrifugal force and electrochemical laws, before realizing they had overestimated the total amount of gold in seawater already in their initial calculations. The project was consequently abandoned.

Gold was around us but Haber discovered its major flaw: it costs more to extract it rather than to take it already minted" [1]. According to the sentence "if you cannot beat them, then join them", chemists resorted to their skills: create gold! Or in better words, they tried to synthesise it artificially.

In the second case, as early as 1922, a wealthy man asked Georges Urbain (1872-1938), member of the French Academy of Science, a feasibility study before launching the enterprise to synthesise gold via radioactive transmutation. Only in recent years – *i.e.* in the atomic age – the transmutation of bare metals into isotopes of gold was made possible. Even though these experiments were experimentally accurate, they also proved that great improvements are still needed to make this "synthesis" economically viable [2].

Presently, gold covers a wide range of applications, some of which are related to cutting-edge innovation in science and technology. A few examples: it is well known that gold wires are the backbone of computers. Gold coatings protect astronauts as well as aerospace equipment from radiation and heat, thanks to gold reflective properties. Gold is a proven material for catalytic converters, but it also plays a key role in innovative tools for medical diagnostics (from well-established Rapid Diagnostic Tests to improved HIV/AIDS diagnosis technologies, based on the use of gold nanoparticles for sensing the presence of a target molecule at ultra-low concentration). Gold-based drugs have been developed and used to treat rheumatoid arthritis and research into the role of gold in cancer treatment is in progress. Gold is also involved in the development of implantable electronics, allowing monitoring of patients' vital signs and warning of potential health problem.

From an environmental point of view, gold nanoparticles are involved in the development of more effective solar cells (including stretchable solar panels that can be integrated into our clothing) and fuel cell catalysts, as well as in solving problems related to groundwater contamination, since gold helps break down contaminants. In broader terms, gold will play an increasingly important role in technologies for the transition to a low carbon and a more sustainable economy, as well in protecting our health and well-being [3].

HISTORY OF THE GOLD-AND-SILVERSMITH DISTRICT IN AREZZO

The Tuscan gold industrial district is located almost exclusively in the province of Arezzo. As it has been well documented by Luciana Lazzeretti [4]. Arezzo, along with Vicenza and Valenza Po, represents one of the highly specialized centres of the Italian goldsmith sector.

The local gold smithery developed between the fourteenth and fifteenth centuries thanks to the growth of power of the rich bourgeoisie and of the confraternities. Initially it was barely able to satisfy the inner market. During the following centuries, the history of gold smithery is closely linked to the development of religious art.

By convention it is established that modern goldsmith industry was born soon after 1900. The province of Arezzo experienced, after World War II, a first significant process of industrialization. It was transformed from a purely agricultural economy to an industrial structure. These changes were facilitated by some exogenous factors that modified the productive network of this territory: in particular the crisis of sharecropping and the birth of numerous small and medium industries.

Citing the study of Luciana Lazzeretti,

… the development of small industry led Arezzo towards

its great economic and social transformation. The city became, in the late sixties, one of the most advanced poles of economic development, not only in Tuscany but also in wider area: Central Italy.
The Arezzo economy grew in size and turnover. It experienced a dizzying growth and a continuous increase in production, which was oriented not only to the local market, but also to foreign markets.
This was made possible by the continuous progress of technology. The development of the goldsmith sector proceeded at a very intense pace in the decade 1961-1971, also favored by the Italian economic boom.

The industrial development suffered a sudden setback in the late seventies, when the price of gold and silver surged, due to problems of a monetary nature, international conjunctures combined with the fierce competitiveness of the other Italian goldsmiths. In the 1980s, the Arezzo industrial economic system lost its initial connotations, i.e. of being an economic center-based on a core of great industries (*e.g.* Lebole, UnoAErre) to attain the characteristics of local system of small and medium firms.

In the 1990s, the use of a new technology, *i.e.* electroforming, took place: it was thus possible to create products with higher added value. Jewels of great value, incredible lightness and difficult shapes were created. With the development of this and other new technologies, the local Arezzo system was able to broaden its products range. It has been able to focus on new markets and satisfy an increasing number of customers.

HISTORY OF TCA

TCA SpA was born in Tuscany, in the pulsating heart of the Italian gold-and-silversmith district [5]. Founded in 1977 in Arezzo, where the headquarters are located, the TCA has two other offices in Vicenza and Valenza Po, for a total of over 100 employees and three industrial installations.

The TCA has a consolidated experience and a deep knowledge of the gold industry. This Tuscan company must be considered a leading company in the global jewellery world.

From the initial specialization in the treatment of ashes containing gold and silver, TCA grows up to expand its skills to the recovery of platinum, palladium and rhodium. With the motto – "*The resources are not infinite, recovering them and recycling them makes them endless*" – TCA has entered the world of modern jewellery.

Increasing the recovery percentage of precious metals means reducing extraction costs and environmental impact: the recovery of metal costs less than its extraction, both in economic terms and in terms of CO_2 emissions. Precious metals are present in many sectors of industry and consequently in many waste materials.

Europe produces 8.7 million tons of electronic waste per year and recycles just over 2 million; in the United States less than 20 percent of electronic waste and only 10 percent of personal computers are recovered. If we consider that a ton of hardware waste contains about 16 grams of precious metals, it is clear that the percentages of recovery of gold and silver could be much higher than the current ones.

Even the quantity of palladium could be increased up to 90 percent, while today only 5-10 percent is recycled. Low recovery rate is also found in jewellery, medical and chemical sectors. Every day TCA faces its own challenge to increase its skills and put them at the service of the environment and the Arezzo area.

AIM OF THE PRESENT SEMINAR

The organization of the Seminary "Precious Metals in the History of Science and Technology" in Arezzo [6] (in May 2018, within the program of events associated with the Gold Fair) belongs to the history of the economic network of this city and its province.

The TCA's sponsorship is a welcome gift to citizens of Arezzo. It is at the same time a message to the public of how dynamic and sensitive the present industry is towards its territory.

The continuous technological progress and the continuous challenges of the variable financial markets, as well as everything that revolves around this world - which we could call "golden world", is of interest not only for insiders (industrialists and technicians of high specialization), but also for economists, historians, chemists, philosophers, physicists and last but not least, for customers, who will certainly be the first to appreciate the history of what they are going to buy, to either to adorn their homes or their bodies.

This transition metal, symbol of both sun and life, has no equal among all the elements of the Mendeleev periodic table. For it wars have been fought, prophecies have been launched and countless theories have been debated. Gold is certainly the most symbiotic element with man and his inclinations (artistic, technical, speculative or scientific).

This Seminar aims to bridge the gap between Academy and Industry; a bridge that connects two opposite banks, the study and the practice of a single river called "knowledge". And for this we hope that this event may be the first of a series of many other meetings between industrial and academic society.

The readers of this volume will meet with technical terms as well as with erudite historical and philosophical terms. In fact, the peculiar aim of this publication is to unite different aspects of current, recent or ancient knowledge around this noble element. The past, the present and even the near future are addressed, particularly in the paper where the use and intrinsic value of gold in the monetary and economic field are discussed. In the paper dedicated to the role and the evolution of gold in alchemy, terms such as *chymistry*, chemistry, alchemy, *chemeia*, and *al-kīmyā* merge, from the dawn of time, into a "crucible" of words embracing either the philosophical aspect (linked to the mutability of matter) or the physical experience of the manipulator, or protoscientist. In other, more strictly technical papers we can observe how man loses his centrality in chemistry to the advantage of the objectivity of the experiment. And perhaps, in recent times, we can observe how gold, once again, changes over time acquiring a haphazard halo of mysticism. We are no more talking about alchemy, proto-chemistry or chemistry, but we can take a glance at macroeconomics and most recent monetary theories.

As a final remark, we would like to thank for their cooperation all the Authors of the papers presented at this seminar. We gratefully acknowledge also the valuable contributions of Prof. Cristina Femoni, Stefano Zacchini and Valerio Zanotti, Department of Industrial Chemistry "Toso Montanari" (University of Bologna) in reviewing some of the manuscripts before publication.

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Apprentices and masters - the transmission of ancient goldsmith techniques

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Abstract. A historical overview from Sumerians to the present day on the goldsmith's craft following two lines: the apprenticeship in the guilds and the ethical and religious value of gold working.

Keywords. Apprentice, master, ancient techniques, goldsmith.

INTRODUCTION

What is the value of knowing the ancient goldsmith techniques today? Is it possible, once rediscovered, to put them into practice again? With which advantages and for whom? The answer to these questions depends on the vision one has of the work: whether it is perceived as a shared activity and integrated into the ethical and political sphere of the community, or whether the consideration of the work is an individualistic one. The shared vision implies the preservation and transmission of experiences since a value as such is recognized to technical abilities. In this case the profit is subordinated to a historical identity kept alive over time. The individualistic vision, on the other hand, has - as its objective - the maximum economic profit in the face of minor expenditure: it is not linked to the context in which it operates, to history, to tradition, it does not imply aesthetic or ethical evaluations. If an individualistic, exclusively economic vision prevails, knowing the ancient goldsmith techniques is of little use: it can be only useful for marketing purposes, regardless the quality of products. But for those who want to give artisan work an ethical, aesthetic and social value, it is necessary to research, study, learn, practice and protect ancient technologies. This contribution, with some brief archaeological and historical examples, wants to remember the importance of a philosophical approach to craft activities, which otherwise are destined to disappear if forced to adapt to the disruptive technological innovations of our day.

Few human activities can continue to use the same working methods over time without them becoming obsolete. The craftsmanship of the workshop is among these: it has changed little over the centuries and today it is undergoing a period of serious crisis, at least in Italy. The validity of the

Figure 1. 22 kt gold classic Greek style earrings, diameter 2.5 cm. Technique: filigree. Author: Alessandro Pacini.

Figure 2. Fibula in gilded silver, garnets and bone. Length 3 cm. Technique: cuttlefish bone fusion, pure gold leaf gilding. Author: Alessandro Pacini.

working methods over time depends on the family-type organization of the artisan laboratory and on the limited and mainly manual production of the artifacts. This gave the crafts a rituality, a respect that sometimes brought them closer to the world of religion or magic. Looking back to the most remote past of the goldsmith's art, we can see that in all ancient civilizations skills and craftsmanship were considered of divine origin. Not all human beings achieved the knowledge of the mysteries which lie in the transformation of matter: among the chosen persons, secrets were shared and transmitted within associations of experts (often constituted in trade associations or corporations). Thus we are witnessing two parallel stories, that of the divine origin of the arts and that of the professional corporations. Mircea Eliade writes: "The smelter, the smith and the alchemist claim a common magical-religious experience […] the secret of this experience […] is transmitted through the initiation rites to crafts" (Eliade 1987, p. 8). And then: "The Celestial Smith completes the creation, organizes the world, establishes culture and guides human beings towards the knowledge of the mysteries" (p.153). There are numerous documentary testimonies of the divine origin of the arts and often in particular of the goldsmith's art, gold having always played a magical role thanks to its beauty and incorruptibility. A list of Sumerian kings (written between 2100 and 1900 BC) states that each sovereign was assigned a semidivine mentor, an Apkallu, to teach all the arts, including that of the government (Pettinato 2004, XXII). In ancient Egypt there were various deities connected more or less directly to the artisan crafts: Ptah (the god of pottery) who dictated the rules of artistic creation, Khnum (who created men by modeling clay on the lathe), Neith (the inventor goddess of the shuttling for weaving), Thot (the god of magic, writing, geometry and mathematics), Maat (the divinity of Harmony and Equilibrium). In Egypt the Houses of Life were already present in the Old Kingdom during the third millennium BC and have continued to exist for many centuries maintaining a multidisciplinary pedagogical vision. They were cultural centers where various arts were taught, including writing, embalming, and magic. Connected to the Royal Palace or the Temple, there were schools of mathematics and geometry for the calculation of proportions, where the artists learned techniques of ornament and sculpture, and the goldsmith arts. The Houses of Life probably were also attended by Zosimos from Panopolis, an alchemist and Gnostic mystic who was one of the first authors of alchemy and who lived between the 3rd and 4th century AD in Egypt which by that time had become a Roman province: "Only with a methodical discipline and treasuring the teachings of the ancients can man heal from poverty, that is the loss of the sense of unity between microcosm and natural and spiritual macrocosm" (Tonelli 2004, p 101). Even the Minoan civilization had deities that supervised the crafts activities, such as Khousor, Kothar and Talo. Some ceramic tablets found in Pilo (a Mycenaean city in Messinia) attest the existence of professional guilds in Crete. In the Royal Palace G of Ebla, in ancient Syria (2400-2250 BC), 17000 ceramic tablets were found with cuneiform inscriptions: some indicate the specialization of the craftsmen of precious objects in detail. Jacopo Pasquali has identified specialized figures in the processing of natural carnelian of light orange color (si-si), and of the heat-treated dark red carnelian (gug-gul). He identified the: puzur-ra-ma-lik lú si (i.e. master cutter of carnelian), the: da-zi-ma-ad (i.e. helper cutter of carnelian), the: ib-du-ma-lik lú si (i.e. expert craftsman in a processing phase of carnelian natural), the: iš-a-ma-lik lú gul-si (i.e. expert craftsman in a processing phase of the carnelian tractors), the: dumu-nita lú si-si (i.e. apprentice cutter), the: dumu-nita-gùn (i.e. apprentice dyer of carnelians) (Pasquali 2005, p.10). Given such a specialized level of processing of each single gem, it is possible that corporative work organizations already existed, although they were controlled by the royal palace. In the Bible we find the action of the holy spirit at the origin of technical abilities: "Moses said to the Israelites: «See, the Lord has called by name Bezaleel, son of Uri, son of Cur, of the tribe of Judah. He has filled him with the spirit of God, so that he will have wisdom, intelligence and science in every kind of work, to conceive projects and make them in gold, silver, copper, to carve the stones to be set, to carve wood and make all sorts of genius work. He also put in his heart the gift of teaching and so he did with Ooliab, son of Achisamach, of the tribe of Dan»". These are the verses 30-35 of the book of Exodus, written between the sixth and fifth century BC, but referring to facts from the mid-thirteenth century BC. In the classical world, artisans played a fundamental economic role and trade corporations were well structured. Plutarch in the *Life of Pericles* lists various crafts and then writes: "Because each art gathered with itself, like a general with his army, the masses of workers and craftsmen […] the various work needs distributed and spread welfare throughout the population" (12, 5-6). Pliny in the XXXIV book of *Natural History* recalls some famous Greek sculptors including: "Silanion, about whom the admirable fact is that he became famous without any teacher" and further on: "Silanion was the most scrupulous in terms of technique and a ruthless judge of himself. He often destroyed the finished statues because he was not satisfied with the result, he was nicknamed the madman". Being self-taught at the time was remarkable, out of the ordinary. A trade was normally learned in a workshop, under the guidance of a teacher, from a young age. Plutarch and Pliny lived in the first century of the Christian era when the tutelary deities of the craftsmen still existed: Sethlans for the Etruscans, Efaistós for the Greeks, Vulcanus for the Romans. It was under the Romans that the professional guilds (collegia) saw their maximum expansion and the highest levels of organization. In the 8th Law of the 12 tables (about 450 BC) it is written: "Sodales legem quam volent, dum ne quid ex publica corrumpant, sibi ferunto", that is: "Corporations may give themselves the legislative system they prefer, provided they are not in contrast with public law". Each collegium, which could count hundreds of members led by the magistri, had its status and its seat (schola). Naturally it was the colleges

Figure 3. Chalice in gothic style, silver, gilded silver, jaspers, travertine. Technique: lost wax casting, embossing, turning, enamels, niello. Author: Alessandro Pacini.

that managed the apprenticeship of young artisans. Such was the importance of craft corporations in Roman times that scholars have identified thirty Latin terms that indicated this type of association. At the end of the Roman empire, under the Roman Barbarian kingdoms, the court laboratories produced precious artifacts for the nobility which had a political value, as gifts of exchange when searching for allies. With the beginning of the Middle Ages the corporations lose power and often disappear, but the apprenticeship continues in the workshop of a master goldsmith who could also be a soldier or an officer or even practice other trades. Some medieval jewelers became famous holding prestigious positions, such as Saint Eligius (588 - 660) a senior official of the court of the Merovingian kings and then bishop of Tournai and Noyon. The guilds continued to exist: Byzantine scholae, Lombard consortes (the word appears in the edict of Rothari, in 643), ministeria in Pavia between the X and XI century. But it was above all the monasteries which preserved and handed down the arts in addition to the classical culture. Between the ninth and twelfth century they ideologically dominated Europe, their great laboratories produced high-end goldsmiths. Moreover, no place was better than the monasteries for associating the profession with spirituality and rituals. Theophilus, probably identified with the Benedictine monk Roger from Helmarshausen, wrote what may be considered the first manual of artistic techniques in Europe. The communal age between the twelfth and fourteenth century saw the birth and triumph of the Arts, that is, the trade guilds that for the first time even had the political control of the cities. Magistri, discipuli and laborantes worked within them in a production context organized in a similar way to a family. The apprenticeship lasted for some years, after which a judging commission composed of the Consoli dell'Arte admitted the Matricole on the basis of the quality of the Masterpiece, a final essay of the technical and artistic skills possessed. At this point the matriculated to the Art could have his mark of production. Cennino Cennini (1370-1427) wrote: "And as soon as you can, begin to put yourself under the guidance of the teacher to learn, and as late as you can, from the teacher you leave". And a century later, in full Renaissance, Lorenzo Ghiberti completes the concept saying: "It is convenient that the artist is expert of writing and trained in geometry and diligently has heard philosophy […] and has heard astrology and is taught in perspective and still is most skilled at drawing […] who has also seen the works of the ancients […] rightly I think that there cannot be professed artists except those who from very young age are trained by similar degrees of discipline and fully familiar with the science of letters" (*I commentari*, I, 2). In the sixteenth century AD, the mercantile ideology contributes significantly to the decadence of the corporations. By then the great merchant companies have more power than the old arts and a clear separation between artist and craftsman comes about. The apprenticeship is less regulated and can be carried out freely by the teacher who considers himself better or more famous. It is no longer necessary to be registered members of a corporation to practice the trade. Benvenuto Cellini for example never registered with the goldsmith's guild: he preferred, still a young boy, to wander around Italy looking for a good teacher. In Pisa, near the Ponte di Mezzo, attracted by a goldsmith's shop, he was invited to enter and "immediately [the goldsmith] gave me to work […] silver gold and joys and the first day provided, in the evening he brought me to his house […] with great love he came to see me at my room that he had given me, seeing that I spent all my hours virtuously, he gave me his love like a father" (*La vita*, X). Cellini stayed there for one year (he was 15). The eighteenth century sees the end of the guilds: in Tuscany they were abolished in 1770 by the Grand Duke Pietro Leopoldo and replaced by an Office of Manufactures. Machines and workers replace shops and craftsmen, there are still small workshops as family units, but the apprenticeship is no longer the exclusive prerogative of craftsmen. In fact, the nineteenth century sees the spread of royal and stately schools, shops of goldsmiths collectors (as the Castellani in Rome), of artisans (entrepreneurs for themselves) and technical schools (established by cultural associations, rural and craft banks, worker's leagues). The quality of the teaching however was however high and the same techniques of previous centuries were preserved, with the drawing always at the basis of the work. A couple of centuries later, under Fascism, on February 5, 1934, a law on corporations was promulgated: "The corporate principle consisted in the subordination of special interests to the national interest, conceived as the superior interest of production" (chapter VIII). Pope Pius XI re-proposes the corporations in the encyclical *Quadragesimo anno* of May 15, 1931: "It happens by natural impulse that […] those who devote themselves to an art form colleges or social bodies; so that these corporations, with their own right, by many are said to be, if not essential to civil society, at least natural" (84). "It is possible to apply to the professional corporations what Leo XIII taught about the form of the political regime, i.e. the choice of the most suitable form is free, provided that justice as well as the common welfare is respected" (87). In those days one could still enter a workshop in the young age and traditional craftsmanship allowed to live in dignity. Over the centuries the sacred prerogatives and the magical potentials went lost, but the craftsmanship still remains an activity protected by our Constitution in the articles 35: "The State takes care of the training and the professional development of the workers" and 45, paragraph 2: "The law provides the protection and development of the crafts". This protection exists only on paper, because in reality the new global economic and cultural forms in Italy have literally disintegrated it. The main causes were new regulations that prevented apprenticeship directly in the workshop, whilst other serious obstacles are due to the incorporation of artisan laboratories in the industry, with an unbearable legislation for the artisans in terms of safety at work and taxation. Various attempts to recover the teaching of artisanal crafts to young people through courses managed by various bureaucratic agencies and financed as projects proved to be a failure.

CONCLUSIONS

The splitting of the transmission of art crafts, which has affected some generations of Italians and Europeans in the second half of the twentieth century, has led to the irreversible loss of most of the ancient craft techniques, including those of the goldsmiths. In recent years, the *coup de grace* has been given by technologies based on computerized systems, combined with new products of chemical synthesis, of which the artisans can neither control the origin nor modify the physico-chemical characteristics, if not in a very limited way. The use of these techniques and these materials can only disrupt the very nature of the craft. These new technologies are no longer linked to the culture of the community or to the history of the territory, nor to any liturgical or ritual form of manual labor, therefore they are compatible with an individualistic vision of work, much less with a shared vision. Although it seems that there is no link between scientific research and traditional craft, we must consider the fact that the discovery of synthetic materials and the invention of technologies for serial production inevitably resulted in the destruction of a working method. This method had existed for centuries, above all the crafts, but now it may end up being relegated to private hobbies or to the amusement of a few enthusiasts, completely emptied of any socio-cultural value, included the fundamental pedagogical one. The freedom of research and experimentation of the scientist, the chemist, should be limited by the awareness that some operations can be harmful to the environment and to society. This limit must be placed by the inventor and not by those holding political and economic power.

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The authenticity of the false

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Abstract. Since its first appearance, the jewel is not a mere expression of vanity and seduction, but it is associated with the decorative function with a multitude of meanings that transform it to all effects into a complex and fascinating communication code [1]. The jewel is a perfect combination of nature, technique and individual creativity that interprets the collective sensibility in the various eras. If we then join up it to its being made of precious metals, it becomes the most advantageous and profitable object of forgery [2]. The fakes and counterfeiters began at much the same time and flourished ever since. Most of the early productions are not very convincing, either stylistically or technically, this was due to a general lack of detailed stylistic information and an almost total ignorance of ancient technology. Until the middle of the last century there was no real science applied to the study of cultural heritage and the falsification or counterfeiting could be unmasked only by stylistic errors or anachronistic details detectable by visual observation although with the help of optical microscopes. With the establishment of Archaeometry, each diagnostic application became a real scientific research [3]. In the present work, the chemical and physical studies on ancient goldsmith's art in the last forty years, highlight the peculiarity of the manufacturing technique and the scientific knowledge of the artisan, which allows not only to discover modern copies, falsifications or counterfeits, but also to unveil the modern experimental approaches implemented for a faithful reproduction of an ancient jewel.

Keywords. Ancient jewellery, archeometry, fakes, Castellani family, Prenestina fibula.

Only micro/nanodiagnostic allows to understand and distinguish jewels made as a copy-replica, jewels inspired by ancient artworks or made as a counterfeit. In fact, all the handicraft and the technical procedures included in the jewel manufacturing sequence pertain to the goldsmith's personality … which cannot be easily reproduced by the forger.

INTRODUCTION

In every civilization luxury products represent, in addition to the desire to embellish the appearance, a sign of social distinction, witnessing the wealth and often the power of those who own them.

The cultures of the ancient ages, including those that were developed in the Italic area, are no exception: in the classification that Pliny the Elder, who lived in Rome in the first century AD, reports in his work, a list of the most coveted goods from his contemporaries, in order of preference

In this list all the materials used in the goldsmith's art appear on time – the processing of precious metals, i.e. gold, silver and their alloy, the electrum – and the glyptic. With this word, deriving from the Greek term γλύφω ("engrave"), we mean either the set of materials of inorganic nature (precious stones and hard stones) and organic materials (amber, ivory, coral, shell) that could be carved and engraved, either the art itself.

As concerns the real products, however, the highest value, among those of the sea, is attributed to the pearls; among those of the earth's surface, to the crystals; among those of the subsoil, to the diamond, to the emeralds, to the gems.... Among the products derived from animals with respiratory system, for terrestrial animals the highest value is the elephant's tusks, for the marine ones the shell of turtles ... between the terrestrial and marine products, the shells and the purple ...
We must not omit to say that gold, for which all mortals do follies, occupies only the tenth place in the scale of values, and the silver, with which gold is alloyed, yes and no the twentieth ... (Pliny the Elder, Naturalis Historia, cap. XXXVII, 204)

Around the eighth century BC, the acceleration of economic-social differentiation processes and the concentration of huge wealth in the hands of the indigenous aristocracies of Etruria, Campania and Lazio induce, in central Tirrenic Italy, the establishment of huge accumulations of precious metals that stimulate the luxuriant development of goldsmith craftsmanship.

Subsequently, with the emergence of Rome power and the extension of its influence due to the territorial conquests and the annexation of new provinces, as early as the first century AD new luxury goods such as hard and precious stones, pearls, ivory, silk, begin to flow along the trade routes that connect Rome with Asia and Africa.

In Italy it is possible to bring back the origins of Italian archaeological jewelry to the excavations of Herculaneum and Pompeii that provided the first jewels, sources of inspiration. Thus the reproductions and the diffusion are more precocious in Naples than in the rest of Italy.

Augusto Castellani in the "Discorso sull' Oreficeria Antica" [4], argues that the first attempts to copy exactly the ancient creations were made in Naples at the beginning of the nineteenth century, in the goldsmith Mariano Sarno's bottega. Later on, this activity would be undertaken by his father Fortunato Pio, in Roma. The goldsmith bottega of Sarno, on the advice and encouragement of learned Neapolitan archaeologists and customers, begins to restore excavation jewels, to imitate them in style and to push their creations to falsification. The goldsmith production, under the guidance of Sarno, had, for a few years, a great success, and then gradually closed its activity [5].

In addition to the well-known Neapolitan archaeological discoveries, in Italy there were many other intense explorations often crowned with unexpected as well as important discoveries like that of the Regolini-Galassi tomb in 1836, in Cerveteri (Caere) or the Bernardini tomb discovered in Palestrina at the end of February 1876 during the excavations financed by the Bernardini brothers [6].

In this last tomb, a dragon-like gold fibula dating back to the mid-7th century B.C was found. A text that constitutes the oldest written testimony in Latin, is engraved on its elongated part, however it has been the subject of doubtful falsification / authenticity issues that raised a twenty years-long discussion.

In the context of the nineteenth century, characterized by the rediscovery of the classical world and the strong diffusion of collecting and the antiquarian market, originals, copies, falsifications and pastiche often live with no particular hardships and difficulties both for the craftsman and for the client. [7].

It was common practice, among the artisans of the age, to touch up, reintegrate and reconstruct damaged or mutilated artefacts to satisfy the needs of an antiquarian market, particularly attentive to the integrity of the object rather than to its authenticity.

These practices sometimes went as far as the meticulous copies of ancient jewels, which however, in the popular imagination of the average purchaser of the time, had the same value as the original ones [8].

A report of Monthly Magazine about the London exhibition of 1862, asserts that "every piece on display is an original copy of a true authentic exemplary of an ancient work; that not only the ornamental style, but the procedures used in ancient times have been followed"

These arguments are enshrined in our Constitution with Article 21 which, in the most rigorous respect for the fundamental principle of freedom of expression, protects the right of every citizen to be able to realize and express their thoughts through the creation and dissemination of their production, without any substantial control over the content of the operations performed.

It is possible also to cite Article 33, which is the principle of freedom of art and science, Article 35 according to which, the Republic protects the work in all its forms and Article 2575 of the Civil Code, which fixes the original character of creativity that identifies the personality of the author and reveals its ability to express an idea, or a feeling. [9]

In 1977 Bloch [10], to describe the phenomenon of ancient reworkings, distinguishes these different types of artifacts:

- **copies-replicas** from a prototype, according to a practice already widespread in the ancient world
- **copies-counterfeits**: products that are exclusively subject to a market law, not by preventing creativity, an essential element of the artist
- **pastiches**, the realization of a work of art, by assembling authentic, i.e. ancient, materials with others of modern production.

The difference between the first two classes of artifacts lies in intentionality, which satisfies a precise practical function, that of placing a responding object in the art market, by means of a malicious operation and under the appearance of truth, to a question that would otherwise be unsatisfied [11].

Ruled by an economic law, the falsification follows the fluctuations of taste and it is no coincidence that the most famous fakes coincide, over time, with the great archaeological discoveries, of which they imitate the findings.

The first Etruscan fakes appear in the eighteenth century, the great era of collecting and of the *etruscan style*. But we must wait for the second half of the nineteenth century, for the production of the finest examples of fakes [12].

The discovery of the Regolini Galassi tomb in the year 1835, sets a very important date as kick off to the development of a goldsmith's art that proposes the study of the ancient technologies, undertaken by the Castellani workshop.

Fortunato Pio, in fact, was called by the papal authority, as a consultant for the restoration and study of Etruscan jewelry and from this moment, a Castellani production of archaeological-style jewelry starts. Alessandro Castellani [8] commented this important discovery in the conference held in London at the Archaeological Institute in 1861[13]:

> *Since there are no scientific studies on ancient goldsmiths' techniques, even if he is a goldsmith with a long experience, he is faced with problems never found in the creation of any jewelry complex.*

The jewel decorative components are, in fact, made with techniques that are not always handed down in full, because in addition to being the creations of the single craftsman, the precious alloys and other non-metallic materials undergo transformation with kinetics of more than 2000 years.

The gold metal does not show many alterations or corrosions, but it is prone to micro-structural evolutions such as recrystallization and discontinuous precipitation, hence it is rather fragile and may present mechanical damage, especially if it consists of thin sheets, connected to each other by welds, which may have been crushed or torn.

Clearly, the Castellani family was aware of the proliferation of fakes and did not want to be associated with them. Augusto Castellani, in the "Discourse on ancient goldsmiths"[13], talking about the activities conducted in the workshop by the goldsmith Sarno, who had a good reputation in the production of faithful reproductions of ancient jewelry, defines the falsification a reprehensible activity and takes the distances:

> *The artists who had been part of the Sarno bottega then set about restoring ancient works of art, and also applied their talent to their falsification. In this last reprehensible activity, they were so wonderfully skilled that Naples became famous for imitations, so astutely made with colored earths, acids and salts, so much to make it difficult and almost impossible to know if an object was ancient or not. Unless they were people who had a long experience in the field of art, and were very experienced in archeology.*

Their archaeological creations and the techniques involved, required a considerable amount of apprenticeship for their artisans, who were asked to apply maximum precision and quality in the execution of the models. This activity led to a revolutionary revival of local craftsmanship, which had its fulcrum in the Castellani bottega, where many Roman goldsmiths at the time carried out their apprenticeship: Fortunato Pio had created a sort of "Roman school" of goldsmiths.

A possible classification of the different types of nineteenth-century "falsification" can be expressed as follows:

1. Antique with modern reworking
2. Antique with modern additions
3. Pastiches of antique pieces
4. Pastiches of ancient and modern pieces
5. Modern with the addition of antique parts
6. Duplicates: pastiches as pendant of ancient pieces
7. Duplicates: modern copies as a pendant of antique pieces
8. Modern artifacts from ancient types
9. Pastiches or modern pieces sold together with antique pieces
10. Pastiches or modern pieces sold together ancient items (false documents)
11. Neoclassical or historicist pieces

Among these categories, the numbers 1, 2, 3 and 6 can be considered "good faith" restoration. Part of the artifacts, which fall into category 8 and those of n. 11 can be classified as imitations.

Categories 4, 5 and part of 8 have counterfeiting intentions. The works that belong to the categories 7, 9 and 10 are false in the strict and legal sense of the term.

According to Hilmeyer [14], the most difficult categories to be distinguished are 4 and 5, which require careful study of all the individual parts of the jewel, which also refers to the techniques of realization of the same. Considering all this, in the study of archaeological goldsmith's art, there is a need to circumscribe the category of "authentic" from that of "reworking".

If it is true that the "fakes", made in the nineteenth century, must be recognized and appreciated as a phenomenon of a specific historical period, it is also true that recognizing the falsifications is an act of honesty towards of visitors and scholars. At the same time, giving back the right identity to authentic works is a moral necessity rather than an historical requisite [15, 16].

From the above described, it is possible to understand how the identification of nineteenth-century reworking has to be considered as a complex study, especially in the specific case of the Castellani's family. In fact, by virtue of their authoritativeness, they could perform "copies", "complete" or "rework" precious objects starting from the direct observation of the authentic pieces, that they had the possibility to handle as long as they needed to study their characteristics and compare them directly with the jewels they reproduced.

If an initial critical observation can direct and help in the identification of originals /fakes, sometimes the stylistic and formal examination is uncertain and not always sufficient to grasp the differences between two objects, even if it is a question of discriminating in the same artifact, antique and modern decorative elements. These latter being formally identical copies of those already present on the original [16].

A useful tool, in this sense, can be provided by the scientific investigation, which, through chemical and physical analyses, allows the technological assessment of the jewel, identifying the details of the construction technique. If the overall system and the construction scheme of a jewel can be reproduced exactly and with relative ease, it will be more difficult to reproduce the original ancient techniques of decoration elements such as granulation and filigree with a resolution of the order of millimeters [17].

In fact, the ancient technologies used have peculiarities, such as the type of alloy, the execution procedure, the assembly, the welding, the traces left by specific instruments, to be used as *diagnostic markers* in the study of a modern example from an ancient one.

Starting from previous studies [18-22] the aim of the present work is to outline how the scientific investigative method, based on the recognition and the temporal and geographical attribution of a goldsmith working process, can be decisive in the attribution of authenticity of an ancient jewel.

MATERIALS AND METHODS

Dealing with jewels, it is right to start from the main metal, gold, that is considered *noble par excellence*, incorruptible, perpetually shining and therefore a symbol linked to the sphere of royalty and the sacred, a sign of power and unalterable wealth over the time.

The precious objects found in the archaeological excavations astonish for their unaltered appearance, even if, on a structural level, we must not neglect that gold, like all metals over time, tends to return to its more stable form, which, in the case of gold, is the metallic face centered cubic crystal structure. Its mechanical properties can be altered by micro and nano-structure modification.

The state of the structure on micro/nano scale becomes complex when alloyed gold is used instead of pure gold: e.g. alloys with silver, copper, often with traces of other metals coming from a possible re-use of metals, such as iron, lead, tin, zinc to cite the most frequent in ancient times. Besides, each of the alloyed metals may contain traces of minerals from which they were extracted by metallurgical processes. Furthermore, in addition to natural ageing, interaction with the environment, often hypogeal, should be considered in view of the function of jewelry in the funeral contexts.

What is described is the basis of archaeological research that aims to trace any clue that bring back to the authenticity of the artifact.

In the choice of the analytical method it is indispensable, in addition to the obvious application of non-destructive techniques, to take into account that it is required to go beyond the visible scale and therefore the dimension of the particular to be investigated is the key parameter for the selection of suitable methods.

The techniques most frequently used in the study of jewels, are based on X-ray radiography, scanning electron microscopy (SEM) coupled with energy dispersive X-ray micro-analysis (EDS) and X fluorescence (XRF), using instrumentations suitable to avoid any micro sampling on the object or surface pretreatment.

With the application of one or more of these techniques on a considerable number of ancient finds, in the last years it has been possible to broaden the knowledge on the activity of goldsmith artisans but also indirectly on their scientific knowledge applied to metal processing [23-25]. From these studies it is possible to obtain a big amount of information that allows to compare technologies belonging to different cultures and to identify the processes linked to the creation of the object, establishing its own characteristics that consent us to trace the genuineness of a finding.

Specifically, each study includes the morphological analysis of the surfaces, by means of images acquired in the various SEM modalities, the elemental analysis of the composition of the pre-existing alloy, by EDS and /or XRF analysis. The critical discussion of the results made it possible to identify the technique of creating jewelry decoration elements such as: granulation, wire form, welding techniques up to the type of tools used and any non-metallic materials included in the artistic composition [26].

The thin border line among the various forms of jewelry remaking, more or less conforming to legal rules, can be highlighted considering the studies carried out on three types of reproduction of objects, from an evident falsification case, to an attribution of authenticity, the fibula Prenestina, passing through nineteenth-century remakes linked, above all, to models derived from studies on the Etruscan jewelry by Castellani's family.

RESULTS AND DISCUSSION

A case of falsification, appeared recently on an auction catalog, is represented by the pair of gold earrings (Fig. 1), consisting of an oval-shaped setting with a frame decorated with short radially engraved strokes, containing a blue-colored dark gem. In the back, on the lower side of the setting, a trapezium-shaped plate is welded to the edge, to which three fixed suspension eyelets are connected. Attached to them are three knurled wires, with the end folded to set three small blue-green beads. So many elements to be verified analytically, when stylistically perfectly consistent with the Roman Imperial jewelry, in particular the type refers to earrings diffused in many variants and defined by the classical sources with the name of "crotalia", a musical instrument that emits the sound from the tinkling of beads. The observation at SEM-EDS (Fig. 2a), highlights the short parallel lines engraved on the frame: they are irregular and imprecise, giving a scarce decorative effect. The central gem presents many imperfections and especially "bubbles" caused by a higher temperature than the glass transition. The glass components have been characterized by EDS analysis (Fig. 2b), showing a composition that can be associated with a modern glass, with a high content of lead and cobalt, the latter to impart the blue color to simulate lapis lazuli.

Figure 1. Earrings attributable to the Roman Imperial period.

Besides, the SEM observations of the surface at microscale, revealed the presence of abrasive material with silicon and aluminum particles to antiquate the surface.

The trick to treat the surface for an antique appearance, is very common in counterfeiting. In another case Fig. 3, the filigree-decorated surface showed, at the SEM observation, a dense covering with a substance which displayed, by EDS analysis, a composition with anachronisms such as nickel and zinc dispersed in an organic matrix.

As written above, the knowledge of ancient jewelry technology through micro and nano diagnostic studies [27], is becoming fundamental for the recognition of counterfeits, but in the case of the 800's jeweler Fortunato Pio Castellani, this type of investigation becomes a discovery of a research method on the Etruscan jewelry that has left its mark on the jewel history.

The study of the Castellani goldsmiths, which include Etruscan jewelry restorations, copies for *experimental archeology*, to use a modern term, and Etruscan-inspired jewelry for sale, offers the possibility of discovering their secrets. The integrated study of a pair of "bauletto" earrings, belonging to the collection of "ancient golds" and another of the same type belonging to "modern gold" has

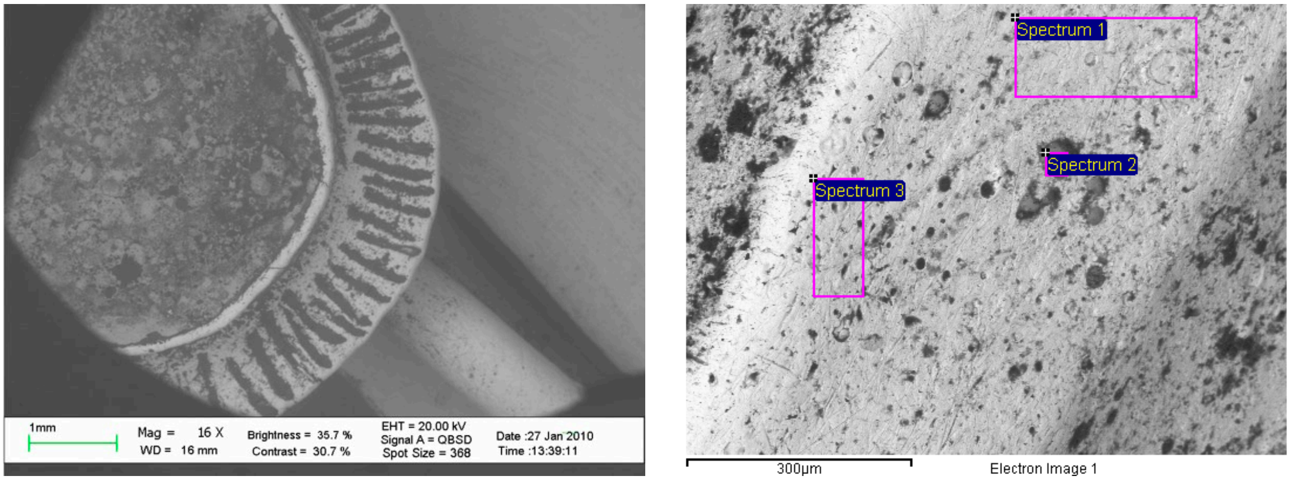
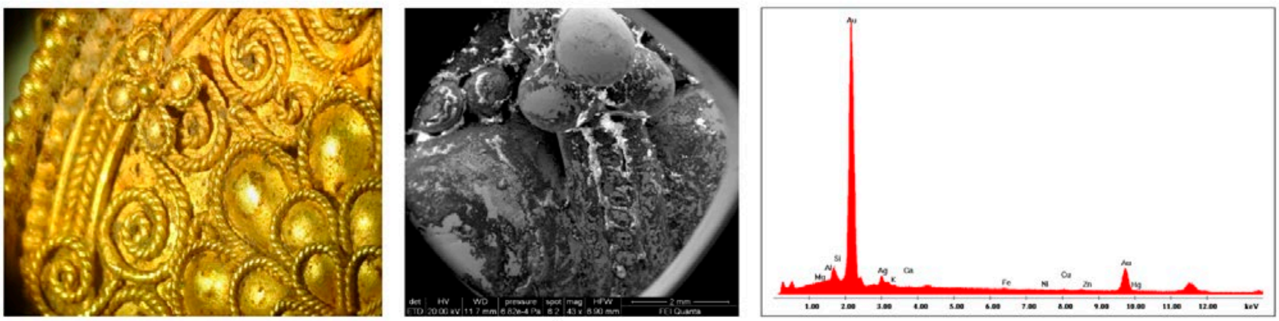


Figure 2. a) Backscattered electrons SEM image, of the part of the bezel with gem b) structure of the glass gemstone with indicated areas analyzed in EDS.



a b c

Figure 3. a) part of a modern jewel made of watermark; b) SEM image in secondary electrons of a part of the decoration; c) EDS analysis of the substance distributed on the surface.

been the subject of an experimental thesis and chemical-physical research [28]. This study gave the opportunity to compare the technologies of execution and realization of the overall plane, and the decoration details of the Castellani work with those of the ancient Etruscan goldsmiths. First of all, the study of the modern earring has been undoubtedly an opportunity to fine-tune the observations and analyses on the technological details used by the Castellani. In the analytical determinations, all the processing technologies related to all the decorative elements of the earring, such as granulation (grain shapes, three-dimensionality, welding), watermark (realization of the threads) and tools traces have been considered. Each particular of the modern production, is to be considered as anachronistic elements in the subsequent study of the so called "Etruscan Collection".

The impossibility of subjecting jewels to invasive instrumental investigations, taking into account the exceptional value of jewels, has led to the selection of appropriate diagnostic techniques. A new type of analytical approach, aimed at highlighting structural differentiations on micro / macro scale between the "hand" of the Castellani and Etruscan goldsmiths has been employed by using modern data processing systems. In fact, the modest variations in composition and the imperfect localization of the Castellani's interventions on a micrometric scale, led to the elaboration of the numerous data obtained from the EDS micro-analysis through the statistical method of the Classification Analysis, allowing to identify correlation areas between elements.

The evaluations of the percentage of the elements constituting the Au-Ag-Cu gold alloy trough EDS is extremely difficult, as the elements are not homogeneously bound, and therefore minimal variations are not immediately observable in order to characterize, for example, one of the various welding processes. The variables selected to discriminate the various soldering techniques have been: brazing agents, Cu salts, silver or other paillons, and the presence of the elements: Cu, Ag, Cd, Au. To avoid undermining the final result, before each classification analysis, their degree of Bivariate Correlation has been calculated using the Pearson Correlation Coefficient, which measures the degree of linear association between two variables.

The values of the coefficient vary between -1 and +1. The sign of the coefficient indicates the direction of the relationship between the two variables: directly proportional in the positive case, inversely proportional in the negative case.

The results made it possible to define the use of Au-Ag alloy for the welding, as traditionally used in the 800s, but there are traces of cadmium that cannot be ignored.

On the use of cadmium in Castellani's work, much has been written [29] and having found it on the pair earrings of Castellani manufacture, it certifies its use.

The skills acquired on Etruscan jewelry and on Castellani's production allow us to recognize the parts subjected to modern intervention with the aim to give the jewel back its original aspect.

This is the case of the "bauletto" earrings Fig. 4, decorated with numerous and dense filigree and granulation motifs.

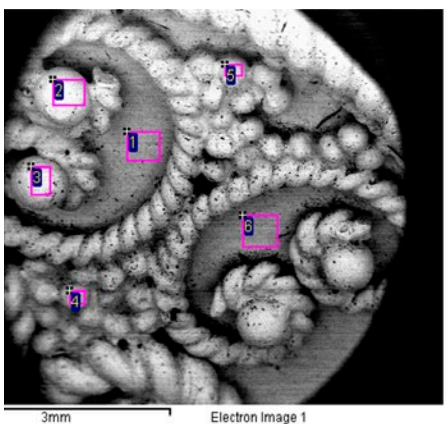
At first glance they appear identical, but a more expert observation reveals several elements of differences. That's why the first studies concluded that they are original Etruscan, but one (N. Inv. 53582) presents many subsequent works, while the other (N. Inv. 53580) has only a few alterations.

If we observe the two earrings at micro/nano scale, many contradictory elements with the Etruscan jewelry are evident. This pair of earrings then falls into the category of antique piece with modern rework.

Figure 4. Pair of earrings, Museum of Villa Giulia N.Inv. 53580 and 53582.

As an example of the analysis carried out in each part of the jewel, we report the representative elements of the Etruscan jewelry, granulation, watermark and knurled thread, are, as highlighted in Fig. 5. As regards the identification of the gold material composition, the SEM investigation has been undertaken by selecting an appropriate focused electron probe and by observing the surface in the backscattered electrons mode. Based on these results, it has been possible to select micro-areas which were homogeneous for morphology and atomic contrast, for the EDS microanalysis. The obtained data are shown in the table of Fig. 5, following the criterion of imposing on the system the evaluation of all the chemical element mentioned in the "probable" Castellani's recipes.

EDS data immediately highlighted the presence of cadmium that, considering only the elements of the gold alloy, ranges from 0.2 to 1.3 wt%.



	Cu	Ag	Cd	Au
1	-	0.9	-	99.1
2	0.3	1.4	1.3	97.0
3	0.4	0.2	0.6	98.8
4	0.8	0.6	0.2	98.4
5	-	6.3	1.3	92.4
6	-	-	-	100.0

Figure 5. Earring N.Inv. 53582 SEM image in backscattered electrons with indicated the areas investigated by EDS method. The table shows the values of the chemical elements in percentage by weight (±0.2%).

The SEM observation, in secondary electrons, of some areas of the jewel, highlighted the welds, whose realization caused an excessive filling of the spaces between the wires and between the granulation spheres.

Focusing on the use of metal wires for the filigree decoration, thanks to SEM (Fig. 6), it is possible to make morphological comparisons that highlight heavy differences between the ancient and the modern parts, certainly not known at the time of the Castellani.

It is possible to observe that the numerous threads do not all have the same technical execution. Some of them show the typical helical grooves, characteristic of the Etruscan construction technique that makes use of a twisted foil strip.

Others, instead have the characteristic parallel streaking, signs that have been produced through the use of a modern wire drawing die.

The excessive heat applied has melted part of the original substance in the upper part and in the external side, making it difficult to locate the welding. In fact, the heating allowed diffusion and or local fusion of the metallic elements.

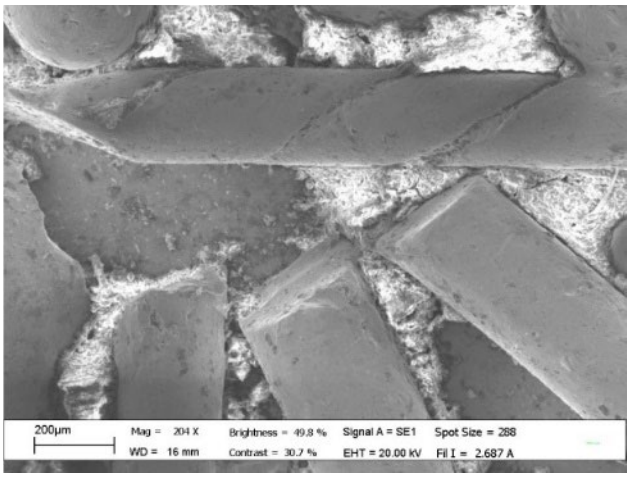


Figure 6. Original wires and threads added during the Castellani restoration.

Therefore, the pair of earrings belonging to the collection of “ancient gold”, given the complexity of the work, have been analyzed by considering each decorative element, in order to obtain more specific information and allow a comparison between them.

The application of Person’s analysis for each earring allowed the creation of correlation matrices (Fig. 7).

The most significant evidence derived from the analysis of elemental composition and correlation of the variables is that the Au concentration decreases in jewel N. Inv. 53580 depends, in equal weight, on the presence of both Cu and Cd. This indicates the presence of welding with Cu salts and addition of modern processing with use of Cd, while, in N. Inv. 53582, it depends primarily on Ag (Ag welding) and then on Cu (copper salts welding).

Moreover, a direct proportionality link between Ag and Cu cannot be found in Inv. No. 53580: this means that in the analyzed areas, the two elements are not correlated and therefore a use of an Ag-Cu alloy is to be excluded. Cadmium is present independently of the Cu in equal measure in the two objects analyzed. Compared to Ag, on the other hand, the Cd has a null bond for Inv. No. 53580, while it becomes important in the case of Inv. No. 53580, a sign that probably Cd has been used in addition to the welds by Ag.

The studies here reported demonstrate how the margin of separation between an attribution of authenticity or falsification is inconsistent, if one does not consider the complexity of chemical-physical information drawn from the study of ancient technological processes.

What has been described, even if it can not necessarily be exhaustive, indicates however an obligatory route for the attribution or for “re-assigning” the authenticity grade to an ancient finding.

A demonstration of this may be the case of the recent restitution of authenticity to a precious object, considered false and deprived of its important historical significance for a long period, the Fibula Prenestina Fig. 8 [30]. The fibula is datable around 670-650 BC and containing the signature of the “Manius” artisan, as well as that of the client. The formula employed is that of the

Matrice di Correlazione N. Inv. 53580

	Cu	Ag	Cd	Au
Cu	1.000	-0.190	0.115	-0.664
Ag	-0.190	1.000	0.282	-0.521
Cd	0.115	0.282	1.000	-0.612
Au	-0.664	-0.521	-0.612	1.000

Matrice di Correlazione N. Inv. 53582

	Cu	Ag	Cd	Au
Cu	1.000	0.283	0.107	-0.704
Ag	0.283	1.000	0.071	-0.877
Cd	0.107	0.071	1.000	-0.173
Au	-0.704	-0.877	-0.173	1.000

Figure 7. Correlation matrices for each of the pair’s earrings in Fig. 4.

Figure 8. Fibula Prenestina 670-650 bC. Pigorini Museum Rome.

"speaking object" by reporting the sentence "Manios fecit for Numasio". These indications have represented the fundamental element used by the legendary etruscologist and archaeologist Raymond Bloch, to fix the birth of the Latin alphabet to the VII century BC.

The writing proceeds from right to left and uses the letters of the Latin archaic alphabet; its wording is influenced by Etruscan, Sabellian and Faliscan languages [31].

So the fibula is considered the oldest document of the Latin language but its authenticity, disputed for years, has been proved not only by linguistic data but also by recent chemical and physical analysis.

It was officially presented for the first time by the German archaeologist Wolfang Helbig, in 1887.

The scholar claimed to have purchased it from a friend in 1876, and indicated the place where it was found as the Bernardini tomb. A princely tomb, discovered in 1851 and excavated from 1871, near the ancient city of Prenestae, the current Palestrina. After years of academic and judicial disputes over its authenticity in 2009, the application of the integrated epigraphic and archaeometric study has demonstrated its authenticity.

The application of the analytical method, to prove the consistency of the techniques used in the construction of the fibula with the ancient working methods, has revealed inconsistencies due to a modern process. However, the real importance of the finding focuses on the verification that the writing has not been performed post-recovery. This has induced studies on the microstructure of the metal, in order to derive useful information for understanding the transformations undergone [32].

As known in its fundamental state, the gold metal has a face-centered cubic crystalline structure (fcc). The specific properties of course are modified when Au is alloyed with other metals such as Cu or Ag. However, while silver is completely soluble in gold at any temperature, copper is soluble in gold only above 410 C, below this temperature Au-Cu intermetallic compounds are formed. It is therefore clear that in the ternary alloys, the parameters and the mechanism of the recrystallizations after the various treatments that the metal undergoes for the realization of the object, are complex [33]. However, the overall process can be reduced to the following general scheme: a) nucleation of crystalline grains, b) growth of crystals, c) irregular grains form more or less regular structures that grow together d) increase of crystalline grains dimensions observable by optical microscope.

Recrystallized structures are clearly identifiable in the SEM image of one of the traces left by the tip used for the inscription (Fig. 9).

Three situations are related to the alloy modification over time and consequently to the observed alteration of the inscription:

1. In the furrow, the marks left by the roughness of the tracer tool are partially interrupted by recrystallization marks (indicating that recrystallization took place after the inscription was traced).
2. If the inscription had been made recently, i.e. after recrystallization of the alloy, the engraving lines would have appeared jagged, following the intergranular lines of lower mechanical resistance: such a feature was not observed.
3. Internal areas of the inscription paths were investigated, using backscattered electron observation with appropriate modifications of the detector operation mode, in order to simulate the effects of grazing light. In this mode, the differences in height between the grooves impressed by the incisor tool and the natural alterations of the metal are high-

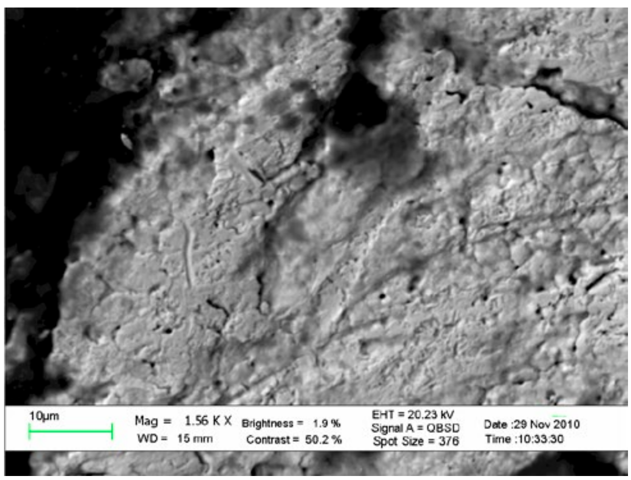


Figure 9. Modification of the metal microstructure (due to recrystallization) inside the incision groove.

lighted. Therefore, SEM observation of the surface in the furrow area confirmed that recrystallization (i.e. natural evolution of the precious alloy over a very long time) took place after tracing the inscription.

This aspect, together with the other scientific information collected with an analytical procedure tailored for the Fibula Prenestina [32], demonstrated that the ancient find contains so many historical, artistic and technological information that we can never say we know everything about it.

This affirmation is particularly true in this case, for which the new investigations, carried out after twenty years of analytical studies on ancient jewelry in general and the Etruscan one in particular, have been able to restore its historical credibility.

CONCLUSIONS

The jewel is the only one among the ancient finds, that contains all the practical and scientific knowledge of the craftsman who has to create a unique work each time. Relying on procedures more or less attested in the period and in the geographic area where it operates, the antique jeweler brings stylistic and technological innovations that gradually become established, and their recognition together with historical artistic elements, allows their chronological collocation. The other important aspect is that the metal, whatever it is, keeps both the information of the operations that have allowed its transformation into a work of art, both of the action of time. The recognition of such transformations provides useful elements for defining its antiquity. The story of ancient gold working is not only related to metallurgical studies, because in the past each object contained meanings and symbolisms, but, at the same time, from another point of view, it is also full of technical and scientific knowledge. Translations, interpretations, hypotheses, assumptions: how many times before an old jewel we met the difficulty to understand it, as well to know its history, the technology used in its realization, the scientific knowledge that led to the manipulation of its constituent material, its origin and so on. However, there is only one universal language, that always existed and always will exist and that is translatable in any language: chemistry. The identification of products and chemical processes that led to the physical realization of wondrous works of art, provides important data to complete the history of the work of art itself, allowing to define also the cultural grade of the contexts in which the object was manufactured.

Someone wrote:

The work of art is born from the idea of form and search for technical means to realize the minimal details. In this sense the artist is at the same time, scientist and technologist.

From this point of view, research turns its attention to the problems of the past with the knowledge of today, trying to identify the chemistry and physics concepts and applications, which, obviously on empirical basis, the ancients had and which we can interpret through scientific laws, now. The treated argument covers the research carried out in recent years on archaeological items in precious metals. The investigation on micro/nano scale is essential for the identification of diagnostic markers that yield the knowledge of particular processes applied to precious metals workings. The collected data on the smallest details of the production procedure of jewels, provide completely objective comparison of the specific techniques adopted in the creation of the artistic object. In fact, as well known, the precious items were always object of treasuring, trades, spoils of war, reaching places far from the original provenance. In this view each jewel contains information on particular geographical areas and/or different socio-cultural situations. Different examples of the described cases studies help to understand the mismatch between scientific investigation and historical knowledge. But the more immediate goal is the transfer of enthusiasm for a research that helps us to appreciate more of our cultural heritage and to suggest that it is not enough to see an object but is much more interesting to know how to see it.

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Electrodeposition and innovative characterization of precious metal alloys for the Galvanic and Jewel industry

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Abstract. In recent years the idea that metals, oil and, more generally, natural resources are not endless has been firmed. Furthermore, people become aware that humanity must not only increase the production of customer-goods, but they also must produce them with respect for the environment, trying to limit either dangerous processing techniques and hazardous materials. The elimination of many metals from alloys has also reduced the possibility to modify or to produce a wide range of precious jewels and new materials. For such reasons it is essential to develop new techniques for manipulation and preparation of precious jewellery products. Nowadays this economic policy drives many companies and even the single craftsmen to a cultural innovation and technological growth. Many small and medium-sized companies ask the University for a technological support, otherwise impossible to achieve alone for high costs. The basic research of University has become an important point for the development of the goldsmith sector and for the increase in production and variety of new jewels. This important collaboration between universities and industries is called "the Third Mission for the University". This collaboration is important from a cultural, as well as from a productive point of view. Nowadays, the symbiosis "Research centre - Goldsmith company", allows the company to expand internationally its market, thus making the whole industrial sector competitive and innovative. This union is extremely important not only for the goldsmith sector but for the entire National economy.

Keywords. Electrodeposition, Surface Analysis, Galvanic, Jewel.

INTRODUCTION

Since several years, industrialists, politicians and scientists have become aware that the energy resources of our planet may sooner or later end since they are limited. Awareness contributed to move towards the development of numerous renewable energy sources. Alternative energies and new renewable sources supported by developing technologies are already a big market creating many, high quality jobs. National research on major societal challenges, such as renewable energies, synthesis of new materials or creation of technological poles, will have more impact if efforts would be combined at the

European level. Besides technological poles and Innovation Centres – widespread across European Union – must help to improve networking and dissemination of experience with entrepreneurs in the industry, universities and civil society organisations.

Some problems have emerged in recent years for all precious metals starting from gold, platinum, silver, copper and even zinc. Then, in 2010, the first official reports were published in Europe [1] and America [2]: these documents highlight the scarce availability of the elements mentioned above, which in a few years will become even rarer [3,4]. In addition to this problem, which is not easy to solve, a second one has been added: the banning of numerous metals regularly used in the jewellery and fashion sectors:

- elimination of lead from brass alloys
- elimination of Nickel from wearables
- the abolition of galvanic baths based on chromium (VI)
- the imminent elimination of cyanides from galvanic baths

These legislative provisions have limited or even eliminated certain galvanic or synthetic processes. For this reason, many techniques employed for decades in the jewellery sector, have been abandoned. It has become necessary to invest in real applied research to find out new ways to meet the market demands. To accomplish this highly qualified and onerous task, a collaboration between the University and Industry has arisen. At a local level as well as international one, this process of collaboration has exacerbated competition among companies: a scientific war has begun between those companies which have invested more or less in new technologies and the other which did not. The future industrial development will penalize countries in which this Industry-University synergy has not yet been created. This costly commercial war left many Italian companies unarmed. The few Italian researchers employed by Italian companies have often been forced to work in conditions of inferiority (in terms of financial resources): without appropriate structures and large-scale investment in research, it was impossible to face the fierce world competition. This led some companies to bankruptcy and has condemned others to remain at the edge of the global scene. The latter category of industries has undergone a much faster and more unexpected cultural aging than it could be imagined.

Some examples are the case of gold galvanic bath in which it is difficult to replace the cyanides with other less dangerous substances; sparing some metals as additives in castings is a major challenge; replacing nickel, with a fundamental metal preventing the diffusion in the solid solution of easily oxidized metals such as silver and copper, is a conceptually and economically titanic undertaking. Not only that, but the scarce availability of gold has triggered the research to decrease the amount of this element in alloys. With low carat alloys of gold and the creation of alloys based on non-precious metals, a "precious-perceived" market has been created. If the economic problems can be limited in this way, the chemical and physical ones cannot be avoided at all, rather they are increased and new ones are added: the corrosion resistance worsens in alloys with a lower gold content. In addition to that also the evaluation of the colorimetric parameters needs some development as well as morphological characterization techniques and new techniques able to examine the composition of the new products.

HISTORY OF GALVANIC INDUSTRY

The history of electroplating begins in the early 18th century [5,6] when, in 1805, L. V. Brugnatelli used the Volta's voltaic pile to plate silver with metallic gold from a gold solution. His discovery was not appreciated from the scientific community and only thirty years later the Russian scientist B. Jacobi devised a process similar to the Brugnatelli's work. Jacobi used the more performing Daniell cell for electroplating copper on metal plates thus rediscovering electroplating [7] and electroforming [8]. The first patent to perform gold and silver deposition were submitted in Birmingham by Henry and George Elkington in 1840. Their use of potassium cyanide as electrolyte led to establish Birmingham as the industrial center for electroplating with the inauguration of the first large-scale plant in 1876. Later, the stability of gold plating bath was improved with the use of ferrocyanides, thus providing the capability of depositing gold alloys containing silver and copper. From then on, electroplating quickly spread throughout the rest of the world and became a common process for depositing precious and non-precious metals. Since then few improvements were made in the following decades, except for the large-scale electric power distribution; only after the Second World War, in 1946, A. Brenner and G. E. Riddell discovered the first autocatalytic metal deposition by adding sodium hypophosphite to a nickel bath giving birth to the "electroless" deposition [9]. Since the early 1950s some baths were implemented by replacing cyanides with acidic solutions obtaining a more manageable and sustainable working environment [10]. In recent years electrodeposition in non-aqueous solution was investigated leading to the development of electrodeposition in ionic liquids and electrophoretic deposition [11]. Ionic liquids are used to deposit metals with a Nernst reduction potential more negative than the evolution of hydrogen in water, e.g. aluminum, [12]. In ionic liquids the electrolyte is composed of anionic and cationic organic species which are in the liquid phase at low temperature; this allows the salts of the metal precursor to solubilize by means of the electroreduction process. Ionic liquids are very sensitive to moisture and therefore they must be employed in a special closed environment with a controlled atmosphere. The electrophoretic deposition process involves the reaction of organic monomeric precursors driven by an external electric potential [13]. Differently from the aqueous-based electrodeposition, the organic molecules not only occur in a redox reaction, but they also form a network leading to the formation of a polymer. The resulting coatings are generally well-adhered and softer than the metal ones with fewer cracking issues. The final polymer could be either conducting or insulating materials. The organic-based coatings tend to be more degradable over time, another issue is the environmental toxicity in the production process due to their precursors. The impact of electroplating on our lives is huge: in 2015 electroplating represented 37 % of the total market share within the metal finishing sectors with applications in automotive, aerospace, building, jewelry and electronics [14,15]. The most commonly galvanically-deposited metals are zinc and zinc alloys (about 15 %), followed by nickel, copper, chromium, tin, and precious metals [16]. According to a recent study published by Future Market Insights the global electroplating market is expected to increase at a compound annual growth rate (CAGR) of 3.7% over the forecast period of 2016-2026, projecting revenues of over US $21 billion by the end of 2026 [17]. The main limit to an even larger expansion of electroplating is the strict environmental regulations: many plating processes involves toxic metals and dangerous chemicals. Another issue facing industrial development is the price volatility of highly on-demand electroplated materials (e.g., gold, copper, and nickel). Although significant technological and processing advancements occurred in the past forty years, industrial firms are still struggling to provide viable solutions to energy conservation, reduction of costs and toxic wastes, as well as strategic challenges such as product durability and corrosion protection [18,19]. Today, a deeper knowledge of the electrochemical mechanisms and the research of new materials and emerging technologies are driving the traditional manufacturing process towards a more reliable, flexible and interconnected production [20]. By exploiting the natural affinity of some elements is possible to obtain a surface-limited reaction that spontaneously generates a single atomic layer. This behavior is very useful from a technological point of view and, therefore, widely studied by the scientific community. Starting from this principle, many techniques have been developed during the last years: Electrochemical Atomic Layer Epitaxy (ECALE) [21,22], Electrochemical Atomic Layer Deposition (E-ALD) [23-25], Selective Electrodesorption-Based Atomic Layer Deposition (SEBALD) [26,27], Electrochemical Liquid-Liquid-Solid growth (ELLS) [28].

HUBBERT PEAK OF PRECIOUS METALS

The World Gold Council estimated that about 190,000 tons of gold have already been mined from Earth [29]. Almost half (48 %) of the total was manufactured in jewellery; almost a quarter (21 %) was channelled into private investments; 17 % in official sector and the remaining 14 % assigned to other sectors such as technology. It is difficult to answer to question of how much gold remains to be extracted. It has been observed that two thirds of the gold already extracted until now occurred after 1950. One might think that if we follow this trend for in the next 100 years we can expect to achieve more hundreds of thousands of tons. Unfortunately, experts estimated that the current underground reserves amount to only 50,000 tons. It is understandable that this relatively modest picture is in contrast with the increasing production and use of gold in recent years.

The idea of peak oil pushed up the price of petroleum, but now another peak theory has emerged, this time involving gold and all the other precious metals. Hubbert's peak, called also Hubbert's curve, is a theory that approximates the production rate of a resource over a period of time. From a careful analysis of the Hubbert's curve we found that the initial production rate follows the increas-

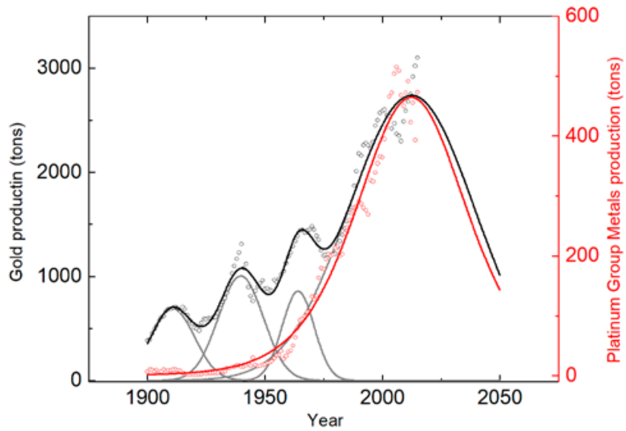

Figure 1. Hubbert peaks of Gold (black) and Platinum Group Metals (red): past production and future previsions.

Figure 2. Price of gold from 1970 to 2019.

ing demand for the new resource, but then it is predicted a loss of correlation and a decreasing in production while the demand still grows up. During this fall, there may be dramatic differences in production and demand as demand continues to rise, but production falls overall.

From the estimations of the remaining unmined gold and its increasing price, many analysts of precious metals and gold miners are taking a cue from the prediction of the Hubbert's theory, according to them the same concept can be applied equally well to the ingots, as well as to the oil, and can lead to outsized investment returns from the purchase of the yellow metal. In this context, the supporters of the golden peak claim that mining has a discrete number of similarities with oil extraction.

Just as the slowing of production and the diminishing reserves observed in the old oil wells, many of the best gold deposits exhibit the same kind of geriatric tendencies, with high quantities extracted long ago. However, after the peak, it was not observed a sustained decline as was the case of the model proposed by Hubbert. The reason could be the evolution of new technologies that provided us the tools to extract oil from unconventional resources. Then, a question arises: does the gold extraction follow this story? The answer is complex; the extraction of gold is connected to something more than just the technology. In fact, the price of the metal itself influences its extraction: it is observed that when gold becomes too cheap the extraction process stops. Furthermore, gold ores becoming increasingly more difficult to access compared to previous decades, and the likelihood of a discovery leading to mine development is very low (less than 0.1% of the proposed sites will lead to a production mine), according to the research of the World Gold Council, even if the 10 % of global gold deposits contain sufficient gold to justify further development, the exploration alone could take up to 10 years and entail heavy costs in terms of geological investigations and chemical analysis.

ELECTRODEPOSITION OF LOW-CARATS GOLD

Galvanic baths containing considerable amount of toxic substances, such as cyanides, and heavy metals, which are also toxic and difficult to remove. For example, cadmium, in the matrix[1] have been used for decades to get one gold alloy containing less than 75% by weight of gold metal (corresponding to a gold alloy of 18 carats or less). These baths allow to get effectively gold deposits having the desired carat value e considerable thickness. However, the presence in them of highly poisonous substances makes them virtually unacceptable for practical use. The alternatives in use, however, exploit products that have only partially solved known problems met with the use of previous galvanic baths and, in addition, do not demonstrate the same suitability for practical use and the same quality of results. In fact, these are generally formulations that only partially eliminate toxic products used and which have limited periods of use or with which an alloy is obtained characteristics of the value of carats, thickness or appearance that do not meet the needs of the intended use. However, baths of this type also include solutions that use cyanide in the matrix or that, though they do not contain cyanide in the matrix, contain other elements or compounds of a certain toxicity. A recent study [30] has opened the possibility to satisfy the above needs due to galvanic alkaline baths containing: gold salts, copper and indium salts, salts of polycarboxylic organic acids, organic amines, and possibly complexing agents, surfactants and other metals in smaller quantities, as gloss additives and refiners of deposits. It is noted that, in contrast to the antecedent technique, cyanide is not present in the bath matrix and its content in the electroplating the solution is caused by its counterion function in the gold salts alone. Cyanide is therefore practically irrelevant, though necessary for the stability of gold in solution.

CHARACTERIZATION OF ELECTROPLATED COATINGS

Color measurements

The determination of the color has a central role in the quality control of electroplated deposits. The color

[1] Matrix is an aqueous solution of organic and inorganic acids and their salts.

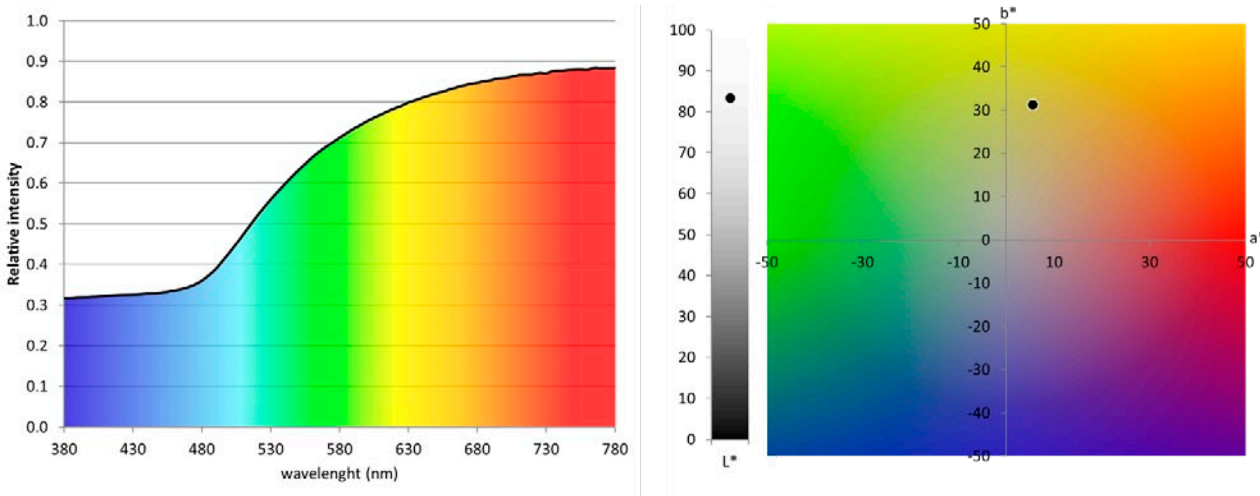

Figure 3. Measured reflectance spectrum (left) and the calculated colorimetric coordinates (right) of a gold sample.

measurement may seem a trivial task, but environmental factors and intrinsic properties of the objects might generate inconsistent data [31]. The formalism used for color assessment is the Lab color space [32] in which the three coordinates L*, a*, and b* are considered. L* identifies the brightness with values from 0 to 100, a* the red-green component (a* > 0 red, a* < 0 green), and b* the yellow-blue component (b* > 0 yellow, b* < 0 blue). The coordinates a* and b* do not have fixed limits but are generally in the range of ±100. The color coordinates a* = b* = 0 represents grays. The color of a sample can be compared with a target with several metrics [33]. The simplest and most commonly used approach defines color difference (ΔE*) as the Euclidean distance between the coordinates of two different colors. It is generally accepted that two colors, placed one next to the other, are not distinguishable ΔE* < 1 [34]. In practice, companies generally tend to give an acceptable range for the single colorimetric coordinates (L* ± dL; a* ± da; b* ± db), whose values are defined by the customer. Colorimetric coordinates are obtained from the mathematical combination of the illuminant, sample reflectance spectra and the average of human eye sensitivity (tristimulus functions) [35]. The main problem in color determination is the inconsistence of the results, even from the same paint or metallic coating, due to instrumental differences (colorimeters are generally used instead of more expensive and accurate spectrophotometers) substrate polishing (reflective or matte), dimensions and irregular patterns and textures [36].

Thickness evaluation

The precise determination of the electrodeposited thickness is a fundamental parameter to characterize a galvanic coating. Mechanical properties are influenced by the thickness, beyond the type of alloy and the succession of the underling layers. A thick deposit can have very high tensile stress and low adhesion. On the other hand, if the layer is too thin, gloss, diffusion, color, and corrosion problems might occur. The most common methods for measuring the thickness are through scanning electron microscopy (SEM) of metallographic cross-sections or using X-ray fluorescence (XRF). Cross-sectional analysis allows acquiring a direct image of the layers' sequence and then measure the thickness. Therefore, quantification is very simple, for thick deposit the cross section can be also measured with an optical microscope. The main disadvantages of this approach are the high cost of the instrument (60,000-200,000 €) and the slow and destructive sample preparation. On the other hand, XRF allows for non-destructive and fast measurements, with an instrumental price of around 40,000-60,000 €. Knowing the composition and sequence of the metallic layers an appropriate calibration curve is made, then the thickness of all the layers can be measured, with a typical 10% standard deviation. The researchers should be knowledgeable *about* the sample under investigation and the impossibility of measuring layers in which a certain element is repeated: for example, in a typical deposition bronze/copper/brass, the copper layer cannot be measured because it is present in both the deposits and brass, while bronze can be evaluated by analyzing the tin and correcting the result based on its percentage in the alloy.

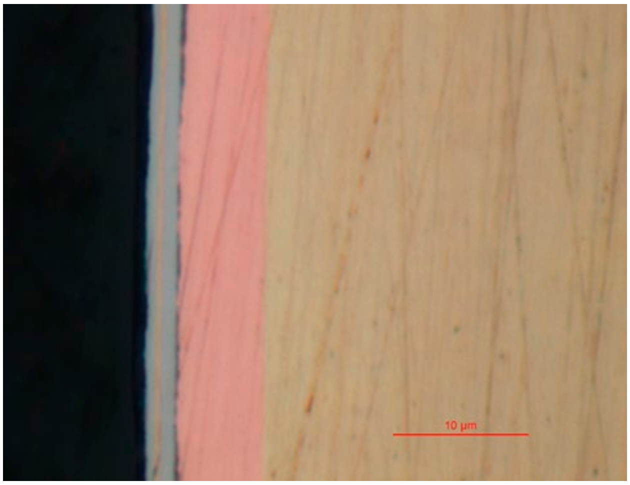

Figure 4. Cross section of typical galvanic deposition analyzed with optical microscope. From left to right it is possible to distinguish: brass substrate, copper, nickel and gold finishing. Before the cut of the sample an additional layer of nickel was deposited on gold to preserve its integrity and sharp edge during the lapping process.

A new methodology based on Energy Dispersive X-ray (EDX) spectroscopy for the determination of the thickness and the composition of electrodeposited thin films was developed in the last year [37]. The proposed method employed a combination of EDX spectra acquisition and Monte Carlo simulation. This method has better lateral resolution than the XRF technique and allows reliable measurement of the thickness on thin metal films, with the capability to determine also the composition of the film in the 1% concentration range. The approach was validated by the analysis of electrodeposited plates with known metal thickness using various approaches and custom-made software. The results were compared with other techniques showing an uncertainty of 9%, which is consistent with the literature data obtained using real standards [38]. The method has been validated on copper-based substrates covered by a layer of nickel, palladium and gold.

CORROSION AND MECHANICAL STRAIN

Product durability is a fundamental aspect which a producer must deal with, therefore mechanical and corrosion test must also be evaluated. The methods for examining the coatings' adhesion are describe by international standards by the qualitative examinations with thermal shock ASTM B571-97:2008, the network of cuts method ISO 2819:2017 and ISO 11644:2009, and the tape test under ISO 11644:2009. The formation of blisters or exfoliations indicates weak adhesion. The effects of time and environment on a sample is simulated with accelerated aging. The corrosion test can be carried out on a new sample or after mechanical tests in order to obtain a more pronounced effect. The most common international corrosion tests are: the effects of exposure to damp heat with or without leather ISO 4611:2010 and ISO 17228:2015, resistance to synthetic sweat ISO 3160-2:2015, salt spray test ISO 9227:2017, and tests with chemicals derived from atmospheric pollution, such as thioacetamide ISO 4538:1978, sulfur dioxide, and nitric acid ISO 4524:2000. Corrosion test generally takes long time (hours to days) to obtain a result and are intrinsically destructive. For these reasons, efforts have recently been made to find faster and non-destructive, or micro/semi-destructive, systems. A probable evolution in this sense could come from electrochemical measurements of Open Circuit Potential (OCP) and Electrochemical Impedance Spectroscopy (EIS).

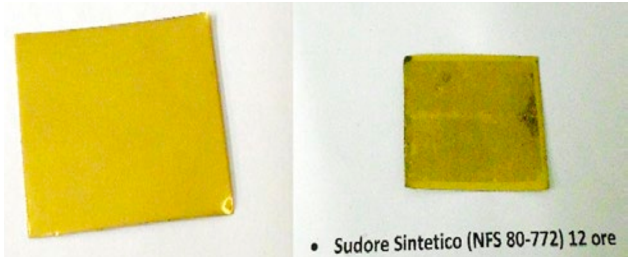

Figure 5. Corrosion test of a gold-plated sample, before (left) and after (right) 12 hours under syntenic sweat test.

FLORENTINE APPLIED ELECTROCHEMISTRY LABORATORY

In the Florentine Laboratory of Applied Electrochemistry, 20 people (professors, researchers, technicians and PhD students) are working. All of them are specialized in the various fields of chemistry and electrochemistry, engineering and materials science. The laboratory is affiliated with the Chemistry Department of the University of Florence. The academic research sectors in which the attention has been focused mainly concern:

1) Study of electrified interfaces with particular attention to the adsorption of electroactive organic substances and inorganic ions on different metals.
2) Study of nanomaterials obtained electrochemically.
3) Morphological and compositional characterization exploiting many technique: Scanning Electron Microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX), X-ray Photoemission Spectroscopy (XPS), Scanning Probe Microscopy (SPM) with par-

ticular regard to Atomic Force Microscopy (AFM). In this field the attention has turned to the morphological characterization of substrates of Technological, Environmental and Biological interest.
4) Microcontact printing and electrodeposition on a nanometric scale.
5) Preparation of modified surfaces of catalytic or technological interest by confined metal electrodeposition.
6) Electrodeposition of ternary or quaternary sulfides for the preparation of surfaces of technological interest in the field of solar cells.
7) Design and implementation of devices in the energy sector with natural materials with low environmental impact and with low energy consumption preparation techniques.

In recent years the laboratory has also been involved in applied research in the industrial field, for the development of sensors in medical use, low-cost instrumentation for oil and wine analysis, absorbent materials for acid spills courses of Basic Microscopy and Galvanic Baths. As previously reported, the Florentine applied electrochemistry laboratory shared the project of the university's third mission activity. The "third mission" of the University addresses the growing societal economic challenges. In reality the term "third mission" is ambiguous because it is used to indicate a multiplicity of activities that relate university research and society. A first fundamental typology is that of technological transfer activities aimed at the evaluation, protection, marketing and marketing of technologies developed in the field of research projects conducted by the academic world and, more generally, for the management of intellectual property in relation with the same projects. In this context laboratory's research activity has been carried out in a very important way, placing the Applied Electrochemistry Laboratory directed by Prof. Innocenti Massimo to a central role in the transfer of knowledge from the University to the industry and vice versa. In addition, the numerous contracts obtained have allowed an exponential growth of this group acquiring high-level instruments, of great impact in the regional production sector. Thanks to the various research activities, the applied electrochemistry laboratory has been able to boast numerous research funds and above all to play a central role for high-level training and the introduction into the working world of numerous graduates and post-doctoral graduates in Chemistry.

MIUR projects financed:

1) PRIN 2004 project financed by the title "Integrated study on the national territory for the characterization and control of atmospheric pollutants (SITECOS)" of which Professor Innocenti was responsible of the Operative Unit of Florence
2) PRIN 2008 project financed by the title "Platinum-free electrocatalytic materials for direct fuel-based fuel cells" of which Professor Innocenti was deputy manager

Projects funded:

Monte dei Paschi di Siena Foundation
1) Monte dei Paschi di Siena Foundation - 2006-2007
He financed the project entitled "Design Synthesis and Characterization of nano-structured composite materials with pre-selected Functional characteristics"

Tuscany region:

1) Gabbrielli 2013 Regional Project 1.3b of the POR CREO 2007-2013 "ECO-SOL".

Research Project "Eco-sustainable and low-cost production of sulphides for photovoltaic applications"

2) ESA 2016, Participant Project Tuscany Region, POR ERDF 2014-2020 Call 2: Research and development projects of SMEs, "New electrolytes for electroforming of yellow gold alloys with low environmental impact" Present and Research Manager of the subcontractor.
3) Regione Toscana Spettrox Project, POR ERDF 2014-2020 Call 2: Research and development projects for SMEs, Present as Researcher INSTM.
4) GADGET Project Call for POR CREO 2014-2020 - DD 3048 of 21/02/18, Call for proposals 2: Research and development projects for SMEs, "Silver, Galvanic, Ecological and Technological Jewelry"
5) EL4ALL Project Bando POR CREO 2014-2020 - DD 3048 of 21/02/18, Call 2: Research and Development Projects of SMEs, "New Aluminum Electrodeposition process on fashion accessories through the development of DES and next coloring "
6) THIN FASHION Project Bando POR CREO 2014-2020 - DD 3048 of 21/02/18, Call 2: Research and development projects for SMEs, "Plasma technologies for the luxury industry: 4.0 approach to additive manufacturing". INSTM . Appropriation 1.995.704,55 Euro (Classified 61, Head of Industry, TEXTS)
7) GALVATRON Project Call for POR CREO 2014-2020 - DD 3048 of 21/02/18, Call 2: Research and Development Projects for SMEs, My Research Group is present as a Subcontractor. Project Approved but Admitted to the Funding with Resource Reserve (probable

Figure 6. Applied Electrochemistry Laboratory group, headed by Professor Innocenti. Department of Chemistry of the University of Florence.

project start by 2018) Budget 469.302,45 Euro (Classified 108, Head of Industry ECO-TECH FINISH)

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Gold and silver: perfection of metals in medieval and early modern alchemy

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Abstract. For a long time alchemy has been considered a sort of intellectual and historiographical enigma, a locus classicus of the debates and controversies on the origin of modern chemistry. The present historiography of science has produced new approaches to the history of alchemy, and the alchemists' roles have been clarified as regards the vicissitudes of Western and Eastern cultures. The paper aims at presenting a synthetic profile of the Western alchemy. The focus is on the question of the transmutation of metals, and the relationships among alchemists, chymists and artisans (goldsmiths, silversmiths) are stressed. One wants to emphasise the specificity of the history of alchemy, without any priority concern about the origins of chemistry.

Keywords. History of alchemy, precious metals, transmutation of metals.

INTRODUCTION

For a long time alchemy has represented a sort of intellectual enigma, a critical difficulty for the philosophical and scientific historiography because of the relationships between alchemy and modern chemistry, which have strongly influenced the reconstructions of the origin of chemistry as a specific and institutionalised discipline. The positivistic tradition constructed and conceptualized alchemy as a form of proto-chemistry, and emphasised the difference between the empirical contents of the alchemical writings which were to be preserved, and the mystic, Hermetic, metaphysical dimension which was to be dropped out owing to its unscientific features. This approach deserves to be praised because it called the attention to the historical relevance of the alchemical writings, to the necessity of their analysis, study and edition. In 1887-1888 Marcelin Berthelot and Charles-Émile Ruelle published the three volume *Collection des anciens alchimistes grecs*, that has been a crucial source for almost a century.[1]

Today Berthelot's approach appears to be unsound because it is obsolete: a suitable historical perspective is to be based on the study of alchemy as a specific, centuries-old form of knowledge, and one must forget or put aside the question of the presumed transmutation of alchemy into chemistry. Without denying the existence of some interactions among alchemy, chymistry and chemistry, one must emphasise that the adventurous events of alchemy, the historical facts concerning the various alchemical traditions are largely different from those of the history of early modern chemistry.

ANCIENT AND MEDIEVAL ALCHEMY

The entry on "Alchemy" of the *New Dictionary of the History of Ideas* (2005) is divided into two sections devoted respectively to *China* and to *Europe and the Middle East* in order to enlighten the historical and conceptual relevance of Chinese and Western alchemy. [2]

Thanks to Joseph Needham and his school the history of the Chinese science represents a substantial chapter of the present history of science, and the volume 5 (two parts, 1974-1976) of their multivolume *Science and Civilisation in China* contains a very detailed reconstruction of Chinese alchemy.[3] Alchemical conceptions and practices were truly present in the Chinese empire, and Chinese alchemy developed during twenty centuries of documented history, and can be divided into two branches: external alchemy, that is the preparation of elixir through the manipulation of substances, and internal alchemy (inner elixir) aimed at the spiritual perfection of the alchemist. In 2005 Fabrizio Pregadio has published a volume entitled *Great Clarity. Daoism and Alchemy in Early Medieval China* in which he states that the crucible was the main tool of the Chinese alchemist from a symbolic, ritual and technical point of view,[4] and such a statement confirms the multifarious dimensions of the alchemical quest for knowledge.

In the Western and Mediterranean contexts alchemy had practical origins in Hellenistic Egypt, during the ruling of the last Ptolemaic Pharaohs and the beginnings of the Roman domination, and was codified between the first and the fourth century A.D. in Alexandria of Egypt. The *chemeia* was originally constituted of practices of artisans and of recipes aimed at the preparation and imitation of natural substances. In Alexandria the first alchemists were devoted to the working of metals, with a particular attention to gold and silver, and to the preparation of artificial, precious stones (pearls and emeralds), and to the colouring cloth using cheaper imitations of the expensive, imperial natural purple. Their activities consisted in the imitation of natural, precious substances and of purple cloths, in colouring silver to look like gold, or copper to look like silver, therefore they were a kind of *bijoutiers*. In Alexandria a middle class probably existed which aspired to a way of life similar to that of the Greek and Roman nobility, and needed some imitations of gems, of precious stones, and of purple because this class could not afford the original and natural ones.

These activities of imitation explain why the first alchemical texts, written in Greek on papyrus, contain about 250 workshop recipes. The Leiden and Stockholm Papyri date from the third century A.D. and present recipes relating to gold, to silver, to precious stones and to textile dyes. In 1981 Robert Halleux edited a new version of the original texts of the Leiden and Stockholm Papyri in a new collection dedicated to *Les Alchimistes Grecs*.[5] Pseudo-Democritus's alchemical writings have been recently published by Matteo Martelli in two critical editions, both in Italian and in English, and these editions confirm the four main sections of the Greek-Egyptian *Chemeia*: production of gold, of silver, of artificial gems, which included making and working glass, and colouring wool with artificial purple.[6] To Martelli we owe some outstanding contributions to the knowledge of the ancient Greek alchemy.[7] In the context of the Greek-Byzantine alchemy the *chemeia* was specified as *chrysopoeia* (the art of making gold) and as *argyropoeia* (the art of making silver).

Alchemy was born as a set of practices but became more and more sophisticated from a philosophical point of view. Alchemy acquired a complex whole of philosophical ideas and conceptions as regards matter and cosmos; Eastern and Greek philosophies became the theoretical base which guided the operations and the experiments, and shaped alchemical language that turned into a difficult and allegorical jargon. Thanks to various philosophical and religious concepts, alchemy was transformed into a true philosophy of nature which was destined to play an important role in western culture until the Eighteenth century. Some particular versions of Platonism, of Stoicism, of Hermetic Gnosticism and a few aspects of Aristotle's theory of the elements are traceable in the alchemical thought which presented itself as something new, specific, well defined in the various historical and cultural contexts.

The corpus of the Greek alchemical writings is composed by anonymous tracts or by pseudonymous tracts ascribed to mythical or famous authors. Zosimos of Panopolis in Egypt (about 300 A.D.) was the first alchemist to sign some systematic treatises of alchemy in which the platonic aspects are coloured by a strong Hermetic dimension. However, in Zosimos's writings an outstanding role is attributed to instruments, and his *Hypomnemata* open with some statements *perì organon kai kaminon*. In her new edition of Zosimos's *Mémoires Authentiques* (2002) Michèle Mertens considers the manuscripts, the preceding editions – Berthelot's and Ruelle's one is qualified as "très mediocre" – the studies on Zosimo. In her detailed introduction Mertens presents a technical introduction devoted to the *appareillage de Zosimo*, to his alchemical instruments and apparatuses.[8] The Byzantine Manuscripts contain many drawings of apparatuses, and Berthelot had tried to reconstruct their structure and their presumed working. The progressive increase of the philosophical and mystical dimension in the alchemical literature did not involve an undervaluation of the experimental and practical aspects. In the Byzantine collections of Greek Alchemical Manuscripts, the book on the production of gold, ascribed to Democritus, has a short introduction devoted to the imitation of purple, and is entitled *Physikà kaì mystikà*, that is *Natural and Secret Things*, according to Lawrence Principe's suitable translation.[9]

In the Middle Age Greek alchemy was preserved by Byzantine culture and from the VII to the XI century the alchemical canon was constructed by Byzantine scholars through selections and collections of texts. Emperors, monks, theologians and scholars were interested in alchemy, and focused their attention on the making of gold and of precious metals, therefore the Byzantine intelligentsia selected a specific type of alchemical tracts which were included in Greek-Byzantine collections, and such collections were translated into Syriac and Arabic. Starting with the VIII century some Arabic alchemical texts were produced in the context of an extraordinary flourishing of the Arabic culture. From the Syriac *kīmīyā* Arabs coined the term *al-kīmyā* which was very successful and was steadfastly used during the whole Middle Age and the Modern Age. Owing to the expansion of the Arabic empire and the spreading of the Arabic as a new common language, in the Islamic world it took place an assimilation of knowledge from the Greek, Persian and Iranian sources. In Islam, alchemical writings show the influences from Egyptian, Syriac, Sabean cultures, too.

Alchemy strongly rooted in the context of the Arabic scientific research, and a Latin manuscript, called the *Morienus*, was translated from Arabic in 1182 as *De compositione alchemiae*, and can be considered as the starting moment of the penetration of the Arabic alchemy into the Latin world: writings ascribed to Jābir ibn Hayyān, alias Geber were the most famous texts of the medieval alchemy. The Islamic alchemy is characterized by various aspects, but the alchemical research was focused on the making of gold, using mercury and sulphur, and on the production of an elixir (*al-`iksīr*) which, when combined with some vile metals, could transform them into gold or silver, and even it could be used as a true elixir, able to guarantee a long life or immortality.[10]

During the XII century the translations from Arabic into Latin composed a very important corpus of alchemical writings, and alchemy attracted the attention of famous scholars and philosophers: Albertus Magnus and Roger Bacon contributed to the development of alchemy in Europe. The art of distillation became a central subject of research: the utilization of minerals, concentrated acids, alcohol, and some new techniques of distillation, which allowed to obtain many distillates and the celebrated quintessence, modified in a substantial and dramatic measure the practices of the alchemists. Thanks to the research of Chiara Crisciani and Michela Pereira, we can now consider the XIV century as the apogee of the Latin alchemy: Arnaldo of Villanova's, pseudo-Ramon Lull's, John of Rupescissa's alchemical works testify to the impressing philosophical level reached by alchemy. Alchemy was a true philosophy of nature, based on some outstanding experimental practices, which was focused on the production of the elixir, on the transmutation of metals into silver and gold[1], and on the use of mercury in various experiments and chymical processes.[11]

It is worth noting that during its long history alchemy evolved but maintained a strong core of knowledge: in medieval and modern texts it is possible find recipes and experimental practices which are identical to those contained in the Greek papyri of Egyptian origins.

RENAISSANCE AND EARLY MODERN ALCHEMY

During the Renaissance and the early modern Era alchemy had a strong influence on various fields, from cosmology to natural philosophy, from religion to the vision of human history, from pharmacy to mineralogy, from metallurgy to medicine. Alchemical texts started being printed with some series of imagines that are still today a resource in order to understand the universe of symbols which nourishes the human psyche. The Sun and the Moon represented Gold and Silver, and these noble metals were also portrayed as the King and the Queen in order to emphasise their primary role in the processes of transformation. The alchemical and astrological symbols of the sun and of the moon were also used during the XVIII century in the Tables of Affinities to paint gold and silver. Metals were considered mixed substances, and like living creatures they were born and grew in the subterranean world: nature had a specific operating time for the maturation of metals in her wombs, and metals composed a sort of ascending ladder to the top of which there were silver and gold. Late medieval alchemist aimed at modifying the times of nature, cooperating with nature, but also surpassing her

[1] This transmutation was also a process of spiritual progress of the alchemist.

in the production of the noble metals. Transmutations were not dreams or fantastic enterprises but were a true project of acceleration of the natural times, based on man's ability to perform, because in its origins alchemy was also the art of making. In Johannes de Monte-Snyder's *Metamorphosis Planetarum*, published in German in 1663, it is possible to read about the metamorphosis of plants and of bodies which are guided by the Sun and the Moon. This text also considers the transformations of metals because mercury and sulphur bind man to the philosophical gold, that is, to the highest principle.

During the Renaissance many collections of alchemical books were published: in 1572 the printer Petrus Perna published in Basle a collection focused on the *Turba Philosophorum* entitled *Auriferae Artis, quam Chemiam vocant* which was reprinted in 1593 in an enlarged edition of two volumes.[12] The *Turba philosophorum* is a Islamic treatise in which the alchemical doctrines are exposed in a sort of congress of the pre-Socratic philosophers that is presided by Pythagoras. In 1546 Janus Lacinius Therapus had published in Venice a collection of theoretical, alchemical works, the first part of which contains the *Pretiosa Margarita Novella* of Petrus Bonus of Ferrara, one of the most important alchemical treatise of the XIV century. [13]

In her important book on *Alchimia. I testi della tradizionale occidentale* Michela Pereira reconstructs the histories of alchemy from the Greek world to the Modern age, and the chapters of this huge book devoted to early modern philosophical and religious contexts clarify the substantial impact of alchemy, in its various forms and declinations, on modern culture.[14] In the age of the Scientific Revolution alchemical texts were firmly rooted in the European cultural landscape. This presence has caused many historiographical controversies concerning alchemy, the Paracelsian tradition, chymistry and chemistry, and so on. Here, I cannot resume these debates but I only want to emphasise that a description of the genesis of modern science cannot ignore the question of alchemy. Andreas Libavius defended alchemy as an art against the Paracelsians,[15] and in 1602 Gaston Duclo published his *Apologia Chrysopoeiae et Argyropoeiae adversus Thomam Erastum*, that contains a defence of the arts of making gold and silver against Thomas Erastus, a professor of medicine in Heidelberg.[16] The controversies about alchemy remained alive and vivid from the Renaissance to the Age of Enlightenment.

The exhibitions devoted to alchemy in its relationships with the figurative arts are frequent in the institutional contexts of Europe and North America. For example, the exhibition of 2004 on *Kunst und Alchemy* at Düsseldorf, was focused on the mystery of the *Verwandlung*, namely transformation.[17] The catalogue of this exhibition contains chapters on the history of alchemy and thematic chapters aimed at illustrating the ties between alchemy and arts. In many seventeenth century pictures it is usual to find representation of alchemical laboratories and some very diversified images of the alchemist. In his mammoth history of the macrocosm and of the microcosm (1617-1624),[18] which is rich of amazing plates, the English physician and philosopher Robert Fludd (1574-1637) presented a mirror of the whole nature and the image of art together with a description of the human arts. These arts were alchemy as regards the mineral world, agriculture as regards the vegetable one, and medicine as to the animal one. Every part of the cosmos is tied to the other parts and these connections produce a complex and linked cosmological whole. Among the various connections one can isolate those between Saturn and lead, Sun and Man, Moon and Woman, but in the underworld Sun and Moon are connected with gold and silver.

In Malachias Geiger's *Microcosmus* (1651) the symbol of the potable gold "chimice praeparati" presents a true image of the macrocosm and of the microcosm in which the human figures of the sun and of the moon are entering in the alchemist's laboratory, and this image confirms that alchemy was both a philosophical cosmology and a series of laboratory practices.

The search for the philosophical stone to be used in the transmutation of metals in gold was still a topical argument in late Seventeenth century because Robert Boyle (1627-1691), the supposed father of modern chemistry, was highly interested in the research of this stone and of the secret of the alchemical transmutations.[19] During his life Isaac Newton (1642-1727) devoted much more time to alchemy, theology and sacred history than to mathematics and physics.[20]

I do not want to emphasise too much the symbolic features of the metallurgical alchemy in the early modern age, and in the final part of my presentation I want to call the attention to the ties between artisans and alchemists, to the relationships among some able goldsmiths, silversmiths, alchemists and chymists in XVII century Europe. In 2007 Vladimír Karpenko published a paper on alchemical coins and medals,[21] but we owe to Lawrence M. Principe's research some outstanding clarifications about the different social contexts of interest in precious metals. Principe has cast light upon the relationships between artisans and natural philosophers, between jewellers and scholars, and has defined the various places and contexts in which the alchemical practices were present in modern age.[22] The types of chymical discourses were numberless, but one needs to emphasise the ties between high culture and the craftsmanship of the artisans.

Johann Rudolph Glauber (1604-1670) was a German chymist, alchemist and pharmacist who was active in Amsterdam. He was very attentive to the practical matter, technological and analytical dimensions of the chymical research which he combined with the interest in alchemy. In 1646-47 he published a two-volumes treatise in German, on the art of distillation, and in 1656-1661 a textbook on the prosperity of Germany. In the latter book, he argued that a systematic application of chymical knowledge to manufacturing of goods would lead to higher prosperity in his native country. In 1658-1659 Glauber published a treatise on the salts, but he had already published (1646) a treatise on the true potable gold, and between 1663 and 1664 he published two treatises on the Hermetic medicine and on the explanation of the true alchemical secrets.[23]

In Amsterdam Glauber became acquainted with the three Grill brothers, German jewellers and silversmiths, who were active in the Low Countries. Anthoni Grill, an aurifaber, criticized some chymical processes used by Glauber and affirmed that the famous chymist did not use a correct process to separate gold from silver. As a jeweller, Grill dedicated his attention to the essaying of the precious metals, and had invented a less expensive technique than those used by chymists and alchemists. Principe has discovered some sources which point that Grill had created a method of producing gold and silver in laboratory, and was able to exhibit some samples of artificially produced gold and silver.[24]

During his long tour across Europe the Danish physician and naturalist Ole Borch (Olaus Borrichius, 1626-1690) met Grill at Amsterdam in 1662. There Grill showed him that the combination for some months of lead with a particular spirit of salt had produced a fine piece of good silver.[25] In The Hague Andries Grill, Anthoni's brother, had a laboratory and a jeweller shop which were visited by European travellers wishing to observe his practices of obtaining gold and silver. In 1659, knowing to his financial debts, Anthoni Grill was obliged to leave Amsterdam, and fled to Sweden where he became a successful public officer in the field of metallurgy, a crucial activity of the Scandinavian country.

In Amsterdam Anthoni Grill had acquired a big house and there he built some large chymical laboratories that after his departure were used by Glauber for a short time. Grill was at the centre of cultural exchanges with travellers, German university professors, visitors of his laboratories and of his shop. They spread all over Europe Grill's practical research.

The case of the German jewellers of the Low Countries, reconstructed by Principe, demonstrates that the traditional dark, witchlike image of the alchemical and of the chymical laboratories does not fit the historical facts. In the Dutch context of the *Gouden eeuw* some fruitful exchanges between artisans and naturalists took place, and were historically significant.

A SHORT CONCLUSION

In Modern age alchemical texts and practices were very popular and alchemists played a crucial role in the history of science because, quoting Tara Nummedal, "in joining the hands on manipulation of matter with more theoretical speculations about its composition and transformation, alchemists (like physicians) modelled the extraordinary potential of the union of head and hand long before it became a hallmark of modern science".[26]

However, alchemy was not able to become a branch of that institutionalised research which produced modern science. In the map of the new knowledge created by the Scientific Revolution that established the academic topics to be investigated one cannot find alchemy. The modern scientific discourse was often engaged to denounce the "dreams" of alchemy.

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"*Antichi Strumenti Orafi*" of the Garuti Collection – The Virtual Exhibition

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Abstract. The "*Antichi Strumenti Orafi*" Virtual Exhibition is a multidisciplinary project developed by The Department of History and Cultures of the University of Bologna in collaboration with the Garuti Collection's owner, Adelmo Garuti. Garuti, a goldsmith in retirement, has been collecting tools and machineries related to his profession for years, and has placed them in Sasso Marconi (Bologna, Italy). This unique Collection shows the inside of the old goldsmiths' workshops, giving us the opportunity to rediscover a world that has changed dramatically since the coming of Information Technology and 3D Computer Graphics in the gold working industry. This Virtual Exhibition (*www.antichistrumentiorafi.it*) (Fig. 1) shows the most relevant objects of the Garuti Collection and describes their functioning, so the visitor can follow each step of the precious metals working process. The objects can also speak on their own about the workshops they belonged and about their producers. That gives the visitor the opportunity to know something more about goldsmithing in Bologna - the main city represented in the Collection – and in general about this sector in Italy between the 19th and 20th century.

Keywords. Virtual exhibition, Ancient Goldsmithing, ancient tools, industrial heritage, industrial archaeology.

The realization of this Virtual Exhibition has requested over three and half years of documentation and study of the huge and heterogeneous Collection set by Adelmo Garuti. Probably there is no such an exhibition in Italy, and maybe in Europe, for the quantity and quality of objects and documents included. They belong different workshops and refer to different ages and come from the 18th century to the second half of the 20th century.

All the objects have been captured in high resolution, classified and dated, including all the hardcopy archive of the Collection, made up of sheets and technical notes from the workshops (Fig. 2), ancient photos, old catalogues, and much more.

Researches in historical archives have been performed to collect information on single workshops or factories, in order to dedicate a special session of the Exhibition to the Industrial Archaeology. The importance of this virtual platform was clear since the early stages of the work. It has the pur-

Figure 1. Home page of "*Antichi Strumenti Orafi*" The Virtual Exhibition.

pose of dissemination to the public, including non-specialist visitors, and also to give the academics new perspectives in the studies concerning ancient metallurgy. It also gives the opportunity to visit the Collection from different parts of the world, without physical barriers and limitations of time. Another purpose of this project is to get in touch with other exhibitions or collections like this around the world, to discuss and share knowledge and experiences.

Very often old workshops definitively close down and all their equipment are sent to dump. Most of the objects and tools of the Garuti Collection have been donated to Garuti through the decades by goldsmiths in retirement or by their families. Many of these objects have also been restored by Garuti himself.

He likes to talk about his Collection, about the circumstances of the recovery of the objects and, above all, about his profession. He started as apprentice in Bologna, in the workshop of a goldsmith, Romano Degli Esposti, in 1960 (Fig. 3). His job became his life and even now he dedicates himself to it, preserving the knowledge of the past and trying to pass it down to the new generations.

Considering how this technical and artistic knowledge was handed down, from one generation to another, during the years of practice, the risk to lose all this heritage with the current industrial progress is real.

The platform chosen for this Virtual Exhibition is a CMS software (Content Management System) that allows to handle different kind of contents, like photos, videos and more.

The Exhibition is designed to guide the visitor through a main path, that starts with the first steps of gold manufacturing.

The main menu, at the top, has several sections, including the one that leads to the heart of the Exhibition: the "Virtual Tour" (*Visita Virtuale*) (Fig. 4). This one is dedicated to the working stages of precious metals

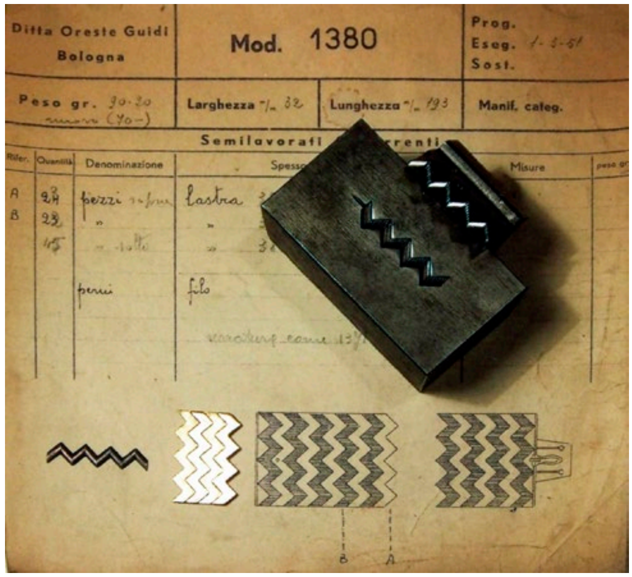

Figure 2. Technical sheet and its mould from Ditta Oreste Guidi.

Figure 3. The "History of the Collection" (*La Storia della Collezione*) page, and a picture of young Adelmo Garuti in the Romano Degli Esposti's workshop.

and starts from the melting of gold, going on with rolling, drawing, engraving and so on. A multi-level menu shows the user how the tour is structured, step by step, so he can choose to follow this *fil rouge* or not.

Every working stage is explained in detail, focusing on the tools and machineries employed, with particular attention to those from the Collection.

Some of them have also dedicated pages, because of their importance in the working process or for their rarity (Fig. 5). After each explanation there is a gallery of

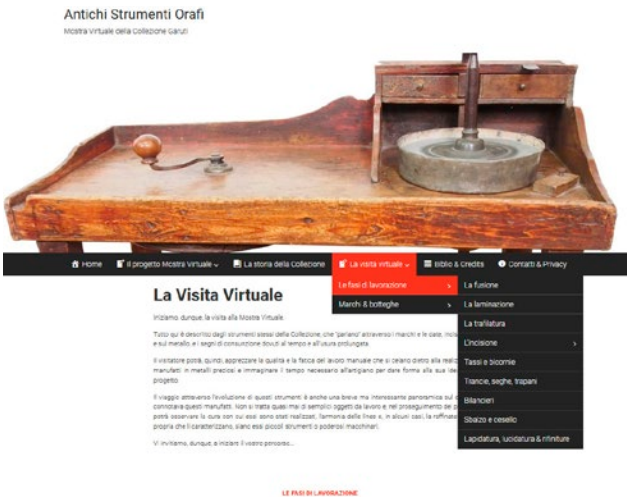

Figure 4. The multi-level menu of the "Virtual Tour".

Figure 5. The multi-level menu and one of its pages, dedicated to relevant objects.

Figure 6. The "lens" tool at work, a square window to see details on the surface.

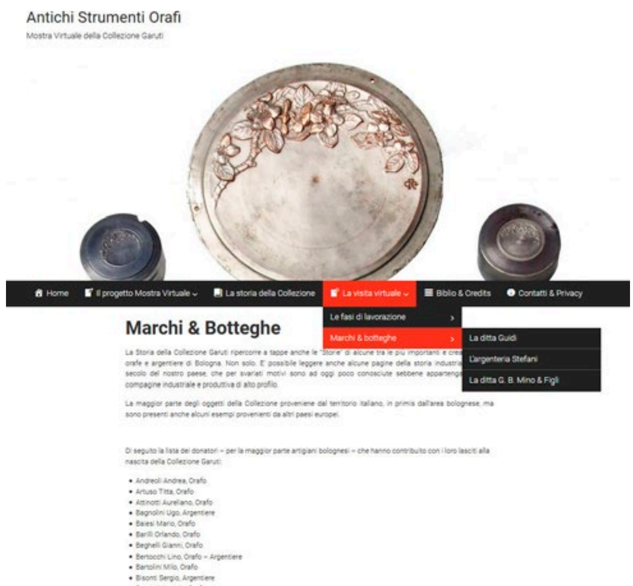

Figure 7. The "Factory Brands and Workshops" page and its related sub-sections.

all the objects referring to the page. The user can watch them one by one, with a slide show. At the end of each section visitors can go on with the guided tour or jump to another section at their will.

Many of the machineries are manually operated and for some of them videos have been provided to show their functioning. More videos will be recorded in the next future to increase that kind of contents.

Every page has links to specific contents, that send back to other sections of the exhibition, or lead to other external contents shared by on-line museums or digital archives.

A dedicated tool gives the visitor the opportunity to look closely into every object with a special lens. It allows the observation of specific details on the surface of the objects, like dates, brands, colours and signs of use (Fig. 6).

Concerning brands, as previously said, there is a special section dedicated to the history of the workshops and producers of the objects exhibited. This section is called "Factory Brands and Workshops" (*Marchi e Botteghe*) and leads to three different sub-sections (Fig. 7). One is dedicated to the Ditta Oreste Guidi, established in Bologna in 1898 and closed before the early 2000s. The second one is about another important workshop in Bologna, established in 1909 by Enea Stefani. Stefani mainly worked silver objects that are still highly renowned and appreciated even after the closing of his shop, occurred in 2015.

The third subsection is dedicated to an Italian factory – established in Alessandria in 1840 by Giovanni Battista Mino – and therefore called G. B. Mino & Figli. The Mino factory produced machineries and tools for goldsmiths and silversmiths and received awards from the Italian Government for its innovations in this sector. The Garuti Collection has numerous objects from Mino, especially rolling mills and drawing plates.

There are also machineries from foreign countries like Germany, France, United Kingdom and from the U.S.A.

The "*Antichi Strumenti Orafi*" Virtual Exhibition is still improving its contents, with researches and new relevant acquisitions. This project cannot be considered completed, it's still in progress and our purpose is to offer the public new sections and increase the current ones. Sharing and dissemination are as important as preserving objects, because we now live in a transition era. Some professions are now referring more and more to machines, therefore we are losing some techniques and know-how that are not reachable in books but are learned from every day practice and from the voice of old artisans.

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Do monetary systems rediscover precious metals in the era of 'bitcoins'?

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Keywords. Monetary systems, bitcoins, precious metals.

Current monetary systems are based on a fiduciary currency. In fact, the international exchange of goods and their valuation is currently in US dollars, despite the unlikely decline of that currency in the times to come. Actually, the question is often asked whether it is possible (when and how) that another system of payment instruments shall replaces the dollar.

Since its historical memory, "La Moneta" has met two needs: value reserve and transport values in time and space. Like a trunk, like a railroad car, like a cart carries, the coins bring the value from one place to another. In a patriarchal economy of floats and trunks, few carriages were needed. Gold, as well as its favourite lieutenants, silver and copper, also indestructible, transferred values in time and space sufficiently. Gold, like other metals, therefore had an intrinsic value, free from the dangers of a regulated and representative currency, from one day to the next, it could have reduced its purchasing power and could have inflated itself; or be treasured, provoking deflation. As described by Mr. Gresham, the coin that always confirms its value, drives away the one that is not able to do it. Gold, as well as silver and copper, took the place of the 'pecunia' (from sheep, livestock) and of the 'salis' (salt, salary), thanks to their uniformity of value in time and space.

Consequently, inflation also occurred in metallic money systems too. The Roman emperors, from Nero up to the 3rd century, they had entrusted themselves to the Augustan system, articulated on four minted metals: gold, silver, orichalcum (copper and zinc alloy, like our brass) and copper. The deception consisted in the reduction of the precious metal contained in the coins: in those of gold and silver it passed from 99% in the Augustan age, to 50% of the times of Caracalla. The situation became unsustainable during the chrisis of the third century and the economic system always collapsed in the time of Diocletian. The military demanded continuous increases in salary, the imperial bureaucracy absorbed most of the resources, and taxation was becoming too high in the countryside.

In 301 A.D., the Emperor issued an Edict which established the prices of the principal goods. For that reason everything stopped, nobody sold goods in exchange for money. The monetary circulation disappeared and it was unnecessary to mint more coins. Thus, one wagon that made one trip a day, was equivalent to seven wagons with one trip per week. The Edict was, as it was to be expected, a complete failure. Shortly, after Costantine he tried again and, unlike Diocletian, did not pretend to stabilize the prices of products by decree. Costantine fixed the parity of the circulating currency with fine gold, instead: in 310 A.D., he introduced a new gold coin, the "*solidus aureus*", beaten to 1/72 of lbs (= 4.54 g) unchanged. The 'solidus' (that comes with the modern Italian term "soldo", that means 'money') guaranteed, the weight and the title in gold for decades, restoring trust to long-distance value relationships between the various part of the vast empire and over time. The fall of the empire would not have happened for monetary reasons thanks to the safety of gold and coins.[1]

Roman monetary affairs of the 3rd century certainly happened also in previous civilizations, and they would be repeated again in the following centuries.

Instead, what happened at the dawn of modernity, at the beginning of the eighteenth century changed the history of money systems and the lives of men. Since the earliest times of which we have witnessed until the Industrial Revolution, especially in England in the eighteenth century, the lifestyle, habits, rhythms and '*traditio*' (cultural heritage) had not undergone sudden changes in any of the great human civilizations on earth. During the centuries, without traumas, economics and exchanges, cultures and ways of thinking, had seen grandparents, fathers and sons "live in the same meanings" with techniques and productions that did not register sudden changes. The massive inflation under Emperor Diocletian[2], but also wars, invasions, famines and the black plague of 1247 in Europe had never been able to settle deep gaps among generations. Until the first half of 1700 the world changed without rapid jumps and heavy falls.

The industrial and monetary revolution, first of all, in England in the eighteenth century, on the contrary, speeded up the changes in the economy and lifestyles in a short time. Originating from three factors, namely technical improvements, capital accumulation and the introduction of paper money, the changes that have occurred in the last three centuries are only comparable, probably, to what happened at the end of the last ice age, before the beginning of the ancient history. Steam trains, assembly line, Taylorism in industrial production, coal, electricity, petroleum, chemistry, plastics, steel, industrial automation, optical fibers, nuclear applications, nanotechnology, spacecraft, and so on, represent the evolution, amazing and fast, of the production techniques of modern time.

In modernity, it could be glimpsed a second factor, the accumulation of capital, whose beginning we can date at the beginning of the seventeenth century, thanks to the return of Sir Francis Drake's flagship Golden Hind. In "the year of grace" 1580, Golden Hind landed in the Thames estuary with the cargo of gold stolen by Drake from the Spaniards by boarding the Galleon Nuestra Señora de la Concepción. The expedition had been financed by Queen Elizabeth of England herself, who personally climbed on the newly moored Golden Hint to meet and greet Sir Francis. The loot, equal to 6 tons of gold, was used to pay the entire substantial foreign debt of the British. There were still £ 40,000[3] left over, invested in the Levant Company in the A.D. 1600, then Company of the East Indies, and imperial British army until 1874. The 'English centuries' began from that moment, time and space of the British global hegemony in history. An essentially maritime domain, based on military projection, with a first-rate and technological background and, as a third factor, due to modern monetary changes, thanks to the monetary projection based on the pound with a golden background. The introduction of paper money by the British Empire in 1694 represents, in fact, an epochal turning point for the history of economics and an instrument of incomparable domination.

Therefore, it was Industrial and Technical Revolution, accumulation of capital and, finally, paper money. Until 1694, in England and elsewhere, the only officially circulating currency was the coined coins. And, as in ancient times or those of Augustus and Constantine, metal coins have always had an ingrained value. Since 1694 a bill was issued, the pound sterling, subsequently produced in series from the early 1700s as gold-based paper money: it corresponded to a fixed exchange with gold deposited at the Bank of England. For that reason, it was called "Gold Standard", but gold did not circulate "physically" any more: in the hands of men from that time the paper was circulating and no longer metal. The paper can be printed without limits, while any metal must be extracted from the mines. The English 'golden system' will remain the foundation of the British Empire until 1914. The issuing banks after 1694 became almost all private (they are still today) and the public coinage and metal will remain

[1] In fact, the fall of imperial Rome in the West occurred in the fifth century for military reasons and political feuds within the Roman Senate, while Constantinople with the new monetary system (the Greek Byzantium) remained standing up for centuries.

[2] It drove silver completely out of circulation.

[3] It is estimated that every pound brought home by Drake has been transformed, in almost three centuries, into 100 thousand pounds thanks to the compound interest of 3.25%.

residual. No one would have been able to verify the carats of gold coinage any more, or the weight of gold kept in deposits. The printing of banknotes allowed to increase of the resources of the state budgets based on the confidence that the banknote received. Alexander the Great in Persepolis and the Inca treasure of Pizzarro had recorded the dispersion of immense quantities of gold and precious. Now the gold that the Rand miners had brought to light was concentrated and buried again in the Central Bank's warehouses.

But the loss of value of "paper money" can sometimes be faster than the "metallic one". The Vladimir Ilič Lenin's (1870-1924) hope, after the end of the British 'Gold standard' in 1914, was that inflation would cause the collapse of capitalims: "governments confiscate with secret hands, promote the 'rentiers', they depress trade". This is the premise for the "revolution in the capitalist countries". Indeed, the post-war economic crisis will have more complex connotations linked primarily to deflation more than inflation. Deflation is not only a problem of the twentieth century. Certainly, the deflation was the origin of the crisis of 1929, illustrated by J. Maynard Keynes (1883-1946). Lord Keynes proved how excess production capacity compared to aggregate demand was the primary cause of deflationary phenomena, provoke even more damage than the German inflation of the Weimar Republic. The British attempt to restore the Gold standard, which lasted until 1931, will produce heavier effects than any loss of purchasing power of the currency. The same Gold has been, during the history of civilizations, a sovereign whose defects have remained hidden by utility. As difficult to reproduce, sometimes monopoly of caves, disputed, the gold and the silver can't in fact transport all the wealth produced by man in times and spaces. The claim of the British Empire, also at its own epilogue in 1930, to repropose the pound at the gold base at the centre of international trade. As Keynes writes, what matters is not the exchange rate between gold and pound that does not involve an increase in production, but the impulse of consumption and aggregate demand: if the products remain unsold and the warehouses are full of stocks, it is useless produce again, while the money saved will not be invested in new plants and machinery. To increase the circulation of money, with the pound tied to a fixed parity with gold, it would have been necessary to discover new mines. It does not happen with the fast pace and lilts of modern technological progress.

Since 1946 the Dollar Standard replaced the pound as international reference currency. Carriages, wagons and trunks were now called Dollars in the new system. Reserve money and world transactions, like the pound sterling until then, flanked the gold with a fixed parity of $ 35 per ounce of gold. The proposal of the 'Bancor' proposed by Keynes in 1943 as part of a project, not implemented, of union for international compensation (International Clearing Union) was discarded in the new American imperial vision. The "*Novus ordo saeculorum*", motto taken from Virgil's Eclogue IV, even printed in US Notes, has a clear meaning. Other quotes from Virgil, the American "Founding Fathers" had, moreover, reported in the 'Great Seal' Usa, such as that readable on the back of the same dollar bill: "*Quid non, mortalia pectora cogis, /* ***Auri sacra fames***"[4]. Keynesian commodity money was therefore discarged. In July 1944 at Bretton Woods, New Hampshire location where the Dollar Standard was approved, US currency was chosen like international currency paper. This exchange system was established by a state under a monopoly regime.

It lasted less than the English currency in the gold exchange and it was abandoned in 1971. Without any link with gold, after 1971, the Dollar is still today the most internationally recognized payment instrument, despite the fact that at the end of the 1999 the so-called derivatives circulating in the world amounted to 30,000 billion dollars, equal to 285% of world GDP; and, only ten years later, at the end of 2009, they had reached the rating of 690,000 billion dollars, that is 1057% of world GDP.

The path of history, of scientific discoveries, of technologies, up to the eighteenth century, initially very slow and then, faster and faster, accompanied by the invention of banknotes, fiduciary money and credit, has determined in the monetary systems the replacement first physically and, subsequently, also of purely theoretical reference of precious metals and of gold in particular. Finally, to the present day, we have passed from Paper banknotes to credit plastic card, to reach Crypto currencies, a pure technological sign far away from concrete goods and services provided. Just the 'digital currency'.

An operation in crypto currency has its own specific ID code, its name and surname and its history. If Romeo buys a meal with coin A (e.g./ ID: 834567), the transaction puts in the archive the passage of currency 'A' from Romeo's wallet to Juliet's in exchange for an asset. The link between a Bitcoin platform and the Cripto currencies, established in 2009, manages transactions and exchanges of information and data in the finance and payment areas. The proof of the passage of the new property is created thanks to a digital signature

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[4] On the American Banknote there is also another quote: 'Annuit coepitis' (**God is in favor of the enterprise**) taken from the Trojan prayer to Jupiter «Audacibus annue coepitis» (**Almighty Jupiter, consents to the audacious undertakings**, aeneid, IX, 625)

of the transaction. In order to use Bitcoin currency as an exchange currency, simply install an application on your computer or mobile phone. The currency of Ethereum, for example, takes its name from a "virtual currency" called "Ether" which itself represents the possibility of producing the shops in cryptocurrency "Ether" by it we can "pay" for the realization of contracts. Ether is basically and concretely a 'token' with an attached digital signature, whose trust is at the base of the Ether or Bitcoin system. Messages are encrypted and access keys are available only to those who are part of the network. The control system, called Blockchain, allows all participants to confirm or not a transaction. Bitcoins are virtual but produce the same effects of traditional banknotes. Therefore they do not represent anything in the physical world, but they have value for the mere fact that people agree to exchange them with goods or services, in order to have an ever greater number on their account, convinced that other people do the same.

The new global computer technologies, based by search engines, artificial intelligences in the service of finance, have magnified the global speculations. The "quick earnings" ('*subiti guadagni*') are also mentioned by Dante Alighieri (1265-1321) with reference to the Black Guelphs in the 13th century Florence. A finance whose wealth expands without control and without limits by the individual nations and the central banks themselves; without the limits that the golden base had, even with its defects, and which had guaranteed the ancient empires. The triumph of the representative credit currency is today at its peak in the world of transnational finance and the introduction of the bitcoins. Modern finance and its many products, hedge funds, the protagonists of speculation, have passed the stage of printing banknotes without a gold standard as in 1694. The new phase registers the use and the loan of money that do not even exist. It has not been printed by any Central Bank. This is the moment of virtual money. Will it last? Will be there any surprises?

In 1930 Irving Fisher (1867-1947), in his work "Monetary illusion", proposed one currency based on a basket of goods. A real currency in which gold could combine real products to guarantee the circulation of money. The Keynesian idea of 'Bancor' could also have foreseen a basket of coins similarly to what was represented today by the IMF's[5] special drawing rights, whose values were based on a basket of national currencies. Will we go, with a delay of over 70 years, in this direction? Will Gold and Silver remain the prerogative of the production of prestigious jewels of the great Goldsmiths in Arezzo and elsewhere, or will they remain deposited in the vaults of the Central Banks? A wagon in a dead track, a trunk in the attic or in a vault are no longer currency, but a store of value.

Gold is to be returned to Goldsmiths only? Or will the monetary systems rediscover the Gold and other precious metals to ensure a circulation without 'volatility', not subject to speculation and ' quick earnings'?

[5] International Monetary Funds.

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Gold parting with nitric acid in gold-silver alloys

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Abstract. This article is an overview of gold parting with nitric acid on a both industrial and laboratory scale, supported by more recently reported experimental and theoretical studies on the gold dealloying process for the fabrication of nanoporous gold material.

Keywords. Parting, assay, gold refining, dealloying, nanoporosity.

INTRODUCTION

Metals have played a fundamental role in human history and were the basis for the development of ancient societies. Precious metals and gold in particular have always been considered status symbols and a measure of power. In all likelihood gold was one of the first known metals due to its presence in native form as grains or nuggets [1]. As soon as gold was discovered, men recognized its extraordinary properties, such as malleability and incorruptibility, which differentiates it from all other metals.

The earliest gold artefacts known to us were found in a pre-historic settlement in southern Bulgaria and date back to 4500-4600 B.C. [2]. However, the metallurgical expertise required to purify gold did not develop until the second millennium B.C. Most gold in its natural state is a gold-silver alloy (*electrum*) containing other base metals as impurities [3]. In the latter case, purification was historically achieved via cupellation, although this metallurgical treatment was originally conceived as an extractive process of the silver contained in lead ores, and only later it also became a refining and assay process of alloy gold metals [4]. However, the separation of gold and silver, generally referred to as gold parting, cannot be done via cupellation. The oldest gold parting process involved salt cementation and the first evidence of this dates back to the 6th century BC in Sardis, Lidia [5]. In this process, silver metal was converted into its chloride salt by alternating thin sheets of gold alloy with layers of a mixture of sodium chloride, brick-dust, vitriol, alum, and other materials which were then heated together in a sealed pot. The main drawback of the cementation process is a tangible loss of material, though a high-grade gold purity can be achieved. With the discovery of the nitric acid synthesis, cementation soon became obsolete. Alchemists were pioneers of this approach as they recognized that this new product was ideal for the purification of gold in silver- and copper-gold alloys. Nitric acid could be made by distilling saltpeter with a specific sulfate salt, the choice of which historically fostered the dissemination of a variety of terms [6]. For example, the term *spiritus nitri* was used when nitric acid was made from saltpeter and alum, while it was called *aqua fortis* when made from saltpeter and vitriol (such as iron sulfate, known as green vitriol) according to the follow reaction:

$$2KNO_3 + FeSO_4{\cdot}7H_2O \rightarrow 2HNO_3 + FeO + K_2SO_4 + 6H_2O \quad (1)$$

The first mention of nitric acid is in the writings of Pseudo-Geber, who described its obtaining from calcining a mixture of saltpeter, alum and blue vitriol (copper sulfate) [7]. However, nitric acid preparation was no simple matter and it is likely that only small amounts of this compound were originally available, thus allowing for only limited-scale treatment. Nitric acid concentration and purity were the main challenges throughout the Middle Ages and the Renaissance. Indeed, hydrochloric acid was often present because saltpeter contamination with potassium chloride and this made nitric acid unsuitable for gold parting. Prior to gold parting, small quantities of pure silver were added to the acid solution as a sacrificial reagent to precipitate chlorides. After Geber, more detailed descriptions of gold parting with nitric acid appear in the writings of Vannoccio Biringuccio [8], Georgius Agricola [9] and Lazarus Ercker [10].

In the nineteenth century, the large-scale nitric acid production using the Birkeland–Eyde, and thereafter the Ostwald process, via nitrogen and ammonia oxidation respectively, allowed extensive use in gold refining on a commercial scale. In the modern period, gold parting with nitric acid has been largely replaced by other treatments such as chlorination using the Miller process [11]. Nonetheless, nitric acid is still used today in the parting stage on the laboratory scale after cupellation assay.

PARTING WITH NITRIC ACID IN GOLD ASSAY AND REFINING

Gold parting consists of a selective corrosion process, also known as leaching or dealloying, which is based on the "incorruptibility" of gold to nitric acid. As a result, in the case of silver-gold alloys with a suitable composition, silver is oxidized and transfers into the solution as silver nitrate. If an alloy contains also other metals, these elements can either be solubilized like silver (*e.g.* copper) or behave in the same way as gold (*e.g.* iridium). In addition to these two borderline cases, other metals can be partially dissolved (*e.g.* palladium) or lead to the formation of insoluble compounds (*e.g.* tin).

On a laboratory scale parting occurs after cupellation, which consists in an oxidative fusion in which samples are melted with lead in a cupel at 1050°C [12, 13]. Atmospheric oxygen reacts with lead to form litharge (lead oxide), which catalyzes the oxidation of the other base metals present in the sample as alloys. Magnesite cupel absorbs the metal oxides, leaving only precious metals in the cupel as small doré bead made up of noble metals, generally silver and gold and PGMs (Platinum Group Metals). This alloy usually contains insufficient quantities of silver to be oxidized by nitric acid. When parting is used as assay, selective dissolution of silver is quantitative and the residual gold compacts enough to be weighed after annealing without powdering on handling. For this purpose, the first operation is designed to make suitable Au-Ag alloys, which consist in three parts of silver and one of gold, hence the term "inquartation process". At this point, the common procedure is to melt bead with pure silver to generate a suitable alloy. After the inquartation process (Figure 1a) and prior to the parting process, bead is hammered (figure 1b), annealed, rolled to a thin strip (Figure 1c), annealed for a second time (Figure 1d) and rolled up to a shape like ionic order column volute (Figure 2). The hammering and rolling stages serve to increase the surface area for the subsequent silver dissolution with nitric acid, while annealing is designed to relieve residual stress. Moreover, a second rolling stage must be carried out to allow the wettability of the whole surface, thus avoiding the occlusion of impurities as oxides obtained from the previous cupellation process. In this regard, the ionic volute is probably better than the cornet shape (Figure 2), as Battaini *et al.* pointed out [14], on the basis of the greater distance between the internal metal walls. The parting process takes place in two stages by keeping the sample in boiling nitric acid inside a Kjeldahl flask, which has a long neck. The first treatment makes use of a 5.6 M nitric acid aqueous solution (22°Bè) and the second one of a 9.4 M nitric acid aqueous solution (32°Bè).

The stoichiometry of pure silver and copper reactions with nitric acid have been the subject of a great deal of enquiries and, in particular for the latter metal, the attribution of the correct reaction coefficient sets is discussed in several articles reported in the literature [15]. The oxidation of silver by nitric acid takes place mainly according with the following parallel reactions [16]:

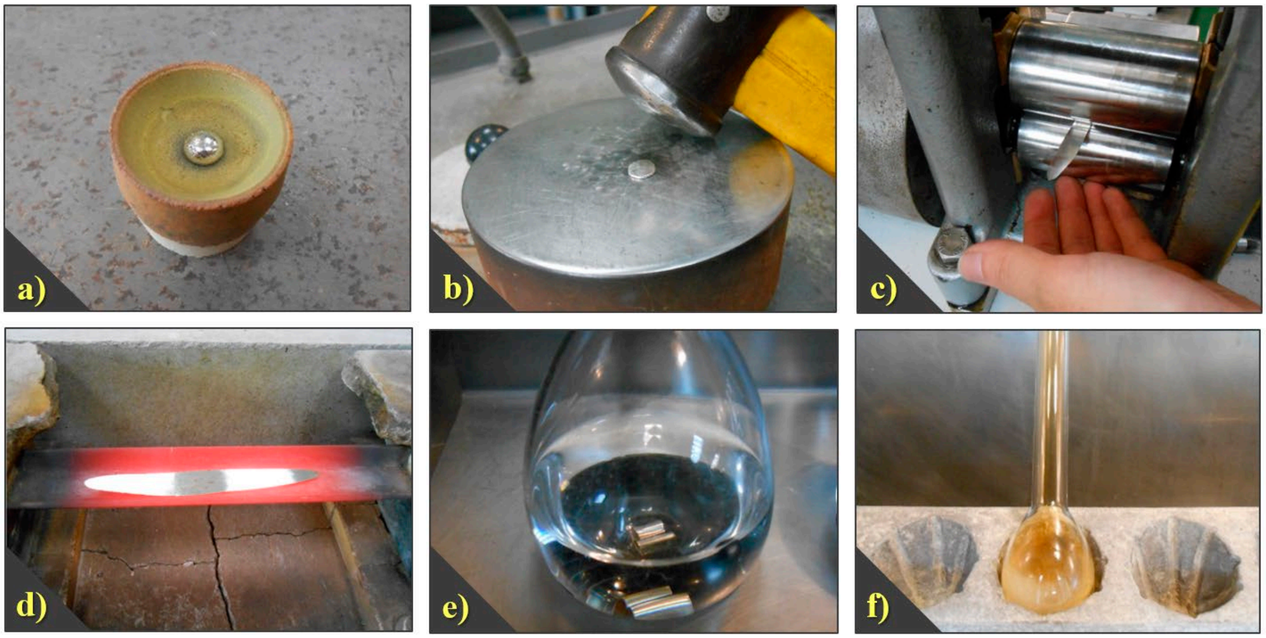

Figure 1. Characteristic gold parting steps on a laboratory scale. After the inquartation stage (a), the precious metal bead is hammered (b), rolled (c) and annealed (d). The parting process occurs inside a Kjeldahl flask (e), keeping the rolled specimen in a boiling acid solution (f).

$$4HNO_3 + 3Ag \rightarrow 3AgNO_3 + NO + 2H_2O \quad (2)$$

$$2HNO_3 + Ag \rightarrow AgNO_3 + NO_2 + H_2O \quad (3)$$

As reported by Martinez *at al.* [17], it is possible to determine the contribution of each reaction by titration of the unreacted nitric acid moles in relation to the moles of silver dissolved. In the case of high concentrated acid (5.3 M) the reaction (3) dominates, on the contrary when the concentration is low (2.5 M), nitric oxide is the main nitrogen product, according to the reaction (2). Similar behavior has been also observed for Au-Ag alloys, suggesting that, during parting stage, reaction (3) represents the main contribute for silver oxidation.

In the case of large-scale refining, a correct balance between a suitable separation gold-silver alloy and the rate of dissolution should be considered. Indeed, gold parting is not necessarily quantitative. In all likelihood, this compromise is the main reason for the different silver content values recommended by scholars which ranges from 60 to 80% [12, 18, 19].

In the case of the laboratory scales discussed above, beads obtained after fire assay are rolled in order to increase the surface area. The same strategy can be used on an industrial scale. The operations involved are similar: first of all, the material is heated to a dull red and chilled in cold water to anneal it. Then it is rolled and the thin foils thus formed are twisted into what

Figure 2. Cornet (top) and volute shapes (bottom) in the same rolled cupellation bead.

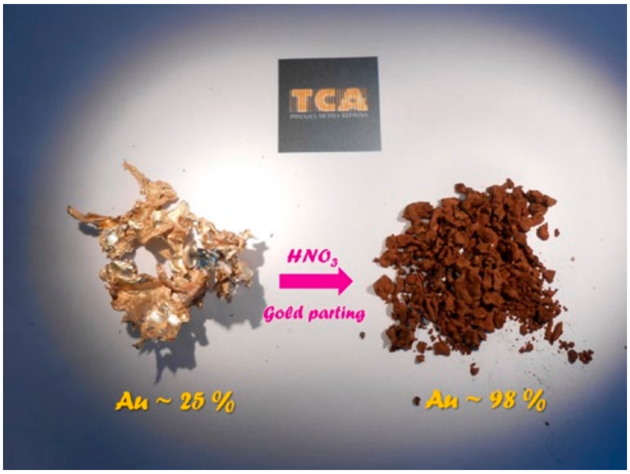

Figure 3. Effect of the silver dissolution by nitric acid on the gold-silver alloy grains.

are called cornets to prevent them from lying flat in the reactor. The second and more common approach is granulation. After melting, the molten alloy is poured into cold water with a thin stream moving the crucible in a circular motion or bobbling air in the water. The grains are small shell shaped (Figure 3).

The parting process takes place in two stages involving nitric acid solutions with different concentration. The solution is often heated only at the beginning because silver dissolution is exothermic. Generally, the nitric acid concentration is lower in the first process than in the second, but this is not a rule and the formulation changes from company to company [19]. A small amount of silver is removed by the second nitric acid treatment and this solution may be used once again in a subsequent parting treatment. When the reaction is finished or the acid is exhausted, hot water is added to have more solution for the decantation of residual gold, avoiding the precipitation of silver nitrate.

In contrast with the laboratory scale, the firmness of the residual gold is not necessary even if it involves different types of reactors and filters. This is due to the fact that gold content varies from a minimum of 1%[1] to a maximum of 35%, close to the value used in assay.

Concerning the reactor, parting is normally carried out in steel vessels including roto-barrels (tumbler machines) or tanks, which are equipped with a rotating basket. The right choice between the two model plants is dictated by the physical form of the final gold product. Indeed, when the gold content in the bullion is low and/or there is a quantitative presence of other base and precious metals, the formation of impure and gluey gold powder requires the use of a rotating basket which is suspended in the tank. This arrangement enables the powder to be continuously separated from the grain and avoids the passivation of the latter. Particle size is related to gold concentration in the alloy, the presence of other metals and reaction conditions. If gold content is less than 1% the dealloying process can lead to the formation of undesirable gold colloids which are difficult to separate[2]. Generally, gold powder is separated using a filter press.

By contrast, when parting is carried out after an inquartation process, the bullion conserves some of its firmness and a roto-barrel can be used for the reaction (Figure 3). This reactor consists of a cylinder tilted to about 20-30 degrees which rotates by means of a motor. In such cases, solid-liquid separation is simpler and industrial Büchner funnels are commonly used. Parting pure Au-Ag alloy alone is rare and the quantitative presence of other metals is common, however only traces of base metals such as tin[3] and antimony should be present for a satisfactory refining [19].

After filtration, parted gold is washed with hot water and finally melted, obtaining bullion ranging from 994 to 999 fine. Moreover, silver is recovered from the spent nitric acid solution as insoluble chloride salt or by means of cementation with a more electropositive metal (*e.g.* iron).

Alternatively, gold parting can be carried out with sulfuric acid. On a laboratory scale this is suitable when the specimen is a silver-rich alloy. From an industrial point of view, sulfuric acid is a cheaper reagent than nitric acid, which incidentally it also has the drawback of generating toxic pollutants such as nitric oxide (NO) and nitrogen dioxide (NO_2) according to reactions (2) and (3).

Nitric oxide reacts instantly[4] and almost quantitatively with atmospheric oxygen to produce nitrogen dioxide [20]. Conversely, the kinetics of the nitrogen dioxide adsorption are relatively slow and large scrubbers are required to provide minimum residence times for complete removal. The scrubbing of nitrogen dioxide with water results in the production of nitric acid and nitric oxide as the following reaction shows:

[1] Note that in this case the separation of the two metals using electrorefining should be taken into account. This approach is cheaper and the final product is pure metal silver (99.95% or more). The impure gold is recovered as sludge and after melting it can be parted with nitric acid.

[2] This problem can be overcome by treating the sol with activated carbon.

[3] Tin is oxidized by nitric acid to gluey insoluble Sn(IV) oxide which passives the grains, hindering their further dissolution.

[4] In the gas phase, this oxidative reaction is second-order in NO because a transient dimer (NO_2) is produced which subsequently collides with oxygen molecules. Because the reaction is second-order, the concentration of NO seriously influences the rate of oxidation. In this case, the high concentration of NO ensures fast oxidation.

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \quad (4)$$

The reaction is exothermic and thus the liquid circulated over the scrubbing equipment may be cooled to increase absorption efficiency. The nitric oxide generated undergoes oxidation by atmospheric oxygen to produce new nitrogen dioxide. As a consequence of this tandem reaction, where the product of one process generates the starting material for another, large scrubbers are required to provide minimum residence times for the NO_x removal in order to fit into legal emission limits. Significant residual NO_x content in the exit gas stream is typically abated by absorption into an alkaline solution in a second tower. Moreover, from an industrial point of view, dilute nitric acid has little or no value and, in practical terms, represents a waste treatment problem[5].

To reduce the volume of the towers, either air or oxygen may be introduced into the gas or liquid phases to improve nitric oxide oxidation rates. Formally, the generation of NO_x by metal dissolution with nitric acid may be overcome by moving the oxidation of nitrogen oxide from the gas phase to the reaction solution. This goal can be achieved using hydrogen peroxide, according to the follow overall reaction [20, 21]:

$$2Ag + 2HNO_3 + H_2O_2 \rightarrow 2AgNO_3 + 2H_2O \quad (5)$$

Another approach is the reduction of NO_x with soluble ammonium nitrate [22]. In this case, the *incipient* formation of NO_x in solution reacts with the ammonium nitrate release of nitrogen gas according to the follow reactions:

$$2NO + 3NH_4NO_3 \rightarrow 3N_2 + 2HNO_3 + 5H_2O \quad (6)$$

$$2NO_2 + NH_4NO_3 \rightarrow N_2 + 2HNO_3 + 5H_2O \quad (7)$$

GOLD PARTING: A MICROSCOPIC ENQUIRY

Gold parting with nitric acid in gold-silver alloy has been the subject of several studies supported by theoretical and experimental data. Martinez *et al.* [17] systematically studied the effect of silver-gold alloy composition on silver dissolution using a 6.56 M nitric acid solution at 80°C for 48 hours. Their experiments showed that such alloys become completely resistant to nitric acid oxidation when the gold content is greater than 40% by weight. This value is the so-called *part limit* above which the dealloying process is quantitative. The various thresholds reported in the literature are due to different reaction conditions such as lower temperatures or lower nitric acid concentration. However, from a practical point of view, the relationship between the dissolution rate and the composition of the alloy should be taken into account. In particular, in the case of the inquartation process, when the gold content is 25% by weight, the dealloying process is slow as compared to that of other silver-rich alloys [17, 23].

During the dealloying process, in the first instance, a static model in which silver ions may exit the alloy lattice only through the holes previously generated by the dissolution of more superficial silver atoms without invoking any type of atomic rearrangement might be assumed. On the basis of this consideration, after the first selective dissolution of silver on the surface, the progress of the reaction depends on composition and alloy metal lattice. The exclusive presence of face centered cubic lattices for any metal Au-Ag composition alloys, partly due to almost identical radii, makes the model easier to describe and analyze. Each atoms in the lattice displays a coordination number of 12 and the probability that a gold displays *n* homometallic contacts can be calculated using statistic equations [17].

Trends in these probabilities against silver-gold alloy composition are reported in Figure 4. In particular, for $Au_{25\%}$-Ag alloys, gold atoms come principally into con-

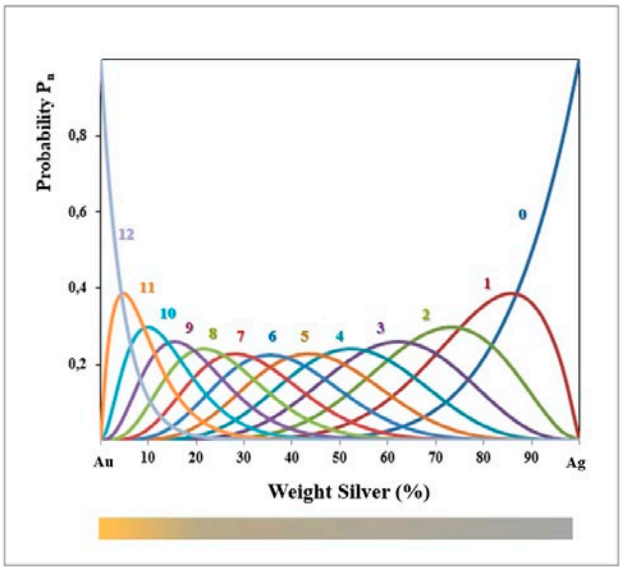

Figure 4. Probability (P_n) for a gold atom to display *n* homometallic contacts against the percentage of weight silver in gold-silver alloys. P_n functions are calculated using the same statistic expression used by Martinez *at al.* [17]. Note: the absence of a mirror plane across 50% of the silver is due to the different weights of the two precious metals.

[5] The dilute nitric acid recovered by this process may be returned to the process. Basically, it is used as "water dose" for the other parting treatments.

tact with one or two other gold atoms, although the presence of gold with three and zero Au-Au contact is not negligible. Thus, with this composition, the random alloy lattice excludes the presence of suitable preformed gold networks as required by a static model in order to justify the lack of powdering. Moreover, without any type of atom surface diffusion, it might be expected that dissolution would stop after about 4-5 metal monolayers have been dissolved, making the separation of the two metals non-quantitative. This is in contrast to experimental values [17] which show quantitative dealloying characterized by a faster dissolution rate than those observed in the case of pure silver (99%).

Thus, a simple static process in which silver is removed by means of nitric acid, which leaves only gold atoms inside the bulk alloy, is not sufficient to describe exactly what happens. From a macroscopic point of view this is corroborated by volume contraction and an unexpected product color obtained after the dealloying process. Indeed, after the parting and subsequent annealing stages, the $Au_{25\%}$-Ag alloy shows characteristic shrinkage, with memory of form, that is particularly visible in the case of laboratory scale assays. Moreover, after the dealloying stage, including when parting is quantitative, gold color is not the characteristic bulk phase yellow but generally brown.

In order to give a qualitative idea of this phenomenon, parting and annealing stages starting from an $Au_{25\%}$-Ag alloy specimen with a TCA logo shape are shown in Figure 5. Dealloying occurred in two stages using 22° and 32° Bè boiling nitric acid for 30 minutes respectively. After parting, these fragile specimens were slowly dried in the oven at 105°C (Figure 5b) and finally put into a furnace at 1050°C (Figure 5c).

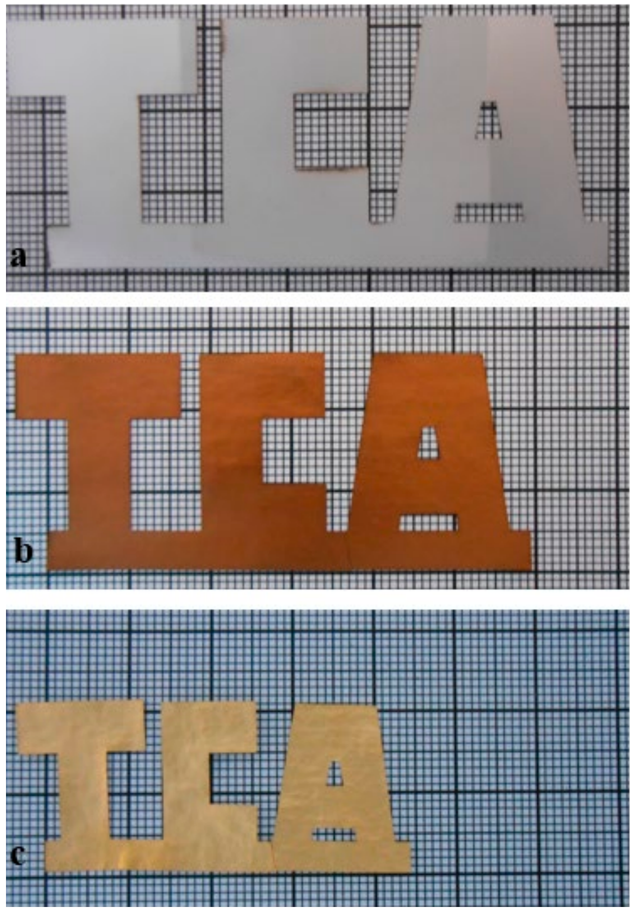

Figure 5. Effect of gold parting (b) and annealing treatments (c) on an $Au_{25\%}$-Ag alloy specimen (a) with TCA logo shape.

Battaini *et al.* [14] described the changes in shape and color during the parting stage with an extensive study by means of scanning electron microscopy, which revealed the nanoporosity architecture obtained after the parting stage. The nanoevolution of porosity during dealloying is well known, and over the last two decades it has received great attention from the scientific community [24-27]. Indeed, the porous gold materials obtained by selective dissolution of silver present numerous potential applications as functional materials on the basis of their chemical stability and unique surface chemistry[6]. As a result, fabrication of newly performed tailor-made porous gold materials, and their related characterizations, have favored an understanding which moves in the direction of a clearer vision of what happens in gold parting.

However, whilst the first detailed look by Forty at the porosity formed by dealloying processes using electron microcopy dates back to 1979 [28], the mechanisms involved in the gold nanoreorganization were studied only two decades later. According to Erlebacher's studies [29-32], during silver dissolution, gold is freed to move along the surface, reorganizing into a three-dimensional network, which generates nanoporosity. The dissolution of silver primarily involves atoms from surface defects, *e.g.* terraces or steps, which are more reactive [30]. This leads to the creation of terrace vacancies that then grow sideways into vacancy clusters as lateral near neighbors are subsequently dissolved. As a consequence of silver oxidation, unsaturated gold atoms, which are thermodynamically unstable, move from low- to high-concentration areas leading to the formation of two-dimensional

[6] Whilst several other methods have been developed to fabricate porous gold materials such as sintering, templating and additive manufacturing, the dealloying approach has attracted remarkable interest on the basis of its simplicity and reproducibility [25]. In addition to chemical gold-silver dealloying, the subject of this work, the selective oxidation of silver may be carried out by electrochemical and liquid metal dealloying.

gold clusters. As dealloying proceeds, new gold-silver layers are exposed to nitric acid solution around the base of the gold islands previously formed in the top layers after dissolution and surface reorganization. The three-dimensional development of such gold islands results in gold covered hills with base perimeters that grow in diameter as dealloying proceeds. This increased surface area requires more gold atoms compared to the gold adatom generated, leading to undercutting and bifurcation of ligaments. The result of this process is a continuous porous structure with gold-rich surface ligaments. The large surface area to volume ratio of these ligaments leads to metastable nanoporous structures. Thus, the length scale of porosity tends to increase over time and, as the atoms move from smaller to larger ligaments, residual silver atoms are exposed and dissolved.

Thus, from a kinetic point of view, the dealloying process can be viewed as a competition between three processes: (i) silver dissolution; (ii) surface diffusion of gold and (iii) mass transport of the dissolved silver ions and the nitric acid through the cavity between the gold nanomounds. The rate-limiting step of nanoporosity evolution is the dissolution of silver from surface defects which is nearly ten orders of magnitude slower than the two other processes. As a result, the dealloying front advances at a constant rate, as shown for a first time by Martinez *et al.* [17] who employed electron microscopy for kinetics studies of an $Au_{25\%}$-Ag alloy. Recently, similar conclusions were reached by Chen-Wiegart *et al.* [33], who studied the dealloying front in an $Au_{30\%}$-Ag alloy by means of transmission X-ray microscopy.

After dealloying, the final gold nanosponge is isotropic and characterized by ligament spacing in the order of 10 nm and surface areas greater than 8 m^2/g [34]. It has been found that the length scale of the porosity inversely increases with the dealloying front velocity. Thus, factors that can be related to the dealloying rate such as acid concentration [23], alloy composition [35] and temperature [36] affect the evolution of nanoporosity. The dealloying process is controlled by the diffusion of gold atoms on the alloy surface, which is strongly dependent on the reaction temperatures [37]. Low dealloying temperatures significantly reduce the interfacial diffusivity of gold atoms and the overall result is an ultrafine nanoporous structure. Obviously, the presence of other metals in the alloy, in addition to silver and gold, may play an active role during the gold nanoevolution but no systematic studies have been reported.

Gold evolution during the dealloying process at nanometric scale justifies the preserving memory of larger size structures such as specimen form (Figure 5a-b). Moreover, the nanoporous structure explains the brown color on the basis of the interaction between light and gold by surface plasmon resonance [38-39]. As previously observed, the high surface area makes the gold sponge thermally unstable. In the annealing stage, higher temperatures increase the surface diffusion of gold atoms leading to thermal coarsening. This process is exothermic in accordance with reduction in the energy of the system moving from high to lower surface material. With the annealing process the nanoporous structures disappear, resulting in a typically yellow gold bulk color. Generally, at 500°C the nanoporous structure is almost completely destroyed [14], although in the case of assays specimens are heated to 1050°C for practical reasons.

CONCLUSIONS

Gold parting with nitric acid substantially contributed to historical knowledge acquisition relating to the development of building furnaces, chemical glassware and synthesis of inorganic acids. With the development of large-scale industrial production of nitric acid, the use of the latter in the parting stage grew, with a peak in the first half of the 20th century. However, more recently, the high cost of nitric acid and the requirement for large NO_x scrubbers have vetoed its extensive use in large-scale industrial refining. As a result, other treatments are now used to refine low-grade gold bullion, such as the Miller process due to its technological development. However, nitric acid is still used at the parting stage on the laboratory scale after cupellation assay. Over the last two decades, the experimental and theoretical studies reported in the literature of dealloying process have allowed the mechanism involved in the formation of nanoporous gold material to be understood.

In conclusion, from a historical point of view, gold parting development occurred as the result of human experience without real scientific understanding of the treatment taking place. Recent academic research on the dealloying process represents a bridge to the understanding of the same phenomenon that occurs during the parting stage in the case of gold refining.

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Hi-Tech waste as "Urban Mines" of precious metals: new sustainable recovery methods

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Abstract. Precious metals (PMs) are valuable components of Hi-Tech goods such as electrical and electronic equipment, catalysts, advanced materials. These relatively recent applications and the growth of their market due to the fast technological development, heavily contribute to the high rate of element consumption and Hi-Tech waste accumulation of the modern consumer society. Looking at these wastes with new eyes, encouraged by the recent world-wide regulations aimed to the sustainable waste management and raw materials preservation, we can appreciate the value contained in and turn them in secondary resources of raw materials. In this context, a sustainable approach in PMs recovery from Hi-Tech waste, built on *green chemistry* principles and addressed to find a ready technological transfer, is described here.

Keywords. Green processes, circular economy, secondary sorces, noble metals recovery, waste electrical and electronic equipments.

OVERVIEW

One of the main aspects related to the modern consumer society is the fast technology development and the inevitable production of high and increasing amount of waste it entails. The assets, especially the Hi-Tech ones, play an essential role in our daily life and their life cycle gradually decreases. Electronic equipment, automotive devices and advanced materials, often contain significant quantities of valuable and even toxic materials which would be destined to landfill, thus generating a serious environmental issue, if not valorized in a different way, *e.g.* through reuse or recycling. European and several other countries regulations on Waste Electrical and Electronic Equipment (WEEE),[1,2] End-of-Life Vehicles (EoLV)[3] and batteries & accumulators,[4] the fastest growing and pollution generating waste streams in the world, ban the uncontrolled disposal of these goods at the end of their life encouraging the implementation of a virtuous circular economy model where the recovered materials, obtained as output of waste valorization processes, are the input raw materials for new productions.[5–7] Sustainable recovery processes are also urged in order to prevent pollution and further waste generation.

In this context, PMs play a key role. Indeed, they are widely used in Hi-Tech goods because of their physical and physicochemical properties. High electrical and thermal conductivity and high resistance to the oxidation (they belong to the noble metals family characterized by high reduction potentials), coupled with their malleability and ductility, make these materials particularly appealing for industrial application mainly as conductors in long lasting high technologies. Besides that, they have limited natural availability and high economic value. For these reasons, and due to the relatively high PMs concentration in Hi-Tech scraps (where often they are present in concentration even higher than in their ores),[8,9,10] their recovery may represent the *driving force* for the profitability of more comprehensive materials recovery processes.

Currently the main methods used industrially to recover valued metals from the main Hi-Tech wastes have been mostly inherited from the well-known processes conventionally applied on ores and jewelry ashes and are mainly based on pyrometallurgy and hydrometallurgy.[11,12] The former, which operates by smelting and refining, generates high financial and environmental costs, while the latter, less energy-intensive, more tunable and predictable but often based on the use of toxic and aggressive substances (*e.g.* cyanides, strong oxidizing acids), can heavily affect the environment, biodiversity and human health, if not strictly controlled for reactants and wastewaters production. A wide research effort is hence required to find new ways for recovering and recycling materials from Hi-Tech scraps able to combine effectiveness to environmental sustainability. A multidisciplinary environmental science approach is needed to face this challenge. The last two decades have seen environmental scientists with different background (*e.g.* chemists, engineers, biologists) and complementary skills, at work for turning this issue into a market, scientific and environmental opportunity. Some interesting results, both in terms of effectiveness and environmental sustainability, have been obtained in the last two decades by Deplano's group of coordination chemists, for gold, palladium and platinum recovery from Hi-Tech wastes by using safe leaching agents and mild condition processes.[13] Here we describe the results obtained for two different families of Hi-Tech waste, following a new *greener* approach, exploiting the interaction between the complexing and oxidizing species in the reaction environment which promotes an effective NMs leaching.

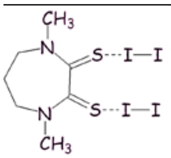
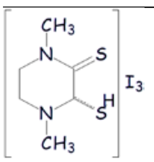
THE CASE OF WEEE

The WEEE family contains all the devices that work with electric current or electromagnetic fields, such as: personal computers, mobile phones, TVs, printers, refrigerators, washing machines, photovoltaic panels, lamps and other small and large appliances. This type of waste contains a variety of different materials that stimulate interest on recycling profitability. At the same time, they make recovery processes a really complex issue. In particular they can contain plastics, glass, copper, aluminum, iron, as well as noble materials, especially metals (*e.g.* gold, silver, palladium), and other critical elements such as "rare earths", often beside toxic substances such as mercury, cadmium and lead, extremely hazardous for the environment and for human health. To understand the greatness of the WEEE phenomenon, it is worth mentioning that world production of WEEE in 2016 was around 45 million tons (+8% by 2014). According to the ONU, this trend is expected to grow further to 52.2 million tons (+17%) by 2021, the fastest increasing rate in the world's solid urban waste.[14] But there is still much to do for turning them into value, recovering materials in an environmentally friendly manner differently from currently used industrial methods. Conventional methods often give a not satisfactory (in terms of recovery rates) and costly (both in terms of economic and environmental impact) answer to this need. An interesting promising contribution in the field of NMs recovery from WEEE - in particular small appliances, Printed Circuit Boards (PCBs), printer cartridges and smartcards - comes from the smart use of coordination chemistry in finding sustainable reactants able to combine oxidizing and complexing properties in a single molecule. It is well-known, indeed, that the presence of a complexing agent is necessary to lower the reduction potential and make feasible the oxidation of metals with highly positive reduction potential such as gold, palladium and platinum (as in the case of cyanides and aqua regia).[11] Molecules coupling complexing and oxidizing moieties show enhanced reactivity with respect of the "free" reagents, as demonstrated in the 1990s by the McAuliffe's group in a pioneering study on the reactivity of $R_3D{\cdot}I_2$ (R = Alkyl; D= As, P) Charge-Transfer (CT) complexes towards crude inactivated metal powders.[15] On these basis, with the view to find safer and more effective leaching agents able to overcome the sustainability issues put by conventional methods, Deplano's group started an extensive study on the use of sulfur-donor/dihalogen CT complexes. In particular, dihalogen/interhalogen adducts of cyclic and acyclic dithiooxamides (DTO), soft chelating ligands bearing two vicinal thionic groups able to favor the square planar geometry preferred by d^8 metal ions, demonstrated to be a powerful class of non-cytotoxic and easily handled lixiviants towards gold,[13,16,17,18] palladium,[13,19] copper,[13] silver,[13,21] and platinum,[22] under very mild conditions, mainly providing complexes of general formula $[M(DTO)_2]^{n+}$ and/or $[M(DTO)I_2]^{(n-2)}$ (M = NM; n = charge of the metal cation) as shown in Table 1.

Among them, the bis-diiodine adduct of the N,N'-dimethyl-perhydrodiazepine-2,3-dithione ($Me_2dazdt{\cdot}2I_2$) behaved as the most effective in the one-pot gold dissolution at room temperature and pressure in common organic solvents, and it was employed fully satisfactorily for the sustainable gold recovery phase in WEEE treatments as patented by the group in the last decade for the lab scale.[23,24] Figure 1 summarizes the patented three-step sustainable process for the treatment of a test specimen consisting in a thin metal powder (diameter=0.4mm) obtained by small appliances and PCBs comminution and deprived by aluminum, ferrous metals and vitreous-plastic materials, consisting in the selective dissolution and recovery of i) base metals; ii) copper; iii) gold.

The described process is based on the use of safe reagents. It is selective and easy to be implemented and managed consisting in just few steps which require mild operative conditions. Moreover, it is effective in the recovery of noble metals, which are obtained almost quantitatively in form of elemental metal by chemical (cementation) or electrochemical (electrowinning) reduction. From the other side, $Me_2dazdt{\cdot}2I_2$, though recyclable at the end of the process, is a reagent not yet available on the market and which works in organic solvent. In order to promote *green chemistry* processes able to meet *green engineering* principles as well for a faster technology transfer on industrial scale,[11,25,26] several

Table 1. Summary of the reactions between cyclic dithioxamides/I_2 leaching agents and Au, Pd, Pt, Ag, Cu powders under mild conditions: room temperature, 2:1 molar ratio; acetone (or THF or CH_3CN).

Leaching agent	Metal	Main product	Ref.
	Au	$[Au(Me_2dazdt)I_2]I_3$	13,16,17
	Ag	-[a]	13
	Pd	$[Pd(Me_2dazdt)_2]I_6$	13,19
	Pt	-[b]	13
$Me_2dazdt{\cdot}2I_2$	Cu	$[Cu(Me_2dazdt)_2]I_3$	13
	Au	$[Au(Me_2pipdt)I_2]I_3$	13
	Ag	$[Ag(Me_2pipdt)I]_2$	13,20
	Pd	$[Pd(Me_2pipdt)_2]I_6$	13
	Pt	$[Pt(Me_2pipdt)_2]I_6$[c]	22
$[HMe_2pipdt]I_3$	Cu	$[Cu(Me_2pipdt)_2]I_3$	13

[a]Unidentified product; [b]unreacted metal; [c]obtained under solvent reflux.

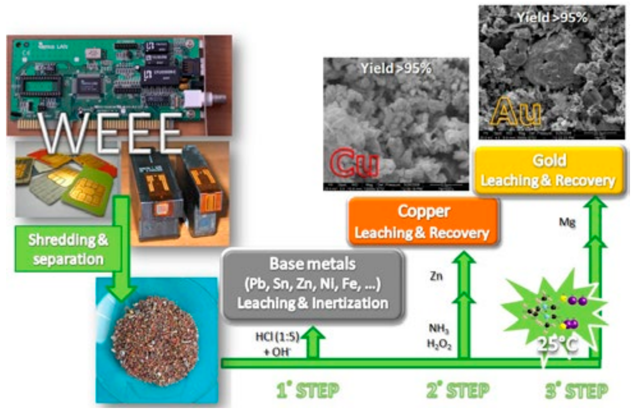


Figure 1. Schematic representation of the Deplano's group Cu and Au recovery method from comminuted WEEE, based on the use of $Me_2dazdt{\cdot}2I_2$ as gold leaching agent.[22,24]

changes in the process were studied and implemented as improvements. In particular:

- 1st step: a refluxing citric acid solution was used in place of HCl, in order to promote the use of weaker natural acids and increase selectivity;
- 2nd step: an alkaline I^-/IO_3^- mixture, able to combine oxidizing with coordinative capability, was used, in the presence of ammonia, as a more reliable alternative to H_2O_2, avoiding effervescence phenomena and promoting in one time the copper leaching and the separation of silver from the solution in form of AgI precipitate;
- 3rd step: a I_2/I^- water solution was used as leaching agent for gold in turn of the $Me_2dazdt{\cdot}2I_2$ solution in organic solvent. Although the demonstrated lower reactivity of the I_2/I^- mixture, the lower cost of the reagents, their availability on the market and, remarkably, the easy recyclability of I_2, make this process really promising for a sustainable application on a large scale.

Satisfactory results (almost quantitative yields in NMs recovery) were obtained on the cited test specimen through this new process design, pursuing a virtuous cycle able to limit the wastewater production.[27] Remarkably, this process demonstrated to be applicable satisfactorily also on coarser materials like shredded PCBs, where a heterogeneous size distribution and the presence of composite materials are present.[28] These last results demonstrate the robustness of the approach which seems appealing also from a costs/benefits ratio point of view[(1)] and open the way for further larger scale experimentations.

[1] The mechanical comminution and separation pre-treatments of the incoming material represent one of the heaviest costs of the whole recovery process

THE CASE OF THREE WAY CATALYSTS (TWC_S)

TWCs are exhaust emission control devices applied to the exhaust of vehicles in order to significantly reduce the polluting emissions (essentially of CO, unburnt hydrocarbons and NO_x), favoring oxidation and/or reduction reactions with formation of non-harmful compounds. Thanks to modern regulations that impose strict limits on vehicles emissions, from the 1st January 1993 the use of TWC is mandatory for all cars in all European countries. Every year, between 6 and 7 million of EoLV, corresponding to 7 and 8 million tonnes of waste, are generated in the European Union which should be managed correctly. Well-known procedures for managing EoLV, reuse of still working parts and processes for the enhancement of bulky materials such as iron, aluminum, glass, etc., have being implemented. Differently, it is still an issue to enhance materials from electronic apparatus, batteries, car fluff (complex mixture of non-ferrous materials including plastics, foam, textiles, rubber and glass residue from car demanufacturing) and catalytic converters.

Among them, in the specific field of noble metals reclamation, catalytic converters represent a rare opportunity. Indeed, they typically consists in a metal case containing the substrate (ceramic or metallic, with a "honeycomb" structure) coated by the wash-coat[(2)] which supports from 5 to 8g (for petrol and diesel engines, respectively) of highly dispersed catalytically active phase formed by a mix of metal platinum, palladium and rhodium. These metals are able to promote the oxidation of carbon monoxide to carbon dioxide and that of unburnt hydrocarbons to carbon dioxide and water (Pd and Pt), and the reduction of nitrogen oxides to nitrogen (Rh).[29] Notably, Pd-only technology has been introduced in catalytic converters in the last years.[30] It is estimated that the car industry alone, which puts about 40 million new cars on the market every year, represents a potential annual resource of $1 billion of Pd recovery.[29] Currently significant but still low (~30%) noble metals recycling from spent car converters[29] is done by non-selective unattractive methods involving unselective pyrometallurgical chlorination[30] or dissolution with strong oxidizing acids[30] in the crucial metal-dissolution step.[31,32] Based on the promising results described above on the use of dithioxamide/I_2 adducts with crude metal palladium, a joint project by Deplano's group, from University of Cagliari, and Graziani's group, from University of Trieste, allowed to check the effectiveness of $Me_2dazdt{\cdot}2I_2$ on model TWCs consisting in a Pd(2.8%)-CeO_2–ZrO_2/Al_2O_3 material underwent simulated aging (1050°C, 200h) for assessing its potential in Pd recovery from spent car converters.[33,19] Almost quantitative Pd-dissolution and recovery rates were achieved through the selective metal leaching by refluxing a Methyl Ethyl Ketone (MEK) solution of the molecular adduct in the presence of the cited test specimen in form of powder for 168 hours, has been patented and summarized as follows (Figure 2).

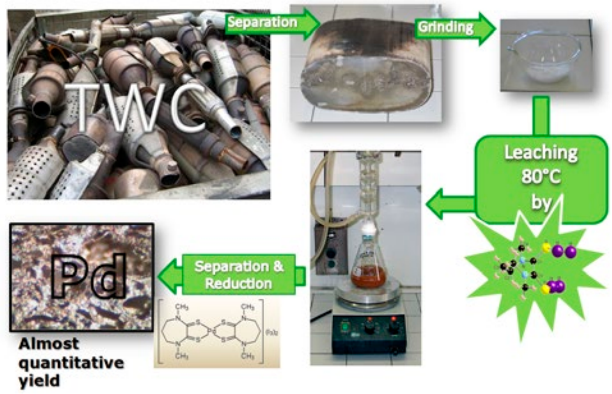


Figure 2. Schematic representation of the Deplano's group Pd recovery method from model aged TWCs based on the use of $Me_2dazdt{\cdot}2I_2$ as palladium leaching agent.[33]

The main recovered product was the $[Pd(Me_2dazdt)_2]I_6$ complex. Pd metal was quantitatively obtained by both chemical and thermal degradation of the molecular compound. Differently, Pd metal recovery attempts by chemical or electrochemical reduction were unsuccessful as expected because of the dithiolenic nature of the dicationic compound.[(3)] Nevertheless, $[Pd(Me_2dazdt)_2]I_6$ complex demonstrated to be successfully applicable in his molecular form as valuable homogeneous catalyst for C-C coupling reactions[34] and as precursor of effective photo-catalysts for H_2 production.[35]

As a cheaper alternative, we recently studied the use of safe fully organic triiodides (organic cations: tetrabuthylammonium, TBA^+; tetraphenilphosphonium, Ph_4P^+; 3,5-bis(phenylamino)-1,2-dithiolylium, $(PhHN)_2DTL^+$) as Pd leaching agents in organic solvents. The presence of an organic cation in the triiodide salt showed to dramatically improve its Pd-leaching properties with respect to those of the fully inorganic KI_3 salt, hampering the formation of PdI_2 coating passivation (typically present in these cases and limiting the leaching reaction to go ahead) by promoting the formation of stable and soluble ionic couples of gen-

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[2] High specific surface layer 40-50 mm thick, of g-alumina or CeO_2–ZrO_2/Al_2O_3 in current technologies

[3] In this class of complexes, the reduction event involves the whole molecule without achieving dissociation into metal and ligand components.

eral formula $Org_2[Pd_2I_6]$.[36] Although the recovery rates achieved using the cited triiodide salts were found slightly lower than those found by $Me_2dazdt{\cdot}2I_2$ solutions in analogous experimental conditions (98%, 83%, 73% for $(PhHN)_2DTLI_3$, Ph_4PI_3 and $TBAI_3$, respectively, *vs* almost quantitative for $Me_2dazdt{\cdot}2I_2$), these reactants seem really appealing for practical application due to their low cost and environmental impact, mild reaction conditions, market availability (or easy synthetic procedures), as well as for the easy metal Pd and reagents recyclability.

CONCLUSIONS AND PERSPECTIVES

The present work highlights how coordination chemistry, which is traditionally involved in the recovery/refining processes of NMs, can give a relevant contribution in designing molecular-level methods able to combine effectiveness with low environmental impact, as promoted by green chemistry principles and required by new legislation. On these basis multidisciplinarity seems the key approach to grew up molecular to industrial scale processes meeting both green chemistry and engineering requirements in order to balance sustainability with economic development. Here, a new promising sustainable approach based on the combined coordinative and oxidizing capability of safe, easy to handle and working in mild conditions charge-transfer compounds towards NMs, has been presented. A further effort is required to the *Environmental Sciences* community for implementing these methods on a larger scale in order to promote the conversion of *Trash into Resource* making the "circular economy" model feasible.

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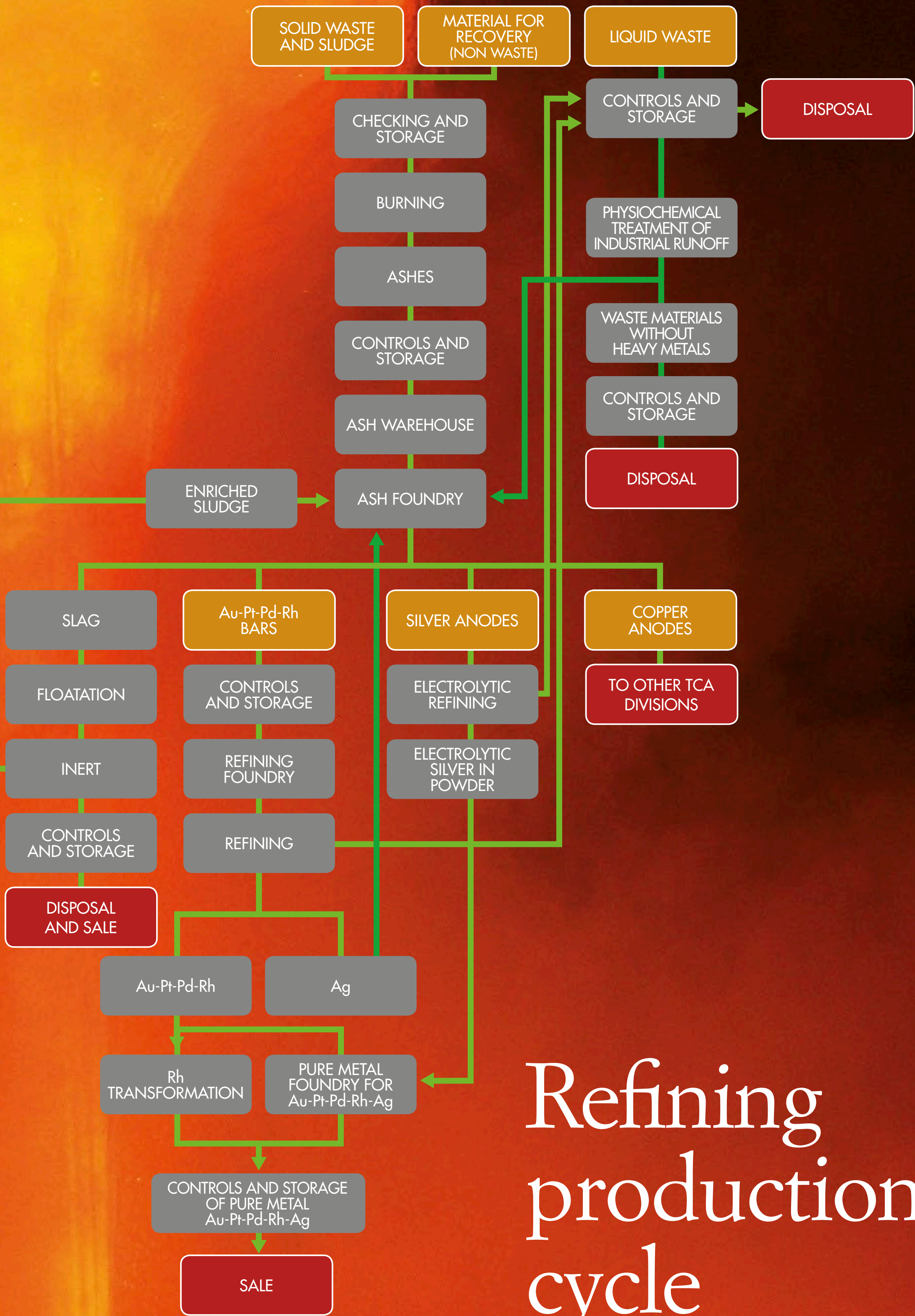

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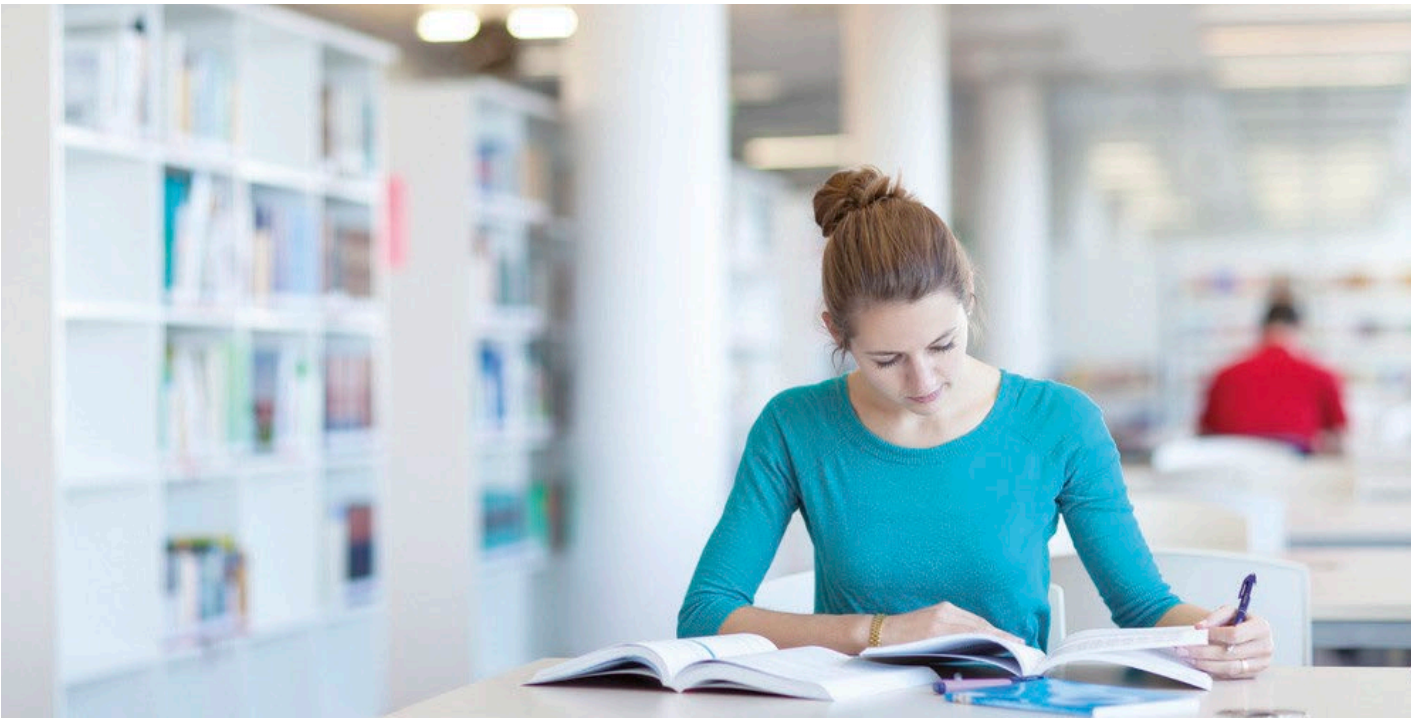

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