

Article

The Destructive/Non-Destructive Identification of Enameled Pottery, Glass Artifacts and Associated Pigments—A Brief Overview

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Abstract: The birth of Chemistry can be found in two main practices: (i) the *Arts du feu* (ceramic and glass, metallurgy, i.e., inorganic and solid state chemistry) and (ii) the preparation of remedies, alcohols and perfumes, dyes, i.e., organic and liquid state chemistry). After a brief survey of the history of (glazed) pottery and (enameled) glass artifacts, the development of destructive and non-destructive analytical techniques during the last few centuries is reviewed. Emphasis is put on mobile non-destructive Raman microspectroscopy of pigments and their glass/glaze host matrices for chronological/technological expertise. The techniques of white opacification, blue, yellow, green, red, and black coloring, are used as examples to point out the interest of pigments as chronological/technological markers.

Keywords: cultural heritage; analysis; pottery; glass; enamel; pigments; spectroscopy

1. Context

The foundation of Chemistry is often related to the practice of ancient alchemists. However, the know-how required for the transformation of matter, the definition of Chemistry, can be found in two main practices: (i) the *Arts du feu*, i.e., the preparation of pottery, glass, and metal artifacts (and related techniques for the selection and preparation of the raw materials used: geology, mining...), in other words Inorganic and Solid State Chemistry; (ii) the preparation of remedies, alcohols and perfumes, pigments, dyes, and binding for frescoes, painting, and textiles, in other words Organic and Liquid

State Chemistry [1–10]. The artifacts were prepared by craftsmen and/or artists, the distinction between them depending on cultural criteria more than technological ones.

For a long time, the search for quality and uniqueness had led masters to develop original techniques in order to make a reproduction by contemporary professionals difficult. Consequently, secrets and master-to-disciple oral transmission were the common law. Greek and Roman literature [11–15] remains the reference for the ‘sciences’ and technologies used in the Western and Mediterranean areas during many centuries, the relative part, transmitted by Western, Byzantine, Syriac, and Nestorian Monks [16], or by Arab scholars [6–8,10], being strongly debated [16]. The technical literature remained scarce until the 17th century [6–10], the onset period of separation between practice and theory. That period also corresponds to the beginning of the large diffusion of book printing. At that time the separation between ‘Chemistry’, ‘Physics’, and Techniques is not yet consumed, and information on the ‘Arts’ of preparing materials and chemicals can be found in books dealing with *Physique Experimentale* [17,18], *Elemens de Chymie Pratique* [19], *Histoire Naturelle* [17,20], *Physique* [18], *etc.* or even *Les Eléments de la Philosophie de l’Art du Feu ou Chemie* (W. Davisson, the first Lecture in Chemistry given in France, published in Latin in 1655, in French in 1661, F. Piot, Paris), a typical title of the Alchemist’ tradition.

Rare documents were, however, published before the *Quattrocento* and *Renaissance* [21–26] and the publication of information about Arts and Sciences truly started in Western Countries afterwards ([27–38] and references therein). The authors were generally scholars, not professionals of the techniques, which limited the precision and reliability of the information. Furthermore, the translation/identification of some terms (raw materials and ingredients, procedures, *etc.*) is very difficult because of the use of metaphoric expressions. The artifacts thus remain the only reliable source to retrieve the information about the technology used and the artisan(s) know-how.

Just like industry companies conduct re-engineering studies in order to identify the innovation of their competitors by dismounting/studying their products, we will show how this approach may be used to retrieve the ancient “secrets” of artists and masters to prepare pottery and glass artifacts. This experimental approach dates back to the 18th century. The works of Macquer [19], Rouelle’ brothers, Fourcroy, Réaumur [37], and Lewis [38] can be considered as very illustrative. The contribution of Hellot has been pointed out by the study of his manuscripts [39]. Then, Brongniard [40,41], Salvétat [42], Bontemps [43], Deck [44], Bastenaire-Daudenart [45], Jacquemart [46], *etc.* also performed comprehensive studies.

The high cultural value and uniqueness of many artifacts imply either a minimization of the (micro)sampling, or the use of non-destructive techniques. Furthermore, displacement of the masterpieces out of their secure locations (Museum, Collectors, and reserve rooms), or their dismounting (building part), is rarely authorized. We will discuss the identification of chronological/technological markers, namely the identification of chromophores, pigments and associated materials, and their glassy silicate matrix, used in ancient masterpieces such as pottery, enamels and enameled glass, pastels, drawings, paintings, *etc.*

2. Pottery and Glass Technology: A Brief Survey

The production of pottery dates back to the Neolithic/Palaeolithic transition (>15,000 B.C. in Japan, Siberia and Africa) and requires heating above 600–650 °C to produce hard and robust artifacts by means of liquid phase sintering. The use and modeling of unfired clay pieces are much older, the first sculptures dating from the Palaeolithic (~30,000 B.P.) [47–49]. However, it has been claimed that the Dolní Věstonice Venus sculpture (25–29,000 B.P., Czech Republic) had probably been heated [48]. Glass paste and glazed artifacts date back to ~3000 B.C. (Mesopotamia) [50]. The crude beads usually formed around a wire have blue and green colors suggesting that they were used to evoke lapis lazuli and turquoise stones. True glass artifacts date back to ~1500–2000 B.C. (Egypt, Phoenicia, and Mesopotamia), colored/opacified with lead antimonate yellow, and calcium antimonate white [50]; heating at ~900–1000 °C was achieved [51–54]. Large glass production stopped for a few hundred years around 1200 B.C., a period of wars accompanied by a trade disruption [50]. Similar interruptions occurred with the decline of the Roman Empire. Centuries before, Chinese Shang and Shang-Zhou proto-porcelains (3000–1500 B.C.) were fired at temperatures from ~950 °C up to ~1200–1250 °C [55].

Roman potters (*sigillata*) and glassmakers experimented mass production [56]. Chinese Eastern Han to Sui potters (2nd B.C. –7th c.) initiated the development of very high temperature firing technology: Yue wares were fired above 1300 °C [55]. White porcelains appeared during Sui and Tang Dynasties (7th–8th c.). At the same period the Islamic potters found how opacification by cassiterite tin oxide combined with low temperature firing could compete with high temperature fired porcelain to produce artifacts with complex depictions [47,48,57,58]. This innovation resulted from the imitation of the

three-color Chinese porcelain wares with lead-rich blue and green glaze dots deposited on a faience/*terra cotta* body covered with an alkaline glaze. The chemical reaction between the two glazes led to precipitation of white cassiterite [57]. This innovation was transmitted to Europe with the extension of the Islamic World (Ifriqaya (7th c.), al Andalous (8th c.), Sicilia (9th c.)) and then Italy (*majolica*, 13th c.) and France (15th–16th c.) [58–61]. Attempts to imitate the Blue-and-white Chinese porcelain were first made in Anatolia with Ottoman Iznik firewares from ~1450 to ~1620 [62–64] and then in Italy with Medici porcelain from ~1575 to 1587 [65,66], as well as in the whole of Europe one century after (18th century porcelain Manufactures) [67–69]. The availability of kaolin permitted the preparation of hard-paste alumina-rich porcelain, though the soft-paste porcelain route, which could be considered as an evolution of the Iznik fritware technology. A revolution took place after 1750 with the development of faience and porcelain factories (Figure 1). A second one occurred during the 20th century with the development of advanced ceramics, in particular dielectric passive components (capacitors, substrates, sockets, *etc.*) at the root of the development of microprocessors and computers [70].

Figure 1 illustrates the innovation law for the porcelain production [71]. It started in rare factories with a very specific technology. Then, attempts to produce similar artifacts were made in different places; with the circulation of persons and information, this number of places first expanded very rapidly and then decreased. Obviously, a differentiation between the first productions is easier, due to the diversity of raw materials and technologies. Indeed, competitors tried to imitate an artifact by using their specific raw materials and technology (Figure 2): therefore composition and/or microstructure

(body) and/or nanostructure (glass, enamels, *etc.*) are different, though the objects look very similar. Then evolution towards the best compromise between cost and quality led to more similar objects.

Figure 1. Evolution of the number of porcelain manufactures in Europe during the 18th century, after P. Ricciardi *et al.* e-preservation, 2009, 22–26. [71].

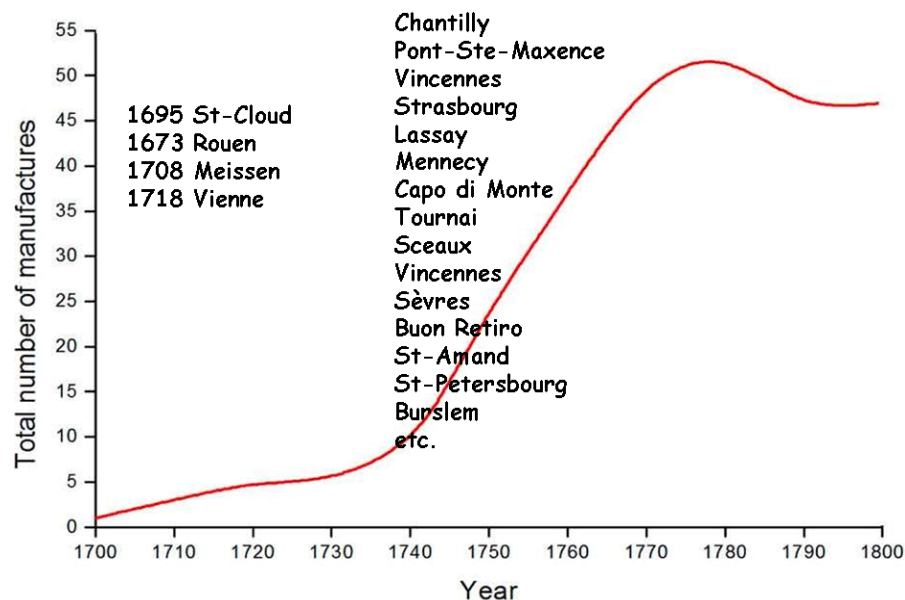
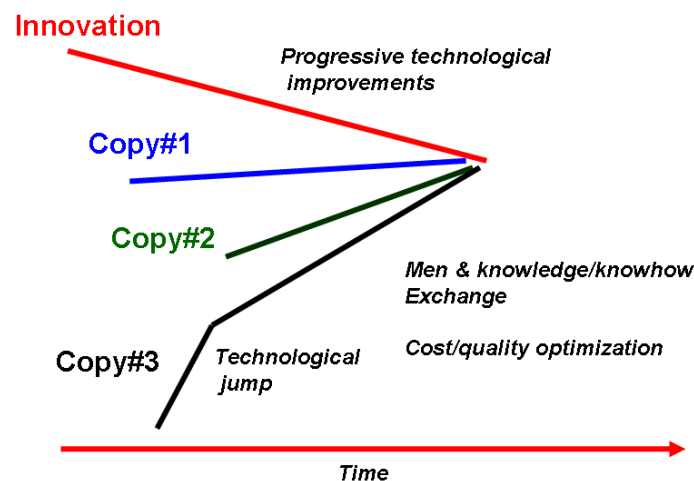


Figure 2. Evolution toward a common technology imposed by cost criteria and facilitated by the circulation of men and their know-how.



There are two difficult tasks in ceramic and glass technologies, (i) the achievement of fine, reactive powders in order to facilitate their reaction, thus melting and the wettability between liquid and solid phases to keep the glaze thickness almost constant, and (ii) the firing and its control. The first pottery clays were iron oxide-rich because a liquid phase appears at $\sim 700^\circ\text{C}$ between FeO and clays, promoting a good sintering in reducing atmospheres [72].

The use of micro-sized Mesopotamian silts allowed a perfect firing at low temperature [57]. The most difficult tasks were the glaze preparation, adhesion, and color control, which require empirical

control at the nanoscale. However, a ceramic always shows a heterogeneous microstructure because the only goal to reach is the formation of a liquid phase at the grain interface in order to develop a soldering between grains. Only in porcelain, a large part of the body volume reaches the liquid state (~30–50%), which permits the final optical translucency [73,74]. On the other hand, the glass and glaze volume reach the liquid state leading to a ‘perfect’ homogeneity at the eye scale. Consequently, differences remain at a much smaller scale, the nano- and subnano-scales.

3. The Development of Solid State Chemistry and Related Technologies Offers Chronological/Technological Milestones

There are two methods to disperse chromophores in a glassy matrix: the first one is to dissolve 3d transition metals (Fe^{2+} , Fe^{3+} , Co^{3+} , Mn^{5+} , Cu^{2+} , *etc.*) or 4f Rare Earth ions (Pr^{3+} , *etc.*) with electronic levels absorbing in the visible range; the second one is the direct dispersion of pigment grains, a matter already containing ions of the kinds mentioned above, or more complex chromophores [75–77]. Note that the chemical and thermal stability of a pigment must be high enough not to be degraded/dissolved by the molten enamel. Each method has advantages and drawbacks. The first one is simple but hues are weak, the colors spread out easily because of the fast diffusion of small coloring ions, and reproducibility of the décor is difficult. The second technique requires sophisticated preparation (synthesis, grinding, flux addition). In both cases, the color palette is drastically reduced when the firing temperature increases.

Nature gives many examples of very vivid colors of another type, the iridescent colors that can be found for instance on blue *Morphos* butterflies, many beetles, opals, nacre, *etc.* The same kind of iridescence has been achieved by potters, centuries ago, in lustre pottery [78–80]. The color arises from scattering, i.e., positive and negative addition of the light waves (interferences) diffracted by more or less organized layers (gratings). Among modern items, the colored reflections of CD surfaces have the same physical origin.

The use of colored materials, natural or synthetic, is one of the most important foundations of Art. Some selected minerals, as well as chemical mixtures extracted from plants, wood, and animals, were used as the first raw materials [81,82].

First glazed artifacts were made of steatite, 4 millennia B.P. [83–85]. In Europe (Celts [79,83,86–88]) and Near-East (Egypt, Mesopotamia [84]) colored enamels and glasses were prepared using different chromophores, mainly metal nanoparticles, transition ions, as well as phases that form precipitates on cooling. However, since the forming elements (antimonates, stanates) [50] are major impurities of lead oxides, the main flux of glass and glaze, their precipitation was not really controlled. Consequently, improved technologies were lost repeatedly: for instance cobalt was used episodically by the Egyptians of the 18th Dynasty (~1500 B.C.) to color glass [89–91], and then stopped for centuries.

The mass production of pottery (*Sigillata* [56,92]) and glass artifacts [93] developed during Roman times. Some new technologies appeared at the end of the Roman Empire: gold tesserae in Ravenna and Byzantium [94], and the use of lapis lazuli as blue glass pigment [95], an unexpected discovery which questions the whole history of pigment technology (see further).

The Chinese chromophore technology was very specific with, for instance, the use of barium derivatives to produce violet, blue, and green colors [96–98] with a composition similar to that of

Egyptian blue and green [99,100]. In actuality, great technological improvements took place during the 8th century in China (Tang porcelains [55,101–103]) and the 9th century in the Ancient World (Abbasids pottery [57,104,105]). The recent discovery of a Tang shipwreck cargo has changed our knowledge on the history of technological exchanges between China and the Mediterranean World [101].

Polychrome lustre pottery was produced for a few decades, only during the first Abbasids Dynasty [78,79,104]. A new technology, namely the yellow coloring of stained glass windows with silver metal nano-precipitates, appeared in the Middle-Ages [22,106]. Red stained glasses, a Celtic innovation [79,86–88], were prepared by alternation of very thin (tenths of micrometer) non-colored and copper metal-containing glass layers [107,108], in order to limit a too-strong light absorption. The controlled reduction of copper ions into metal nano-particles was used to make *Jun*, *Flammés*, and *Sang-de-Pigeon* Chinese porcelains. *Cloisonnés* enamels on metals, a technology that also emerged during Celtic times, continued during Byzantium, and flourished in Spain during the Middle-Ages [109]. Then, at Limoges (France), the enameling technique allowed the production of black-and-white and colored enamels on copper plates, depicting Greek, Roman, Christian, and then historical scenes [109,110]. The technology spread to China and then Japan [111], an example of West-to-East technology exchange. At the same time, Mamluks pushed the glass enameling to a very high level [112,113].

Painters of the *Quattrocento* and *Renaissance* used enamels and pigments developed by potters [114]. The first Technological Books became largely available [27–31] at that period.

The Ottoman Court, through the *Nakashane* Office, promoted the production of exquisite Fine Arts [64,65,104,115–117]. This involved a prodigious development of the ceramic pigment technology that spread out in many countries. The cross-over between the ancient praxis and beginning of the Science and Technology Epoch took place in the 18th century with the New Chemistry and the Encyclopaedists. Many books describing preparation procedures were published [34–46]. Many manufactures were founded and routes explaining the reactions leading to specific chemicals and products, e.g., the Macquer' dictionary, became available [19]. With the turn between the 18th and 19th centuries, industrial workshops and the related innovations developed by mean of an increasing knowledge in solid and liquid state chemistry. Commercial colouring agents became more complex—different coloring agents/pigments were mixed together in a patented formula—which offered accurate chronological markers [40–45].

The onset of the development of organic chemistry took place around 1850, together with the race for the related innovating steps. People having experiences in both ceramic technology and science theory wrote books [118].

Cost and hazardous properties became very important criteria at the end of the 20th c. for environmental reasons, e.g., the limitation and then the replacement of lead in glass/enamel composition. This continuous evolution gives us a variety of markers to trace production place and time.

4. The Analytical Techniques of Artworks: Toward Non-Destructive Procedures

To date, the history of the scientific study of ancient artifacts is poorly documented. Alexandre Brongniart (1770–1847), with his *Traité des Arts Céramiques ou des poteries considérées dans leur*

Histoire, leur Pratique et leur Théorie [41], can be considered as one of the founders of this kind of approach, at least for ceramic and glass technologies. He was a follower of the Encyclopaedists and of the rare precursors such as Ehrenfried Walther von Tschirnhaus (1651–1708) [116], René-Antoine Ferchaud de Réaumur (1683–1757) [37], Pierre-Joseph Macquer (1718–1784) [19], and Georges Leclerc Comte de Buffon (1707–1788) [20]. However, his books [40,41] were the first devoted to the potters and glassmakers rather than scholars. Productions from all over the world are described and a careful attention is paid to the identification of the raw materials used and to the firing techniques. For instance, A. Brongniard noted that in Corsica, female potters produced the first ceramic matrix reinforced composites, mixing asbestos long fibres with a calcareous clay [41,117].

In the third part of the 19th century, many technical books were rapidly published, especially in the famous Roret Encyclopédie series that covers most of the Fine Arts techniques [118]. Among books on ceramic technology and its history, '*La Faïence*' from Théodore Deck (1823–1891) can be distinguished [44].

The first chemical analyses of the different parts of ancient pottery (body, glaze, lustre, *etc.*) was conducted by Duke of Luynes, A. Salvétat [41,42], and other famous chemists. Their studies were highly destructive.

A great improvement took place one century after (~1950), with the development of neutron activation techniques [119,120]. The development of X-Ray Fluorescence (XRF) instruments in the sixties, with the bore glass bead technique (boric acid or lithium tetraborate is added as a flux to solubilise about 1 g of ceramic in a Pt crucible and form a glass bead permitting quantitative composition measurement) [120–123] can be considered as the true onset of archeometry literature with the help of data processing (Principal Component Analysis, Cluster variation methods, *etc.*) [124–127]. The increasing sensitivity and versatility of instruments (Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS), Energy Dispersive Spectroscopy coupled with a Scanning Electron Microscope (EDS-SEM), *etc.*) significantly decreased the sampling size [90,91,128,129]. Microsampling is achieved with Laser Induced Breakdown Spectroscopy (LIBS) [130–133]. The development of accelerators with extracted particle beam gives opportunity, in rare laboratories, to study art pieces by Particle Induced X-ray Emission (PIXE), Rutherford Backscattering Spectroscopy (RBS), *etc.* [134–137]. Synchrotron sources offer new tools (XRF and diffraction-microbeam, Infrared microspectrometry) that have been extensively used for a few years [138–140]. However, though the brilliance of the source decreases the recording time, similar or even better results can be obtained—at a much lower cost - by using classical instruments.

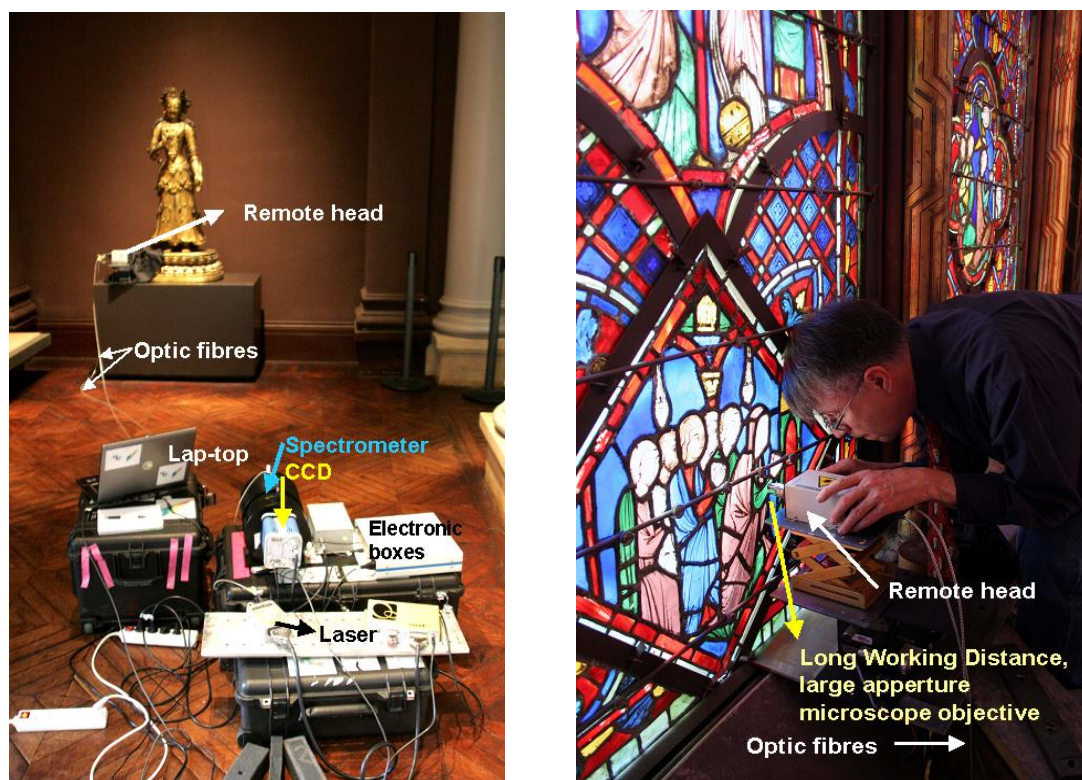
Today the composition of most materials can be qualitatively determined in a micro-destructive/non-destructive way using portable XRF instruments [141–145]. In some cases (homogeneous materials, flat surfaces) the measurement can be quantitative: LIBS instruments [145,146] allow profiling the composition from the surface to the bulk, by means of a few microns-sized laser beam that drills the sample.

5. The Development of Mobile/Remote Raman Microspectroscopy

Irradiation of matter by a coherent electromagnetic wave induces coupling with the oscillating distribution of charges; in other words, with the chemical bonds in the system. Polarization of the

excited dipoles generates a scattered electric field and associated waves [147–149]. A small part of the incident light is scattered with an energy different from the initial one due to energy exchange with the chemical bonds, and the prediction of this effect dates back to the beginning of the 20th century (L. Brillouin in France, A. Smekal in Russia [150,151]). First experimental evidences were given in the same month, in 1928, by different groups: two in France (Y. Rocard & M. Ponte and J. Cabannes [152,153]), one in Berlin (P. Pringsheim & B. Rosen [154]), one in Russia (G. Landsberg & L. Mandelstram [154]), and one in India (K.S. Krisnan and C.V. Raman [155]). Although the latter group was not the first to publish its work, it obtained the Nobel Prize in 1930 (Raman sent many preprints all over the world and received a high impact). The effect was called ‘*Raman effect*’. In actually, the technique relying on this phenomenon was developed in the 1970s with only the availability of Ar⁺ and Kr⁺ ion lasers. The development of Charge Coupled Devices and photodiode arrays in the 1980s, and then of CCD matrices in place of photomultipliers, increased the detection level by several orders of magnitude [147]. Replacement of the first monochromator stage (a diffraction grating) with Notch photonic crystals or Edge dielectric layered filters increased the detectivity significantly. Miniaturization and improvement of computers and electronic boxes allowed the size reduction of all the Raman set-up, and the conception of dedicated transportable/mobile spectrometers free of any moving parts (Figure 3). Today hand set-ups are available, but have reduced capabilities (poor resolution, low sensitivity).

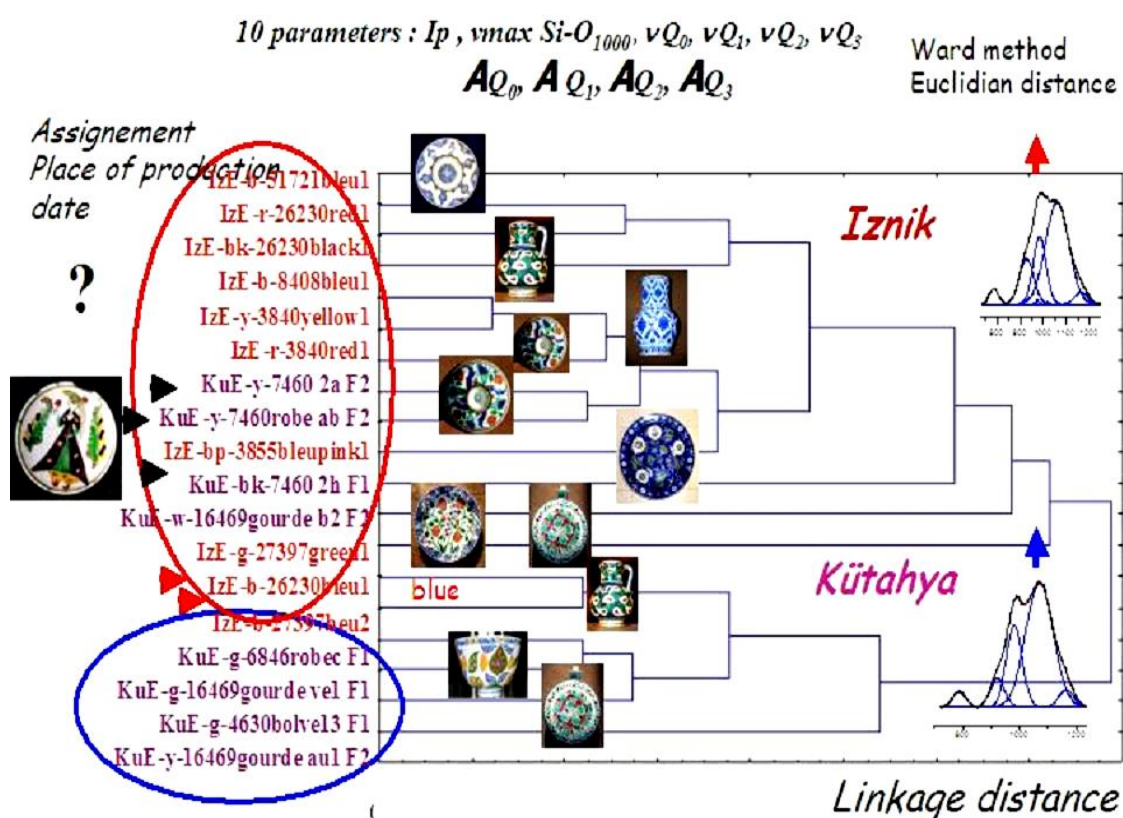
Figure 3. Examples of on-site measurements with a mobile Raman set-up [144,156]; detail about the positioning of the remote optical head is given.



Our group is playing a pioneering role in the development of on-site Raman study of ancient (glazed) pottery [62,63,65,66], enameled glass [112,113], Limoges and Cloisonnés enamels on

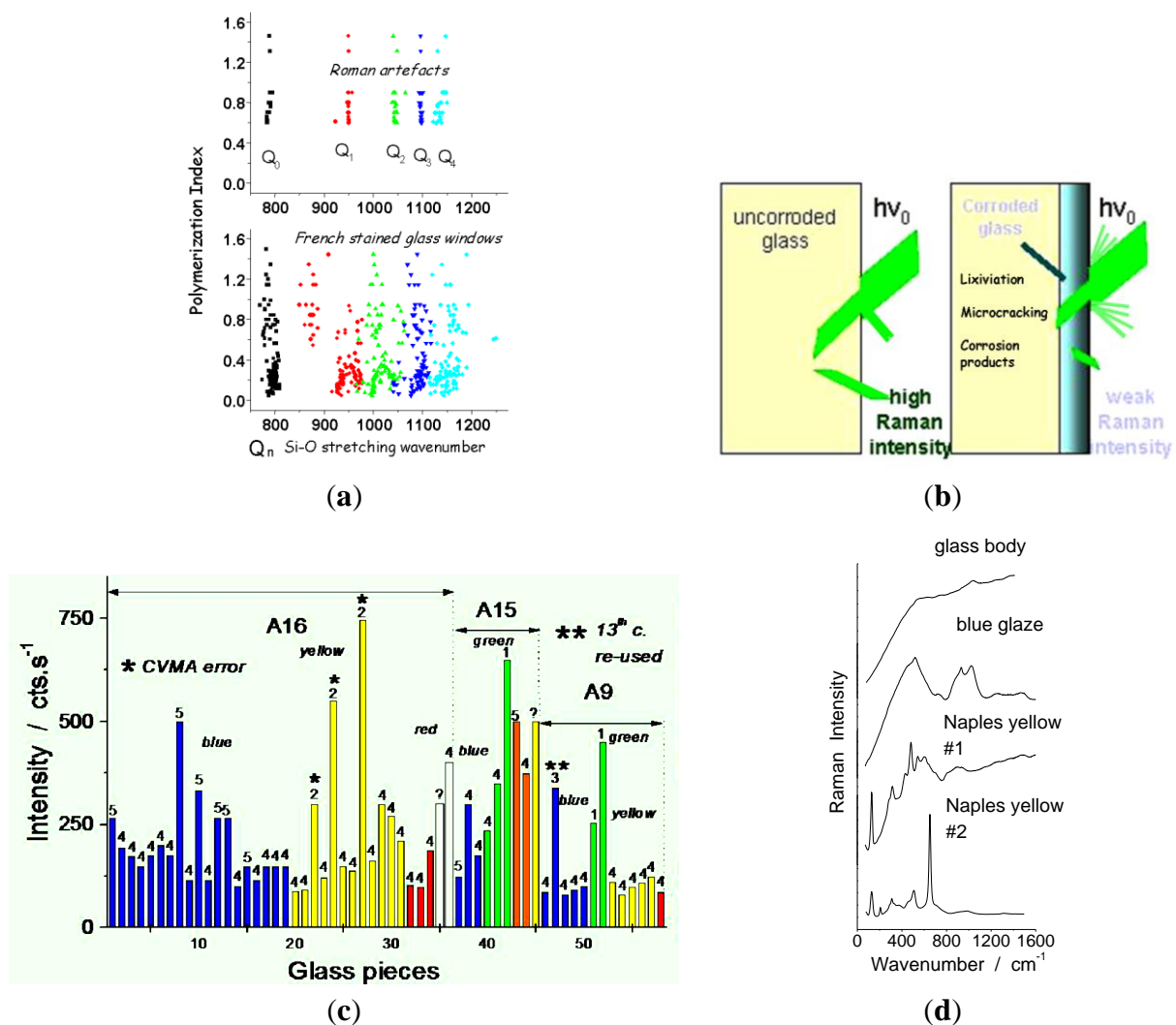
metal [109–111], paintings and drawings [157,158], patinated bronzes [144], rock art paintings [159], etc. (Figure 3). The poor resolution and complex background of spectra recorded with mobile Raman set-ups require the development of models expliciting the Raman signature and associated parameters in relation to the micro and nanostructure of matter, as well as the use of multivariate chemometric techniques [160–164] (Figures 4–6). The recent availability of small size laser sources with different colors is a new asset: typically, blue to green lasers are better for inorganic and light colored compounds, whereas red to infrared lasers show advantages for the study of organic and black compounds. However, red and yellow pigments are easily detected by using excitation of the red (typically 633 and 785 nm) [165]. Sophisticated optics, such as objectives optimized for the laser wavelength, with a large aperture to collect the scattered light with high efficiency, and a long working distance between the focus point and the front lens (to avoid any contact with precious items), are mandatory.

Figure 4. Parameters extracted by modeling the Raman signatures of the glazes of various artifacts assigned to Iznik and Kütahya Ottoman production were classified using the cluster classification technique to establish a procedure of indentification [65,66].



An analytical study of the Raman signal can be used to identify the phases present in the volume of the analyzed system. Typically, many non-colored minerals and compounds can be identified by simple comparison with reference spectra found in databases [75,165–172]. The narrower bandwidth of many signatures leads to a better detectivity of minor phases by Raman spectroscopy than by IR spectroscopy. However, the large variation of the Raman signal intensity with chemical bond polarizabilities (no spectrum for ionic bonding compounds, intense spectrum for covalent bonding compounds) renders quantitative analysis difficult.

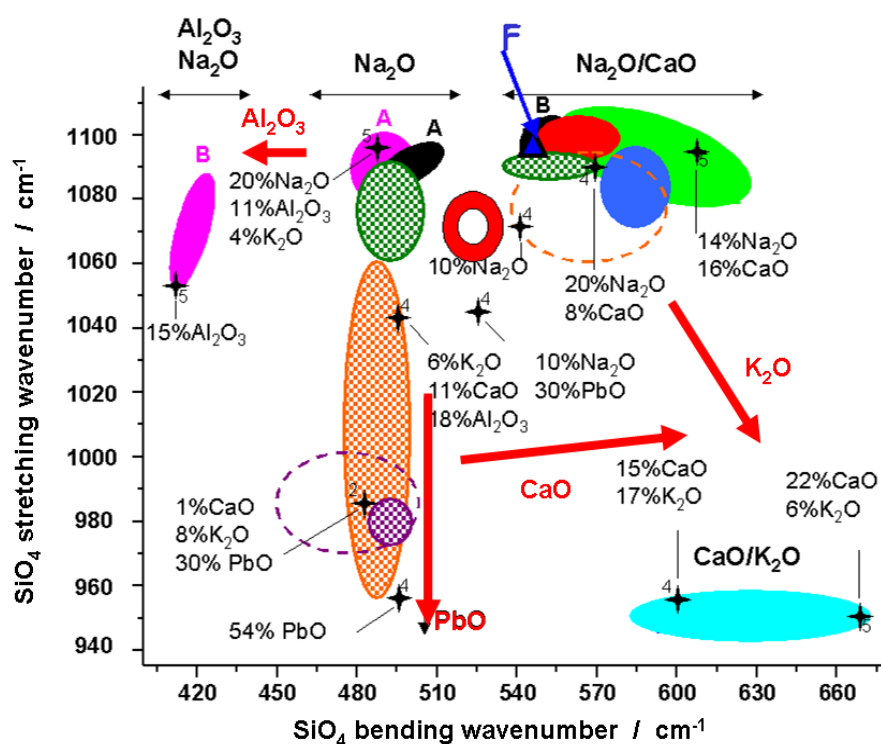
Figure 5. (a) The limited scattering of the Q_n stretching components of SiO_4 tetrahedra indifferent Roman glass artifacts excavated in France, Italy, and Tunisia results from the controlled mass production using a single composition; on the other hand, the dispersed data measured for stained glass windows from Northern and Eastern France medieval churches arise from production by many different workshops [163]; (b) the absolute intensity of the Raman signal decreases with time because of the surface degradation of glass artifacts (leaching and microcracking); (c) the example given for Sainte-Chapelle (Paris) Rose window shows the easy differentiation by comparing as-recorded peak intensity between middle-aged and 19th century restored pieces [156]: #5, 1 and 2-type glass pieces are restored pieces; #4-type pieces are original weathered stained glass pieces ; (d) examples of Raman spectra as-recorded on enameled artifact with a mobile Raman set-up: the signature of pigments (two Naples yellow glaze) and colored glaze (cobalt blue glaze) is recorded with a rather good intensity, when the signature of non-colored glass consists of tiny broad peaks on the complex background due to the Edge filter.



Recently available (portable) IR spectrometers give very useful information in the case of samples with flat, glossy surfaces [173,174].

The specific interaction between the laser light and the electronic levels of chromophores [117, 173–175] gives rise to Raman resonance that leads to a high detectability, but requires a deep understanding of the phenomenon and, therefore, prevents from using databases. Instead, a Solid State Physico-Chemist approach is mandatory [176–179]. This approach, through the modeling of the Raman signal, allows for the analysis of the micro and nanostructure of matter, thus detecting many technological signatures in the objects: second phases, short range-order and structural distortions, grain orientation and shape, etc. A discussion of the different models developed, especially for poor crystalline materials (Figure 6), is out of the range of this text but can be found in refs [160–164].

Figure 6. Diagram built with the highest wavenumber of bending and stretching bands in silicate glass signatures; each couple is characteristic of a given composition/nanostructure. Examples of typical compositions are given (stars). See references for details [108,109,111–113,160–164,179,180].



6. Case Studies: White, Blue, Yellow, Green, Red, and Black Pigments and Coloring Agents

In order to illustrate the interest of chronological/technical markers we shall consider the different techniques used to achieve colors in glass and pottery.

6.1. White

The white color of a glass is obtained by dispersing a second phase within the glassy matrix; the dispersed phase must have a higher optical index than the matrix, to give a very efficient opacification. The particle/heterogeneity size must be smaller than the eye resolution, a few μm or less, typically. The opacification of a glaze masks the body coloration in order to depict a decor. Glaze, like any

enameling, must have a thermal expansion slightly higher than the body to avoid cracking or scaling [174].

The simplest way to opacify a glass (Table 1) is by dispersion of micronic bubbles (e.g., in Celadon [177,178] and first Meissen porcelains [179]). Other ways are the dispersion of micrometric grains of quartz [62], the precipitation of antimonates [58–61,180], wollastonite [66,67], cassiterite [57,58,67,105], fluorite [111], calcium phosphates (bone opacification) [65,112,113], arsenates [109], as well as the addition of rutile, anatase and zircon in modern productions [76]. White slips and deposits, fired or not, are also used to obtain a white décor on *terra cotta*. Many of these phases are *post quem* markers. Many of the above compounds were also used in paintings, frescoes, illuminating manuscripts, etc. e.g., in refs [81,180–185].

Table 1. White pigments and opacifiers. Dates of innovation (first production) are given.

Color	Composition	Date
Bone white	$\text{Ca}_2(\text{PO}_4)_2$	Antiquity
Chalk (calcite)	CaCO_3	Antiquity
Cerussite	PbCO_3	Antiquity
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Antiquity
Bassanite	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$?
Anhydrite	CaSO_4	Antiquity
Antimoniate	CaSb_2O_7 , CaSb_2O_6	Antiquity
Kaolin	Al_2O_3 , 2SiO_2 , $2\text{H}_2\text{O}$	Antiquity
Lead white ceruse	$\text{Pb}(\text{OH})_2$	500 BC
Cassiterite	SnO_2	9th
Fluorite	CaF_2	14th?
Quartz	SiO_2	16th.
Arsenates	$(\text{Ca,Pb})_{1.5}\text{AsO}_4$	17th
Zinc white	ZnO	1781 (1834)
Lithopone	ZnS - BaSO_4	1874 (Western)
Titanium white	TiO_2 anatase	1916 (1923)
	TiO_2 rutile	19th?
Freeman' white	PbSO_4	19th
Hamburg white	PbCO_3 , BaSO_4	19th
Barium white	BaSO_4	19th (Western)
Zirconia	ZrO_2	20th
Zircon	ZrSiO_4	20th

6.2. Blue

Egyptian blue, a more or less crystalline copper-lime silicate (Table 2), can be considered the first synthetic pigment [99]. Besides, the earlier white (or yellow) antimoniate pigments may result from natural precipitation, once saturation is achieved during the cooling of the melt. Millennia later, Chinese Han potters developed a Baryum homolog to Egyptian blue [97,98] for the decoration of the famous terra cotta army of the Qui Shi Huang Xiang mausoleum.

The turquoise blue color was first obtained in Egypt by firing silicawares (synthetic or natural stone) in a copper-rich paste leading to a turquoise blue glazing of the object surface [41,84].

Episodically (18th Dynasty), cobalt was used instead [88,89]. These techniques use the dissolution of $3d\text{ Cu}^{2+}$ or Co^{2+} ions in the glassy silicate.

Table 2. Name and composition of blue pigments and coloring agents. Dates of innovation (first production) are given.

Color	Hue	Composition	Date
Egyptian blue	Light blue	$\text{CaCuSi}_4\text{O}_{10}$	3000 BC
Turquoise		Cu^{2+} in alkaline glass	2000 BC
Han blue		$\text{BaCuSi}_4\text{O}_{10}$	200–500 BC
Han violet		$\text{BaCuSi}_2\text{O}_6$	200 BC
Smalt	Light blue	CoO n SiO_2 ; Co-containing glass	Antiquity
Lapis Lazuli (Lazurite)	ultramarine	$\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}_n$	Roman
Cobalt, -manganese-iron ores		dissolved	9th
Indigo		$\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ indigotin	<10th?
Prussian blue		$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{--}16\text{H}_2\text{O}$	1704
Cobalt blue	Dark blue	CoSiO_2 olivine	18th
Cobalt blue	Dark blue	CoAl_2O_4 spinel	1775 (1802)
Cerulean	Dark blue	Co_2SnO_4 spinel	1810 (1821)
Cobalt chromite		$\text{Co}(\text{Al},\text{Cr})_2\text{O}_4$ spinel	
Synthetic ultramarine			1826
Cobalt spinel		$(\text{Co},\text{Zn})\text{Al}_2\text{O}_4$ spinel	19th
		$\text{CoAl}_2\text{O}_4/\text{Co}_2\text{SnO}_4$ spinel	
Spinel aluminate blue	Blue	Al_2O_3 ; 0,5 ZnO; 0,5 CoO	~1900
	Turquoise blue	Al_2O_3 ; 0,2–0,4 CoO; 0,6–0,8 ZnO	
	Dark blue	Al_2O_3 , 2 $(\text{PO}_4)_2\text{Co}_3$ ou 2 $(\text{AsO}_4)_3\text{Co}_3$	
	Violet	Al_2O_3 ; 0,5 CoO; 0,5–1 MgO	
	Blue grey	Al_2O_3 ; 0,6–0,8 CoO; 0,4–1,2 NiO	
	Dark blue green	Al_2O_3 ; CoO; Cr_2O_3	
	Light blue green	Al_2O_3 ; CrO_4 ; CoO; ZnO	
Zircon blue	Light blue	ZrO_2 , SiO_2 + V_2O_5 (<1%)	~1950
	Turquoise	+ NaCl or NaF	
	Light blue	+ Na_2CO_3	
Cobalt oxide	Dark blue	Co_3O_4	
Zincochromite	Dark blue	ZnCr_2O_4	
Cobalt zinc oxide	Light blue	ZnCo_2O_4	
Posnjakite		$\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$	
Cyprium		$\text{Na}_3\text{Ca}(\text{Al}_3\text{Si}_3\text{O}_{12})$	
Vivianite		$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	
Phtalocyanine blue		$\text{C}_{32}\text{H}_{16}\text{CuN}_8$	20th
Manganese blue		BaMnO_4	20th

The preparative chemistry of cobalt (chromium, *etc.*) is difficult: a small addition of cobalt (0.5–2 wt %) is sufficient to color a silicate glass, while higher cobalt-levels generally lead to precipitation of cobalt silicate (lead-rich glass) [67,75] or cobalt-aluminate (alumina-rich glaze) [186,187]. Consequently, before the 19th century, cobalt sources were natural ores containing very

large amount of other transition metals such as manganese, iron, or chromium [90,91,177,188]. For instance Chinese/Vietnamese cobalt sources were manganese- and iron-rich ores, and the porcelain firing was performed under strongly reducing atmosphere so that the dark color of $Mn^{4/5+}$ and Fe^{3+} ions would not obscure the blue hue [188 and references herein]. Since cobalt ores remain rare, recycling of blue glass was reported in remote antiquity.

The main alternative to obtain a nice blue color is the use of lapis lazuli, a stone associating lazurite or hauyne feldspars (colored by some S_2^- ions located in site of the feldspar structure) with pyrite and diposide. Sources of lapis lazuli, are scarce: mainly in Afghanistan, and for a minor part in Baikal Lake mines and in Chile [189–192]. Moreover, the access to Afghanistan mountains mines was difficult, and stopped in different periods of history, especially during Sassanid Dynasties. Consequently, many scholars in Western Countries considered lapis lazuli as a very rare material and therefore rejected its use in glass and ceramic. Raman studies have shown that this view was erroneous. The first evidence for the use of lapis lazuli as a glaze pigment was given by Clark *et al.* on pottery excavated in a 14th c. Swabian-Normand-Islamic context [193–195]. If cobalt was easily detected by analytical techniques such as ICP or XRF [91,92,192,196,197], the detection of lapis lazuli small grains, dispersed in a silicate matrix by the same methodology, was not possible: first, because the composition of the feldspar host framework is close to that of the glass, and second, because the S traces are masked by SO_4 traces, common in ancient glasses. On the contrary, the Raman resonance of the S_2^- chromophore under green laser excitation allowed detecting the presence of S-doped feldspar very easily [95,113,157,180,193]. Thus, it was demonstrated that both cobalt and lapis lazuli could be used simultaneously in the glaze of a rather common *Lâjvardina* artifact, contradicting the alleged high cost of these pigments at the period considered (14th c.) [190]. It is now obvious that during the 14th–15th centuries, lapis lazuli was a common blue pigment. A recent study also points out that a Roman enameled glass, the Lübsow beaker, already contained lapis lazuli as blue pigment [95]. Mamluk enameled glass objects as well as the blue enamel of the famous Begram Treasure [198] were also made using this blue pigment [113]. In addition, the discovery of glass shards in Frederick II Melfi's castle, dated from the second half of the 13th-first half of 14th century, gives arguments in support to a direct link between Roman-Byzantine glassmakers/potters and Islamic ones through the Swabian-Normand Court [193–195].

An unexpected use of Lapis lazuli was observed in the first hard-paste Meissen porcelains made by J.F. Böttger [179]: the selected kaolin has iron oxide traces and the fired body remains gray, not white. The opacification of the glaze was only achieved by dispersion of micronic bubbles, a technique not sufficient to completely cover the gray color of the body. To achieve a white color, Böttger, educated as lapidarian expert, added lapis lazuli blue grains at the body-glaze interface: the artifact looked as white as the Chinese model, made with Kaolin of higher quality. Different modern ceramic pigments are now available to obtain blue color [76,77,165,187,199].

6.3. Yellow

Stable yellow colors are difficult to prepare. The easiest way to obtain a yellow glaze is to saturate a silicate with lead, inducing precipitation of massicot PbO [58]. With the development of *majolica* wares, Naples yellow, a large pyrochlore solid solution between $PbO-SnO_2-Sb_2O_3/Sb_2O_5$ with addition

of SiO_2 , Fe_2O_3 , and ZnO became the most widely used pigment [59–61]. Because of the very large range of the solid solution, the composition actually achieved is specific to a factory and, therefore, a good production marker [112,200].

Table 3. Name and composition of yellow pigments and coloring agents. Dates of innovation (first production) are given.

Color	Composition	Date
Ochre	$\text{FeO}(\text{OH})$ goethite	Neolithic
Massicot	PbO	Antiquity
Orpiment & pararealgar	As_2S_3 - As_4S_4	Antiquity?
Saffron	$\text{C}_{20}\text{H}_{24}\text{O}_4$ crocetin	Antiquity
Ocre	Fe_2O_3 H_2O + clays + SiO_2	Neolithic
Naples yellow	$\text{Pb}_2\text{Sb}_2\text{O}_7$ pyrochlore	1500 BC
Lead-antimony yellow		
Palmatine	$[\text{C}_{21}\text{H}_{18}\text{NO}_4]^+ \text{X}^-$	Antiquity
Naples yellow	Pb_2SnO_4	Antiquity
Lead-tin yellow type I		
Berberine	$[\text{C}_{20}\text{H}_{18}\text{NO}_4]^+$	Antiquity
Silver yellow	Ag nanoparticles in glass matrix	12th
Or mussif	SnS_2	13th.
Indian yellow	$\text{MgC}_{19}\text{H}_{16}\text{O}_{11} \cdot 5\text{H}_2\text{O}$	15th.
Naples yellow	$\text{PbSn}_x\text{Si}_x\text{O}_3$	15th?
Lead-tin yellow type II		
Strontium yellow	SrCrO_4	1800
Barium yellow	BaCrO_4	19th.
Cadmium yellow	CdS (+ CdSe)	1829 (1845)
Chrome yellow/orange	PbCrO_4 (+ PbO)	1809 (1820)
Aureolin	$\text{K}_3[\text{CO}(\text{NO}_2)_6] \cdot n\text{H}_2\text{O}$	1861
Cambodia yellow	$\text{C}_{38}\text{H}_{44}\text{O}_8$ et $\text{C}_{29}\text{H}_{36}\text{O}_6$	
Rutile yellow	$(\text{Ti}, \text{Ni}, \text{Nb})\text{O}_2$ rutile	20th
Cassiterite yellow	$(\text{Sn}, \text{V})\text{O}_2$ cassiterite	20th
Primrose yellow	$2\text{Ni}, 3\text{BaO}, 17\text{TiO}_2$ priderite	20th
Zinc yellow	ZnCrO_4	1809 (1850)
Curcuma	$\text{C}_{21}\text{H}_{20}\text{O}_6$	
Uranium yellow	PbUO_4	19th
Stibine	Sb_2O_5	
Malayite yellow	CaSnSiO_5 sphene malayite	20th
Praseodymium yellow		20th

New pigments were searched for during the 19th and 20th centuries (Table 3) to obtain a variety of yellow hues, such as uranium yellow, zinc-chrome yellow, rutile yellow, Praseodymium yellow, etc. [76,77,165,199].

A specific mention must be made of silver yellow: yellow glasses are prepared by diffusion of Ag^+ silver ion from the glass surface inward and then *in situ* reduction into metal nanoparticles to obtain coloration by the Ag^0 plasmon light absorption. This technique was first described in middle-age

reports [22,79,106]. Because the plasmon absorption is very strong, the layer colored by silver metal particles must be very thin to keep its transparency (see further the discussion for red copper glass).

Note that the huge plasmon absorption peak makes the observation of low wavenumber nanoparticle modes difficult under excitation with absorbed laser wavelength [79]. In this case, the Raman spectrum only reflects the nanostructure around the metal nanoparticle and does not correspond to the glass matrix [57,79,106,108,201].

6.4. Green

Green glasses and glazes have been obtained since the Egyptian times: Egyptian potters and glassmakers prepared a greenish derivative of Egyptian blue (different composition, different crystallinity) by diffusion of copper ions into a silica-rich body—or stone—from a Cu-rich paste in which the artifact was wrapped [41,84,85,165,199].

Roman craftsmen prepared copper-containing lead-based glass. This technique remained the only one for a while, inducing in China [101–103], before the use of chromium-rich ores by Iznik Ottoman potters developed [62,63]. However, other minerals were used as pigments for paintings and illuminating manuscripts (Table 4): malachite, green earths, *vert-de-gris*, etc. [81,165,183–185,199].

Table 4. Name and composition of green pigments and coloring agents. Dates of innovation (first production) are given.

Color	Composition	Date
Malachite	$\text{CuCO}_3 \text{ Cu(OH)}_2$	Antiquity
Atacamite	$\text{CuCl}_2 \cdot 3\text{Cu(OH)}_2$	Antiquity
Green earth	$\text{K}[(\text{Al}^{3+}, \text{Fe}^{3+})(\text{Fe}^{2+}, \text{Mg}^{2+})], (\text{AlSi}_3, \text{Si}_4)\text{O}_{10}(\text{OH})_2$	Antiquity
Vert-de-gris	$\text{Cu(CH}_3\text{COO)}_2$	Middle age
	$[\text{Cu(CH}_3\text{COO)}_2]_2 \text{ Cu(OH)}_2 \cdot 5\text{H}_2\text{O}$	
	$\text{Cu(CH}_3\text{COO)}_2 \text{ Cu(OH)}_2$	
Green	Cr in glass	Ottoman
Scheele green	$\text{Cu(AsO}_2)_2$	1778
Cobalt green	$\text{CoO} \cdot n\text{ZnO}$	1780, >1830
Dark green	Cr_2O_3 haematite	1800
Emerald green	$\text{Cu[C}_2\text{H}_3\text{O}_2] \cdot 3\text{Cu[AsO}_2)_2$	1814
Viridian	$\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	1838 (1859)
Victoria green	$3\text{CaO}, \text{Cr}_2\text{O}_3, 3\text{SiO}_2$	19th
	Yellow green: + CaCl_2 & CaF_2	
	Dark green: + CaF_2	
	Middle green: + LiF	
Chromium Green	Light green: $\text{ZrO}_2, \text{SiO}_2, \text{Na}_2\text{WO}_4, \text{K}_2\text{Cr}_2\text{O}_7, \text{NaCl}$	
	Olive: $\text{ZrO}_2, \text{SiO}_2, \text{Na}_2\text{WO}_4, \text{NaCl}$	
Nickel green	Ni_2SiO_4 olivine	
Chromite green	CoCr_2O_4 spinel	
Cobalt green	Co_2TiO_4 spinel	
Yellow + blue	Yellow pigments in blue matrix	18th

Green color is also achieved by dispersing yellow pigments in a blue matrix [75]. Chromium-based pigments were developed during the 18th century and still compete with organic chromophores for many applications.

6.5. Red

The technique to obtain red glass using a dispersion of copper nanoparticles can be considered, with the pottery technology itself, as the first example of nanotechnology [79,80,106]. Indeed, the possibility to prepare, at relatively low temperature, a variety of ceramic is directly related to the nanosized character of clay particles, which allows their dispersion in water as colloid or gel. The control of the rheology, plasticity, and high reactivity of the latter phases then permits the low firing temperature [202]. The controlled dispersion of a small quantity of copper (red), silver (yellow to brown) and gold (red) metal nanoparticles in an optically clear glass gives rise to colorful materials through the specific interaction of light with the electron gas at the particle surface, the so-called plasmon resonance (Figure 7). This leads to narrow peak absorption and more complex features related to the particle composition, size, and shape [57,79,106,201].

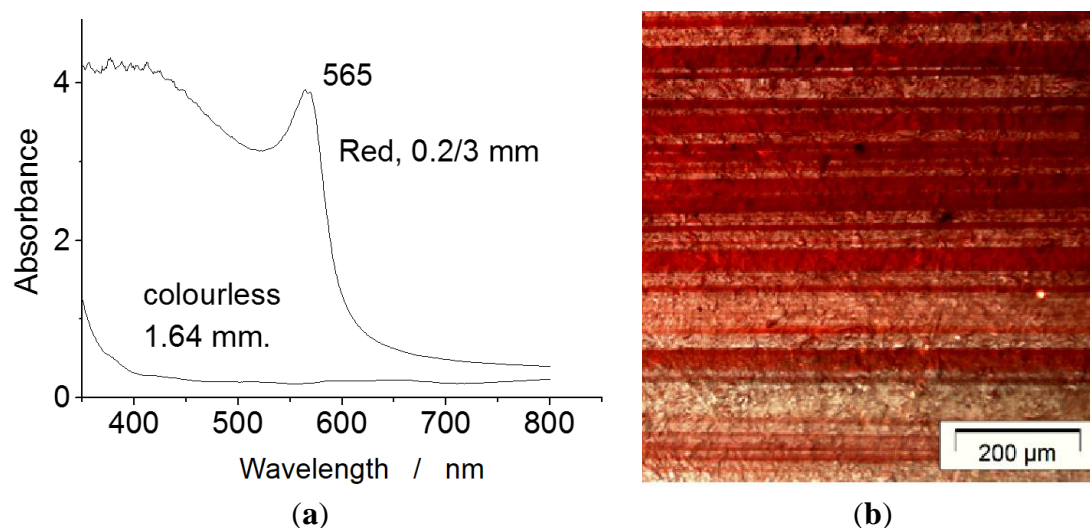
Table 5. Name and composition of red pigments and coloring agents. Dates of innovation (first production) are given.

Color	Composition	Date
Copper red	Co metal nanoparticles in glass matrix	Neolithic
Vermillion	HgS	Neolithic
Ochre & Earths	Fe ₂ O ₃ + clay + SiO ₂	Neolithic
Haematite	α -Fe ₂ O ₃	Neolithic
Purpurin	C ₁₄ H ₁₈ O ₅	3000 BC
Tyr purple	C ₁₆ H ₁₀ Br ₂ N ₂ O ₂	1400 BC
Litharge	PbO	Antiquity
Minium	Pb ₃ O ₄	Antiquity
Kermes	C ₁₆ H ₁₀ O ₈	Antiquity
Realgar	As ₄ S ₄	Antiquity
Haematite/hercynite	Fe ₂ O ₃ + SiO ₂	Antiquity
Umbria earth	Fe ₂ O ₃ , MnO ₂ + clay + SiO ₂	
Cassius' purple	Au metal nanoparticles in glass matrix	Roman?
Kinkel' red		
Madder	C ₁₄ H ₈ O ₄	Middle-age
Carmin	C ₁₄ H ₈ O ₄ (alizarin) + purpurin	16th.
Armenian Bole	Fe ₂ O ₃ + clay + SiO ₂	14th
Thiviers sandstone	Fe ₂ O ₃ + SiO ₂	17th
Mars red	Fe ₂ O ₃ synthetic, nanosized	<18th.
Mendipite	Pb ₃ O ₂ Cl ₂	
Cadmium red	CdS (+ CdSe)	1907

Copper dispersion in glass was controlled by Celts, millennia ago [79,86–88], and red Roman mosaic tesserae were prepared with the same technique [180,203]. Silver dispersion was largely used to prepare yellow middle-age stained glass windows [26,106,118], and gold ruby glasses made by

Renaissance glass-makers are famous [108,116,118,196,197,204,205]. Rare artifacts such as the Licurgus cup (4th century) [79,206,207] or some Roman *tesserae* contain both copper/silver and gold [203], indicating that ruby gold glasses date back at least to the end of the Roman Empire.

Figure 7. (a) UV-visible absorbance curve of a 19th century typical glass, free from or with a 200 μm thick Cu° -containing layer exhibiting a plasmon peak; (b) optical micrograph of a Middle-Age red flashed glass showing alternate colored and non-colored glass. This example shows the sophistication of the ancient technology (after [108]).



Another way to obtain a nice red or orange color is the use of nanosized haematite or parent structures. The size reduction of particles, by broadening the electronic absorption bands, decreases the electronic gap, leading to a small change of color. This phenomenon is at the origin of the nice color of Roman *Sigillatta* [56], where the orange to red color of the fired slip arises from the association of micronic haematite and corundum grains. Rather similar fine microstructures are observed for Iznik red (Armenian bole) [64,65], red Meissen décor, and French faience red décor obtained using Thiviers sandstone as red pigment precursor [208]. Note that fake red dots made with organic pigments can be observed on ancient Islamic masterpieces, “embellished” in order to improve their commercial value [112].

6.6. Black

Although the black color is easily obtained from carbon by controlled firing of organic precursors (plants, bones, ivory, *etc.*) [157,158,165,199], the preparation of a black glaze/enamel in association with other colors is very difficult, especially in oxidizing firing atmospheres [209] and dates from the Ottoman period in Western Countries (Table 6). Song potters produced outstanding black glazed artifacts that continue to attract the interest of modern potters [210]. On the other hand, black *terra cotta* décors had been obtained since the beginning of pottery, and achieved a very high level in the Greek period by controlled reduction of iron-rich clays and slips [211,212].

Note the early use of Bismuth [205]. New ceramic pigments were developed during the 19th century.

Table 6. Name and composition of black pigments and colouring agents. Dates of innovation (first production) are given.

Color	Composition	Date
Carbon black	C	Neolithic
Earths	MnO ₂ , clays, Fe(OH) ₃	Neolithic
Bismuth black	Bi	>15th
Spinel black	Cr ₂ MnO ₄ spinel	15th
Tin-massicot	Pb ₂ SnO ₄	
Copper black	CuO	
Cobalt black	CoO	

7. Lustre, Another Way to Master the Color

Rare ancient reports suggest that iridescent glass has been prepared in (late) Roman times [118], but to date no actual artifacts has been described and *a fortiori* studied. Some scholars say that the first lustres were made on glass artifacts a few decades before Abbasids lustre pottery (Mesopotamia, 9th century) [104]. However, examination of the objects—in their more or less preserved state—points out that their lustre level is very limited. Further studies are necessary to clarify the lustre origin.

Lustre coloration is obtained by combination of plasmon absorption and interferences [78,79]. An interference-built color requires a very specific orientation of the observer's eyes *vs.* the artifact and the source of light (Figure 8), as well as a very specific micro/nanostructure of the material, made of a transparent matrix with an 'organized' dispersion of silver, copper, or gold nanoparticles.

Figure 8. (a) The Transmission Electronic Microscopy micrograph of a modern lustre replica prepared by combined oxidizing- CO reducing sequences shows the metal nanoparticle-rich layers in the silicate matrix (Courtesy of Ph. Sciau, CEMES, Toulouse); (b) the copper nanoparticle-containing lustre glaze exhibits the well-defined Plasmon peak in the yellow-green range, the color of the plasmon peak depending on the nanoparticles shape and size. For most of the observation angles, this Fatimid's lustre (Fustât excavation, Egypt) looks reddish but for a specific orientation *vs.* the enamel surface, the viewer and the light source, the diffraction takes place, giving a golden shining. Metal nanoparticle-containing glasses, called dichroic glasses, have different color in reflexion and transmission.

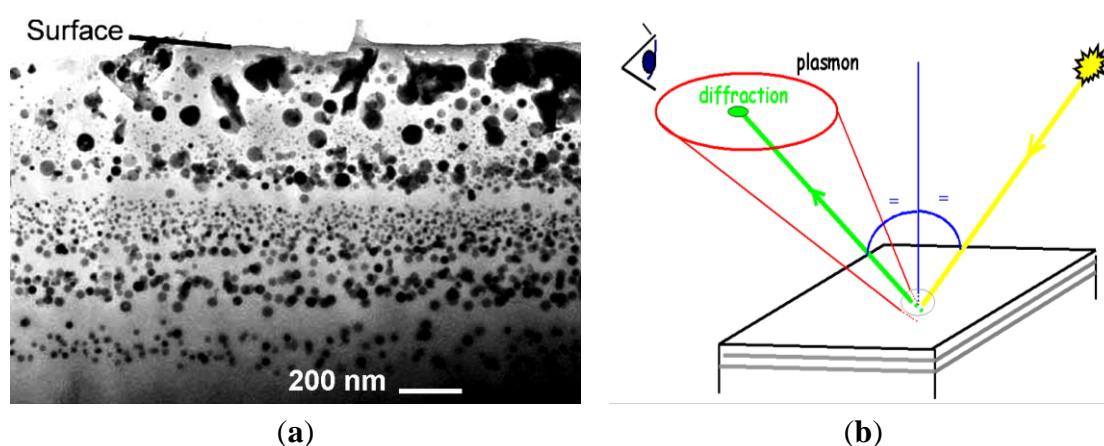


Figure 8a shows the near surface section of the Fatimid lustre shard. Metal particles appear in dark. So the upper region appears free from metal particles and the alternation of layers with and without metal particles is obvious. The precise chemical analysis of the dark particles shows that they consist of small silver and copper, rarely alloyed, single crystals [79,80]. Copper can exist both as Cu^0 metal particles and as dissolved Cu^+ or Cu^{2+} ions. The upper oxidized particle-free layer plays an important role for the optical properties. Namely, this impedance adaptation layer promotes penetration of light down to the metal-containing layers, maximizing the scattering and hence the single color lustre shining in combination with the number of layers, with and without metal nanoparticles. Large disorder in the particle shape and size distribution destroys the interference contribution, letting the color be determined by the plasmon absorption: red for copper, golden brown for silver. Abbasid and Fatimid Lustres show well-defined interferences and lustre shining [78–80].

Rare polychrome Lustre pottery shards have been excavated from Susa and Samara. The best example is the tile series forming the décor of Kairuan mosque (Tunisia, [78]): for a given observation angle, blue and green lustres are observed on a tile simultaneously. Such high-quality polychrome lustres seem to have been produced only during a few decades. Majolica and Mudejar lustres do not exhibit various colors [78–80], and are very similar to more modern lustres like Meissen, Burgos, or Lüdersdorff productions, or even bismuth-based metallization [118].

8. Conclusion: Master's Secrets as Chronological/Technological Milestones

The use of mobile, non-destructive Raman spectroscopy, notwithstanding the important instrumental limits *vs.* fixed instruments excited with a variety of laser wavelength, has allowed the achievement of important results. It outlines the technologies, with the essential advantage of preserving the objects in their museum rooms. The development of new mobile Raman instruments able to perform mapping (as under development for Mars explorations) and/or excited with blue or UV laser should improve the efficiency of the mobile Raman technique for the study of these and other artifacts.

Raman analysis of several examples of enameled glass objects and glazed pottery/porcelain yielded important information both on the coloring agents/pigments used and on the technological procedures employed. As an illustration, Table 7 lists remarkable case studies, pointing out specific use of Lapis lazuli and/or unexpected white opacifiers identified by Raman scattering. Identification of these unexpected pigments offers criteria to follow the transmission of a technology as well as to differentiate genuine, embellished/restored, or fake artifacts.

Table 7. Technologies used to obtain blue and white hues as evidenced by Raman microscopy.

Artifact	Period	Technology	Ref.
Begram glass Treasure	1 st century AD Roman Empire	Lapis lazuli	[198]
Ptolemaic faience pottery	1 st century AD Roman Empire	Lapis lazuli	[213]
Lübsov glass beaker	2 nd century AD Roman Empire	Lapis lazuli as blue & calcium antimonate as white pigments	[95]

Table 7. Cont.

Artifact	Period	Technology	Ref.
Abbasid pottery	9 th c.	Cassiterite opacifier; Lustre	[57]
Lâjvadina pottery, Iran	13 th c.	Lapis lazuli and cobalt as blue glaze pigments	[189,190]
Enameled glass and Pottery, Frederic II Souabian Court, Apuglia	13 th –14 th c.	Lapis lazuli as blue & calcium phosphate as white pigments	[195]
Mamluk mosque lamps	13 th –14 th c.	Lapis lazuli as blue & calcium phosphate as white glaze pigments	[113,198]
Medici porcelain Florence	1575–1587	Calcium phosphate Feldspar & wollastonite	[65]
Böttger porcelain Meissen	1700–1708	Lapis lazuli grains at the body-glaze interface. Bubble as opacifier.	[179]

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