THE APPLICATION OF SCIENTIFIC METHODS OF INVESTIGATION TO WORKS OF ART AND ARCHAEOLOGICAL OBJECTS*

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In this review a resumed historical background on the application of scientific methods of investigation to works of art and archeological objects is presented. Special emphasis is given to the description the personnel and activities developed at the *Laboratoire du Louvre* in France, today known as the *Laboratoire de Recherché des Musées de France*. Several examples of the application of different physical and physical-chemical methods of analysis are presented, as for instance, optical and microscopies, X-ray radiography and diffraction, infrared and UV-vis spectroscopies and gas chromatography among others. Examples have been given in which several techniques were used to ensure authenticity of works of art and archeological objects as well as to provide information that can be used to guarantee better methods for the restoration of art objects.

Keywords: analytical methods; art objects; laboratoire de recherché des musées de France.

HISTORICAL BACKGROUND

The relations between art and the use of scientific techniques have already a history. As early as the XVIIth century, artists and scientists work together for the glory of the kings. The heritage of the Renaissance is still present, when a single man could cover the entire knowledge of the world. At that time artists are not differentiated from scientists and both attempt to propose an explanation of the world around them. The XVIIIth century, the "Siècle des Lumières", has done much to bring closer sciences and the artistic evolutions. The french revolution has developed the museums, at the same time for the artistic creation as well as for science and nature. At that time the different fields of learning are not distinct, and separated by walls as they often have been since. The fracture between the two begins in fact in our XXth century and it will probably disappear. There are signs of a renewed interest in the hard sciences for the humanities and vice-versa.

The examination of works of art considered as materials has been immensely boosted by the discovery of the X-rays by Röentgen, exactly 100 years ago today. Röentgen himself, who was very inventive had already examined paintings and a bunch of ancient coins stuck together by corrosion. In France, it all started during the first World War when some doctors examined radiographs of paintings in a military ambulance.

The first laboratories were created in Berlin and in London in the late twenties.

THE LABORATOIRE DES MUSÉES DE FRANCE

Formally, the Laboratoire du Louvre was created in 1931 and it became the Laboratoire de Recherche des Musées de France in the 60's.

It is located within the Louvre. This is of importance because it benefits from the security organization of a large museum and the art works under study within the laboratory are considered to be safe by the curators in charge of the collections.

It has moved very recently into a new space, 4000 m^2 and entirely underground, below the level of the Tuileries garden which is above it.

Its role is to provide assistance to the public collections, before new acquisitions for instance or, more frequently, before the restorations are performed. Indeed, before they start with their difficult task, the restorers are keen to get as much information as possible concerning the nature of materials, the techniques that have been used for the fabrication and all that is hidden under the surface. Through their catalogue, major exhibits are often the opportunity to finalize research on a painter or an artist or a school. Therefore, this is also a good opportunity for the laboratory to have its say. Finally, one of the main tasks of the lab is to perform investigations into various research topics whenever they appear to be ready for further advance.

The director of the laboratory is Jean-Pierre Mohen, a curator and a well-known prehistorian. About 65 people are employed permanently, among them, at present, 8 doctor's thesis candidates. The training of half of them is in the humanities, or they are radiographs or photographs, the other half has a standard background of chemist or physicist. However, the essential characteristics of this laboratory is the intimate mixing of both cultures. A good understanding of the other's approach and reasoning is essential for the success of the research projects. This mixture is at the same time a strength and a challenge.

The work at the laboratory can be subdivided into two types. One is related to the examinations, the other to analysis. Let us now describe the various types of investigations which are conducted and the best is to present examples, taken from the activity during the last years.

THE EXAMINATIONS

The tools available for the examinations are microscopes, whether by transmission or reflection, binoculars, X-ray radiography, infrared, ultraviolet examinations and the scanning electron microscope.

Made with tools other than the normal light and the naked eye, the examinations show the invisible. Examples of **unexpected findings** are very numerous.

- The Louvre egyptian collections, for instance, include many animal mummies and some species were adored. Mummies of cats of the Late period were radiographed. In some of them, there was the remain of an animal, in others not. The existence of fake mummies is taken by

* Palestra Convidada pela Divisão de Química de Materiais, proferida na Reunião Anual da SBQ, Caxambu, 1995.

the specialists as an indication of a decline in the religious practice from this period.

- The "Gobeur d'oursins" was painted by Picasso in Antibes during the last world war, when there was a shortage of painting material and supply was difficult. The radiography of this painting shows that he had used another painting which he did not like or appreciate, the portrait of the general Vandenberghe, the most important donator of the Antibes museum. Incidentally, this raises a basic question concerning the authenticity of an art work and the choices to make before restoration.
- A virgin with child, a stucco from the Renaissance museum in Ecouen, has been restored in the past and at this occasion, for some unknown reason, the restorers left behind strange material inside. One may see on the radiograph a compass, a file, a hook for fixing tiles etc..., a real and unexpected tool box!
- Sometimes the discovery is of a greater historical importance. Clay Mesopotamian bubbles of the IVth millenium were found to contain small objects of a strange appearance. Opening was of course impossible. To get a clearer view, an X-ray scanner was used and it was found that these objects were tetrahedra, disks, rods or cones and that some had superficial marks. It is considered that these bubbles are a sort of a receipt of a commercial transaction. They could be one of the first signs of accounting and writing.

The examinations are always a help in understanding the technique of an artist, sometimes they show his hesitancies, his successive attempts, his quest towards the final expression.

- Georges de la Tour had painted the same subject several times. It is not clear why and the historians would usually like to know which painting was done first. When the paintings and the radiographs are alike, one cannot say anything. Such is the case of the "Tricheurs" where the only difference is the nature of the ace in the hands of the cheater, diamonds on the Louvre version, clubs on the Fort Worth's museum. On the other hand, when differences may be found, the laboratory can be of help. Take the example of the flames on the two "St Sebastien soigné par Irène", one from Berlin, the other from the Louvre. The visible flames are identical but on the radiographs one may see that there are several attempts on the Louvre version whereas the gesture on the Berlin one is perfectly assured. Although it is not a definite proof, one may think that the Berlin painting was done later, the artist at the second time knowing exactly how to paint the flames on a torch.
- Infrared reflectography may give many indications on the preparatory work of a painting at least when there was one. The examination with an infrared camera, which is sensitive only to the chosen wavelength in the infrared, may disclose what is under the painting layers, particularly the drawings and sketches made before, often with carbon material. Dutch paintings often yield interesting informations of this type. Many examples show the drawings, the cross-hatchings to increase shadows and relief, sometimes indicating the color to be used. There is a discussion on the origin of these color indications: were they from the master at the intention of the helping hands or to the artist from the person who had commissioned and paid the painting?
- Carole Fritz uses the depth of focus of the scanning electron microscope to study engraved paleolithic stones and bones. This allows to disclose the details of the technique, the nature of the tools, the sharpening of the flint stones used, almost the gesture of the artist, whether he was clever, expert or clumsy.

A recurrent question concerns the **authenticity** of the works of art, and it is not the simplest one. The answers of the laboratory are seldom clear cut, they bring another type of indication which is in general complementary to the intuitive and immense knowledge of the art expert. The final conclusion comes from the sum of these arguments.

- Raphael has painted a Holy Family for the Pope Jules II, which was placed in the church of Santa Maria del Popolo in Rome and has become known as the Madonna de Lorette. It was long believed that this painting had disappeared and that only copies remained and there were many of them. A well-known british expert, Cecil Gould suspected in the seventies that the Chantilly museum version could be the original Raphael's. The radiograph showed that the St Joseph in the background on the right had been added and that an initial version showed a window and a landscape instead. All the other paintings which have the St Joseph right from the start, could be all copies. All other technical elements such as the sketching shown by the infrared examination or the nature of the painting layers as seen on samples examined under the microscope are well compatible with Raphael's technique. It is now generally accepted that the painting in Chantilly is the original.
- An example to the contrary is given by a Virgin and child, which is not an original XVth painting from Sienna. First, the eyes of the Virgin do not have the typical Giotto's aspect, and the way her hands are crossed is unusual. The preparation is a thick layer of zinc sulfide and baryum carbonate completely different from the seven layers of gesso recommended by Cennini and commonly used in Sienna at this period. The radiograph does not show the usual lead white currently used for the carnations. Finally the red pigment found on one of the samples is a cadmium containing red which has been synthesized only in the XIXth century. The case seems clear, it is a XIXth century copy.

The **restoration** is an important activity which always benefits from the assistance of the tools of the laboratory. The restorer has a very tricky task and he is always much better off to know as much as possible about the nature of the materials used and everything which is underneath, below, behind, hidden to his eyes.

- The **"Noces de Cana"** is one of the largest paintings in the Louvre, it is 70 m^2. It was painted by Veronese in 1563 to decorate the dining hall of the benedictine convent of San Giorgio Maggiore in Venice. It was restored recently, during two years, under the eyes of the public and was in particular entirely radiographed by the laboratory, of course *in situ*. More than 150 samples of the painting material have been taken and analyzed, which increased largely our knowledge of Veronese's techniques. There was one major discovery: the mantle of the superintendent, an important character in the center of the painting, which was a brownish red, had been initially green. It is a very ancient modification since a first copy of the painting, only some fifty years after, show already a red mantle. After long discussions between the experts, it was decided to turn back to the original green color which is what you may see now in the Louvre. Another discovery was the addition of a face painted on paper, glued onto the painting probably some years after the original had been in place. Is it the portrait of the new superior named in 1564 and who wished to be present on the painting? There are arguments about the identity and the origin of this addition.

NARCISSE AND THE MODERN TREATMENT OF IMAGES

The laboratory, as you may understand from my first examples, produces many images. It is equipped with some 1200 m^2 of photographic spaces, for taking the photographs,

printing, enlarging black and white photographs and radiographs. There are in storage more than 80,000 radiographs of paintings and objects and as many photographs. This has been the initial motivation of M. Lahanier to initiate a project named Narcisse. It consists of scanning the images and, as well, of storing all the technical information available in the reports on optical disks. This allows first to preserve this information which does not age well on film supports and secondly to make it available to the entire community of the people interested throughout the world by using the new information networks which are beginning to be set up. To make all this information usable by the specialist communities, it has first been necessary to get the agreement of all experts on the exact use of every word, not only in France but also in the other countries for the various languages in which the system is or will be available. The scanned image opens also the possibility to use the computer programs now available for image analysis, for comparisons, superpositions, counting, color measurement, etc. The Thomson company has built for this project a special scanner which gives a 6000 x 8000 pixels image of a 30cm x 40cm radiograph or other in 9 seconds. The quality of the colors is also as perfect as it is technically possible today.

Thanks to this equipment and all the preliminary work already done, the laboratory has recently prepared a commercial by-product in the form of a CD Rom on Poussin which is commercialized by the "Réunion des Musées Nationaux", the body which handles in France all the commercial aspects of the national museums. 40 paintings by Poussin which had been studied are described in this CD-Rom. In addition to the images which can be looked at leisure with a magnification of 64 with respect to the original photograph, all the technical information available on these paintings, radiographs, details, UV and IR images, analytical results, etc. Are included and can be consulted with great comfort through the techniques of hypertext. It is already in five languages including portuguese. Other CD-Roms are in preparation on Corot, Picasso and the Limoges medieval enamels.

ANALYTICAL TECHNIQUES

The analytical techniques used in the laboratory are either structural or elemental. Fourier transform infrared spectrography, gas chromatography, X-ray diffraction and microchemical methods allow to determine the nature of the compounds. The elemental techniques are the UV emission spec-troscopy, the X-ray fluorescence, the scanning electron mi-croscope equipped with energy dispersive system and lastly the ion beam accelerator.

The accelerator, named AGLAE, a 2 MV tandem machine gives the possibility to use all the analytical techniques wich the ion beams make possible. These are the X-ray emission under the ion impingement named PIXE, the back scattering of ions named RBS and above all the nuclear reactions. The latter are the most promising because there are many reactions with all the elements, including the lightest ones down to hydrogen. An additional potential advantage comes from the resonant nuclear reactions. These occur for a particular energy, which may allow to measure the concentration of the reacting element within the depth of the specimen by varying the incident energy and therefore to measure concentration profiles on a thickness of some tens of micrometers. The ion beam techniques are superficial, non destructive, rapid and accurate. An external beam allows to analyze the objects without the need to take sample or to place the object under vacuum. This is of great advantage because many precious ancient objects cannot stand the vacuum and sample removing is always problematic and should be avoided as much as possible. Another beam line is a microbeam with a diameter of about 1 micrometer whereas the other two beams have a diameter of 1 mm. It allows to analyse very fine details and particles and to draw the map of the distribution of the elements in the chosen area.

The **purposes of the analyses** can be very diverse. One may simply wish to identify the materials used and this is often the starting point of many investigations. Constituting the data base of the materials used by a given culture or artist or school is often the prerequisite for further studies such as the provenances or the understanding of the techniques used. They are also the basis for most of the authentication or dating activity.

- A good example of the interest of answering the simple question "what is it made of?" is the recent work on egyptian pectorals from the Louvre. The egyptian antiquities department has among other treasures three pectorals which were found together in the Serapeum in Memphis. All the materials used have been identified and it was surprising to find that they were quite different from one pectoral to the other. One of them had very pure gold and precious stones, lapis lazuli, turquoise and tourmaline; another one had a gold heavily alloyed with copper and silver, a more crude fabrication technique and no precious stones at all but glass, egyptian blue and frit. The third one was somewhat intermediate. These observations were somewhat surprising for the curators in charge and raised several questions such as the existence of several sources of materials and places of fabrication or on the definition of what is precious.

In many instances nothing is known about the materials or the technology used in such and such period. This is the case, for instance, with enamels for which it is important, first, to identify the various metals or the components of the glasses, or with manuscripts where an important activity is going on inks and pigments identification.

- The lead and tin yellow is an example where the analysis may help the authentication. This pigment was used until the XVIIIth century. It is a double oxide of lead and tin which has two varieties. The first is well defined crystallographically, it is a quadratic Pb_2SnO_4, the second one is less well defined, it contains a partly glassy phase containing lead and silicon and crystals of cubic $PbSnO_3$. It is simple to recognize the second variety with EDS on the scanning electron microscope because of the presence of the silicon. A large number of paintings of the XIVth and XVth century have been examined and it was found that the first variety was no longer used from around 1440. The reason for such a change is not known, it may be related to the use of a glass, but this transition may help dating some paintings.

Provenance is an extremely important question because it may give indications on the commercial relations and therefore on the exchanges that may or not have taken place. The sort of fingerprint of the material which is given by the spectrum of the existing trace impurities can often be used. Such an investigation is presently under way at the laboratory on the flint stones of the Paris area, which is a former sea with chalk and many possible and identified sites of flint production. The work consists of analysing specimens taken from every site and trying to find discriminant elements or combinations of elements which may be characteristic of each. Preliminary results are encouraging.

Outside from the simple identification and data base compilation, the analyses may bring determinant information on the **techniques** used and their evolution.

- For instance, another work presently in progress by Martine Regert concerns the adhesives used by the pre-historic men to glue the tools on their handles. This is a difficult task of microchemistry, the specimens are less than 1mg, and it is complicated by the degradation due to aging and the modifications which occurred in the soil. It is generally

assumed that the ancient man used the bark of birch trees characterized by the betulin but the dehydration modifies the spectra.

- Starting from work on decorated objects found in caves in Ariège in the south of France, Menu and Walter have been led to study all the colored material used in these caves. To make a long story short, they have discovered that our ancestors had an elaborate technique and not the instinctive gesture which was previously imagined. They used a charge material such as potassic feldspath to dilute the coloring material and facilitate its adherence to the wall. They ground the pigments differently depending on lhe color to be obtained, they mixed them carefully with the charge and certainly a binder such as grease or oil. This work also allowed to relate the techniques used for the objects, which incidentally can be dated, to that used on the walls, thus giving a possibility to identify chronological steps in the decoration of the caves. It was found that these caves were in fact decorated during more significant periods than previously thought.

Although it is not an analytical technique, mention must be made here of the **thermoluminescence** which is the only dating technique used in the laboratory and which can date the ceramics. The preparation of the samples is lengthy, tedious and must be very constant, this is why a robot has been built to make the preparations automatically.

The thermoluminescence is based on the existence of defects in geological materials due to bombardment by cosmic rays or natural radioactivity, which emit visible light when they disappear. Heating this material, as when the clay is turned into a ceramic, anneals out these defects and the clock is set to zero. Then, the ceramic is in its turn submitted to the same radiations and new defects form again. There will be the more of them, the longer the ceramic is irradiated, i.e. the older it is since its first fabrication. If the ceramic is heated once more today, one can measure all these defects which have accumulated. This technique is widely used to detect modern copies. With a more complete experimental procedure and a good knowledge of the surroundings and of the composition of the material, one can also date the ceramics, to about 7% at best. This is very useful for the archaeologists since ceramics are one of the most common remaining material in excavations and they are used to date the different layers.

- Recently the laboratory has received strange tiles from the cathedral of Meaux, a gothic cathedral at the east of Paris. They were partially covered with colored glazing in the form of bands which could, when properly assembled, form a design. The date we found coincided exactly with the known date of construction of the cathedral, in the beginning of the XIIIth century. This means that the original roof of the cathedral was colored and decorated.

As mentioned in the beginning, some longer term investigations are also made. They are very diverse and bear for the most part on the modifications the works of art have undergone since their original creation. In addition to those made by the author himself or during restorations, modifications may come from the simple **use of the object** when it is a practical one or from the **aging and deteriorations** which all materials have to suffer.

- A flint tool for instance has in general been used. It would be exciting to know for which use. Many archaeologists study the physical traces, that is the more or less lustreous appearance which can be observed on the edge of the flints. This gives some hints to the type of material which was worked with the tool but the interpretation is problematic. With the accelerator, again, Christensen, Menu and Walter have tried to see if some of the material being worked did not remain within the asperities of the rough flint surface, like the butter on a piece of bread. This was positive with the apatite when a bone was worked with the tool or with the elements characteristic of various woods. Indeed, the results of experimental work with modern flint were extremely encouraging and some applications to ancient tools have shown the feasibility of extending this work to the prehistoric material.
- Some of the modifications can be put to a profitable use for dating some objects. A recent investigation which was Walter's doctor's thesis has dealt with the determination of the processes of diffusion of fluorine in the complex silicate material, the flint stone. Once abandoned in the soil, the flint receives natural waters which always contain some fluorine. A resonant nuclear reaction (p, aγ) on ^{19}F, with accelerated protons allows the determination of the fluorine concentration profile within the flint, thus allowing to determine the duration of the stay in the soil. This may provide a method to date flint objects, which is impossible today.
- The pigment named smalt is an interesting case. It is a ground potassium glass, colored in blue by cobalt ions, up to 10% in volume. It has been used as pigment from the XVIth to the XVIIIth centuries. Very often, it looses its color in oil paintings, such as can be seen on the **"Noces de Cana"** for instance. It is not systematic and the causes are not identified. The alteration proceeds from the outside to the center. There is an interaction with the oil in which one finds cobalt ions, and the potassium seems to disappear. The mechanism remains to be elucidated.
- Several XIXth century artists have tried to innovate and used non proven techniques which now raise new problems of conservation and of restoration. They show accelerated aging, giving premature large cracks such as on paintings by Prudhon. This comes from differences in the drying rates and in the mechanical properties of the different layers. The diagnosis may identify an excess of lead drying agent, the hardening due to the use of natural resins or the addition of tar or, on the contrary, a lack of drying agent. These XIXth century paintings open a large range of necessary studies.

Many of these studies are presently under way and there are also several projected actions. We are interested for instance in the beginnings of the copper fabrication. It is known that, at first, native copper was used. When was it first melted? When was the transition between native material and metal elaborated from natural ores? Copper was then smelted from oxides or carbonates then from sulfides, which are more difficult to use. When was the transition from the easier ores to the more difficult ones? We are attempting to answer these questions by measuring, with the accelerator, impurities which are not usually analyzed such as carbon, oxygen, sulfur, phosphorus or nitrogen.

The description of examples of investigations in progress or terminated could go on but it is necessary to come to the conclusion.

CONCLUSIONS

The scientific methods give a new way of approaching the artistic gesture. Understanding the materials choices and the techniques helps us to know the artist more intimately and from a different angle. We try to guess what he knew, what he had learned and from whom or eventually what his genius brought him to discover. This way of looking at art objects is complementary to that of the art historian. The combination of the two approaches is often enlightening, although often conflictual. The assurance of the scientist, sitting on his scientific proof and the strength of the experimental approach, is sometimes difficult to accept by the humanist who has an immense memory, a close familiarity with the artist or his period and has acquired a strong

conviction. To bring conclusive evidence against, or even in favor, of his truth, is often shocking. It is necessary to build up a climate of confidence and to convince of the interest and the advantages of the scientific approach. The approval of the curator in charge is imperatively needed, because, anyhow, they have the responsibility of the collections.

There is one area in which the scientific approach is unique and has an unquestionable advantage, that is the conservation of the materials which make the artistic work. The scientific tools are then the only ones which may make the diagnosis, measure the damage and help to slow down the inexorable deterioration of all the human heritage. There is an immense field of phenomena, very complex ones, which require the involvement of good scientists. Some of these investigations can be tackled by the international community but I feel strongly that also the local conditions justify the involvement of every country and the adaptation to the local conditions of aggression and all the local relevant situations.

For the moment restoration is doing its best but one cannot restore indefinitely. There is the need for the scientific approach to really understand the phenomena that are operating and to fight the degradation from the start and perhaps even reconstruct the initial material, atom by atom. This will be the challenge for the future generation of chemists such as those assembled here at this annual congress.

FURTHER READING.

Many of the examples described in this article are taken from the review TECHNE, which is edited by the laboratory. The first issue (1994) contains articles on "Poussin and the French painting in the XVIIth century", the second one (1995) is an "Autoportrait of the laboratory". They may be acquired from the Reunion des Musées Nationaux or by writing to the Laboratory. The postal address is 6 rue des Pyramides, 75041 Paris Cedex 01, France.

See also the special issue of the french art magazine "Connaissance des Arts" Hors serie Nº 68, 1995.