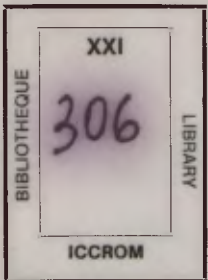


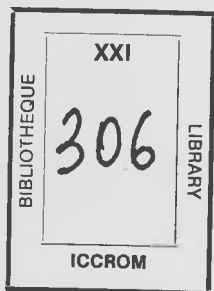
Scientific Investigations of Works of Art

MARCO FERRETTI



ICCROM

1993



SCIENTIFIC INVESTIGATIONS OF WORKS OF ART

Marco Ferretti



Rome, 1993



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OF WORKS OF ART

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CONTENTS

Introduction	1
ANALYTICAL METHODS	5
1. NEUTRON ACTIVATION ANALYSIS (NAA)	7
2. X-RAY FLUORESCENCE (XRF)	11
3. PARTICLE-INDUCED X-RAY EMISSION (PIXE)	19
4. ATOMIC ABSORPTION SPECTROSCOPY (AAS)	23
5. INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY (ICP-AES)	25
6. ION CHROMATOGRAPHY (IC)	29
7. INFRARED SPECTROSCOPY (IRS)	33
8. X-RAY DIFFRACTION (XRD)	39
9. SCANNING ELECTRON MICROSCOPY (SEM)	43
STRUCTURAL METHODS	47
10. PHOTOGRAMMETRY	49
11. ENDOSCOPY	51
12. SPECIAL PHOTOGRAPHIC TECHNIQUES (SPT)	53
13. REFLECTOGRAPHY	57
14. STRUCTURAL ANALYSIS WITH THE FINITE ELEMENT METHOD (FEM)	59
15. STRAIN GAUGE MEASUREMENTS	61
16. LASER INTERFEROMETRY	63
17. ACOUSTIC EMISSION (AE)	67
18. RADIOGRAPHY	71
19. ULTRASOUND	75
20. THERMOGRAPHY	79



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INTRODUCTION

It has not been long, probably no more than 30 to 40 years, since the world of works of art has been studied with scientific criteria, and disciplines such as chemistry, physics, biology, engineering, mathematics and computer science have been brought to bear on the question.

Here, as in every branch of science, enthusiasm for a new application has often led people to overestimate the capabilities of a method and the power of technology in general. This attitude has produced situations where the expense of means was totally out of proportion to, and inappropriate for the actual diagnostic problem. Therefore, some time has been (and still is) necessary in order for specialists to find the optimum application ranges, where costs are balanced by the significance of results.

At present, it seems to be clear that sophisticated technologies are not sufficient by themselves to solve complex problems, and that it is more important to be able to integrate different types of information to produce a reasonably complete and self-consistent knowledge of the work of art under investigation. In such a context, computer science (the capability of which has probably been overestimated as well) can perhaps find one of its most important roles, i.e. making large amounts of data easily available, processable and comparable.

There are probably two major conditions for the establishment of an integrated information system. The first concerns the working environment, which has to be highly interconnected: specialists with different backgrounds – art historians, restorers, physicists, chemists, biologists and engineers – have to work together under the same roof on the same problems. They must be able to interact at every stage of the study, not only when discussing the final results.

The second condition is the existence of a coordinator who has a deep knowledge both of the problems of studying and conserving cultural heritage and of the field of use, characteristics and limitations of the most important investigation techniques. This person should be able to plan a complete diagnostic campaign, or at least large parts of it, as well as to read, interpret and integrate the data coming from the specialists.

The above considerations have been made to emphasize that the study of works of art by scientific methods is not, or at least is not only, a matter of technology and that the cultural composition and interconnection of the working environment are probably much more important.

We should also stress the fact that these technical notes were developed to support participants in ICCROM's course on Scientific Principles of Conservation (SPC) with regard to the unit on scientific methods of investigation. The extremely large number of technologies, as well as the limited time available for the lectures force these notes to be similar to a list of methods.

Owing to the fact that other major units of the SPC course are devoted to study of materials and related analytical problems, we preferred here to stress the working principles of the diagnostic techniques, as well as their merits and drawbacks, in order to give an idea of the types of problems one can expect to solve with a given method. For this purpose, only a few examples are given without the pretence of exhausting the subject.

These notes are divided into two parts, one on analytical investigation methods and the other on structural investigation methods. From an historical point of view, the former are probably the first to have been applied to this field.

It is important to observe that these analytical techniques are not used only for conservation purposes: for instance, the detection of trace elements is very often employed to characterize archaeological objects. These types of analyses are the scientific basis for provenance studies of pottery, metals and other archaeological materials, due to the fact that such materials, although made of the same major components, very often differ with regard to the composition of trace elements, depending on the provenance of the base minerals.

As far as conservation in the strict sense is concerned, all the analytical techniques mentioned in these notes have important applications. Ion chromatography, X-ray diffraction and the scanning electron microscope, for example, are widely used for the study of deterioration processes of stone and metals.

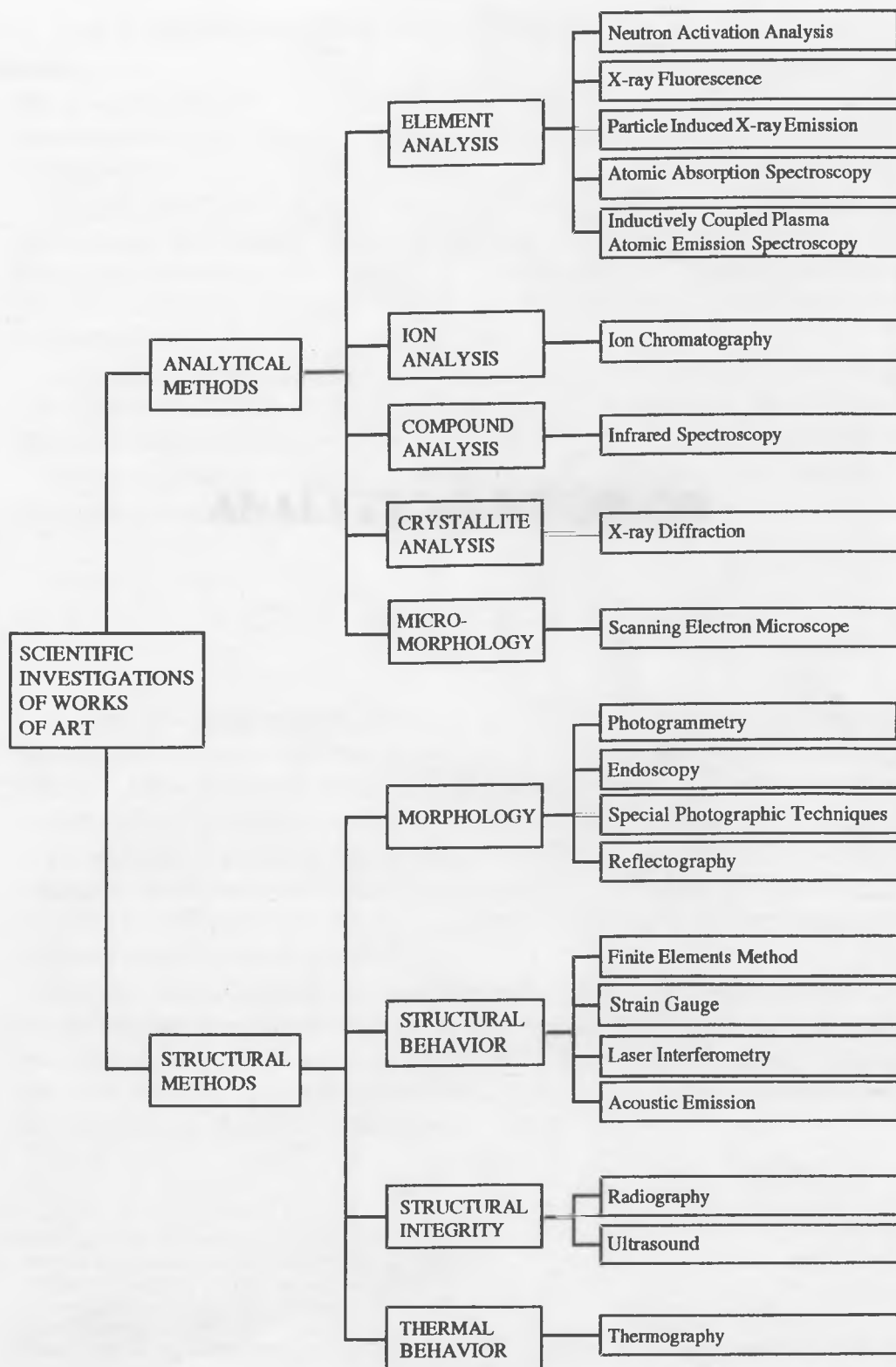
The application of structural methods to the study and conservation of works of art is more recent (except radiography, perhaps) in comparison to analytical methods and is more closely related to the problems of conservation.

Several of the structural methods (endoscopy, strain gauge, laser interferometry, acoustic emission, radiography, ultrasound, thermography) were developed in other fields such as materials science, quality control of industrial products and maintenance (of aircraft, for example) and are mainly concerned with the detection of faults in the matter, cracks in particular.

It is self-evident that such methodologies would find important applications for the study of the stress conditions of structures of artistic interest (every object can be regarded as a structure) and for the study of deterioration processes involving the creation and propagation of cracks and other defects.

Other techniques such as reflectography, special photographic techniques and the already-mentioned thermography use the peculiarities of the interaction of matter with electromagnetic radiation to give images of objects under radiation wavelengths other than visible light. Such imaging techniques can show aspects and details of the object that are not visible to the human eye.

The block diagram in fig. 1 gives an overview of the investigation methods described in the following notes and groups them according to the type of information they supply.



ANALYTICAL METHODS

ANALYTICAL METHODS

1. NEUTRON ACTIVATION ANALYSIS (NAA)

Physical principles [1]

Neutron activation techniques are based on the detection of γ -rays produced by the decay of unstable nuclei.

Unstable nuclei are usually produced in the sample by reactions of neutron¹ capture. Thermal neutrons are generally employed due to the high cross-sections²; nevertheless it may be convenient to use fast neutrons, as shown in reference [4]. Activation can also be induced by other particles, such as charged particles and photons, but these methods are less widely used.

After a neutron is absorbed, the target nucleus tends to reach a more stable configuration with a series of nuclear transitions that involve β^- decay and, above all, the emission of characteristic γ -rays that can be detected, analyzed and used to identify the parent nucleus.

The relative weight of the parameters involved in the activation process can be understood by considering the following equation:

$$A(t_r, t_a) = \Phi \frac{N_0}{A_i} \sigma_{i,j} \left\{ 1 - \exp \left[-\frac{t_r}{\tau_j} \right] \right\} \exp \left[-\frac{t_a}{\tau_j} \right]$$

where $A(t_r, t_a)$ is the activity of the sample that was kept t_r seconds in the irradiation facility and measured t_a seconds after being extracted, Φ is the neutron flux, N_0 is the Avogadro number, A_i and $\sigma_{i,j}$ are the mass number and the capture cross-section of the parent nuclide, respectively, and τ_j is the mean life of the daughter nucleus.

The equation of activation can be manipulated to show that the detection limit is inversely proportional to the neutron flux; this explains why reasonably low detection limits can be achieved only by means of such expensive, complicated and cumbersome structures as nuclear research reactors.

A further consideration is that the background of the measurement can be considerably reduced by properly managing the irradiation and waiting times. Long waiting times can be used in the detection of long-lived isotopes, allowing the short-lived ones to decay. In contrast, the detection of short-lived isotopes is improved by reducing the irradiation time and, consequently, the activity of long-lived isotopes.

¹ With regard to their energy, neutrons are commonly classified as follows:

- thermal neutrons: Maxwell distribution with $E_m = 0.025$ eV;
- epithermal neutrons: 0.4 (Cd cut-off) $< E < 1$ keV;
- intermediate neutrons: 1 keV $< E < 100$ keV;
- fast neutrons: 100 keV $< E < 10$ MeV.

² The quantity "cross-section," indicated with σ , accounts for the probability that a certain reaction will take place.

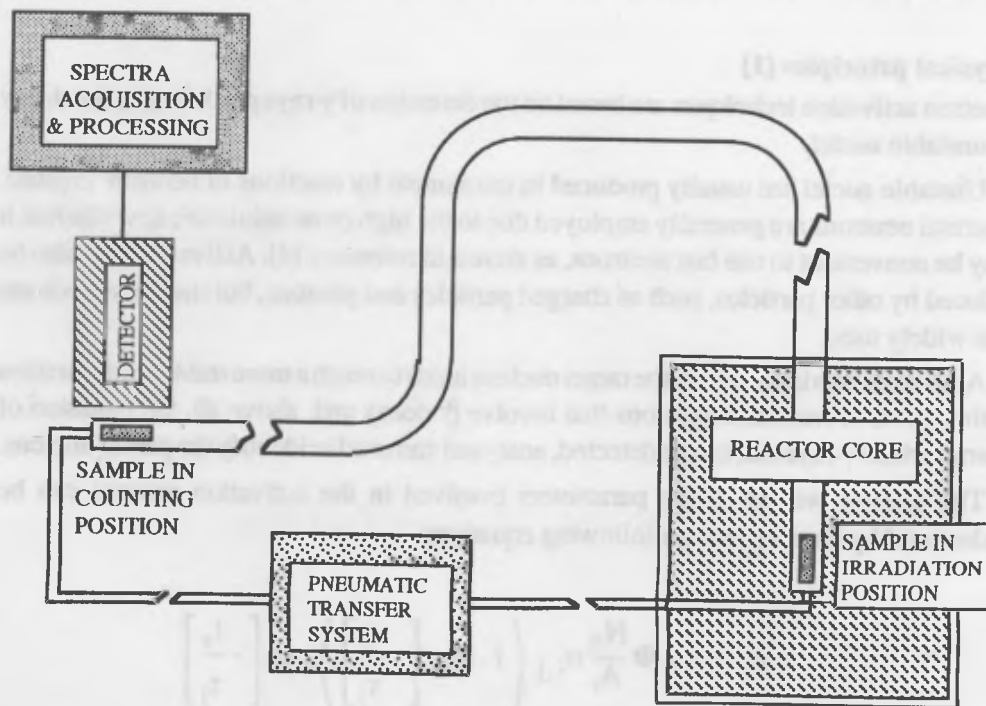


Figure 1 – Diagram of an NAA facility.

Instrumentation

Figure 1 [1] schematically shows an NAA facility composed of the three following systems:

- 1) NUCLEAR RESEARCH REACTOR, which supplies fast or thermal neutrons at extremely high fluxes. Neutrons are generated by fission reactions in uranium.
- 2) SAMPLE TRANSFER SYSTEM, which is pneumatically operated and provides rapid transfers of the samples between the irradiation position, inside the reactor core, and the measurement position, which is generally several tens of meters away from the reactor.
- 3) COUNTING SYSTEM, which is similar to those of XRF, PIXE and SEM. The systems differ slightly with regard to the detector (of the HPGe well-type), which is optimized for the detection of photons of much higher energy than X-rays.

Features and limits

It is possible to demonstrate that the detection limit of activation techniques is inversely proportional to the neutron flux, to the capture cross-section and to the number of target

atoms. Cross-sections vary by orders of magnitude with the mass number; for very light and very heavy elements, for example, they are low [2] and detection limits unacceptably high. For most of the remaining elements, realistic figures are in the range of 0.1-10 ppb for thermal neutron fluxes of $10^{13} \text{ cm}^{-2}\text{s}^{-1}$ and sample weight of 100-200 mg [1, 3]. The latter figure shows that, although substantially destructive, NAA requires very small amounts of sample. Due to the large number of peaks that most elements show, the effect of interference on the detection limits should be also considered: such effects can be reduced by properly managing the irradiation times and by mathematically correcting the experimental data.

Quantitative analyses require calibration with standards but do not require sample pre-treatment, because the high penetration into the matter of both neutrons and γ -rays always assures that the entire sample volume is concerned in the analysis.

The most important limitation of NAA is the necessity of a nuclear reactor; in fact, even if in principle radioisotopic neutron sources can also be used, in this case fluxes would be so low as to increase the detection limit by a factor of 500,000, which makes NAA much less attractive in comparison with other techniques.

Applications in fields of artistic interest

Reference [4] describes the study of the composition of 60 Islamic glass stamps and monetary weights, covering the periods of Umayyads (A.D. 661 - 750), Abbassids (750 - 870), Tulunids (870 - 905), Fatimids (969 - 1171) and Mamelukes (1251 - 1517). NAA was chosen due to the poor representativeness of such surface analyses as XRF or PIXE. The objects were first irradiated with thermal neutrons from a moderated ^{252}Cf source, in order to determine the Mn content. Subsequently, fast neutrons from a cyclotron were employed at short (30 s) irradiation times to determine the content in Mg, Al, Si, K and at long (5 to 40 min) times for Na, Ca, Ti, Fe, Co, Ni, Cu, Zn, As, Rb, Y, Zr, Sn, Sb, Ba, Ce, Pb.

The classification of objects was done by statistic methods that allow grouping of different elements with similar behavior. Three groups were distinguished: the first, characterized by all the objects belonging to the period 90 - 162 of Egire (A.D. 576), an intermediate group and the third one including all the objects of Fatimides and Mamelukes dated after 341 of Egire. The passage from the first to the second group shows a decrease of Al, Fe, Ti and an increase of Ca; this can be attributed to the change in composition of the sand employed for the fabrication of glass. The passage from the first two groups to the third one is characterized by a considerable increase of K, Mg, Mn; this can be attributed to changes in fabrication technology: the flux passed from a sodium base to a vegetable ash base.

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2. X-RAY FLUORESCENCE (XRF)

Physical principles [1]

The transition of electrons between two atomic shells may cause the emission of a photon whose energy is strictly related to the energy difference between the shells.

The inner shells of an atom are indicated with the letters K, L and M, and the corresponding binding energies, indicated with B_K , B_L and B_M , depend not only on the type (whether it is K, L or M) but also on the atomic number Z ; this means, for example, that B_K in silver is different from B_K in copper.

If a photon strikes an atom and its energy is sufficiently high, one of the inner electrons may be ejected; the vacancy that is created tends to be filled by an electron from the outer shells, and other bound electrons fill the new vacancies in cascade.

The transition of electrons to more tightly bound states may involve the release of an X-ray and its energy is the difference between the binding energies of the two states. For example, if the transition takes place from the L to K-shell, the X-ray energy is given by:

$$E_x = B_K - B_L$$

On the basis of these considerations, the composition of a sample can be non-destructively investigated by irradiating it with photons of sufficiently high energy and by analyzing the exiting fluorescence radiation in terms of energy and intensity (count-rate): the former characterizes the element, the latter its abundance. Figure 1 shows a typical XRF spectrum from a bronze alloy; the horizontal position accounts for the energy and the height of the peaks indicates the count-rate.

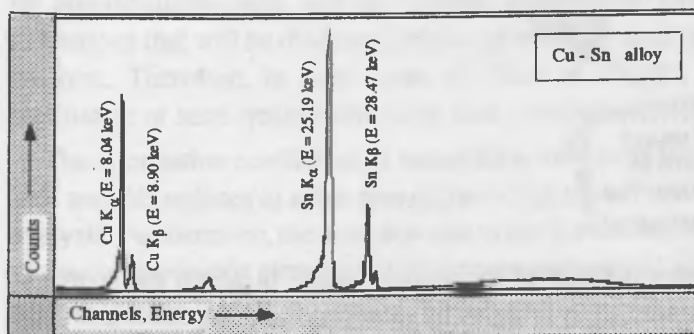


Figure 1 – X-ray spectrum of a Cu-Ag alloy.

X-ray fluorescence is also induced by charged particles, apart from photons, and this characteristic is employed in other analytical techniques (PIXE and electron microprobe) which will be described later on.

Instrumentation

Figures 2 to 4 illustrate three types of XRF systems, designed to be used in different experimental situations and with different sensitivity requirements.

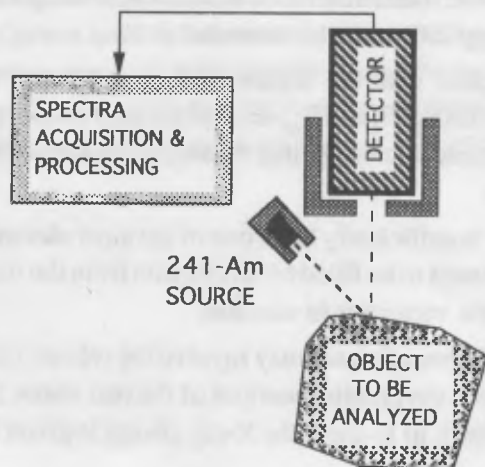


Figure 2 – XRF system employing a radioactive source.

The system in figure 2 was widely used for field investigations. The use of a radioactive source considerably reduces the overall weight but the sensitivity is relatively poor due to the low photon output of the source; further difficulties arise from current legislation which severely restricts the transport of radioactive sources.

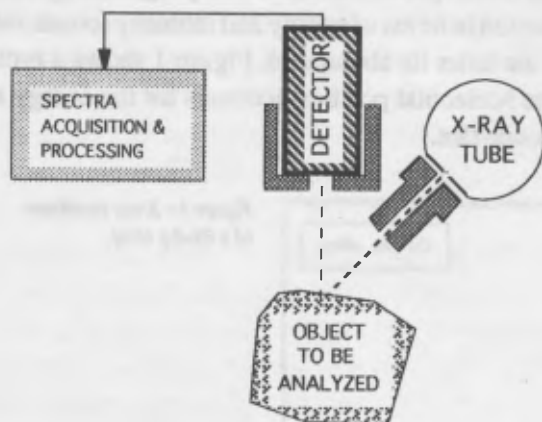


Figure 3 – XRF system employing an X-ray tube.

Figure 3 shows a major improvement of the above system, in which the source is replaced by an X-ray tube. The sensitivity is higher by some orders of magnitude and there are no legislative restrictions on transport, but the system is heavy, cumbersome and complicated to manage.

This setup is currently used for the analysis of paintings and archaeological objects.

Finally, a laboratory device for quantitative analysis of thin layers is shown in figure 4. The presence of a secondary target should be noted; the sample is a layer of some

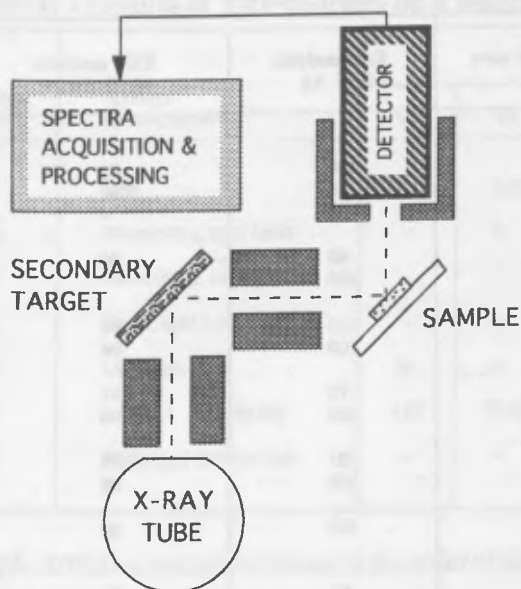


Figure 4 – XRF system employing an X-ray tube with secondary target.

hundreds of mg/cm^2 obtained by solubilization and deposition on a filter. Under these conditions, the count-rate depends only on the concentration of the element under observation, and accurate quantitative determinations can easily be performed.

This method was used for the bronze alloys of the Marcus Aurelius statue: 200 mg of sample were drilled from the inside and processed as described.

Features and limits

XRF is considered an indispensable tool for the study of artistic materials, mainly due to its non-destructiveness and the rapidity of analysis. Unfortunately, due to intrinsic limitations that will be discussed below, quantitative determinations are quite difficult to perform. Therefore, in most cases of practical interest, it should be regarded as a qualitative or semi-quantitative analytical technique.

The attenuation coefficient of materials is extremely high at energies of some tens of keV and this reduces to a few tens of μm below the surface of the layer concerned by the analysis. Furthermore, the detection rate of the X-rays depends not only on the abundance of the corresponding element but also on the presence of all the other components of the sample (matrix effect).

In order to take these effects into account, the system must be calibrated. The closer the standards are to the samples to be analyzed, the more accurate the measurements. The extreme difficulty of producing standards with the same surface conditions as the artistic artifacts (roughness, corrosion and homogeneity) explains why quantitative measurements are so difficult to perform.

Table I - Results of XRF analyses on Roman silver objects

Object and inventory no.	Measurement area	R/C analysis wt % Ag	XRF analysis wt: % Ag
Double-handled plate IV-2599	Front central	100	93
	Back central	99	92
	Handle	99	-
Small double-handled plate IV-25313	Front central	99	92
	Back central	100	
Basket cover V-25343	External	100	94
	Internal	100	94
Small mug XIII-25290	Lateral	73	91
	Other lateral	100	95
Small mug XIII-25291	Lateral	97	94
	Other lateral	100	95
Single-handled cup IV-25691	Bottom	100	93
Handled pot III-25262	Bottom	91	95
Cup with fragments of lamina IV-25373	Lamina	100	90
	Lateral of cup	100	83
Plate with flat bottom III-25350	Front	90	93
	Back	98	93
Plate with flat bottom III-25351	Front	91	93
	Back	96	91
Mug IV-116330	Lateral	83	92
	Other lateral	63	89
Mug IV-116332	Lateral	81	92
	Other lateral	73	91
Fragment of cup lamina XVI-25565	Lateral	94	73
	Bottom	93	93
Mug with fragments of lamina XVII-25578	Lamina	92	83
	Lateral of int. element	77	83
Mug with lamina XVI-25301	Lateral of lamina	88	87
	Other lateral of lamina	54	81
	Bottom	96	94
Mug with lamina XVI-25300	Lateral of lamina	94	79
	Lateral of int. element	99	79
Double-handled cup IV-110846	Bottom	93	87

As far as sensitivity is concerned, one must consider that even if detection limits have been achieved in the range of some tens of p.p.m. under particular experimental conditions, yet in most practical cases they are much higher.

Table II - Results of XRF analyses on a Botticelli painting

Meas. no.	Area of measurement	Count-rates (1/s)					
		Ca	Fe	Cu	Pb	Sr	Sb
17	Lips	—	1.19	—	51.35	9.27	—
2	Retouching, right hand	—	tr.	—	86.28	—	20.76
14	Retouching, neck	—	—	—	67.19	—	27.69
1	Flesh, right hand	—	tr.	—	83.63	—	—
12	Light part, neck	tr.	tr.	tr.	90.10	—	—
13	" " " (15 kV)	1.57	15.02	—	14.21	n.d.	n.d.
15	White part close to hair	—	—	—	90.22	—	—

Typical relative uncertainties are in the order of some percents for the major components of metal alloys.

Applications of artistic interest

Tables I to III show some relevant experimental results obtained with the systems illustrated in figures 2 to 4, respectively.

Roman silver objects from Herculaneum and Pompeii, exhibited at the National Museum of Naples, were analyzed and the measured concentrations of silver are given in table I [2].

The surface composition (XRF method) of the artifact very often differs from the bulk's (R/C method), as was previously pointed out, due to the presence of thick patinas; the hypothesis of selective corrosion processes was advanced to explain these discrepancies.

Table II gives some of the results of the measurements performed on Botticelli's *Portrait with Medal*, from the Uffizi Gallery, Florence [3].

For the sake of brevity, only the whites and flesh tones are reported and discussed. The results are essentially qualitative or, at most, semi-quantitative because several layers overlap one another and, even on the same layer, the brushstrokes are not homogeneous.

This method is particularly useful when colors with similar chromatic yield have to be compared. In table II, for example, the retouching is characterized by the presence of Sb (Naples yellow is made of lead antimonate) whereas the original flesh tones contain Pb and Fe (probably white lead with an ochre or an earth); the white point shows only Pb (white lead).

The bronze alloys of the Marcus Aurelius were analyzed by means of XRF [4]. Table 3 shows some of the most meaningful results of the analyses; the uncertainties are quoted at 68% confidence level.

Table III - Results of XRF analyses on the bronze alloys of Marcus Aurelius

Sample no.	Area of sampling	Sample composition [wt. %]		
		Copper	Tin	Lead
Horse				
1	Left hind leg, shin	80.04 ± 0.57	10.36 ± 0.41	9.60 ± 0.19
2	Left hind leg, forearm	80.49 ± 0.57	8.77 ± 0.41	10.22 ± 0.19
3	Right foreleg, shin	82.05 ± 0.72	8.42 ± 0.46	9.53 ± 0.18
4	Right foreleg, forearm	79.66 ± 0.57	8.30 ± 0.40	12.03 ± 0.20
15	Belly, right side	79.34 ± 0.70	7.27 ± 0.52	13.40 ± 0.22
32	Belly, right side	78.41 ± 0.56	5.32 ± 0.38	16.27 ± 0.23
47	Belly, right side	82.15 ± 0.70	5.98 ± 0.47	11.87 ± 0.20
35	Belly, left side	81.55 ± 0.57	4.38 ± 0.38	14.07 ± 0.22
46	Belly, left side	78.93 ± 0.67	7.05 ± 0.49	13.64 ± 0.21
28	Left chest	79.71 ± 0.56	6.73 ± 0.39	13.05 ± 0.21
31c	Left chest	78.36 ± 1.34	7.76 ± 0.48	13.49 ± 0.73
58	Head, left side	78.74 ± 0.56	8.23 ± 0.33	12.54 ± 0.26
Rider				
42	Right knee	82.38 ± 0.58	7.09 ± 0.39	10.10 ± 0.19
43	Right thigh	83.89 ± 0.71	7.19 ± 0.50	8.42 ± 0.18
44	Cloak, right edge	82.43 ± 0.71	6.01 ± 0.50	11.56 ± 0.21
Original welding				
48	Rampant leg	79.11 ± 0.67	4.08 ± 0.49	19.81 ± 0.26
49	Neck, left side	74.86 ± 0.66	6.48 ± 0.50	18.32 ± 0.25
50	Belly, median line	73.88 ± 0.54	7.89 ± 0.33	18.22 ± 0.29
59	Head	74.30 ± 0.55	9.16 ± 0.34	16.55 ± 0.29

The measurements show a clear difference between the elemental composition of the original parts and the welds. The high lead content probably assured the flowability of the welding alloy and facilitated the finishing of the bead. Significant variations of composition are also observed in different points of the same part, probably due to inhomogeneities in the alloy.

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Figure 1. The XRF system.

With the beam path and the sample all perfectly collimated, the detector is positioned at a distance from the sample surface by a fixed cylindrical window. If a parallel beam of X-rays is incident on the sample, the detector is positioned at a distance from the sample surface by a fixed cylindrical window. This arrangement also prevents overexposure.

3. PARTICLE-INDUCED X-RAY EMISSION (PIXE)

Physical principles

The emission of characteristic X-rays can be induced not only by photons, but also by charged particles such as electrons, protons, α -particles, deuterons or heavy ions. This chapter will focus only on protons, which are used in most cases.

The ionization process is described as a Coulomb interaction in which the energy transfer between the accelerated proton and one electron of the inner shells causes the electron to be ejected. The consequent de-excitation of the atom takes place with the modalities described in the XRF chapter and the analysis of the exiting fluorescence radiation is performed in the same way and for the same purposes.

Instrumentation

Figure 1 [1] shows a diagram of the components in a PIXE experimental arrangement. The accelerator is generally of the single-ended or tandem type and produces protons with energy of some MeV and with beam currents of 1 to 100 mA.

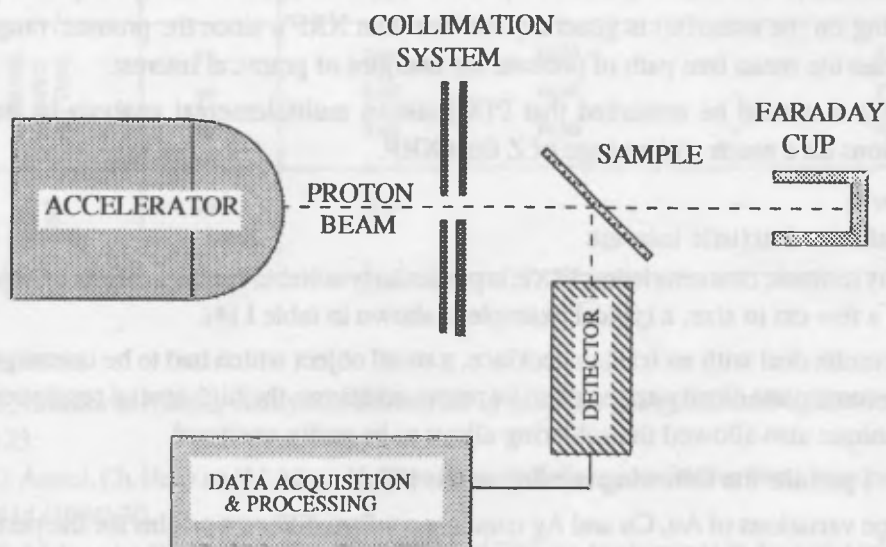


Figure 1 – PIXE experimental setup.

Both the beam path and the sample are generally under vacuum and the detector is separated from the sample chamber by a thin beryllium window. It is possible, however, to have external proton beams; by means of a thin Al window, the vacuum system is separated from the sample chamber; the sample is in air or helium. This arrangement also prevents overheating.

Features and limits [1-3]

Ion beams are produced by accelerators, which are much more expensive, complicated to manage and cumbersome than simple radioactive sources or X-ray tubes; this explains the relatively limited use of analytical techniques based on PIXE.

One of the main reasons people choose PIXE is its extremely high sensitivity, which is in the range of p.p.m., with sample weights in the range of mg's. High spatial resolution can also be achieved because the beam can be focused down to 1 μm in diameter. These features make PIXE one of the most powerful methods for identifying the technological processes in archaeo-metallurgical investigations.

Like XRF, PIXE quantitative analyses require calibration; relative accuracies of 5+10% can be achieved using well-chosen standards.

A serious problem is the energy deposition of the incoming protons, which can damage the surface of the sample; the employment of external beam systems, in which the sample is in an air or helium atmosphere, can prevent surface overheating.

In comparison with the electron microprobe and XRF, PIXE sensitivity is higher by roughly one order of magnitude, at least in the range of low atomic numbers (Z's), whereas heavy elements are better detected by XRF. PIXE's depth of analysis (1+30 μm , depending on the material) is generally smaller than XRF's since the protons' range is lower than the mean free path of photons for energies of practical interest.

Finally, it should be remarked that PIXE allows multielemental analysis in single irradiations on a much wider range of Z than XRF.

Applications of artistic interest

Due to its intrinsic characteristics, PIXE is particularly suitable for the analysis of objects that are a few cm in size; a typical example is shown in table I [4].

The results deal with an Iranian necklace, a small object which had to be investigated because some parts clearly appeared to be recent additions; the high spatial resolution of the technique also allowed the soldering alloys to be easily analyzed.

Table I permits the following considerations [4]:

- large variations of Au, Cu and Ag contents confirm different origins for the parts of the necklace
- the Cd concentration is higher in the neighborhood of solders
- the rear of the setting of the emerald is extremely inhomogeneous
- soldering alloys are extremely rich in Ag and relatively rich in Cu
- the composition of the almond-shaped setting is less rich in Au but seems to be more homogeneous than other parts
- the Ag content of the wire suspending the pearl is below the detection limit.

Table I - Results of PIXE analyses on an Iranian necklace

Meas. area	Meas. no.	Composition [wt. %]			
		Cu	Ag	Cd	Au
REAR SETTING OF THE EMERALD STONE	2	4.85	6.50	0.25	88.40
	3	5.00	12.45	—	82.55
	4	0.50	0.25	—	99.25
	5	4.35	5.70	—	89.95
	6	0.65	0.20	—	99.15
	8	1.00	0.25	—	98.75
SOLDERS	9	6.65	20.05	0.20	73.10
	10	5.45	26.80	0.30	67.45
	12	7.80	14.90	0.20	77.10
	23	9.55	31.35	0.40	58.70
	24	16.80	25.50	0.55	57.15
ALMOND SHAPED SETTING	15	2.80	19.55	—	77.65
	16	3.95	18.35	—	77.70
	17	3.45	15.55	—	80.90
PEARL WIRE	25	5.10	—	—	94.90

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4. ATOMIC ABSORPTION SPECTROSCOPY (AAS)

Physical principles [1, 2]

In the energy range of visible light, the interaction of electromagnetic radiation with matter takes place by excitation of the outer electrons of atoms. This can be experimentally observed by considering a continuous-spectrum optical radiation that passes through a cloud of free atoms; the transmitted spectrum shows some dark lines, which are characteristic of the type of atom: the missing photons have been totally absorbed and have caused the transition of outer atomic electrons to the excited state. The inverse transition can be observed on excited atoms (see ICP-AES): some lines of the emission spectrum, which are caused by the return of electrons to the ground state, exactly overlap the dark absorption lines.

Measuring the ratio between the intensities of the attenuated and unattenuated radiation, as a function of wavelength, is an extremely sensitive method of quantitative analysis; the method requires calibration by means of reference standards of accurately known composition.

Instrumentation

Figure 1 shows a block diagram of an AAS system.

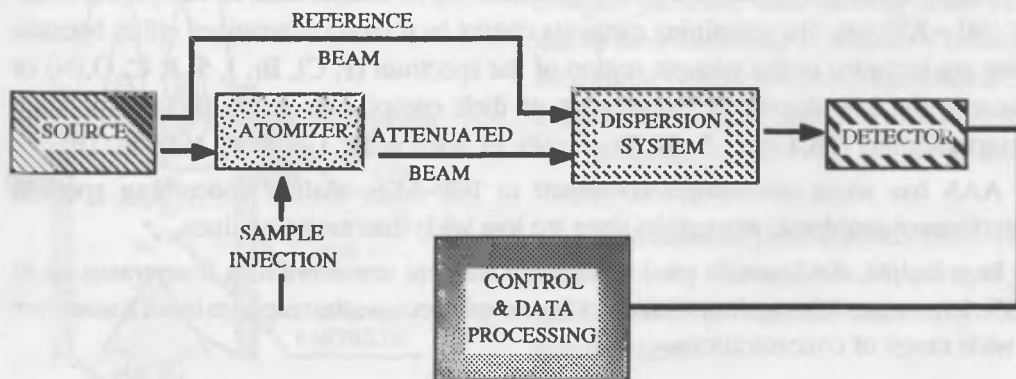


Figure 1 – Block diagram of an AAS system.

The system is composed of the following components [1]:

SOURCE - The radiation emitter; a typical structure is the so-called hollow cathode lamp, in which the light is obtained by exciting the emission of the same element as that to be measured in the sample.

ATOMIZER - Breaks the chemical bonds by heating the sample and produces free, neutral atoms of the analyte; the most widely used are of the flame and furnace types.

DISPERSION SYSTEM - Separates the single components of the observed light: radiations of different wavelengths are diffracted at different angles.

DETECTOR - Detects the diffracted light and transforms the signal into electric pulses; the most commonly used are of the photomultiplier type.

OPTICAL SYSTEM - Provides focusing and propagation of attenuated and unattenuated light beams.

CONTROL SYSTEM - Is generally a computer, which, besides processing, recording and displaying the signals collected, also provides automatic setting of the AAS system parameters according to the element to be analyzed.

Features and limits

AAS is one of the most widely used analytical methods for the determination of trace elements. The experimental setup discussed above clearly shows that only one, or at most two elements are analyzed at a time; furthermore, the operator has to decide *a priori* what elements to analyze and choose the corresponding lamps.

The detection limits are highly dependent on the structure of the system and, in particular, on the type of atomizer; typical figures are $10^{-1} + 1$ ppb for furnace atomizers and $10^1 + 10^3$ ppb for flame atomizers [3].

Provided the sample can be brought to the liquid state, generally by solubilization, this method is able to detect traces of 70 elements having resonance lines in the spectral range of 190 + 850 nm. The remaining elements cannot be directly determined either because they are included in the vacuum region of the spectrum (F, Cl, Br, I, S, P, C, O, N) or because the low degree of atomization of their compounds is insufficient for trace determinations (Th, Ce, U, B, W, Ta, La, Nb, Zr, Re, Lu, Hf, Gd, Ir, Pr, Nd, Sm, Tb) [4].

AAS has some advantages compared to ICP-AES, mainly concerning spectral interference problems: absorption lines are less wide than emission lines.

In principle, AAS can be used to measure element concentrations from traces up to 50%, in practice this requires dilution of the sample because the response is not linear over a wide range of concentrations.

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5. INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY (ICP-AES)

Physical principles [1, 2]

The transitions of the outer electrons of atoms, or ions, between the excited and the ground state, or between two excited states, involve the absorption or release of electromagnetic energy in the range of visible light or in its immediate neighborhoods. The wavelength (or energy) at which absorption or emission takes place is characteristic of the atom; the intensity is proportional to its abundance.

The emission of characteristic radiation requires the atoms to be taken to a neutral unbound state¹, then to be excited; in ICP-AES, both steps are achieved by merging the sample particles into a stream of argon plasma.

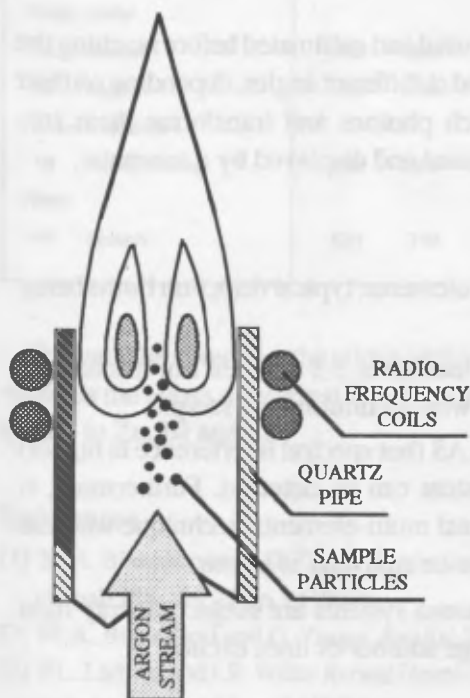


Figure 1 – Diagram of a plasma source.

A plasma is defined as a conducting gas containing ions, electrons and neutral particles but no net charge. In the ICP systems, it is obtained by coupling an argon stream with a radio-frequency electromagnetic field. The field, which is variable in time, accelerates the seeds of charged particles; their motion heats the gas by the Joule effect and induces further ionization. Typical working parameters are: temperatures on the order of 5000+8000 °K, electrical powers of 1+1.5 W and frequencies of 27 MHz [3].

A diagram of the plasma source is shown in figure 1, the sample is normally introduced as an aerosol carried by the argon stream.

Instrumentation

Figure 2 shows a block diagram of an ICP-AES device.

¹ Atomization, that is producing neutral free atoms, is necessary because valence electrons are also concerned with the excitation process.

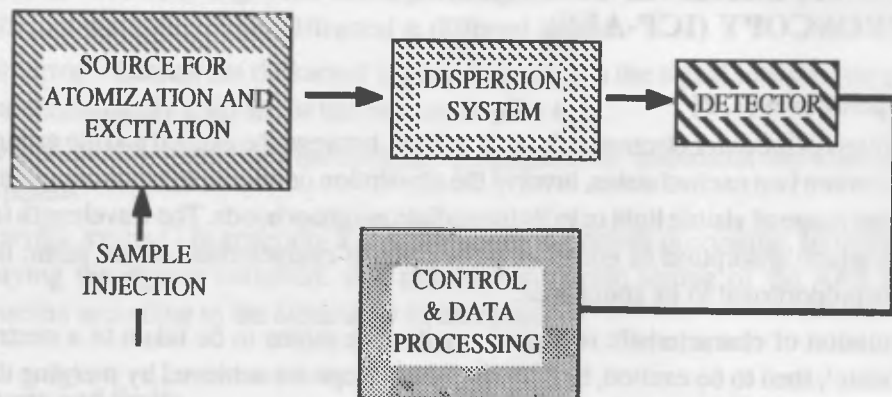


Figure 2 – Block diagram of an ICP-AES device.

The light coming from the plasma source is focused and collimated before reaching the dispersion system, where the photons are diffracted at different angles, depending on their wavelength. A photomultiplier tube detects such photons and transforms them into electrical pulses; the resulting spectrum is processed and displayed by a computer.

Features and limits

ICP-AES is widely used for the detection of trace elements, typical detection limits being in the range of $1 + 100$ ppb [4].

Unlike AAS, the response of the technique is linear over 3-5 decades. For this reason, both traces and major elements can be analyzed without diluting the sample.

Chemical interference is much lower than in AAS (but spectral interference is higher) and almost all the elements of the periodic system can be detected. Furthermore, if equipped with a polychromator², ICP-AES is a real multi-elemental technique whereas AAS only allows one or, at most, two elements to be analyzed at a time.

On the other hand, besides their high cost, plasma systems are subject to stray light problems and spectral interference due to the large number of lines excited.

Applications of artistic interest

ICP-AES was used, in combination with XRF, to characterize the alloys of the equestrian statue of Marcus Aurelius; in particular, ICP-AES was used for trace determination [5]. The results are given in table I.

² A polychromator is an optical system that resolves the single wavelengths of a polychromatic radiation simultaneously or in rapid sequence.

Table I - Results of ICP-AES measurements on the statue of Marcus Aurelius

No. and area of sampling	Trace elements [ppm]								
	Fe	Zn	Sb	As	Ni	Co	Ag	Bi	Si
<i>Horse, Right Side</i>									
3 section	1400	400	680	600	380	30	16	3	97
4 section	1100	370	720	720	440	330	19	3	40
10 b section	1120	1350	950	830	460	50	16	29	0
15 section	830	650	950	630	320	30	14	29	15
16 section	440	620	770	600	330	20	14	0	0
33 section	810	510	860	660	460	38	25	3	150
41 section	730	660	920	700	330	20	14	57	0
18 repair welding	140	1580	1200	640	290	30	12	82	0
48 assembly welding	500	70	1000	510	370	20	19	3	120
<i>Horse, Belly</i>									
32 section	1360	1330	920	650	330	36	15	17	67
35 section	780	1160	960	630	340	20	14	15	72
<i>Horse, Left Side</i>									
19 repair welding	280	2350	6620	1870	720	0	34	82	4
<i>Rider</i>									
42 section	520	710	1130	650	390	30	14	40	8

It should be noted that the alloys of the original sections do not show major differences, whereas the alloys of original weldings differ considerably from the repair weldings with regard to Zn, Bi and Si.

References

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6. ION CHROMATOGRAPHY (IC)

Physico-chemical principles and instrumentation [1]

Ion chromatography is based on the separation effect that ionic species undergo when passing through a properly chosen ion-exchange resin column. A cation-exchange resin and an anion-exchange resin are used for the analysis of cations and anions, respectively.

The retention time of each ion inside the column is closely related to its affinity for the exchange resin; this causes different ion species to leave the column at different times.

The block diagram of a typical IC device is shown in figure 1.

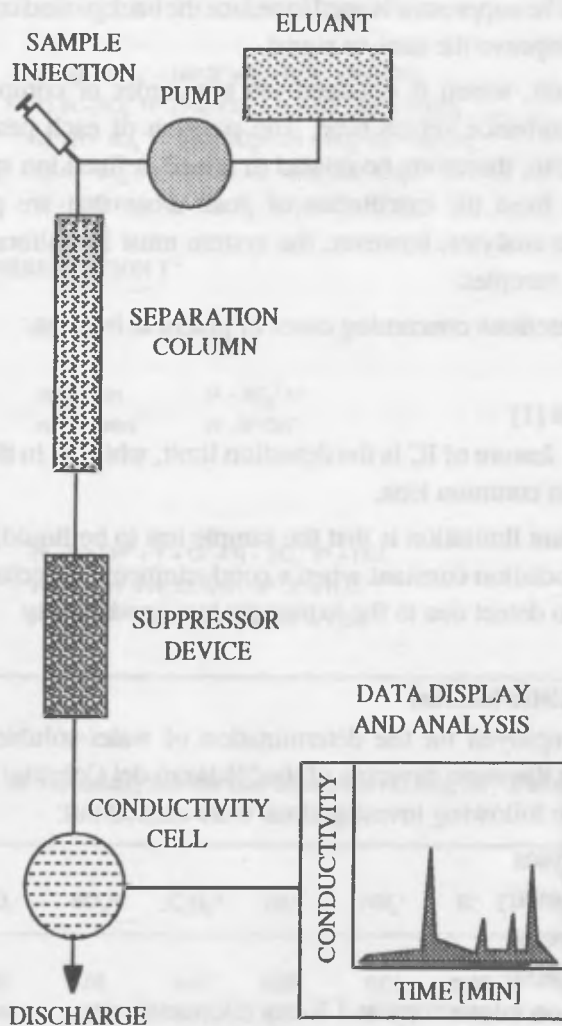


Figure 1 – Schematic diagram of an IC system.

A continuous eluant stream flows through the system. The affinity of the eluant ions and of the sample ions for the exchange resin should be comparable.

When the sample is injected into the system and carried through the column by the eluant, its ions are combined with the resin. After a time (which depends on the corresponding affinity), the sample ions are replaced by the eluant ions, make another step downstream and are combined again with the resin.

When leaving the separating column, in principle the ions are ready to be detected. Detectors generally measure either the total conductivity or the absorbance towards UV radiation, depending on the type of ion.

When a conductometric detector is used, a suppressor device is put in series with the separation column. The suppressor is used to reduce the background conductivity from the eluant and then to improve the analyte signal.

The chromatogram, which is obtained via a recorder or computer, is the plot of conductivity or absorbance versus time. The position of each peak accounts for the retention time and can, therefore, be related to a well-defined ion species; quantitative results are derived from the calculation of peak areas that are proportional to the concentration of the analytes; however, the system must be calibrated with a suitable number of standard samples.

Table I reports reactions concerning cases of practical interest.

Features and limits [1]

The most important feature of IC is the detection limit, which is in the range of 0.1 ppm for many of the most common ions.

The most important limitation is that the sample has to be liquid; further limitations come from the dissociation constant when a conductometric detector is used: ions with $pK > 7$ are difficult to detect due to the extremely low conductivity.

Applications of artistic interest

IC is commonly employed for the determination of water-soluble salts in stone; an example concerning the stone covering of the "Palazzo dei Celestini" in Lecce is shown in reference [2]. The following investigations were carried out:

- biological analyses
- X-ray diffractometry
- optical microscopy
- ion chromatography
- scanning electron microscopy and X-ray microanalysis.

With regard to the IC measurements, the samples were dessiccated, weighed and subjected to extraction with deionized water, according to the standardized procedure described in reference [3]. The results are reported in table II.

Table I - Reactions of practical interest in ion chromatography

ANALYSIS OF A GENERIC ANION X^-	
Eluants:	1) NaHCO_3 2) Na_2CO_3 3) NaOH
Types of resin:	<i>separation</i> $\text{R} - \text{N}^+ \text{HCO}_3^-$ <i>suppression</i> $\text{R} - \text{SO}_3^- \text{H}^+$
Reactions:	
<i>separation</i>	$\text{R} - \text{N}^+ \text{HCO}_3^- + \text{Na}^+ \text{X}^- = \text{R} - \text{N}^+ \text{X}^- + \text{NaHCO}_3$
<i>suppression</i>	1) $\text{R} - \text{SO}_3^- \text{H}^+ + \text{NaHCO}_3 = \text{R} - \text{SO}_3^- \text{Na}^+ + \text{H}_2\text{CO}_3$ 2) $2\text{R} - \text{SO}_3^- \text{H}^+ + \text{Na}_2\text{CO}_3 = 2\text{R} - \text{SO}_3^- \text{Na}^+ + \text{H}_2\text{CO}_3$ 3) $\text{R} - \text{SO}_3^- \text{H}^+ + \text{NaOH} = \text{R} - \text{SO}_3^- \text{Na}^+ + \text{H}_2\text{O}$ $\text{R} - \text{SO}_3^- \text{H}^+ + \text{Na}^+ \text{X}^- = \text{R} - \text{SO}_3^- \text{Na}^+ + \text{H}^+ \text{X}^-$
ANALYSIS OF A GENERIC CATION Y^+	
Eluant:	HCl
Types of resin:	<i>separation</i> $\text{R} - \text{SO}_3^- \text{H}^+$ <i>suppression</i> $\text{R} - \text{N}^+ \text{OH}^-$
Reactions:	
<i>Separation</i>	$\text{R} - \text{SO}_3^- \text{H}^+ + \text{Y}^+ \text{Cl}^- = \text{R} - \text{SO}_3^- \text{Y}^+ + \text{HCl}$
<i>Suppression</i>	$\text{R} - \text{N}^+ \text{OH}^- + \text{H}^+ \text{Cl}^- = \text{R} - \text{N}^+ \text{Cl}^- + \text{H}_2\text{O}$ $\text{R} - \text{N}^+ \text{OH}^- + \text{Y}^+ \text{Cl}^- = \text{R} - \text{N}^+ \text{Cl}^- + \text{YOH}$

Table II - Results of IC analyses on the stone covering of "Palazzo dei Celestini" in Lecce

No.	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻²	C ₂ O ₄ ⁻²	Na ⁺	NH ₄ ⁺	K ⁺	Mg ⁺²	Ca ⁺²
A2	0.25	0.35	5.52	0.17	0.25	0.01	0.10	0.06	3.14
A3	0.15	0.58	6.62	0.11	0.15	0.01	0.14	0.12	3.49
A4	0.09	0.07	5.75	0.10	0.09	0.03	0.03	0.09	3.30
A6	0.10	0.06	0.90	0.05	0.03	3.12	—	—	—
A7	0.25	0.44	2.51	0.14	0.16	0.01	0.08	0.08	2.01
A8	0.20	0.36	9.47	0.21	0.13	—	0.06	0.73	4.15

It is possible to observe that the most abundant ions are Ca^{+2} and SO_4^{-2} ; the good correlation indicates the presence of gypsum. A good correlation is also shown by Na^+ and Cl^- as well as by NO_3^- and Mg^{+2} ; extremely low amounts were found of K^+ , $\text{C}_2\text{O}_4^{-2}$ and NH_4^+ . The predominant type of deterioration is connected to the presence of water-soluble salts, mainly to gypsum, which is the reaction product of calcite with acid sulfurated pollutants. The presence of NaCl and nitrates can probably be related to cycles of crystallization-solubilization.

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7. INFRARED SPECTROSCOPY (IRS)

Physical principles [1]

IRS is concerned with the interaction of quanta of electromagnetic radiation with organic and inorganic¹ compounds in the wavelength range $2.8\text{--}33\text{ }\mu\text{m}$, the so-called fundamental infrared region.

The mechanism of the interaction is such that molecules can be likened to mechanical oscillators in which atoms are the masses and bonds are the springs. If, and only in this case, one or more of the possible oscillating configurations involves a periodical change in the dipole moment of the molecule, then coupling of the oscillator with the electromagnetic wave may take place at the resonance frequency.

Such frequency depends on the relative masses of the atoms, the force constants of the bonds and the geometry of the atoms.

If molecules of an organic or inorganic compound are immersed in an electromagnetic field, photons at the resonance frequency are absorbed and the spectrum of the transmitted radiation shows characteristic dark lines (or missing frequencies). De-excitation of molecules takes place by releasing energy, mainly in the form of heat.

The position of the dark lines in the wavelength axis supplies information about the type of the oscillating molecule or group, whereas the intensity accounts for the abundance.

A diagram of the possible types of molecular vibration is shown in figure 1 [1].

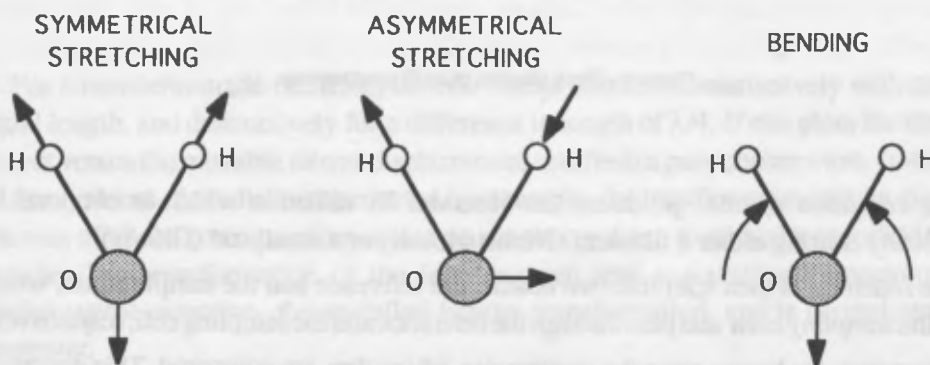


Figure 1 – Types of molecular vibration.

¹ Although inorganic substances show a response to IR radiation, sometimes they do not give definitive spectra; for this reason, IRS is mainly used for organic compounds.

In particular, *stretching* consists of oscillations along the bond axis with periodical changes of interatomic distance. *Bending* may consist of either the change in the angles between the bonds with a common atom or in the rigid movement of a group of atoms with respect to the remainder of the molecule.

Instrumentation

A block diagram of an IR spectrometer is shown in figure 2.

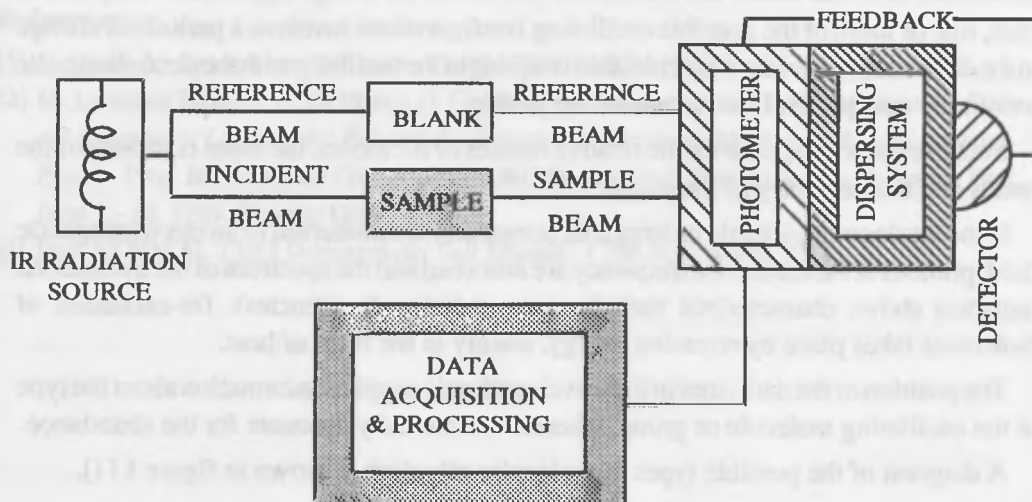


Figure 2 – Block diagram of an IR spectrometer.

The *radiation source* produces the observed IR radiation which is obtained by electrically heating either a filament (Nernst glower) or a small rod (Globalar).

The radiation is then split into two beams, the reference and the sample beam, which enter the *sampling area* and pass through the reference and the sampling cell, respectively.

Afterwards the beams enter the *photometer* where they are compared. This operation is driven by the *detector* and consists in attenuating the reference beam down to the intensity of the sample beam. The level of attenuation, which is a direct measurement of the sample absorption, is transmitted to the *data acquisition and processing system*.

The *dispersing system* provides the wavelength resolution of the radiation, whose intensity is measured by the *detector*. The latter closes the feedback chain to the *photometer*.

An important development of IR spectrometers is the so-called Fourier transform IR spectrometer, or interferometer spectrometer [2].

In this instrument, all the wavelengths are measured simultaneously, thus allowing a more efficient utilization of IR radiation. The basic design of the interferometer is shown in figure 3 [2].

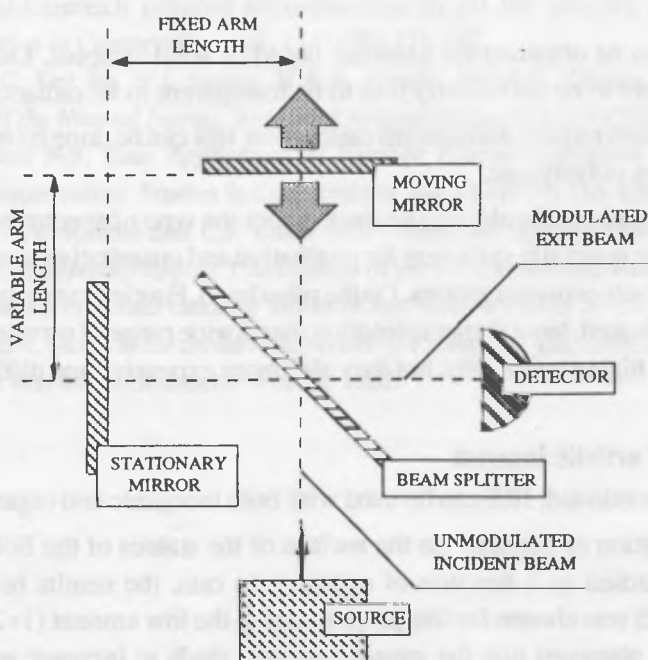


Figure 3 – Schematic diagram of an Interferometer.

For a monochromatic radiation, the two beams interfere constructively with arms of equal length, and destructively for a difference in length of $\lambda/4$. If one plots the detector output versus the movable mirror displacement, one finds a pure cosine wave. In the case of a polychromatic radiation attenuated by a sample, the interferogram will be given by the sum of all the corresponding cosine waves except those specifically absorbed by the sample. The transformation of the interferogram into a wavelength spectrum is a mathematical operation, the so-called Fourier transformation, and is carried out by a computer.

It also performs the necessary spectra manipulations such as smoothing and background subtraction, as well as providing library data for automatic searching of reference spectra.

However, digital data-processing devices can be employed with dispersive spectrometers as well, and the same operations can be carried out.

Features and limits

Different types of information can be obtained from different parts of the IR spectrum. The short wavelength region, for example, is mainly concerned with functional groups such

as OH, NH and C=O; the intermediate portion is usually referred to as the "fingerprint" region and is probably unique for each molecular species. It can be used to identify the presence of relatively simple compounds. Typical sensitivities are in the order of 1% in weight [2].

IR spectra can be obtained for gaseous, liquid or solid samples. Liquids and solids require the sample to be sufficiently thin to be transparent to IR radiation.

IR spectrometers require wavelength calibration; this can be done by means of reliable standards such as polystyrene.

Some considerations should also be made about the type of spectrometer. Dispersive spectrometers are generally sufficient for qualitative and quantitative analyses, as well as for molecular structure investigations. On the other hand, Fourier transform spectrometers are more sophisticated, have higher resolution over a wide range of wavelengths, are more rapid and have a higher sensitivity, but they also more expensive and difficult to manage.

Applications of artistic interest

As previously mentioned, IRS can be used with both inorganic and organic compounds.

The accumulation of gypsum² on the surface of the statues of the Boboli Gardens in Florence was studied as a function of exposure to rain, the results being reported in reference [3]. IRS was chosen for this purpose due to the low amount (1+2 mg) of sample required. It was observed that the gypsum deposit tends to increase with time on the surfaces protected from rain, whereas it is washed away on the exposed surfaces.

Investigations on organic compounds are reported in references [4 - 6]. The results concern the identification of pigments, media, ivory, linseed oil, paper and pigments. In reference [7], attempts were made to relate the causes of papyrus deterioration to the corresponding IR spectra.

Finally, Botticelli's *Primavera* was studied in reference [8] with regard to the binders in the preparation, in which non-polymerized oils were found, and on the protective varnish, which was probably applied during the twentieth century. A further thin greyish layer, found under the varnish, contained calcium sulfate, calcium oxalate, silicates, fats and proteic materials; it was thought that these substances belonged to a previous egg-based protective layer that was exposed for a long time to the atmosphere.

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² It is well known that gypsum is produced by the reaction of marble with acid sulfated pollutants.

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8. X-RAY DIFFRACTION (XRD)

Physical principles [1]

Diffraction is the name given to a class of phenomena concerning the interaction of any type of wave with objects whose dimensions are comparable with the wavelength.

The presence of the object causes variations of amplitude and/or phase of the impinging waves, thus giving rise to interference, which can be constructive or destructive, respectively, according to whether the waves are in phase or in opposition.

In particular the interaction of monochromatic X-rays with a crystalline solid may give rise to constructive interference if the following Bragg equation is satisfied:

$$n \lambda = 2 d \sin \theta$$

The meaning of the symbols is displayed in figure 1 with λ indicating the wavelength of the impinging radiation, d the distance between the crystalline planes and n any integer number.

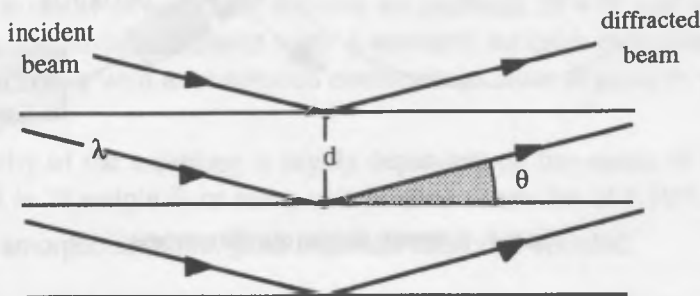


Figure 1 – Diagram of a diffraction process.

In practice, most diffractometric investigations are carried out on powders of about 300 mesh (53 μm), rather than on single crystals. The great number of randomly oriented crystallites statistically ensures that there will be at least one crystallite in the correct diffracting position for each of the possible crystallographic planes in the crystal.

The result of the analysis (diffractogram) is a plot of the intensity of diffracted X-rays versus 2θ (which is actually considered instead of θ); according to the previous considerations, even for a single species, there will be several peaks, each corresponding to one of the crystallographic planes. The relative geometrical position of the peaks accounts for the shape and size of the unit cell, as also shown by the Bragg equation, whereas the relative weight of the areas accounts for the spatial relationships between the atoms in the cell.

Such characteristics make the diffraction pattern a sort of fingerprint of a crystalline material that can be used to detect its presence and, in principle, its abundance in the sample under observation.

Instrumentation [1]

Figure 2 shows a diagram of a diffractometer.

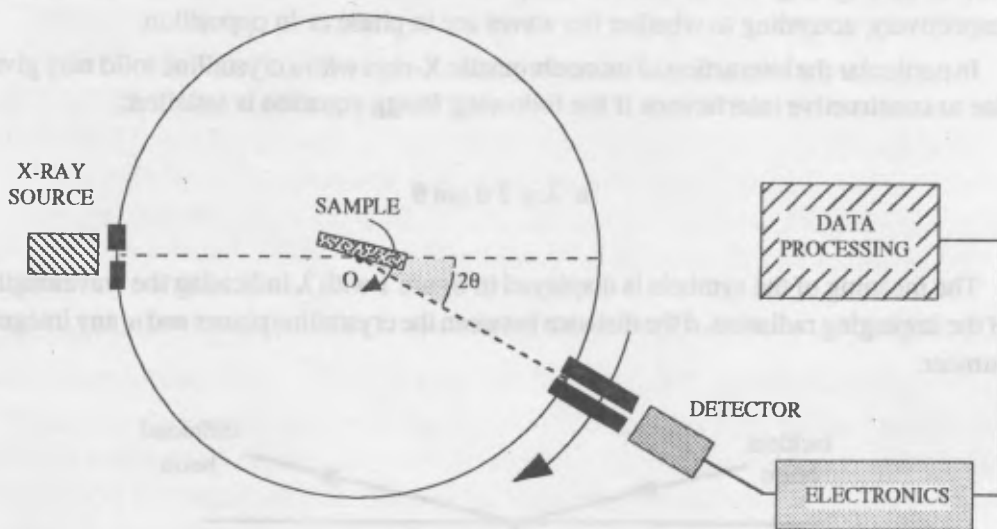


Figure 2 – Schematic diagram of a diffractometer.

The X-ray source is normally kept still, whereas the sample and the detector are rotated with angular velocities of ω and 2ω , respectively, around the same axis O; most information is obtained in the range $5^\circ \leq 2\theta \leq 70^\circ$.

Monochromatic X-rays (normally Cu- K_α line, 8.04 keV) are provided by an X-ray tube with copper target, equipped with suitable filters in order to reduce both the Cu- K_β line and continuous “white” radiation. Typical working parameters are 40 kV and 16+20 mA with stabilities better than 0.1%.

The primary and diffracted beams are collimated as much as possible in order to reduce the background from stray radiation and to improve the resolution of the system.

Scintillators coupled with photomultiplier tubes are normally used as detectors due to the possibility of resolving the energy of diffracted photons; a large part of the unwanted noise can, therefore, be eliminated by simply introducing a single-channel analyzer in the electronic chain.

The detector count-rate versus 2θ is recorded on a strip chart or stored in a computer memory for further processing. The position of the peaks accounts for the type of crystalline material, whereas the area beneath the peaks is connected to its abundance.

The data are interpreted by means of indexes which include most of the known crystalline phases with the corresponding eight most intense lines. In recent systems, indexes are stored in the libraries of computers, which also provide peak search, spectrum smoothing, background subtraction and area calculation.

The sample preparation is extremely important because the reliability of quantitative determinations is connected to this step. The mineral should be ground to obtain a ~ 300 mesh ($53 \mu\text{m}$) size powder and packed, eventually with the help of a binding fluid, into a depression on a glass or metal plate; the sample weight is in the range of 1+100 mg.

Features and limits [1]

In fields of artistic interest, XRD techniques are generally used to identify crystalline materials, essentially from a qualitative or, at most, semi-quantitative point of view. In fact, even if possible in principle, quantitative analyses are extremely difficult to perform, mainly due to self-absorption problems in the sample.

Due to the difficulty of accurately defining the positions $2\theta = 0^\circ$ and $2\theta = 180^\circ$, the diffractometer should be calibrated with a standard material of accurately known d -spacings, preferably with an absorption coefficient as close as possible to that of the unknown sample.

The sensitivity of the technique is highly dependent on the nature of the material, ranging from 1 to 25 weight % or more, with relative accuracies of 5-10%.

Given their amorphous nature, glass materials cannot be detected.

Applications of artistic interest

Reference [2] shows an example in which XRD is used in combination with SEM and microprobe.

The investigations concerned the Madonna and Child on the main portal of Orvieto cathedral; the aim was to chemically characterize the remains of the rich decoration and to improve the knowledge of the painting technique. The following three layers were examined.

GILDINGS - The most ancient preparation is essentially made of gypsum; as will be shown below, the corresponding gilding is probably the only original one. The second type of preparation is made of lead white, in which Pb is always associated with K; the crystalline compounds $\text{K}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$ and $\text{K}_2\text{C}_2\text{O}_4$ were found by XRD. The third type of preparation essentially contains Ca with lower amounts of S and, in some cases, traces of Fe; it was probably obtained with S. Giovanni white, gypsum and, sometimes, small additions of ochre.

BROWN LAYER - It is essentially made of Ca, Si and Fe, with traces of Al, S, Cl and K; the detected crystalline phases were weddellite and whewellite, the latter always in smaller amounts than the former. It is a layer containing ochres and black pigments; calcite was totally absent and sulfur was found only in traces; therefore, the use of lime and gypsum as binders can be excluded. This layer is particularly interesting because it also covers the hand of the Madonna, which was replaced in the eighteenth century. Therefore, it allows a rough dating of the layers, depending on whether they are under or on the brown layer.

YELLOW-GREEN LAYER - It is essentially made of Fe, Ca and Si, with variable amounts of K and S; the pigments are supposed to be yellow ochre, green raw and charcoal black. Since at least in one case this layer is on the brown one, it has to be considered as a late repainting, following the eighteenth century.

RED-VIOLET LAYER - Microprobe analyses detected the presence of Pb and traces of K. Pigments containing lead such as minium or litagiriun are to be excluded because they were not found by XRD. The hypothesis of the authors is that it is an organic pigment used as a glaze to give a warmer tone to the gold.

The following substances and elements were also found:

- gypsum in the outer layers, probably due to pollution
- P, mainly on the horizontal surfaces, probably due to pigeon guano
- traces of Cu, probably due to corrosion products from the overhanging bronze baldachin.

References

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- [2] M. Laurenzi Tabasso, G. Guidi and F. Pierdominici *Duomo di Orvieto - Portale Centrale: Madonna in Trono con Bambino - Studio della Polocromia* Proceedings of the 2nd International Conference on Non-destructive Testing, Microanalytical Methods and Environment Evaluation for Study and Conservation of Works of Art. Perugia April 17-20, 1988; II/10.1.

9. SCANNING ELECTRON MICROSCOPY (SEM)

Physical principles [1]

When a radiation is employed to “illuminate” an object, the possibility of resolving details is limited by the wavelength of the radiation. For this reason, optical microscopes have a $2000\text{\AA}$ resolution whereas electron microscopes are in the range of 2 to $20\text{\AA}$.

The interaction of electrons with matter can give rise to the following effects, among others:

- production of secondary electrons
- backscattering of primary electrons
- production of Auger electrons
- transmission of primary electrons
- emission of characteristic X-rays.

If detected, these effects can supply information about the nature of the sample observed.

For example, the morphology of the object is related to secondary, backscattered and transmitted electrons; crystallographical information is related to the same parameters and to X-rays; the elemental composition is described by X-rays, backscattered and Auger electrons; finally, the chemical bonds are related to Auger electrons and X-rays.

In SEM, two synchronized electron beams are used: one scans the sample and the other scans a cathode-ray tube (CRT) display so that every point on the sample has a corresponding point on the CRT. The scanning velocity is sufficiently high to yield a complete image, similar to what a TV screen does.

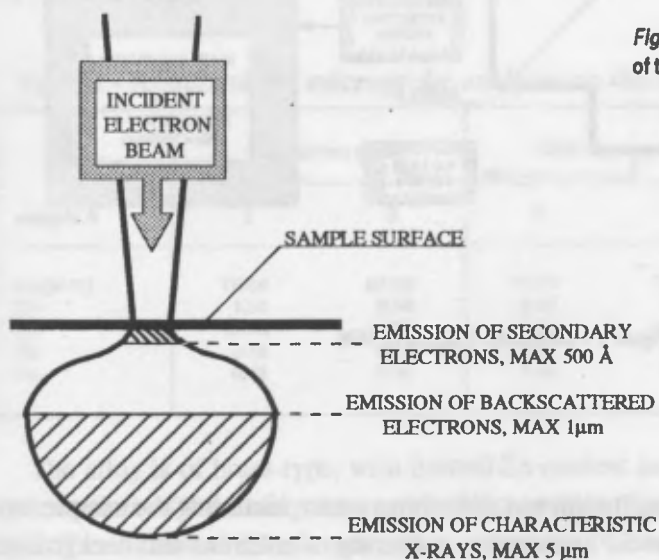


Figure 1 – Schematic diagram of the signal emission volume.

The interaction of the beam with the sample produces different types of images and information, according to the above-described effects. Depending on the energy of primary electrons, on the sample atomic number and on the particle that produces the image, the analysis concerns different depths of matter, typically less than $500\text{\AA}$ for secondary electrons, $1000\text{\AA}+1\mu\text{m}$ for backscattered electrons and $5000\text{\AA}+5\mu\text{m}$ for X-rays. A schematic diagram of the signal emission volume is shown in figure 1.

Instrumentation

Figure 2 shows a schematic diagram of SEM.

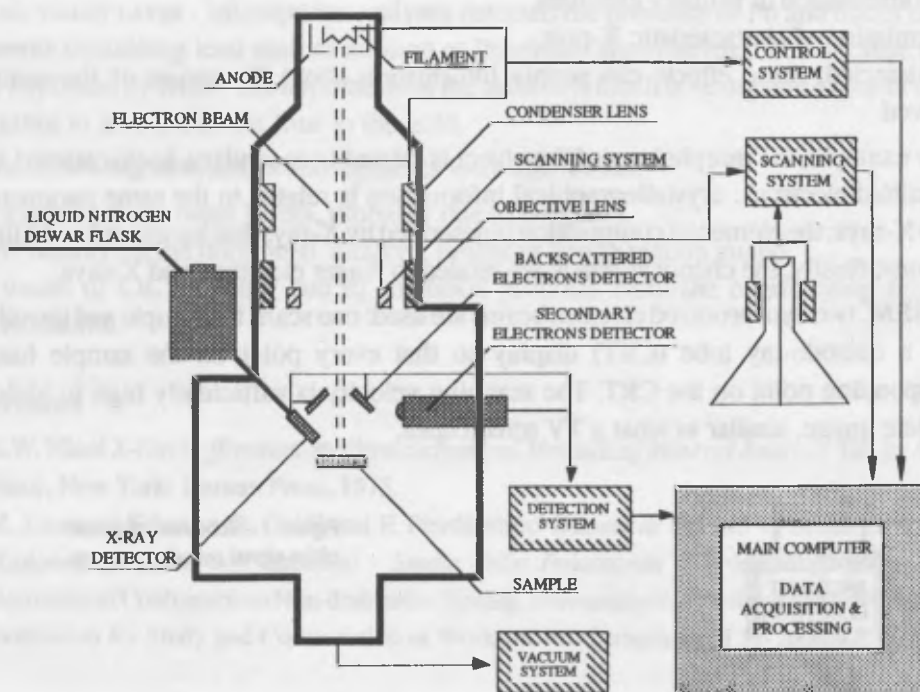


Figure 2 – Schematic diagram of SEM.

All the components of the excitation and detection system, including the sample, are kept in a vacuum in order to avoid attenuation, scattering of electrons and background from argon X-rays.

The electrons, emitted by a heated tungsten filament, are accelerated by potentials up to several tens of kV; before striking the sample, the beam is finely focused by electronic optics down to diameters of several tens of Å to several tens of μm . A scanning system pilots in synchronism both the primary and the CRT electron beams.

Electrons are generally detected by a scintillator coupled with a photomultiplier tube and X-rays by a Si(Li) semiconductor detector. The resulting electric signal is processed by a computer, used to modulate the brightness of the CRT and recorded.

Sample preparation also requires some care because the sample has to be conductive; if it is not, it has to be covered by a thin metallic film, generally gold, obtained by evaporation.

Features and limits [1]

The highest resolution presently obtainable with SEM is about $10\text{\AA}$. If used for X-ray spectrometry, the detection limit is in the range of $10 + 1000$ ppm in weight concentration or $10^{-5} + 10^{-11}\text{g}$ in absolute weight, depending on the element.

Applications in fields of artistic interest

Reference [2] gives an example of the combined use of SEM and microprobe. The object is an African metal scepter, surmounted by an equestrian group, called a *sono*. The *sono* was taken apart, the components slightly de-patinated at the points of measurement and entirely inserted in the vacuum chamber (dimensions $250 \times 250 \times 250$ mm) of a Cambridge 250 MK3 SEM equipped with a Link 860-II microprobe; samples were taken of the rod because it was too long (580 mm) to fit into the chamber. Table I shows the results obtained by microprobe analysis.

Table I - Results of the microprobe analyses on the *sono*

sample #	Equestrian group		Globular element		Rod	
	1	2	3	4	5	6
Cu [w.%]	75.69	84.00	74.75	73.28	78.55	78.15
Sn "	1.53	0.38	0.33	0.65	3.80	1.17
Zn "	19.98	14.86	19.86	21.01	16.72	20.04
Pb "	3.16	0.49	n.d.	0.14	n.d.	n.d.
Fe "	0.45	0.32	0.48	0.64	0.91	0.65

The alloy is of brass-type, with limited Zn content and Pb, Sn impurities. The SEM observations of the casting show oxide skins, cavities of interdendritic shrinkage, crystals of ZnS and a remarkable presence of interdendritic Pb isles, especially in point 1. Similar behavior is observed in the globular element.

The presence of ZnS indicates that impure materials were used for the alloy, probably coming from the processing of silver minerals. Moreover, the inhomogeneity of the dendrites shows that the scepter did not undergo thermal treatment. Finally the composition of the parts is relatively homogeneous, thus showing that they belong to the same original object.

References

- [1] *The Scanning Microscope as a System* in Jeol News (Manufacturer's technical notes).
- [2] F. Pierdominici, G. Guidi and R. Pesoli *Nuove Facilities nel Campo della Microscopia Elettronica Applicate alle Opere d'Arte. Studio Microstrutturale Non-Distruttivo di un Oggetto di Bronzo di Particolare Interesse Etnografico: il Scono* Proceedings of the 2nd International Conference on Non-Destructive Testing, Microanalytical Methods and Environment Evaluation for Study and Conservation of Works of Art. Perugia April 17-20, 1988; II/17.1.



Part	Material	Weight (g)	Volume (cm³)	Density (g/cm³)	Composition (%)
Sample	Brass	10.0	0.5	20.0	70 Cu, 30 Zn
Detector	Aluminum	5.0	0.2	25.0	99.9 Al
Electron Gun	Wolfram	0.5	0.01	50.0	99.99 W
Lenses	Steel	2.0	0.1	20.0	99.9 Fe
Control Unit	Plastic	1.0	0.05	20.0	99.9 PC
Signal Processor	Glass	0.5	0.02	25.0	99.9 SiO₂

STRUCTURAL METHODS

Applications in the field of bridge internet

10. PHOTOGRAMMETRY

Description of the method [1, 2]

Photogrammetry is a method that allows a completely objective description of three-dimensional surfaces, in both graphic and numerical form; the result is independent of any hypothesis that can be made *a priori* about the geometrical shape and the relative spatial position of the surfaces. The survey does not require any physical contact with the object.

The method is based on the same principles as human binocular vision, i.e., observing the same object from two different points of view. If two pictures, taken with the above criteria, are simultaneously observed by means of a stereoscope, the resulting image restitutes the object in its three-dimensional form and its dimensions are in agreement with the principles of linear perspective.

Photogrammetric images are obtained by means of a photogrammetric camera and a system for stereo-restitution of the image, which also provides the plotting of contours.

Applications in fields of artistic interest

The great importance of photogrammetry in the study of works of art arises not only from the possibility of accurate geometrical documentation, but also from the availability of numerical data for the construction of mathematical and physical models.

A typical example is given by the equestrian statue of Marcus Aurelius [3, 4] whose 1/5 scale photogrammetry was the starting point for the construction of the 1/5 model, obtained from the integration of the contours, and for the structural calculations with the finite element method. In this statue, the photogrammetry contour spacing was 5 mm and mean square deviations of ± 1 mm.

Further applications concerning the study of fresco techniques, survey of architectonic structures and the study of thickness distribution in bronze panels are given in reference [1].

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11. ENDOSCOPY

Physical principles and instrumentation [1]

Endoscopy is an optical technique that allows the inspection of parts of an object that cannot be directly observed by eye.

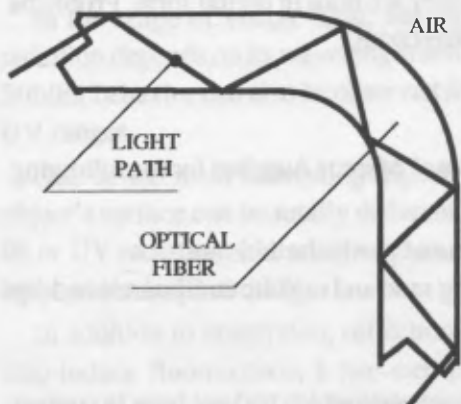


Figure 1 – Light path inside an optical fiber.

Modern endoscopes are based on the peculiar properties of optical fibers (fiberscopes), which are thin wires of glass or quartz. The difference in density between glass and air causes a light beam which enters the fiber to be totally reflected when it reaches the glass-air interface. The path of the light will therefore “bounce” between the walls of the fiber, as shown in figure 1.

Present-day fiberscopes employ two fiber bundles (see figure 2), one of which is used to illuminate the area being observed. The image is transmitted by the second bundle, which is made of up to 100,000 fibers, each of $9+12\text{ }\mu\text{m}$ diameter, disposed in the same order at both extremities (coherent fibers). The definition of the image, which appears as an assembly of luminous points, increases as the fiber diameter decreases.

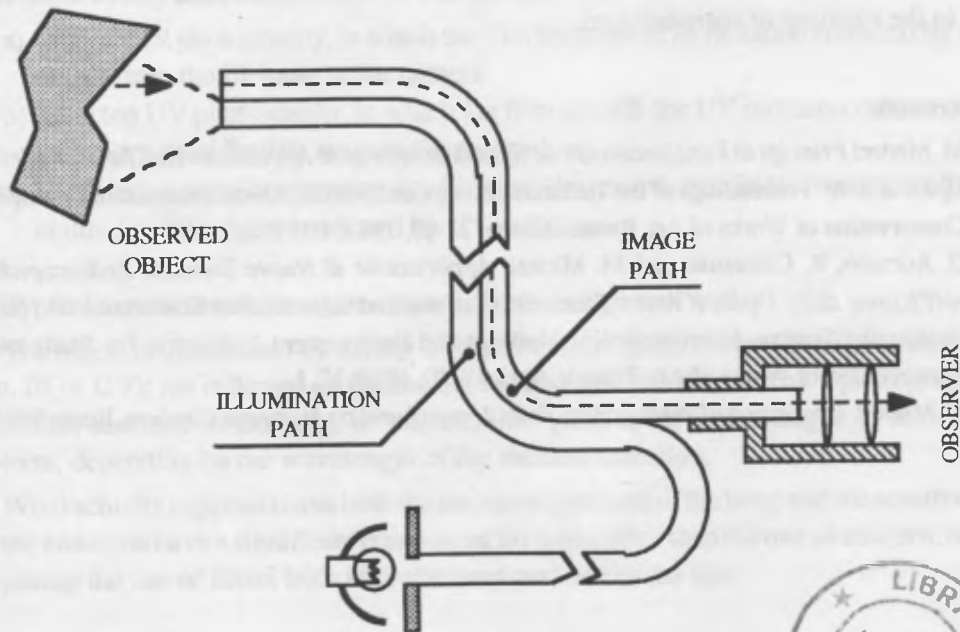


Figure 2 – Schematic diagram of a fiberscope.

Features and limits [2]

The main limitations of fiberscopes are the limited length and fragility of the instrument, due to the optical and mechanical characteristics of the fibers, and the definition of the image, which is limited by the number of fibers.

Recently developed endoscopes overcome such limitations; the replacement of fibers with a miniaturized TV-camera greatly improves the definition, the possibility of manipulation and the recording of images, since they are born in digital form. Problems concerned with the length of the probe are also overcome.

Applications of artistic interest [3]

A fiberscope was employed on the equestrian statue of Marcus Aurelius for the following purposes:

- 1) photographic documentation of internal areas of particular interest
- 2) search for materials to analyze, such as casting sand and organic compounds in deep cavities
- 3) integration of radiographic information.

The most significant results were obtained in those parts which had not been in contact with the external environment, such as the rampant leg and the left hind leg.

With regard to the former, the shape and constraints of an iron bracket were observed as well as its deep corrosion in the lower part. Iron brackets were also observed in the left hind leg as well as in the rider's right shoulder to support the extended arm; the latter was anchored to the statue with four bronze collars, two of which, the central pair, were broken due to the swelling of corroded iron.

References

- [1] M. Medori *Principi di Funzionamento degli Endoscopi e Loro Applicazioni nel Restauro delle Opere d'Arte* Proceedings of the 1st International Conference on Non-Destructive Testing in Conservation of Works of Art. Rome October 27-29, 1983; I/19.1.
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- [3] M. Medori *Ispezione dell'Interno* Cat. Exib. *Marco Aurelio - Mostra di Cantiere*, Roma 1984.

12. SPECIAL PHOTOGRAPHIC TECHNIQUES (SPT)

Physical principles and instrumentation

The interaction of matter with electromagnetic radiation gives rise to a large number of phenomena and is, in general, a function of the radiation wavelength and of the characteristics of the irradiated matter.

In the range of visible light, the capacity of a surface to absorb or reflect incident radiation depends on its wavelength and is the cause of what the human eye sees as colors. Similar behavior can also be observed for non-visible radiation, particularly in the IR and UV ranges.

One of the most interesting aspects of these phenomena is that the behavior of an object's surface can be totally different, depending on whether it is irradiated by visible, IR or UV radiation. Materials such as glass, for example, are transparent to visible light and opaque to IR and UV.

In addition to absorption, reflection and transmission, electromagnetic radiation can also induce fluorescence, a two-step process in which the excitation of the irradiated material is followed by a de-excitation consisting of the emission of higher wavelength radiation. If the exciting radiation is in the UV range, the fluorescence radiation that leaves is in the range of visible light and can be detected by a normal photographic emulsion.

The special photographic techniques use the above-described principles to detect different materials in a work of art or to show some modifications that may have occurred. The most widely used methods are as follows:

- a) reflected IR photography, in which the film records the IR radiation reflected by the object from the IR lamp to the camera
- b) reflected UV photography, in which the film records the UV radiation reflected by the object from the UV lamp to the camera
- c) UV fluorescence photography, in which the film records the visible fluorescent light emitted by the object irradiated by UV radiation.

Typical experimental arrangements are shown in figures 1 to 3.

The object is illuminated by a lamp with an emission spectrum in the range of interest (i.e. IR or UV); the reflected or fluorescent radiation is then detected by a photographic emulsion sensitive in the range of interest, thus yielding different images of the same objects, depending on the wavelength of the incident radiation.

What actually happens is that both the emission spectrum of the lamp and the sensitivity of the emulsion have a significant component in ranges other than the one of concern, thus requiring the use of filters both after the lamp and before the film.

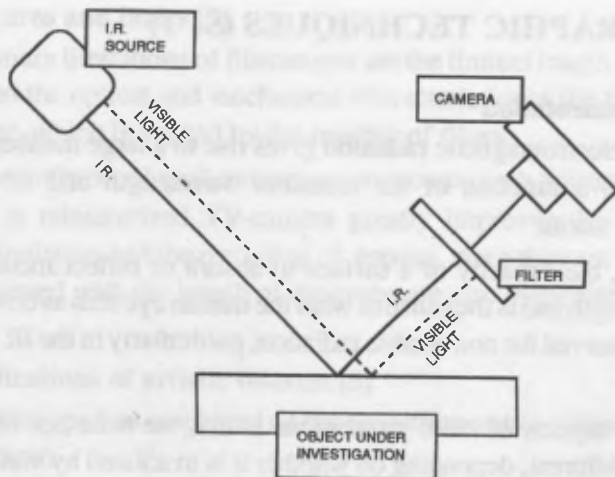


Figure 1 – Experimental setup for reflected IR photography.

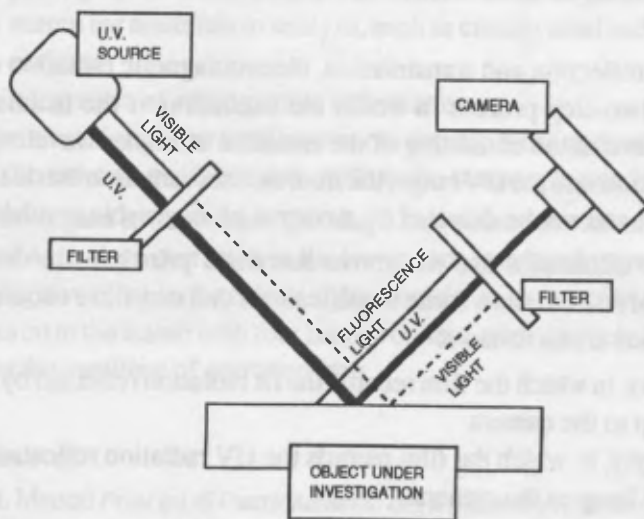


Figure 2 – Experimental setup for reflected UV photography.

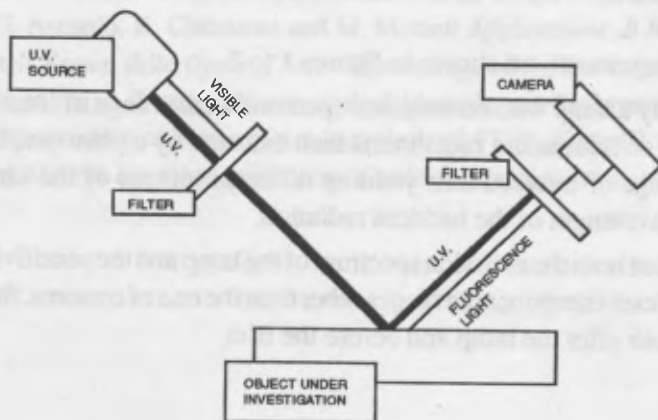


Figure 3 – Experimental setup for UV fluorescence photography.

Features and limits

As far as the IR range is concerned, it must be considered that the sensitivity in terms of wavelength of presently available films does not go beyond $0.9\text{ }\mu\text{m}$ and $1.3\text{ }\mu\text{m}$ for normal and special films, respectively, and that higher-wavelength radiation cannot be detected. Given these limitations, reflected IR photography generally inspects less deep layers than reflectography due to the fact that the latter employs more penetrating radiation.

In the UV range, the main limitations come from the optics and the emulsion. The opacity of glass to UV makes it impossible to use normal glass optics below $0.32\text{ }\mu\text{m}$; for lower-wavelength radiation ($0.32 - 0.25\text{ }\mu\text{m}$), quartz optics must be used. Similar problems are encountered with the gelatine, which is opaque to radiation wavelengths below $0.25\text{ }\mu\text{m}$.

Applications of artistic interest

The above-described techniques find important applications in the study of paintings.

According to the principles described in the previous paragraphs and in the reflectography chapter, it can happen that the old varnishes of a painting, the glazings or even some parts of the paint layer, although opaque to visible light, may be transparent to IR. Although investigation by IR photography does not generally reach the preparatory drawing, which is visible by reflectography, it can still be usefully employed to collect information for restoration and authentication.

Reflected IR photography can use both black-and-white and color films, the use of color sometimes improving the readability of the IR images. For example, some pigments that have the same color in the range of visible light may give rise to different colors on an IR color film. This may help to detect restorations performed with different pigments of the same color.

Reflected UV photography is mainly used to differentiate painting materials and can, therefore, be used to identify previous restorations in a painting. White pigments are detected particularly well by this technique.

UV fluorescence photography is widely used for the study of restorations in paintings. It must be considered that most polymeric painting materials give very similar fluorescence colors and cannot, therefore, be distinguished one from the other. These colors range from light green to yellow to light orange. A particularly high fluorescence is given off by the resins contained in varnishes.

For this reason, in a varnished painting, the fluorescence of the pigments beneath is generally masked by that of the varnish.

During restoration, however, after the varnish has been removed, UV fluorescence photography can be used to detect some painting materials. The ageing of pigments and binders gives rise to the formation of compounds that have high fluorescence yields, whereas recently added materials do not give fluorescence. Therefore, recent restorations

are generally visible in an UV fluorescence image as dark areas on a light yellow-green fluorescent background.

This technique has also been employed to detect some pigments on the basis of their particular fluorescence colors; in this context, the light yellow fluorescence of zinc white, the pink-orange fluorescence of garanza lake and the gold-yellow fluorescence of Indian yellow are well known.

For the reasons described above, UV fluorescence photography is also used to highlight ambers in excavation blocks.

All these special photographic techniques can be usefully employed in microphotography for stratigraphic analysis.

References

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13. REFLECTOGRAPHY

Physical principles and instrumentation [1]

The chromatic characteristics of materials depend on their property of absorbing and reflecting electromagnetic radiation in the range of visible light; such properties are a function of the radiation wavelength: some materials are transparent to visible light and opaque to IR, glass for example, whereas others are opaque to visible light and transparent to IR. That is the property on which reflectography is based. An example is given by relatively thin layers of particles, such as pigments, which scatter IR much less than visible light, thus allowing the radiation to "illuminate" the underlying layers. Furthermore, it is possible for materials with similar behaviors in the visible range to show completely different properties in the IR range. This feature makes it easy to tell them apart.

The instrumental components of reflectography are a source of radiation (an IR lamp with tungsten filament) and a TV camera equipped with a Vidicon tube, which is sensitive to radiations in the range of reflectographic IR. The images can also be recorded and processed by means of computer-assisted devices.

Features and limits

The wavelengths used in reflectography are between 1.2 and 2 μm , whereas thermography usually works in the neighborhood of 10 μm .

Like other types of IR images (see thermography), interpretation problems arise due to the fact that the behavior of individual materials is not sufficiently known and cannot be predicted in advance.

Applications of artistic interest [1, 2]

Reflectographic investigations are particularly helpful in the detection of preparatory drawings, provided the painted layer is sufficiently thin. The best results are generally obtained in red, white and brown areas, whereas copper-based pigments show poor transparency to IR. Preparatory drawings are easily detected if done with charcoal black; on the contrary, if iron oxide is used, the drawings can hardly be distinguished from the gypsum and glue preparation.

Reflectography is also widely used to show previous restorations, *pentimenti* and underlying paintings. Reference [2] describes the investigations carried out on Raffaello's *Marriage of the Virgin*.

References

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14. STRUCTURAL ANALYSIS WITH THE FINITE ELEMENT METHOD (FEM)

Description of the method [1]

In most cases of practical interest, the problem of calculating the stress distribution in a complex structure cannot be solved in a purely analytical way. The need to simplify the problem, from both the mathematical and the geometrical point of view, led to the development of numerical methods, some of which, FEM for example, were expressly designed to be employed in the form of calculation codes with today's fast and powerful computers.

The principle of FEM is based on the assumption that a complex continuous structure can be described as an assembly of a certain number of discrete contiguous elements. Such elements, which are of finite volume and simple shape, are connected to one another along the borders in a finite number of points called nodes. Code libraries are provided with several standard types of element configuration for the best approximation of the actual structure.

It should be noted that although in principle the accuracy of the method is improved by increasing the number of elements (that is, dividing the structure into smaller elements), this may not be convenient due to the extremely high cost of CPU time — the time in which the computer is engaged in calculations. For this reason, prior optimization work has to be done when setting up calculations.

The method approximates the actual loaded structure with such a configuration of the element assembly to satisfy the consistency between the node displacements, which are the unknown quantities of the problem, and the external loads and constraint conditions; subsequently the stresses in each node are calculated as linear functions of the corresponding displacements (Hooke's law).

The propagation of displacements from the starting element through the structure is assured by functions known *a priori*, contained in the code library, which are characteristic of each element type.

Applications of artistic interest

An interesting example of an application is described in reference [2]: it is a part of the investigations carried out on the equestrian statue of Marcus Aurelius.

Calculation and experimental techniques were used in combination to determine the stress distribution in the horse, also taking into account its irregular geometrical shape and the local distribution of thicknesses, discontinuities and flaws.

The experimental analysis of the relationship between stresses and deformations is usually performed by sticking strain gauges on significant points of the structure. In the case of Marcus Aurelius, this was an extremely critical operation due to the possible damage to the bronze surface caused by attaching strain gauges.

In order to optimize the number and position of the transducers on the statue, a FEM calculation code was employed to evaluate the stress distribution; subsequently calculations were compared to extensometric measurements performed on a 1/5 bronze model of the horse (see strain gauge and photogrammetry chapters).

The coordinates of the nodes were identified according to the photogrammetric results and a total number of 125 nodes was chosen for the finite element model. The elements were of the shell and beam type, 102 and 35 in number, respectively.

The results show that the structure behaves like a rigid body on the legs, by moving forward on the right when loaded. The calculated bend displacements were compared with those caused by the application of known loads on both the model and the statue, the latter being measured by mechanical comparators; FEM results were found to be in good agreement with the experiments. The small discrepancies were probably due to the presence of structural irregularities such as welding beads which were not considered in the finite element model.

References

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15. STRAIN GAUGE MEASUREMENTS

Physical principles and instrumentation

Strain-gauge techniques are used to measure the elongation of stressed structures. The working principle is based on the reduction of cross-sectional area that a metal wire undergoes when subjected to traction. If current flows through the wire, the change in physical dimensions will cause a corresponding change in the electric resistance, according to the formula:

$$R = l \rho / S$$

where ρ is the resistance of the material, l the length and S the cross-section area of the wire.

A typical transducer for measuring elongation is shown in figure 1.

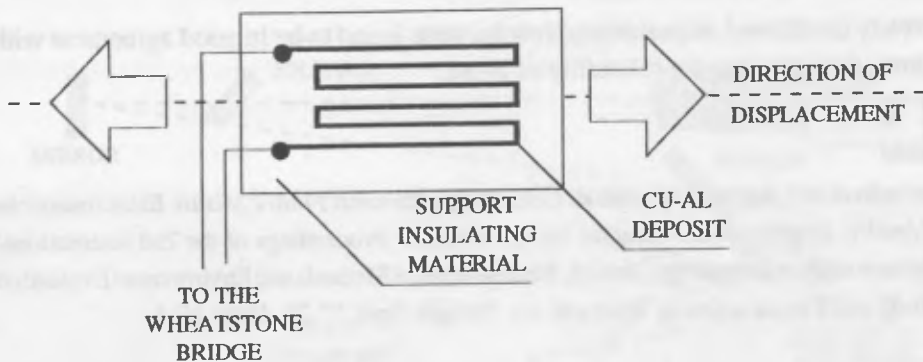


Figure 1 – Schematic diagram of strain gauge.

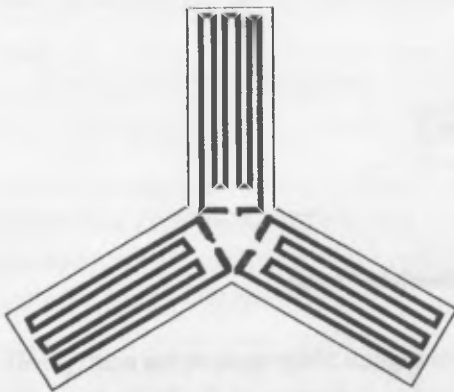


Figure 2 – Transducer used for Marcus Aurelius measurements.

A thin, wire-shaped copper-aluminum deposit is supported by a sheet of insulating material. During the measurement, the sheet is stuck to the structure and the ends of the wire are connected to a resistance measuring device (typically a Wheatstone bridge).

More complex stress configurations require several strain gauges arranged on the same support to monitor deformations along different axes. Figure 2 schematically shows the type of transducer used for investigations on Marcus Aurelius.

Applications of artistic interest

Strain-gauge measurements were largely employed, in combination with FEM, for structural characterization of the Marcus Aurelius statue [1]. In preliminary measurements, extensometers were not stuck directly on the statue; instead, experiments were carried out on a 1/5 bronze model. The model was progressively loaded by a dynamometer and its behavior observed by means of ten strain rosettes.

According to FEM calculations, the stresses were expected to reach maximum values at the junction of the left foreleg. Therefore, eight of the ten rosettes were positioned in the neighborhood of the junction and the other two were stuck on the belly, where the stresses were found to be modest.

Two sets of measurements were carried out under different constraint conditions. In the first set, the horse's legs were free to slip over the bearing plane; in the second, slipping was prevented. The constraints could be regarded as three "double carriages" in the first case and three "hinges" in the second.

As already mentioned, experimental results were found to be in good agreement with calculations, thus proving the reliability of FEM.

References

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16. LASER INTERFEROMETRY

Physical principles and instrumentation

The availability of lasers as strictly coherent and monochromatic sources of light has allowed the development of interferometric techniques that can be employed to observe the deformation of structures ranging from several mm down to half radiation wavelength ($\lambda = 541.5 \text{ nm}$ for argon laser).

Two types of laser interferometry will be described below; one of these was used to measure the deformations of the horse in the equestrian statue of Marcus Aurelius.

HOLOGRAPHIC INTERFEROMETRY (HI) [1, 2] - This technique relies on a unique feature of holograms, which are capable of storing information on both the intensity and the phase of the object-scattered light. A typical experimental setup is shown in figure 1.

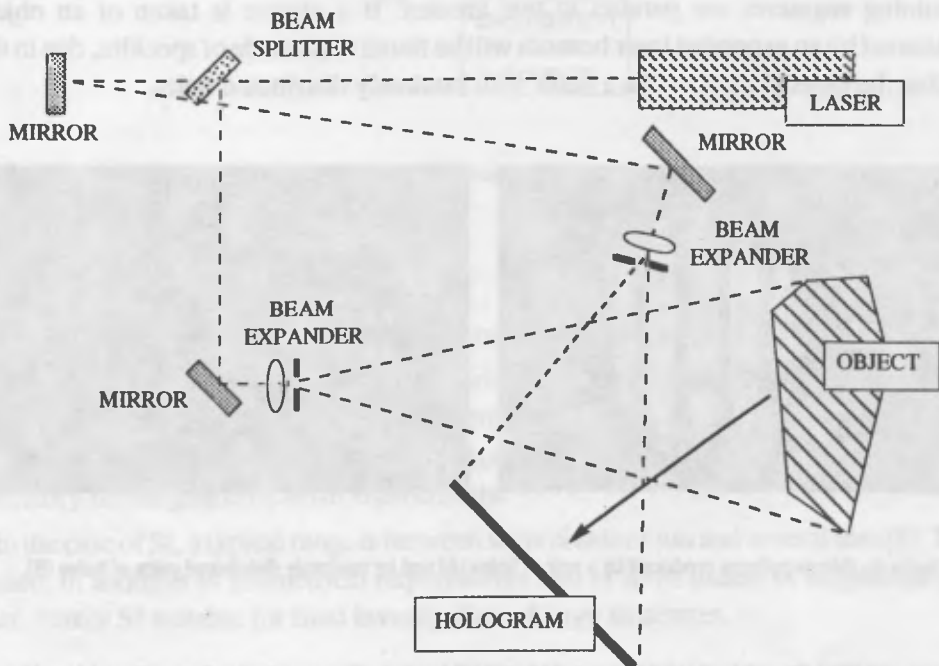


Figure 1 – Schematic diagram of a HI system.

Holograms are photographic images obtained by splitting the output of a laser into two beams, one of which is expanded and used to illuminate the object, whereas the other (reference beam), expanded as well, strikes the photographic plate directly. Each point of the recorded image is the result of interference among the reference beam and the beams coming from all the points of the object. The hologram is read in the same position in which

it was recorded; when illuminated with the reference beam, it behaves like a window opened on the object: a virtual image of the object, with all its characteristics of three-dimensionality and parallax, can be seen through the hologram. Small changes in the object's shape, on the order of hundreds of nm, can be detected by impressing the same plate before and after the deformation. When illuminated by the reference beam, the two images interfere with each other and the object appears to be furrowed by interference fringes. The spatial frequency of the fringes is directly related to the magnitude of deformation and can be used to evaluate stress concentration, just as discontinuities in fringes can be used to locate discontinuities in materials.

SPECKLE INTERFEROMETRY (SI) [3] - When an opaque mask with two holes is illuminated by laser light, interference takes place and a set of parallel fringes can be observed on a properly positioned screen. The spatial frequency of the fringes is a known function of the distance between the holes and the orientation is perpendicular to the joining segment. The same behaviour can be observed in the case of randomly distributed pairs of holes, provided the joining segments are parallel to one another. If a picture is taken of an object illuminated by an expanded laser beam, it will be found to be made of speckles, due to the fact that the object behaves like a mask with randomly distributed holes.

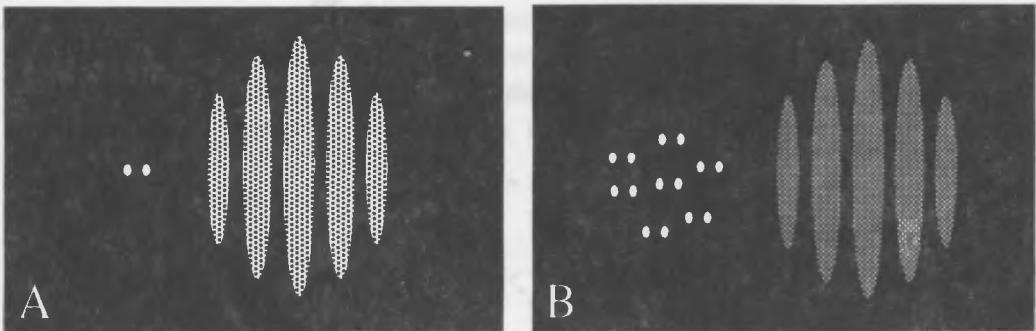


Figure 2 – Fringe patterns produced by a pair of holes (A) and by randomly distributed pairs of holes (B).

Suppose that the object undergoes deformation due, for example, to external loads and that both configurations are recorded on the same film; when a small area of the film is illuminated by an unexpanded laser beam (see figure 2), it behaves like a mask with randomly distributed pairs of holes and produces sets of parallel interference fringes.

The magnitude and orientation of deformations in the whole structure can be measured by scanning the picture with the laser beam, provided the magnification of the camera is known.

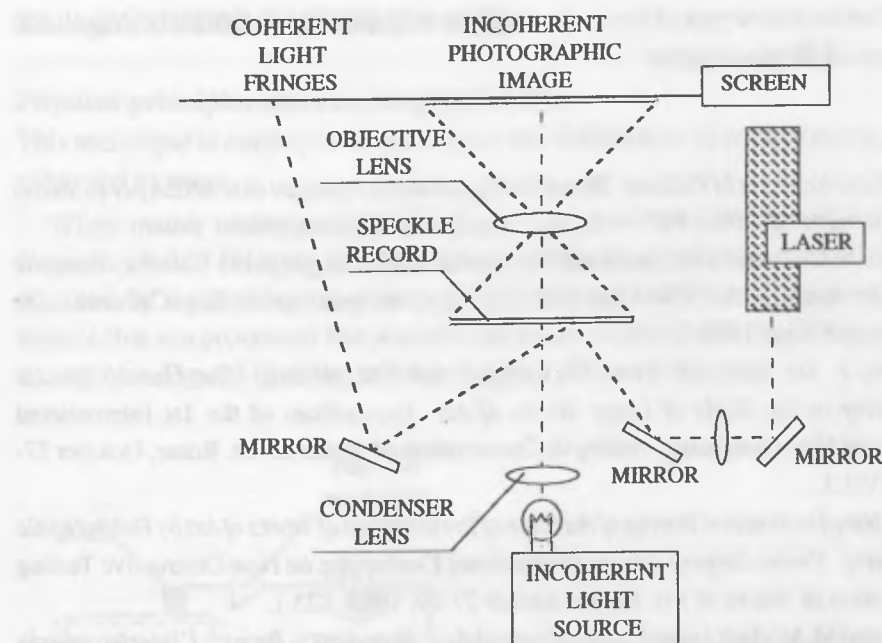


Figure 3 – System for observing speckle Interferograms.

Features and limits

Although measuring the same quantity, the two techniques work in different ranges.

HI measures displacements roughly included between 0.1λ and 10λ , with $\lambda = 541.5$ nm for argon laser; moreover, the components of the system need to be geometrically stable within a small fraction of wavelength. These features make HI suitable for laboratory investigation of small rigid objects.

In the case of SI, a typical range is between several tens of μm and several mm [3]. This feature, in addition to geometrical requirements two or three orders of magnitude less strict, makes SI suitable for field investigation of large structures.

Applications of artistic interest

Laser interferometry is employed to approach a wide range of structural problems.

HI can provide useful information about detachments in paintings [4], the effects of reversible assembly systems on bronze statues [5], the deterioration of stone surfaces [6] and the stress-deformation characteristics on bronze statues [7].

SI was employed to investigate the Marcus Aurelius group with regard to stress-deformation characteristics [3]. With a load of 150 kg on the horse's back, a maximum displacement of 3 mm was measured on the neck. The effects of an ancient repair were

also detected on the lower part of the neck, owing to non-smooth variations of magnitude and orientation of displacements.

References

- [1] F. Gori in *Tecnologie per la Cultura - Tecniche Diagnostiche Avanzate dell'ENEA per lo Studio e la Conservazione dei Beni Culturali*, De Luca Edizioni d'Arte, 1988.
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17. ACOUSTIC EMISSION (AE)

Physical principles and instrumentation [1]

This technique is employed to investigate the behavior of structures and materials when subjected to stress.

When matter undergoes alterations, an energy release takes place in form of high-frequency (>100 MHz) mechanical vibrations. In AE measurements, such vibrations are detected by a piezoelectric probe and transformed into attenuated electric sinusoidal signals that are processed and analyzed in terms of amplitude, frequency and energy by a computer. Fig. 1 [1] shows a block diagram of the system.

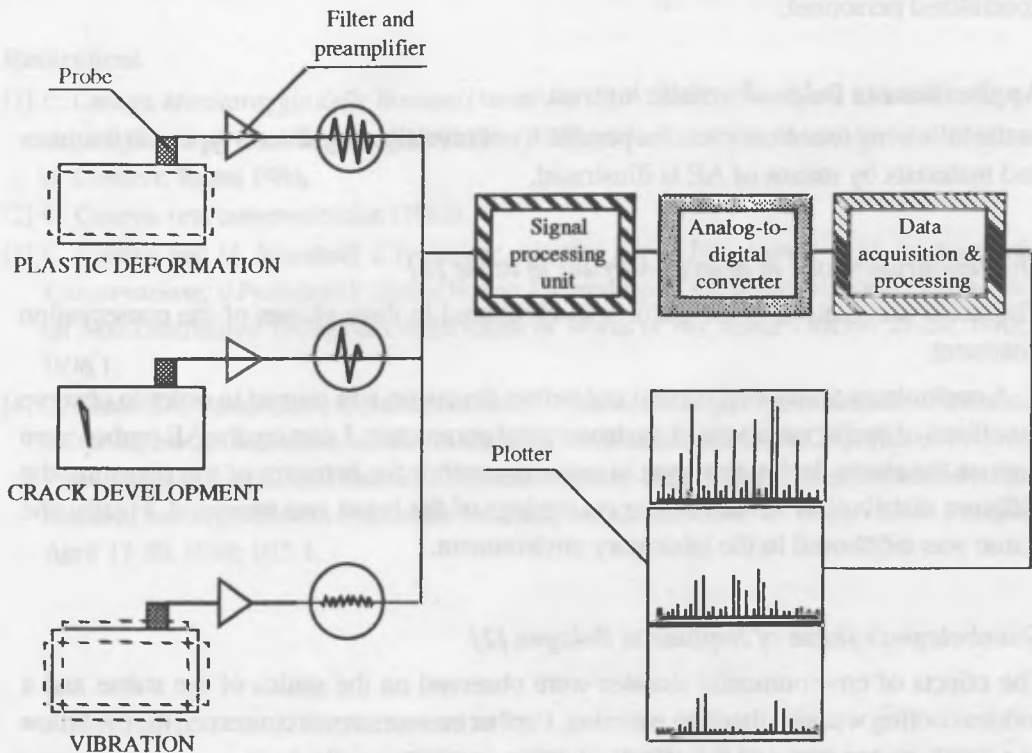


Figure 1 – Block diagram of an AE system.

Different wave shapes of the signals are also shown, corresponding to different alterations of the structure, i.e. plastic deformation, crack evolution and vibrations. It is also possible to locate the alteration in space and evaluate its intensity.

Features and limits

AE is a non-destructive technique that can be employed to monitor the interaction between the structure and its environment, and its reaction to stresses. It is also used to verify the effectiveness of conservation treatments. The instrumentation is portable, so the investigations can be performed *in situ*.

In order to correlate the alterations to the corresponding causes, AE has to be employed in combination with other methods for monitoring environmental parameters such as humidity, temperature, solar irradiation and so on.

Further features of AE are that the analysis is performed in real time and that its applicability is not limited by the type of material, whether metal, stone or wood.

On the other hand, this instrumentation is very expensive and has to be operated by specialized personnel.

Applications in fields of artistic interest

In the following four examples, the possibility of investigating several types of structures and materials by means of AE is illustrated.

The equestrian statue of Marcus Aurelius in Rome [1]

The stress distribution of the statue was monitored in three phases of the conservation treatment.

A preliminary study was carried out before the statue was moved in order to observe the effects of cyclic variations of environmental parameters. Later on, the AE probes were kept on the statue during transport in order to monitor the behavior of the structure: the different distribution of the stresses on the legs of the horse was observed. Finally, the statue was monitored in the laboratory environment.

Giambologna's statue of Neptune in Bologna [2]

The effects of environmental stresses were observed on the statics of the statue and a sudden cooling was simulated by watering. Further measurements concerned the evolution of a crack on one arm and the effects of stress-corrosion on the base.

AE was used in combination with strain gauge and surface conductivity measurements.

The portal of S. Zeno church in Verona [3]

The portal is made of a wooden structure covered with bronze panels; two thirds of the stresses on the structure are due to the presence of the panels. AE was applied in combination with other techniques.

The causes of degradation were identified in the overstresses induced in the structure by solar irradiation: the panels were expanded by heating, whereas the wood shrank due to loss of humidity.

The corporal in Orvieto cathedral [4]

This object is a large reliquary made of gold and silver with enamels. The degradation was of a chemico-physical type; in addition, a progressive detachment of the enamels was observed. The causes were found to be the thermal shocks that the corporal suffered when transferred from a cold strongbox, where it was kept at night, to the chapel, where it was exhibited during the day. Strain gauge and vibration analyses were also performed on the entire structure.

References

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18. RADIOGRAPHY

Physical principles

Radiographic techniques are based on the capacity of ionizing radiations to blacken photographic plates or films, the intensity of blackening being proportional to the flux of the impinging particles. In the common meaning of the words, both radiography and gammagraphy denote methods employing photons: X-rays and γ -rays, respectively.

A typical experimental arrangement for radiographic techniques is shown in figure 1.

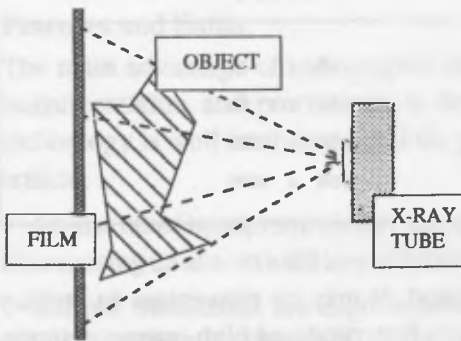


Figure 1 – Radiographic experimental setup.

The blackening of the film depends on the attenuation properties of the object, which are a direct function of the thickness and density of the material and an inverse function of the energy of the X or γ -rays. Variations in the material's thickness and/or density can be studied by considering the corresponding variations in the grey levels of the radiogram.

The energy of the impinging photons has to be increased when the thickness and/or density of the object to be investigated increases.

Instrumentation

The experimental arrangement of radiographic techniques has already been shown in figure 1; depending on the dimensions and thickness of the object, the radiation source can be either an X-ray tube or a radioisotopic source.

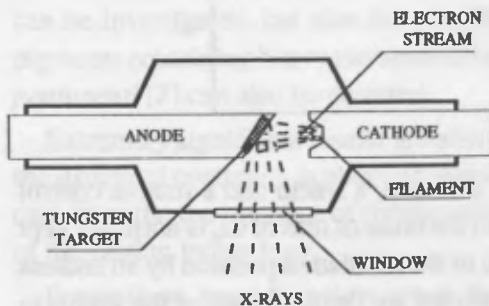


Figure 2 – Schematic diagram of an X-ray tube.

Figure 2 shows a typical X-ray tube. The electrons emitted by an electrically heated filament (cathode) strike a target (anode) after being accelerated by a potential (HV) on the order of tens or hundreds of kV; the interaction of such electrons with the electric field of the target atoms is called "bremsstrahlung" and produces broad-spectrum X-rays.

The mean energy of the spectrum is affected only by the high voltage, whereas the photon flux density is also affected by the filament current. Both parameters can be adjusted but the most important is HV, which should be kept as low as allowed by reasonably short exposure times to have good contrast and resolution of the image.

Optimization is an essentially empirical operation and depends on the type of object to be investigated; typical HV ranges are given in table I [1].

Table I - HV ranges for objects of artistic interest

Type of object	HV [kV]
drawings, paintings on canvas and wood	5 + 30
wooden statues, pottery, laminae	30 + 80
bronzes and other metals	80 + 250
large bronze statues, stone	250 + 1000

If large statues or stone have to be investigated, it may be convenient to employ γ -sources instead of X-ray tubes; nuclear decay, in fact, produces high-energy photons, able to penetrate large thicknesses of materials. Typical nuclides used for gammagraphic techniques are shown in table II.

Table II - Nuclides employed in gammagraphy

Nuclide	Energy [MeV]
^{192}Ir	0.20 – 0.61
^{137}Cs	0.66
^{60}Co	1.17 – 1.33

The irradiation device generally consists of a source, a shield and a remote control system. The source, whose activity is generally in the order of tens of Ci, is normally kept inside an uranium shield from which it is carried to the irradiation position by an endless screw running into a pipe; both the screw and the pipe are flexible to allow the source to be positioned comfortably.

A considerable quality improvement can be achieved in radiographic images by digital processing. Digitalization is performed by means of a computer interfaced to an image acquisition device. It consists of converting the original image, which is continuous both from the geometric and the chromatic point of view, into a finite set of elementary areas,

so-called "pixels," each characterized by its position in the frame and by a code accounting for the grey level in that point. The final result is a numerical representation of the image which can be mathematically processed to highlight information that exists in the original image but cannot be easily observed. The enhancement of contrast, a better definition of the outlines and the reduction of noise are typical operations that can be performed by digital processing.

This procedure is particularly useful for gammagraphic techniques, which generally have poor contrast and resolution due to the effect of Compton electrons generated in the film (blurring).

Features and limits

The main advantage of radiographic techniques is that they do not need sophisticated instrumentation and procedures, at least in the most common versions: X-ray tube technology is well established and the parameters affecting the experiments are not too critical.

On the other hand, intrinsically three-dimensional objects are projected onto a plane, thus causing an almost total loss of information in the direction perpendicular to the plane.

Further limitations are represented by the radiological hazard, particularly when radioisotopic sources are used. According to current Italian legislation, a health physicist must supervise the irradiations and, if necessary, order the removal of personnel from the area for the duration of the experiments.

Applications of artistic interest

Radiographic investigations can be employed whenever structural details are displayed by differences in the attenuation of X or γ -rays.

With regard to paintings, not only the structure and state of conservation of the support can be investigated, but also the spreading of colors and brush strokes, mainly when pigments containing heavy elements are used (e.g. lead white). The presence of gaps and *pentimenti* [2] can also be detected.

Extremely significant results are also achieved on bronze statues [3]: information on the structural continuity is obtained; original sections can often be distinguished from the cast-on parts; the presence of repairs and welds can be easily detected, as well as details of the casting technology.

Precautions must be taken when thermoluminescence measurements have to be performed on casting sand or pottery: in these cases, a sample has to be taken before irradiation; enamels can be damaged due to radiochemical reactions [1].

References

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19. ULTRASOUND

Physical principles and instrumentation

The name “ultrasound” is conventionally given to acoustic waves in the frequency range of 15 kHz to 100 MHz, but only frequencies between 22 kHz and 10+20 MHz are considered for practical applications.

Typical ultrasonic transducers are made of small oscillating elements in which electrical high-frequency signals are transformed into pressure waves and vice versa by a piezoelectric effect¹; such transducers can work as both transmitters and receivers.

The propagation of ultrasound takes place along a straight line and, like all other types of pressure waves, it requires the presence of a medium, which is characterized in terms of acoustic impedance and propagation velocity. It can be demonstrated that the interface between two media totally reflects the incident wave if the acoustic impedance of the first one is much higher than the second; this is the case of liquid and solid substances interfaced to gases.

The properties described above can be used in measuring thickness, detecting discontinuities or flaws and investigating the mechanical characteristics of materials; a typical experimental arrangement is shown in figure 1. The ultrasonic probe is made of two transducers – one transmitting, the other receiving; a fluid couples the probe to the material to avoid reflection problems. An oscilloscope, connected to the ultrasonic system, measures the time employed to receive the echoed wavefront, thus allowing the following quantities to be derived:

- 1) If the medium sound velocity is known, the thickness can be derived ($x = v \cdot t$); in practice such measurements are performed by calibrating the instrument with standards of known thickness and composition.
- 2) The presence and location of defects can be detected if the measured thickness is smaller than the expected one.
- 3) The velocity and elasticity modulus can be derived if the ultrasound path length is known ($v = s / t$).

Applications of artistic interest

Ultrasound was used on the equestrian statue of Marcus Aurelius in combination with radiographic techniques [1]. The latter permitted identification of the regions of interest and the sample areas where ultrasonic measurements should be performed. Ultrasound

¹ When a quartz crystal is subjected to a potential difference, it changes its dimensions; conversely, if it is mechanically forced to change its dimensions, a potential difference can be measured on its surface. Due to efficiency problems, present-day transducers are made of ceramic materials such as barium titanate, lead titanate and zirconate and lead metanyobate.

² The acoustic impedance accounts for the resistance offered by the medium to wave propagation and is given by the product of density times velocity. The velocity depends on the composition of the material and is closely related to its elasticity modulus.

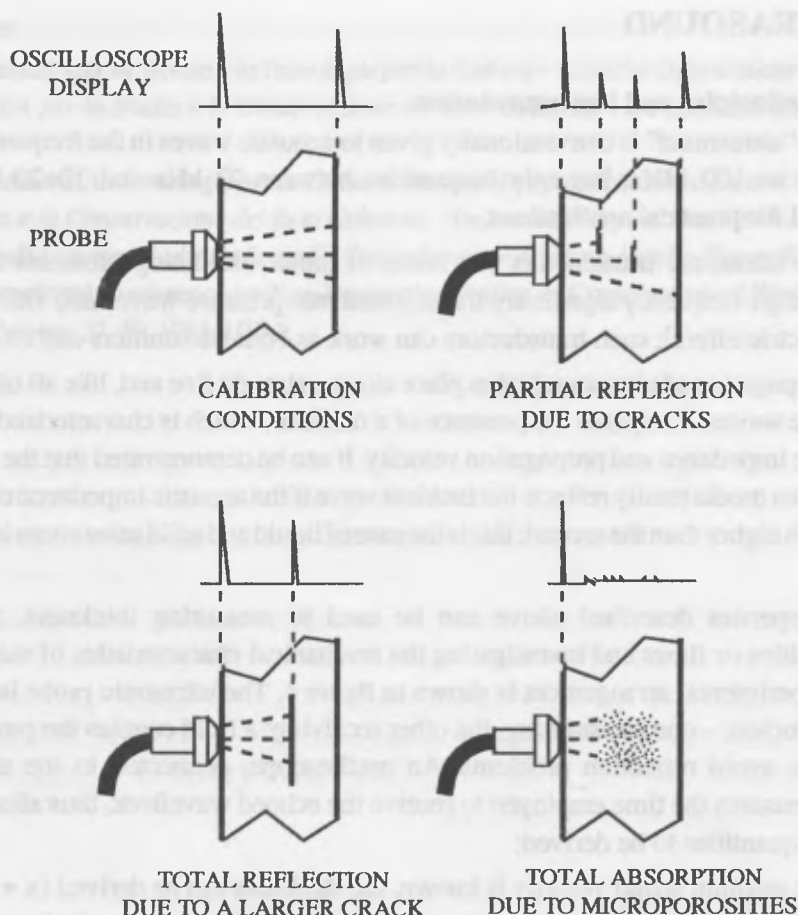


Figure 1 – Experimental setup for ultrasound measurements.

showed the presence of defects parallel to the surface of the statue, which, therefore, could not be detected by radiography.

In most cases, the measurements were carried out on sample areas, chosen to be representative of the whole region of interest. Besides the thickness distribution, the measurements also provided the means of normalizing the grey level of radiographs; the average thickness was found to be about 6 mm, with minimum and maximum values of 3 and 8 mm.

The investigations on weldings showed widespread discontinuities between structural parts and welding beads; in most cases, thicknesses in the neighborhood of the beads were found to be lower than would be required for a perfect adhesion between the welding and the structural material, thus making the welding more similar to a mechanical anchorage.

Other examples of application of ultrasonic techniques can be found in [2] and [3]. Reference [2] concerns the Fontana Maggiore in Perugia; longitudinal crack dimensions and the elastic modulus of the stone were measured; the adhesion of panels and slabs to the concrete structure of the basins was also non-destructively tested. Reference [3] concerns an assessment of the consolidating and protective effectiveness of a water mixture containing lime water, acrylic emulsion and potassium silicate.

References

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20. THERMOGRAPHY

Physical principles

It can be experimentally observed that all bodies at temperatures above absolute zero emit electromagnetic radiation, the wavelength depending on the absolute temperature; for temperatures of practical interest in the field of conservation, the emission is in the range of thermal infrared (around $10\text{ }\mu\text{m}$).

With regard to the so-called “black body,” which is an ideal object in which the capability of emitting or absorbing radiant energy does not depend on the radiation wavelength, the laws of physics state that the wavelength distribution shows a maximum which is inversely proportional to the absolute temperature and that the power emitted by irradiation is proportional to the fourth power of the absolute temperature. Compared to the black body, real objects always show a capacity to exchange energy by irradiation (emissivity), which is lower and wavelength-dependent.

If the corresponding emissivity is known, the surface temperature of an object can be derived, without physical contact, by simply measuring the radiant power: this is the working principle of thermographic instruments.

It has to be considered that the temperature distribution is related not only to the interaction of the object with the environment, but also to the presence of discontinuities and dishomogeneities which may cause changes in thermal conductivity and capacity.

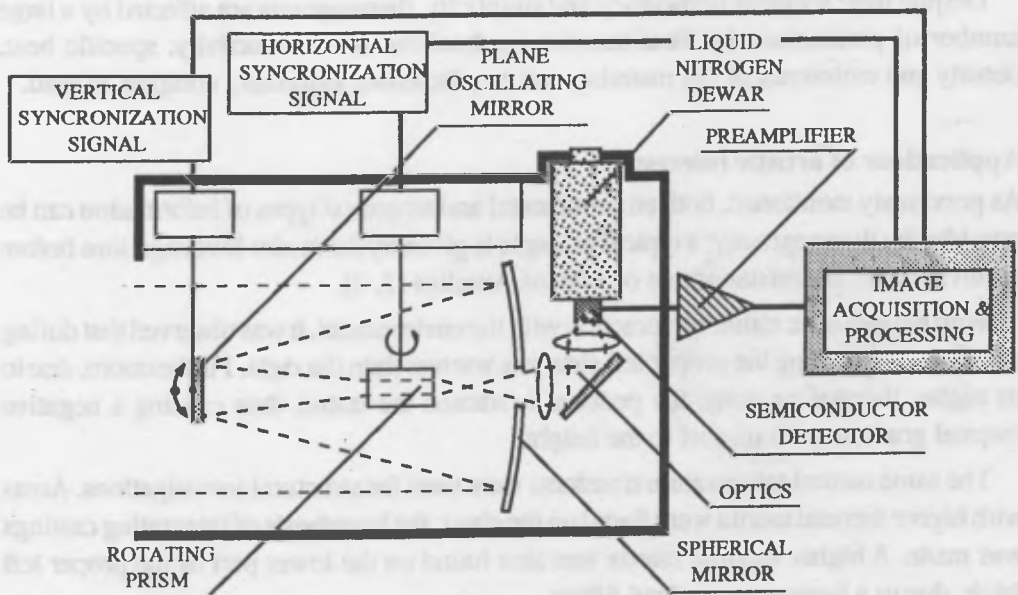


Figure 1 – Diagram of a thermographic system.

Instrumentation [1]

Modern thermography is usually performed by means of scanning devices, schematically shown in figure 1.

Electrically operated optical systems successively focus small areas of the object, the whole image being scanned in about 0.1 s, and direct the radiation beam on one or more detectors, generally of the semiconductor type. The output electric signal, which is proportional to the radiant power of the focused area, is amplified, digitalized and sent to an image processing system, which, besides the reconstruction of the image, also provides filtering operations such as reducing the noise, enhancing the outlines, etc.

Features and limits

Typical working parameters of a thermographic device are listed below, with reference to the Marconi TICM II system [1].

Spectral band	8 + 13 μm
Thermal resolution	< 0.1 $^{\circ}\text{C}$ at 30 $^{\circ}\text{C}$
Spatial resolution	2.27 $\times 10^{-3}$ sterad
Survey frequency	2.5 images / s
Detection system	8 det. HgCdTe

Despite their seeming immediacy and simplicity, thermograms are affected by a large number of parameters, i.e. heat-transfer mechanisms and conductivity, specific heat, density and emissivity of the material, and are, therefore, extremely complex to read.

Applications of artistic interest

As previously mentioned, both environmental and structural types of information can be provided by thermography; a typical example is given by the *in situ* investigations before removal of the equestrian statue of Marcus Aurelius [2, 3].

With regard to the statue's interaction with the environment, it was observed that during the nocturnal cooling the proper left side was warmer than the right. Furthermore, due to its higher thermal capacity, the pedestal irradiated the statue, thus causing a negative thermal gradient with respect to the height.

The same natural temperature transients were used for structural investigations. Areas with higher thermal inertia were found on the chest; the hypothesis of integrating castings was made. A higher thermal inertia was also found on the lower part of the proper left thigh, due to a homogeneous lead filling.

Thermography is also helpful for investigations of building works [4]. The following peculiarities can be observed, due to their effect on the thermal behavior of the structure:

- detachment of frescoes
- consolidations
- presence of humidity
- ancient, subsequently filled apertures
- micro and macro-fractures over extended areas
- voids.

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