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"Energy Dispersive X-Ray Fluorescence for the Analysis of Works of Art"

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Introduction

When a sample of any form and nature is irradiated by a beam of X-or gamma rays of proper energy and intensity, it emits X-rays of characteristic energy and intensity, depending on the elements present in the sample and on their intensity. The analysis of emitted X-rays, and therefore the related analytical methods is called Energy Dispersive X-Ray Fluorescence (EDXRF)(1).

The physical process of excitation and deexcitation of a sample with emission of characteristic X-rays will be discussed in Section 2. It is important now to point out that EDXRF provides a simple and sensitive method for multi-element analysis of elements with atomic number Z larger than about 15.

The EDXRF technique presents the following characteristics:

- -it is intrinsecally non-destructive;
- -it requires measuring times typically of the order of 100 s;
- -it is a multielemental technique;
- -it is a surface analysis, as information comes from a thin layer of the specimen (see Section 2);
- -it presents a wide dynamic range of analysis, from about ppb (parts per billion per weight) to percent of concentration.

  EDXRF is therefore very useful for elemental analysis of works of art, such as paintings of all types, alloys, potteries and so on.
- -it is able to analyze all elements from the periodic Table, except those with low atomic number (approximately elements below atomic number 15, due to the strong absorption of the emitted low energy-X-rays by the air and the detector-window).

2. Physical principles

2.1 Interaction of radiation with matter

Radiation, i.e. X-and low energy gamma rays, may interact with matter in various ways. The most important, in the energy range of interest for XRF-analysis, namely 10-150 keV, is the photoelectric effect, which gives rise to the emission of fluorescent X-rays. In the photoelectric effect an incident photon of proper energy interact with an electron from the internal shell of the atom (Figure 2.1). The electron is ejected from the atom and begins to pass through the surrounding matter. The electron rapidly loses its energy and moves only a relatively short distance from its original location. The photon's energy is,therefore, deposited in the matter close to the site of the photoelectric interaction. Since the interaction creates a vacancy in one of the electron shells, typically the K or L, an electron moves down to fill in. The drop in energy of the filling electron produces, with some probability, a characteristic X-ray photon (Fig.2.2). The energy of the characteristic radiation depends on the binding energy of the electron involved. This radiation is called fluorescent radiation. The photoelectric effect

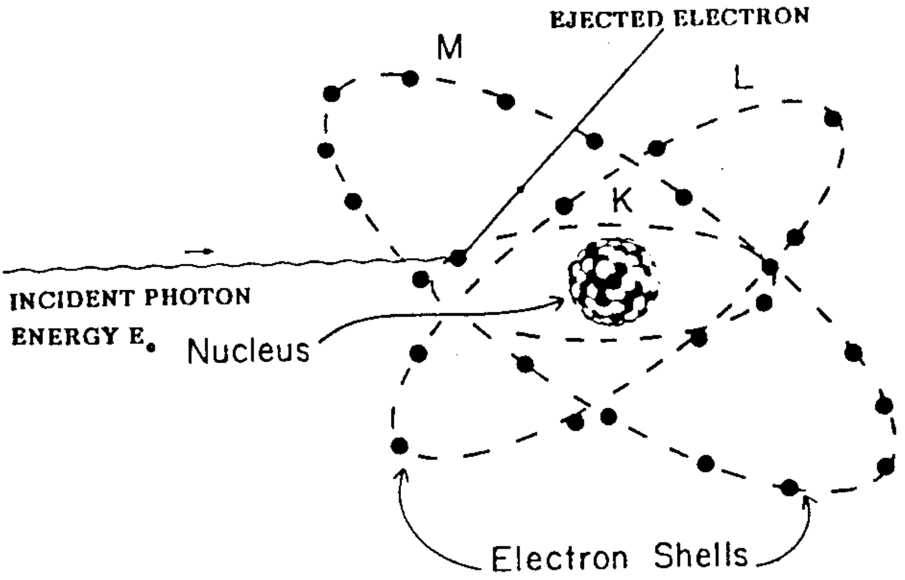


Fig. 2.1 Structure of an atom and scheme of the photoelectric effect.

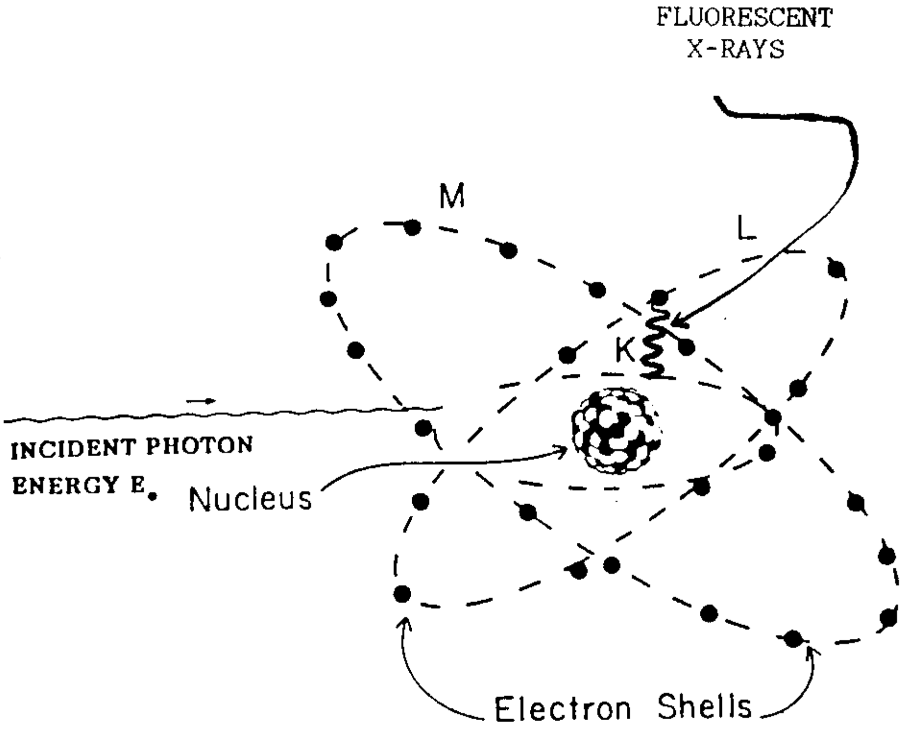


Fig. 2.2 - X-ray emission by an excited atom. After the photoelectric effect and the ejection of a K-electron, the vacancy is filled by photons of energy characteristic of the atomic number of the involved atom (fluorescent X-rays).

converts, in some way, X-or gamma rays into X-rays of lower energy, characterizing the atomic number of the irradiated atom.
The probability of photoelectric interactions is strongly dependent on the energy of the incident photon and its relationship to the binding energy of the electron. Figure 2.3 shows the relationship between the probability of photoelectric effect for iodine (atomic number Z=53) and photon energy. This graph shows two significant features. One is that the probability value decreases rapidly with increased photon energy. The other important feature is that the probability changes abruptly at one particular energy: the binding energy of the shell electrons.
The K-electron binding energy is 33 keV for iodine. The reason for the sudden change is apparent if it is recalled that photons must have energies equal or slightly greater than the binding energy of the electrons with which they interact.

From the energy determination of the X-rays emitted from an irradiated sample, i.e. from the "X-ray spectrum" ,the elements present in it can be identified. From the number of photons corresponding to a single X-ray peak, the amount of the element can be also quantitatively determined.
When a sample containing for example two elements a and b is irradiated by an X-ray source, characteristic X-rays of elements a and b are emitted from the sample. Typical X-ray peaks of some elements are shown in Figure 2.4.
The photoelectric effect is not the only possible interaction between an incident photon and matter. Another common interaction is due to the Compton effect, in which only a portion of the energy is absorbed and a photon is produced of reduced energy. The photon leaves the site of the interaction in a direction different from that of the original photon, as shown in Figure 2.5.
This type of interaction is classified as a scattering process and is a "disturbing" effect, both in radiology than in X-ray fluorescence, in which it is originating a background contribution.

2.2 Attenuation of radiation

Let us observe what happens when a beam of photons encounters a slice of material, as illustrated in Figure 2.6. Some of the photons interact with the material, and some of them pass on through. The interactions, either photoelectric or Compton, remove some of the photons from the beam in a process known as attenuation. A certain percentage of the photons will interact in the material, the rest will cross it. These percentages may be calculated through the Beer-Lambert law:

$$N = N_0 \exp -(\mu x) \qquad (1)$$

in which:
N_0 and N represent the number of photons before and after crossing a slice of material of thickness x (in cm);
μ (in cm^{-1}) is the linear attenuation coefficient of the material,

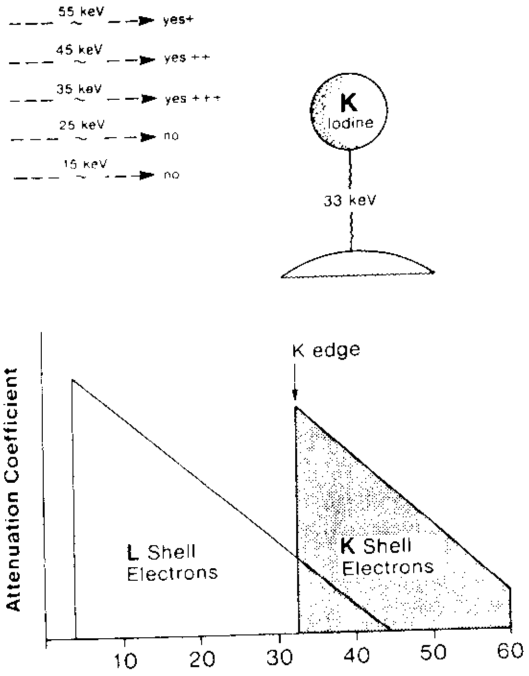
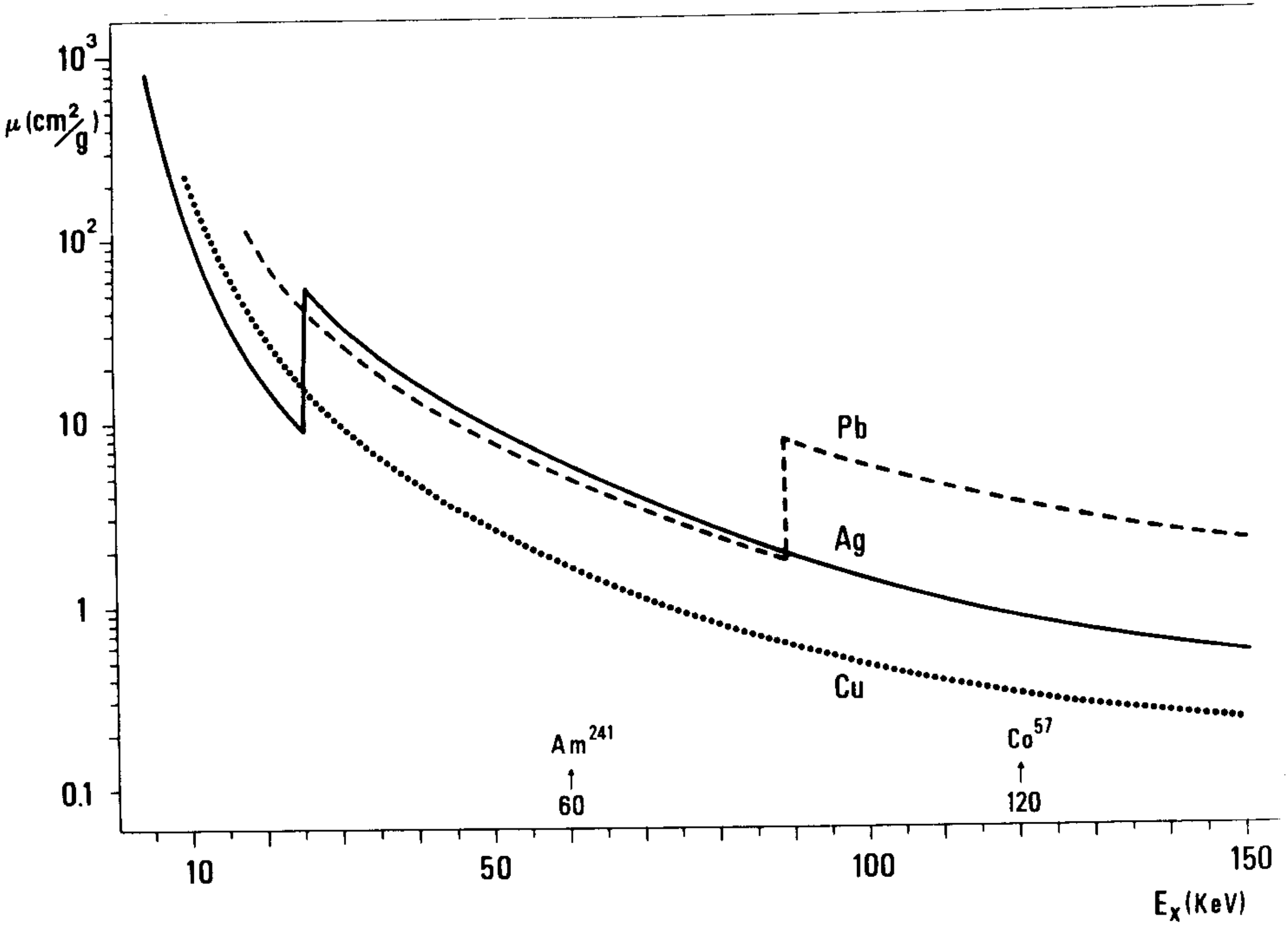


Fig. 2.3 - Relationship between the probability of photoelectric interaction and photon energy; the probability, or attenuation coefficient, shows characteristic jumps corresponding to the minimum energy for ejecting an electron from its orbit. Above, the attenuation coefficient for iodine, showing the L-and K-shell contribution; below the attenuation coefficient for Cu, Ag and Pb, with the characteristi jumps at 9 keV (not visible), 25.5 keV and 88 keV respectively.



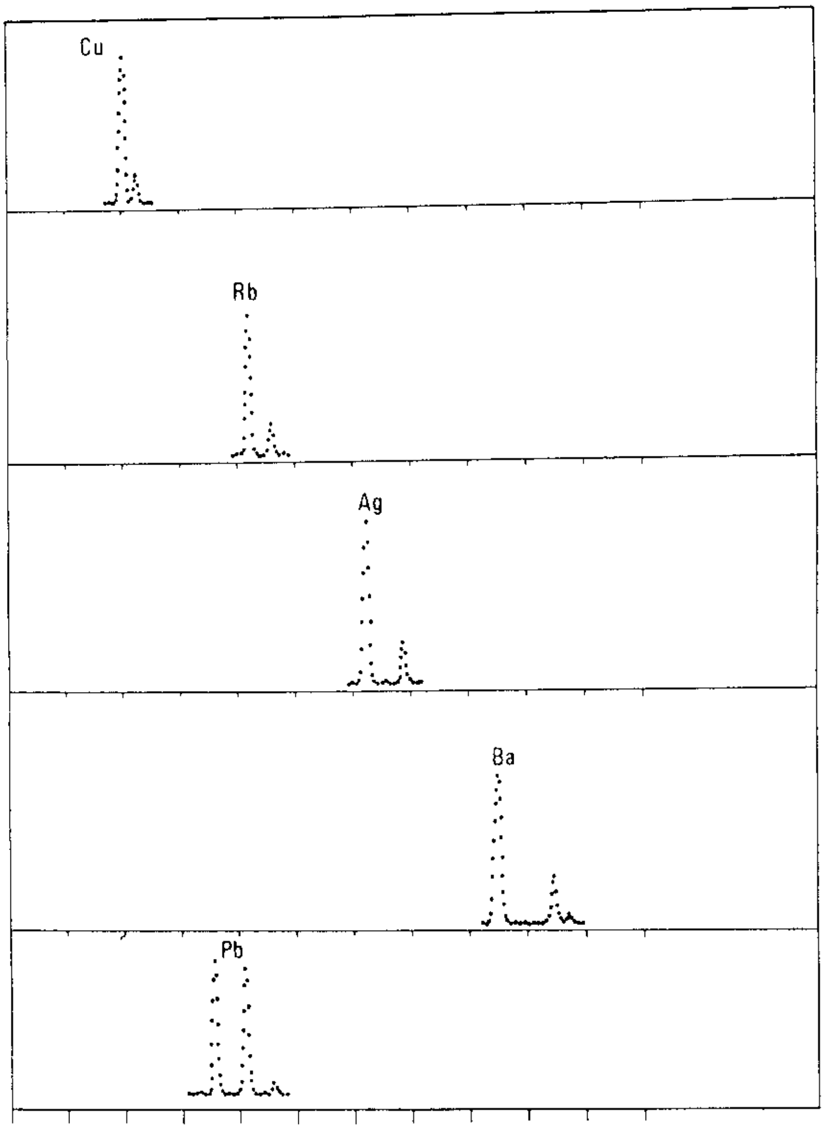


Fig. 2.4 - X-ray fluorescence peaks emitted by some typical elements. K-lines are composed by K_α and K_β -lines with an intensity ratio of about 6 to 1. L -lines are composed by L_α, L_β and L_γ-lines with an approximate intensity ratio of 1 - 1 - 0.2.

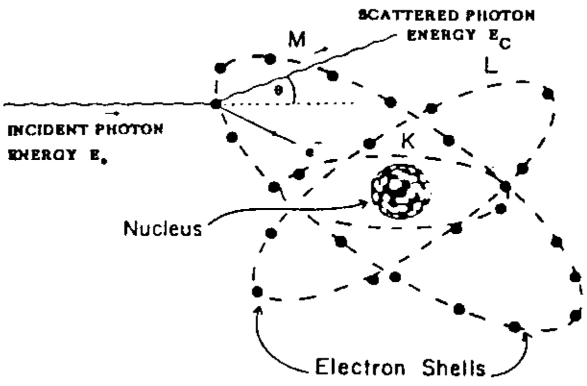


Fig. 2.5 - Scheme of the Compton effect. The incident photon is scattered and part of the energy is taken by a secondary electron.

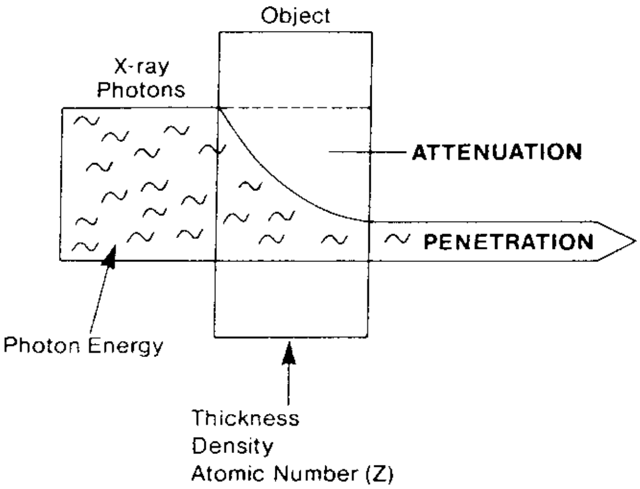


Fig. 2.6 Factors that Affect the Penetration of Radiation through a Specific Object (A)

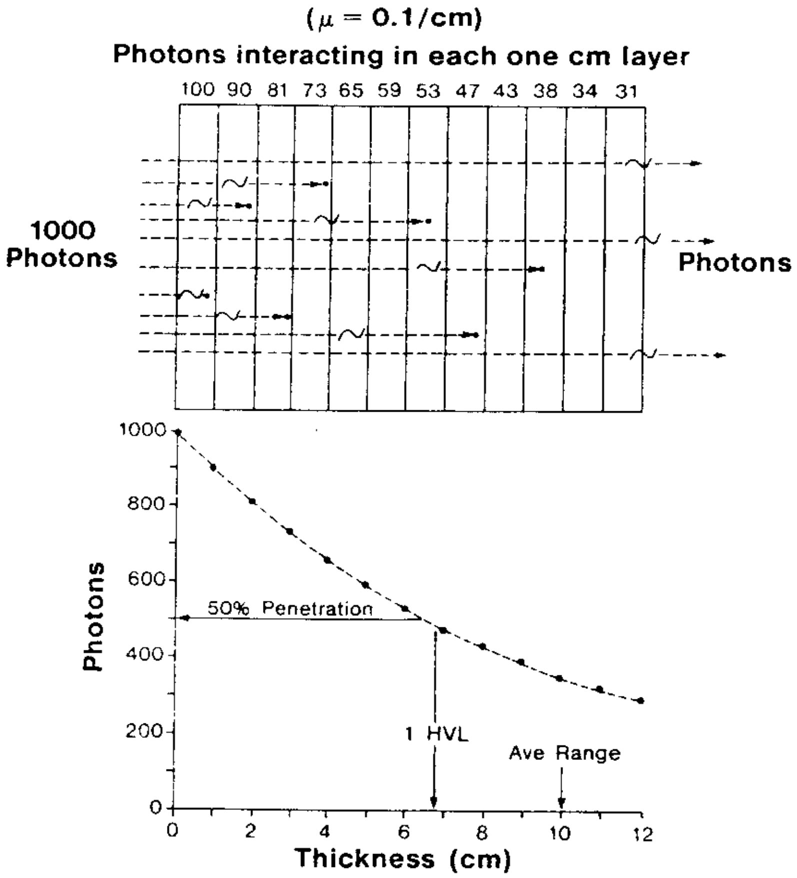


Fig. 2.6. Penetration Range of Individual Photons (B)

indicating the rate at which photons interact as they move through material. The linear attenuation coefficient is a sum of the photoeletric and of the Compton attenuation coefficient.
Linear attenuation coefficient and probability of an interaction are equivalent concepts.
The linear attenuation coefficient is determined by the energy of the incident photons and the atomic number and density of the material. Higher the atomic number and the density, higher the attenuation coefficient (see Figure 2.7).

2.3 Radiation penetration

It might be helpful in understanding the characteristics of radiation penetration to first consider the distance traveled by the individual photons before they are absorbed or scattered. Let us consider a beam of monoenergetic photons entering an object, as shown in Figure 2.6A.If we count the number of photons through each thickness of material, we observe the exponential attenuation described by Eq. (1). Half value layer (HVL) is the most frequently used factor to describe both the penetrating ability of specific radiations and the penetration through specific objects. HVL is the thickness of material penetrated by one half of the incident photons.

Considering Eq.(1), it turns out to be:

$$HVL = 0.693/\mu \qquad (2)$$

The attenuation coefficient of any element, substance or mixture is tabulated versus energy. It is therefore extremely easy to calculate the HVL value for any type of specimen.
In Table 1 are for example shown the HVL values for wood, bronzes, silver and gold alloys versus energy of incident radiation.
It is evident, from the data of Table 1, that the radiation penetrates only a superficial layer. The EDXRF-analysis is, therefore a surface and not a volume analysis, and is therefore extremely dependent on the surface composition. In all cases in which the surface composition is not representative of the whole sample composition, such as in the case of patina or corrosion, a superficial layer should be removed in order to correctly analyze the sample.

3. Apparatus for EDXRF

As observed in Section 1, when a sample is irradiated by X-rays of proper energy, it emits secondary X-rays, characteristic of the sample composition. For analytical purposes these secondary X-rays should be detected and processed.
To this aim, the following apparatus are needed (Figure 3.1):

1. a source of excitation, generally constituted by a X-ray tube;
2. a X-ray detector;
3. an amplification chain;
4. a multi channel analyzer for the representation and processing of the secondary X-Ray spectrum.

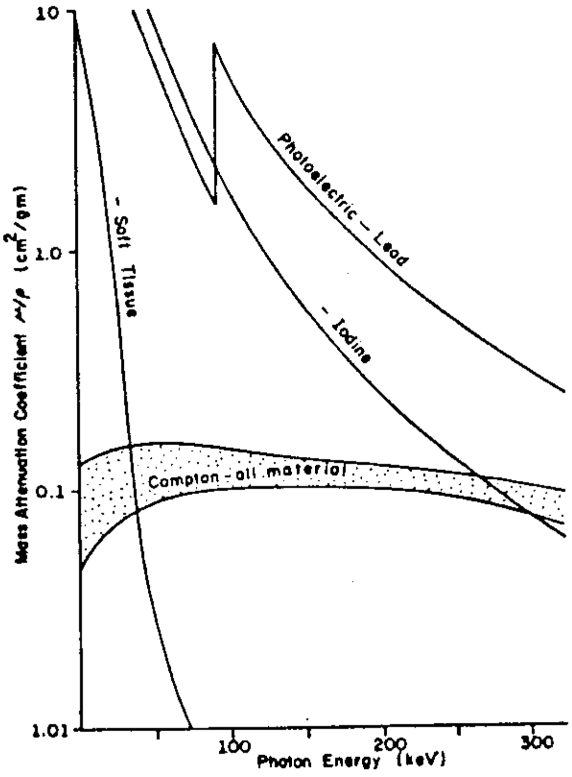


Fig. 2.7 - Attenuation coefficient versus energy for various materials, showing separately the contribution of photoelectric and Compton effect.

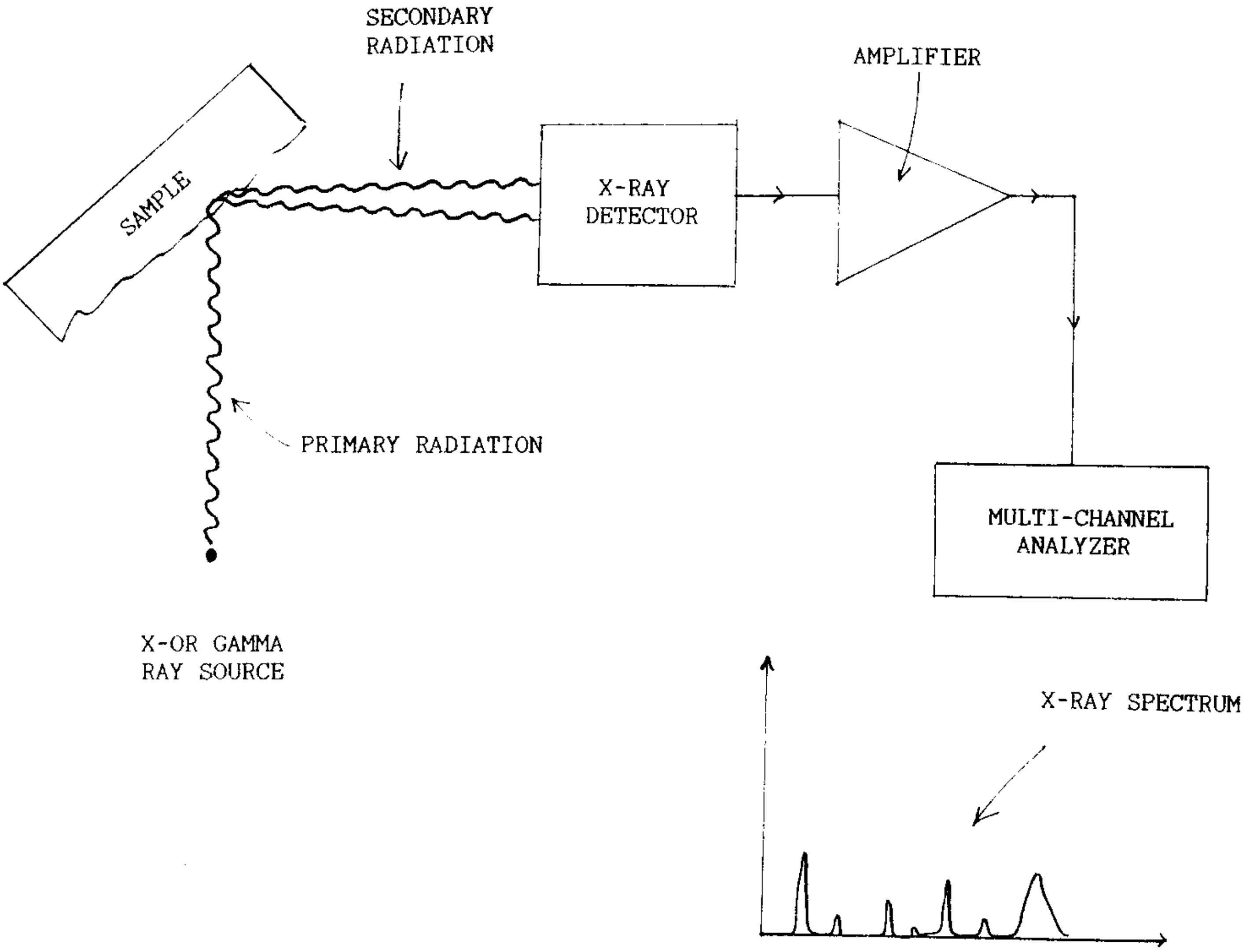


Fig. 3.1 - Schematic set-up of a EDXRF-equipment, showing X-ray source, detector, electronics and multi-channel analyzer.

The details of the single apparatus are described in the following:

3.1 Excitation source

For the best EDXRF conditions, a X-Ray source would be required, with the following characteristics:

- -to be portable, or at least transportable;
- -to emit monoenergetic or quasi monoenergetic radiation of variable energy between about 20 and about 90 keV;
- -to emit radiation with a photon flux of about 10^7 - 10^8 photons per cm^2 per s;

Various radioisotopes could be employed for EDXRF, emitting monoenergetic radiation, but they are relatively expensive, of low intensity and do not cover the whole range of excitation.

The best solution is, therefore, to use a X-ray tube (Fig. 3.2) and to partially monochromatize its output by proper filtration. In fact a X-ray tube is emitting radiation with a continuum spectrum,from about zero to a maximum value (in keV) correponding to the high voltage of the anode. For example,if a X-ray tube is working at 30, 40 and 50 kV, the radiation emitted from the tube has a spectrum between 0 and 30, 40 and 50 keV respectively (Figure 3.3).

This spectrum can be filtered or modified in several manner, by employing targets or filters of proper elements, and by utilizing their photoelectric effect (Figure 3.4). The secondary radiation is composed by quasi monoenergetic radiation of variable energy (by varying the target or the filter) and of adequate intensity (2).

3.2 X-Ray detector

Various types of detectors may be employed for the detection of X-rays, depending mainly on the analytical problem.

A detector may be characterized by its ability to separate lines of close energy (energy resolution) and on the number of detected photons per 100 incident photons (efficiency).

The most sophisticated detector for analysis of X-rays is represented by the cooled Ge-or Si-detector.

3.3 Electronics and multi-channel analyzer

Associated to the detector, a preamplifier and an amplifier are generally needed, and a single-channel analyzer with timer-scaler, or a multi-channel analyzer.

3.4 Evolution of the equipment versus time

When the programme "EDXRF in archaeometry" was started, in 1971, the equipment was characterized by (3):

- -radioactive sources;
- -a proportional gas counter;
- -a multi-channel analyzer.

The time for an analysis was relatively long (minutes) because of the low-intensity sources, the overlap between the X-ray peaks was high, due to the poor energy resolution of the detector, making the interpretation of the results sometimes difficult, and

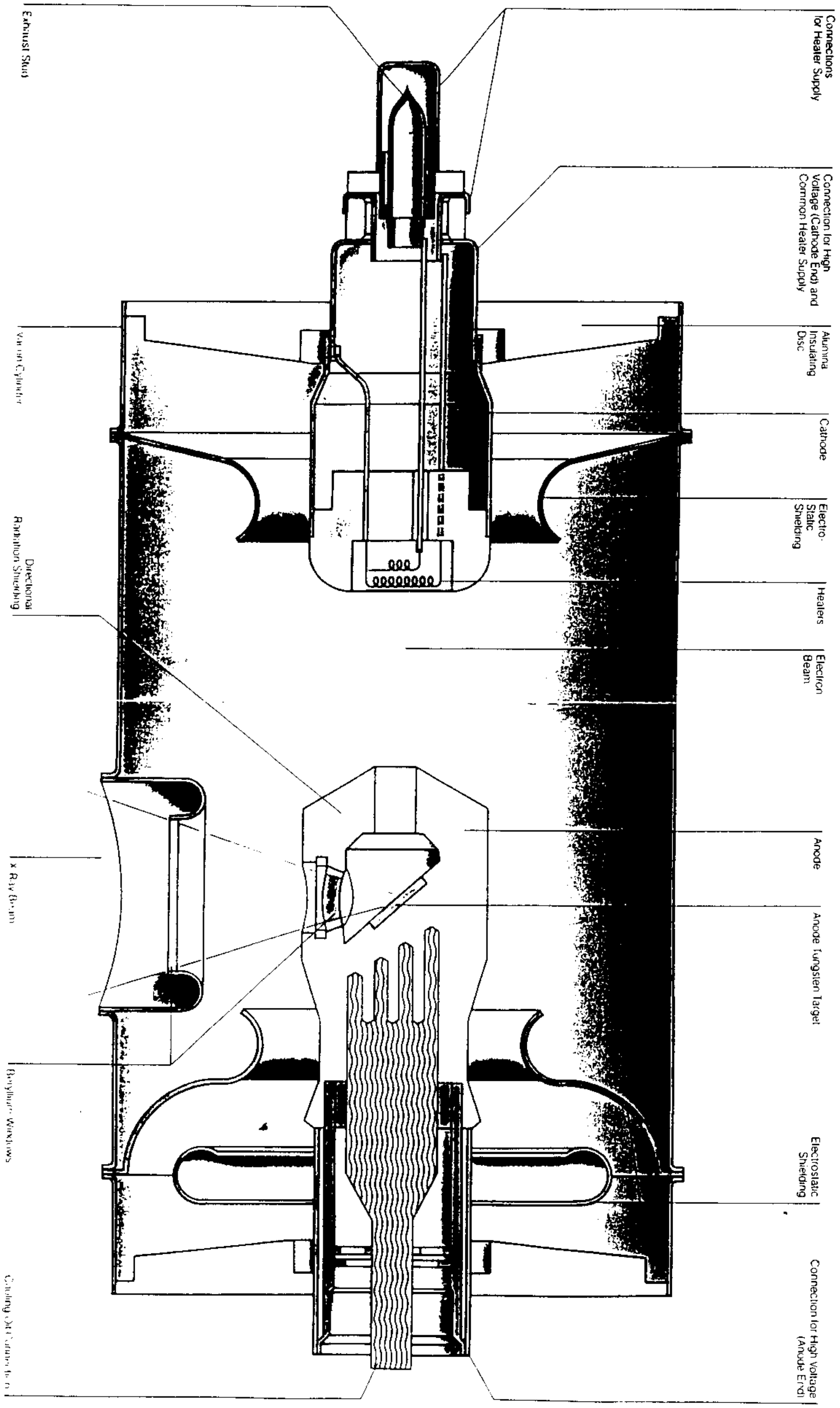


Fig. 3.2 - Schematic view of a X-ray tube.

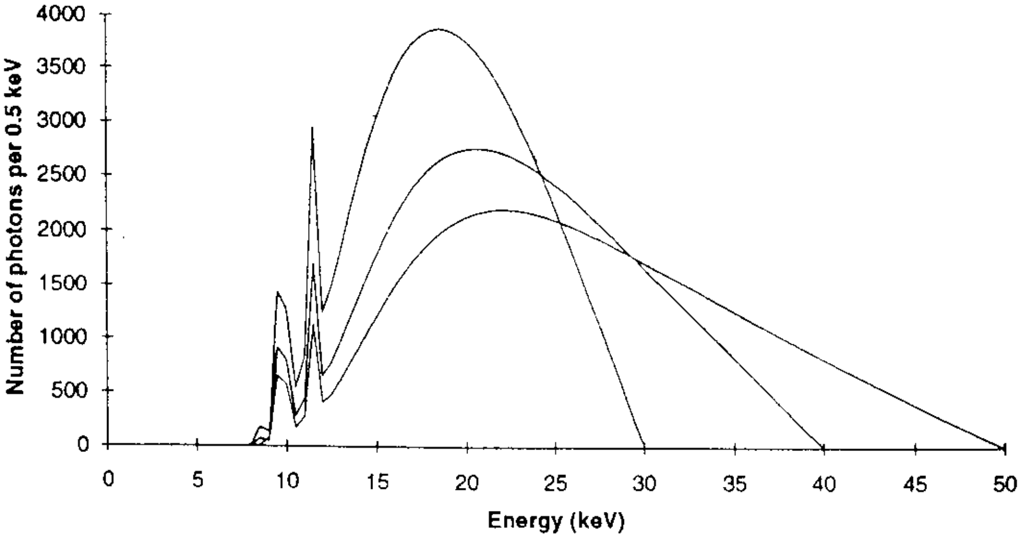


Fig. 3.3 - Bremsstrahlung spectra emitted from a W-tube working at 30, 40 and 50 kV respectively. The peaks at the left are the W-L fluorescence lines.

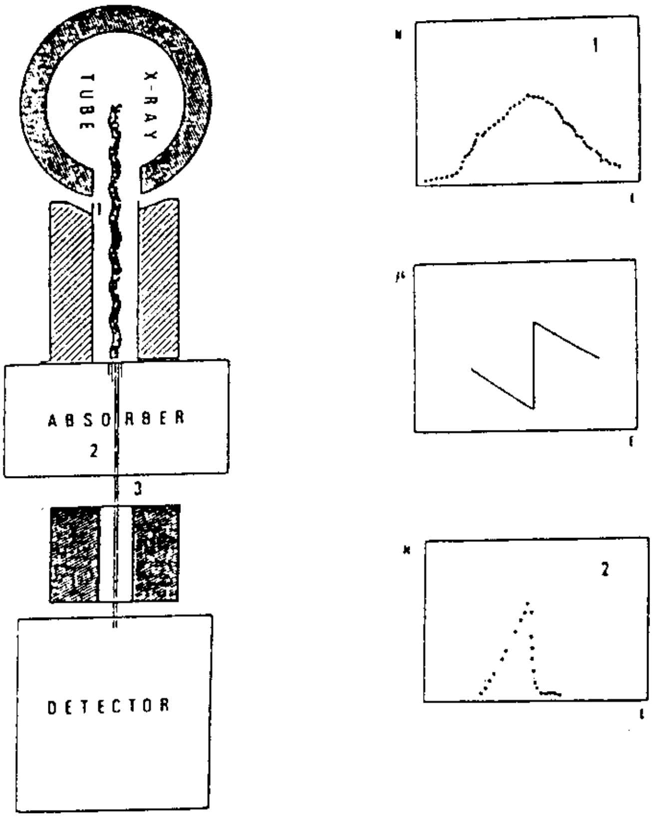


Fig. 3.4 A

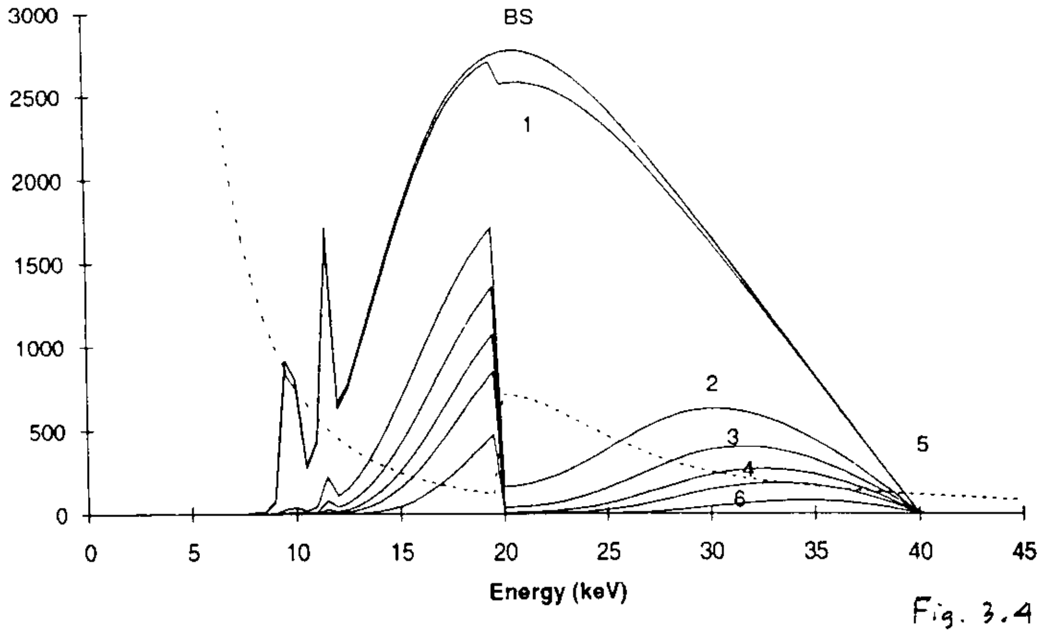


Fig. 3.4 B

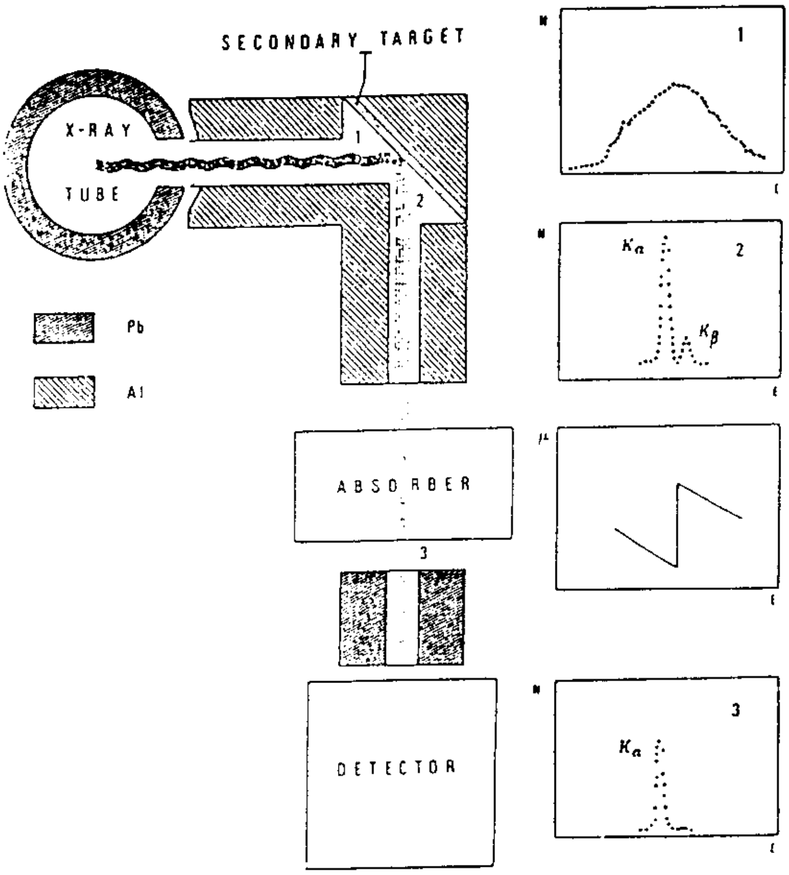
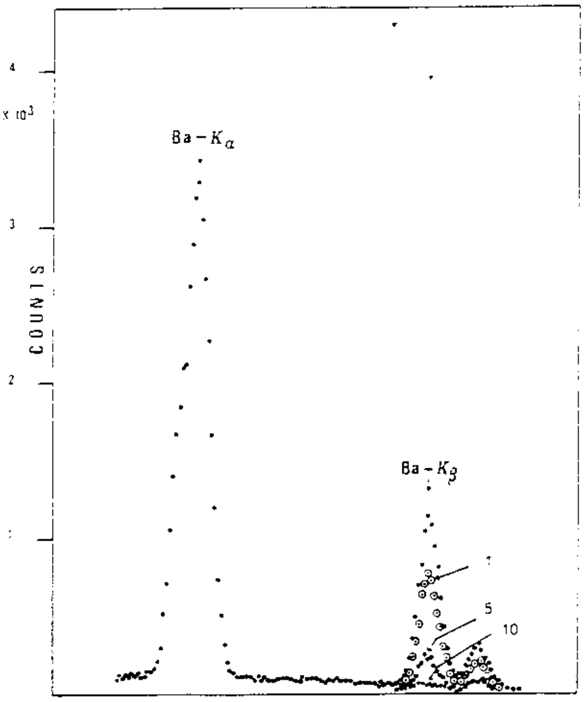


Fig. 3.4 C



D

Fig. 3.4 - Filtration of the bremsstrahlung radiation with absorbers, for monochromatizing the radiation (A)
Effect of filtrating the bremsstrahlung radiation with 40, 60, 100 and 150 microns of Mo (B).
Filtration of bremsstrahlung radiation with "diffusion targets" for monochromatizing the radiation (C).
Effect of the filtering process, showing the K_α and the K_β -peaks. When a completely monoenergetic peak is required, the K_β -peaks can be reduced or almost completely eliminated by employing a filter characterized by a photoelectric-discontinuity energy between K_α and K_β -lines (in the Figure iodine solutions at 1,5 and 10% concentration) (D).

the weight of the total apparatus also high, due to the old multi-channel analyzers.

In the portable version, employed for analysis of bronzes,brasses and golds (4), the multi-channel analyzer was substituted with a modified single-chennal analyzer (see Figure 3.5) with prefixed and precalibrated windows.

With the introduction of cooled Si(Li) X-ray detectors, the analysis of paintings and alloys could be improved, because of the much better energy resolution of those detectors (5).

At the beginning of the 1980 s, new technological progresses improved this field: the HpGe-detectors and the multichannel cards for PCs and the portable X-ray tubes for excitation of X-ray fluorescence.

A successive important technological improvement was given by the introduction of the room-temperature (or Peltier cooled) HgI (6) and Si-PIN semiconductor detectors, having, the first, an energy resolution comparable to that of the cooled semiconductor detectors, the second an energy resolution three times larger (about 650 eV between 5 and 30 keV) sufficient for EDXRF analysis of a large number of different objects. Currently, the EDXRF-apparatus is totally portable, and could be composed by: a portable, light X-ray tube; a Peltier-cooled HgI_2 or Si-PIN detector; a portable multi-channel analyzer.

The total weight of the apparatus can be about 10 Kg, and the cost about 30000 US$.

4. Analyzed area

The area analyzed by EDXRF corresponds to the area irradiated by the incident radiation, and is therefore depending on the size of the X-ray beam irradiating the sample. From a practicle point of view, beam-sizes of the order of 1 mm to 1 cm can be typically generated by properly collimating the X-ray tube output, but smaller sizes are obtainable, according to the characteristics of the sample. In some cases, especially when a surface sample cleaning is required, such as for bronzes, brasses and silver alloys, it would be desired to strongly collimate the beam, in order to clean only a very small surface. In other cases, such as in the case of paintings, gold alloys and others, it would be more useful to irradiate a larger surface, in order to have a mean concentration value over a larger area.

5. Qualitative and quantitative EDXRF analysis

The final result of a EDXRF-measurement is generally given by a X-Ray spectrum (Fig.5.1),in which peaks of a given energy and intensity can be correlated to the excited atoms of the elements present in the sample, and therefore to the elements itself (to a peak of given energy is corresponding a well known element) and the intensity is in some way correlated (but not always linearly) the the concentration of the element.

The correlation between energy of the peaks and element is always valid, because to a given element are always corresponding peaks of a given energy (see Table 2). On the other side, the correla-

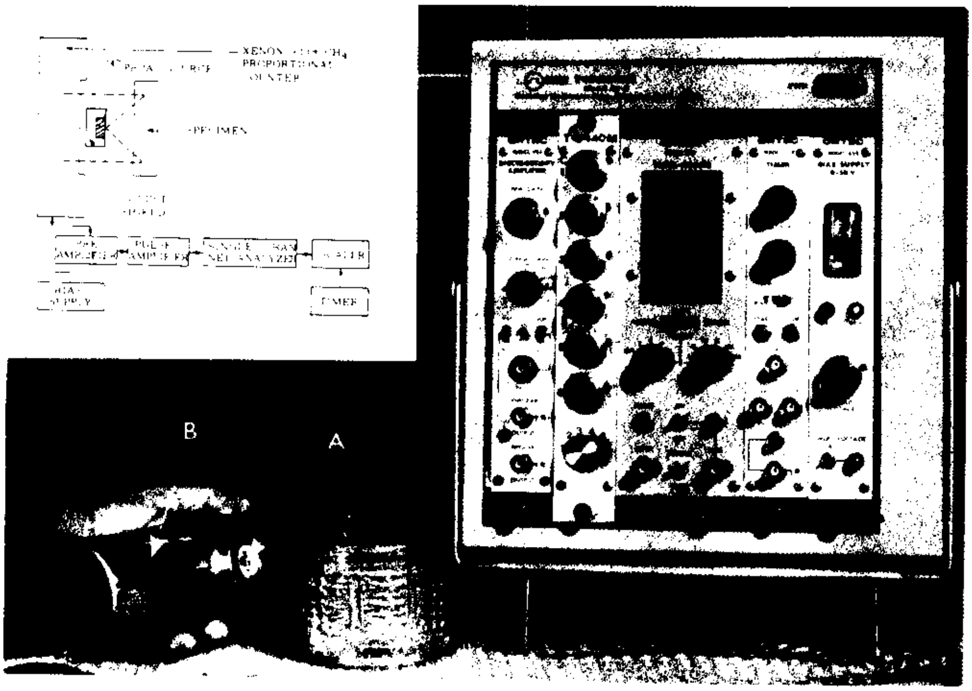


Fig. [illegible] - Portable apparatus for EDXRF-analysis of alloys (bronzes, brasses, gold alloys, silver alloys and so on).

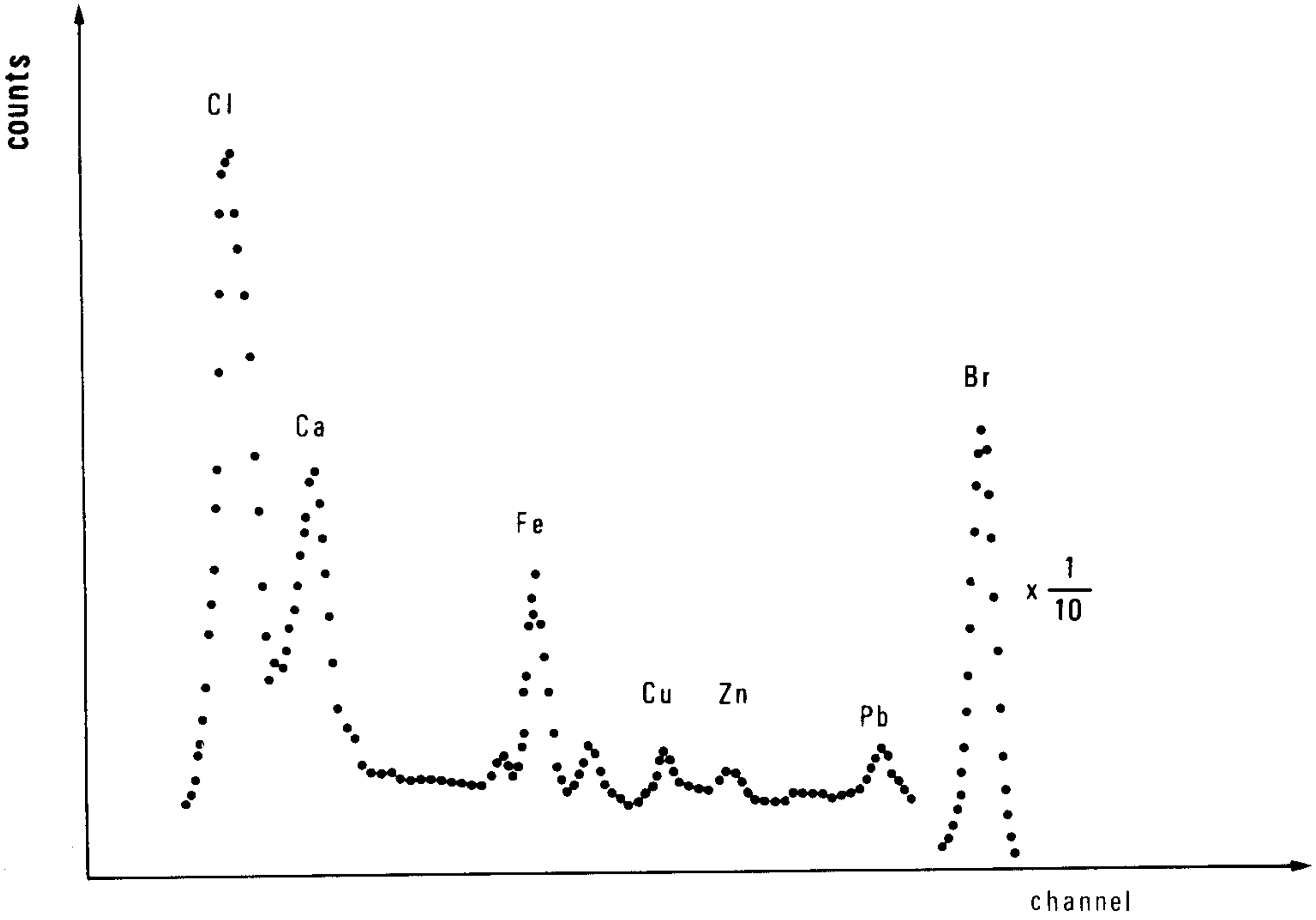


Fig. 5.1 - Typical EDXRF-spectrum.

tion between area of the peak (or number of detected photons) and concentration of the corresponding element in the sample is depending on a large number of parameters such as the energy of the incident radiation, the thickness of the sample (two types of samples can be characterized: the "infinitely thin" and the "thick" sample) and the characteristics of the detector in terms of efficiency for the analyzed X-rays). Only when the sample can be considered as infinitely thin, there is a linear correlation between the area of the peaks and the concentration of the elements and no matrix effects are present (Fig. 5.2). In all other cases, interelement effects give rise to a non-linear correlation .

In EDXRF there are, therefore, different situations: in many cases a qualitative or semiquantitative approach is sufficient. For example, when a painting is analyzed, then a qualitative evaluation of the elements in the pigments is generally sufficient for its determination.

On the contrary, in the case of alloys, an accurate determination of the major component concentration is required for its analysis and classification. In such cases, the most common procedure is to use several samples, having a known composition of the major elements.

An example of the two different situations is shown in Figure 5.3.

6. Results

6.1 Paintings

The EDXRF-analysis seems to be particularly suited for the analysis of paintings, because the penetration of radiation is of the same order of magnitude of the paint layer, the concentration of chemical elements sufficiently high and generally no surface phenomena occur, altering the pigment composition. Finally, only a semiquantitative analysis is required.

A systematic study on a large number of paintings was performed, in situ, including: Raffaello: Deposizione and La Fornarina; Michelangelo: Holy Family; Caravaggio: Boy with a basket of fruits and others; L. Lotto: Giudizio di Santa Lucia. The non-destructive analysis of chemical elements in pigments turned out to be very useful for the following reasons (3):

a) the presence of elements like chromium, titanium or zinc allows one to state that a painting has been recently made or restored. White, for example, may be produced with white lead,zinc or titanium oxides, but zinc oxide was not produced before 1832 and titanium oxide before 1912;

b) it is possible to determine the pigments that the painter used in order to obtain chromatic effects;

c) a great number of measurements carried out on many works of the same author will make it possible to determine the "Tavolozza" of the painter and the techniques which characterize the "Bottega" even in its temporal location.

A typical result of the EDXRF analysis on a particular of the Lotto's painting (mantle of the monk) during the restoration

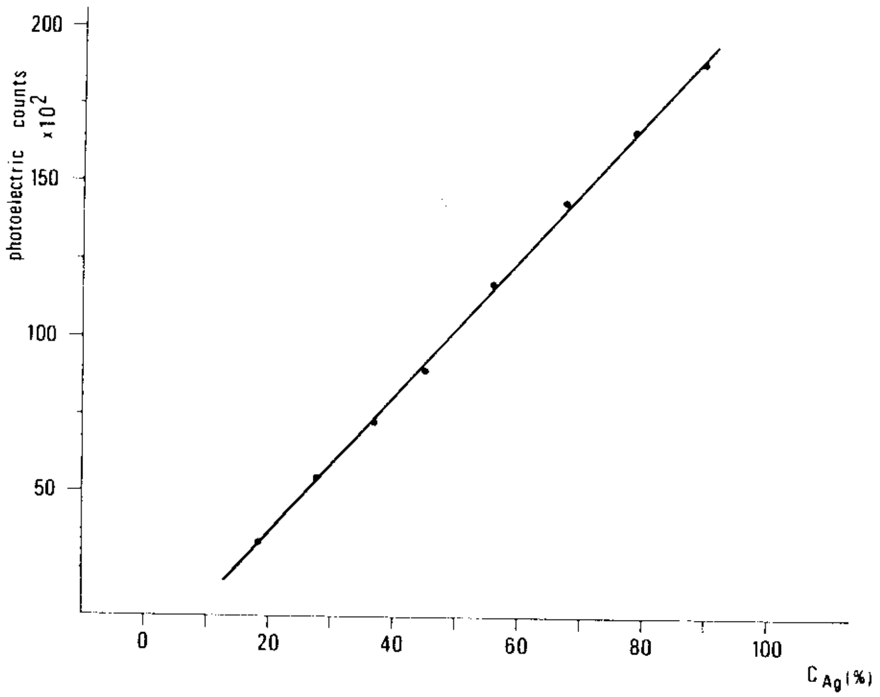


Fig. 5.2 - Linear plot of fluorescent counts versus silver content, for standard Ag-Cu samples.

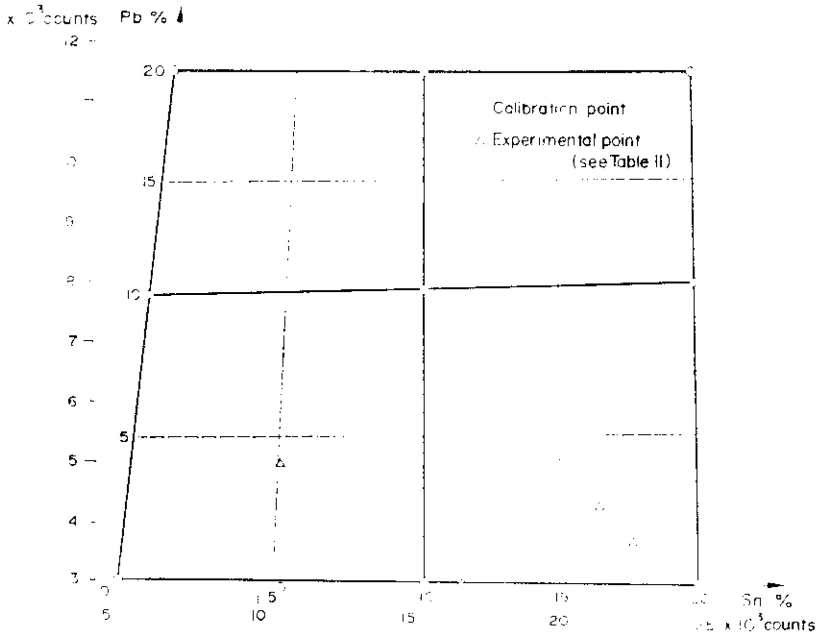


Fig. 5.3 - Use of standard samples for calibration of bronzes. Several standard bronzes having a known concentration of Cu, Sn and Pb were employed (circles) and counts versus concentration were reported in the nomograph. From this calibration nomograph, the tin and lead concentration of bronzes of unknown concentration was determined (triangles).

process is shown in Figure 6.1. The superimposition of three layers of paint from recent restorations was clearly observed (7). Another example of application of the EDXRF technique is related to the analysis of a painting supposed of the 18th century venetian school; remarkable amounts of chromium and zinc in a large number of areas suggests that the painting has been made in recent days (3).

6.2 Bronzes and brasses

In this case, the penetration of radiation is generally very small compared to the alloy thickness, and therefore the analyzed area should be completely cleaned, in order to ensure that the analysis correspond to a "volume analysis".

Further, the analysis should be quantitative, and determine with sufficient precision the major elements in the alloy.

Considering only elements present at a concentration level larger than about 1%,bronzes are generally characterized by the elements copper,lead and tin; those elements vary in concentration according to the epoch and to the geographic area.

Sometimes, in oriental bronzes, also arsenic and antimony are present.

A typical bronze spectrum is shown in Figure 6.2.

Brasses are characterized, besides copper, by lead and tin, in lower amounts that in the case of bronzes, and by zinc in considerable amounts.

Due to the reduced number of elements to be analyzed, generally four, a simpler equipment can be employed in such cases, characterized by a single-channel analyzer + timer-scaler (see Figure 5.3. Standard bronzes and brasses were employed for the calibration of the instrumentation.

A large number of bronzes have been analyzed with EDXRF: etruscan,greek,roman (8), nuragic (9), oriental and so on. Then, important Doors on bronze or brass have been analyzed (10). The analyzed area was carefully cleaned before EDXRF-analysis.

The results can be summarized in the following manner:

- no lead is generally present in etruscan bronzes and in bronzes of the same age, for example nuragic;
- no zinc is generally present in bronzes B.C.;
- bronzes can be generally grouped according to the melting epoch and the geographic location.

6.3 Gold objects

In the case of gold, the "patina" or enrichment effects at the surface of the alloy is extremely reduced; for that reason, EDXRF-analysis is again very suited for gold analysis.

Gold alloys are generally composed by gold, silver and copper. For that reason, also in the case of gold, a very simple and portable instrumentation can be employed (cfr. Fig. 5.3).

Etruscan gold alloys from the VII Century B.C. were analyzed (11), and some ancient gold samples from Mexico (12).

A typical gold spectrum is shown in Figure 6.4.

The results are summarized in Figure 6.5.

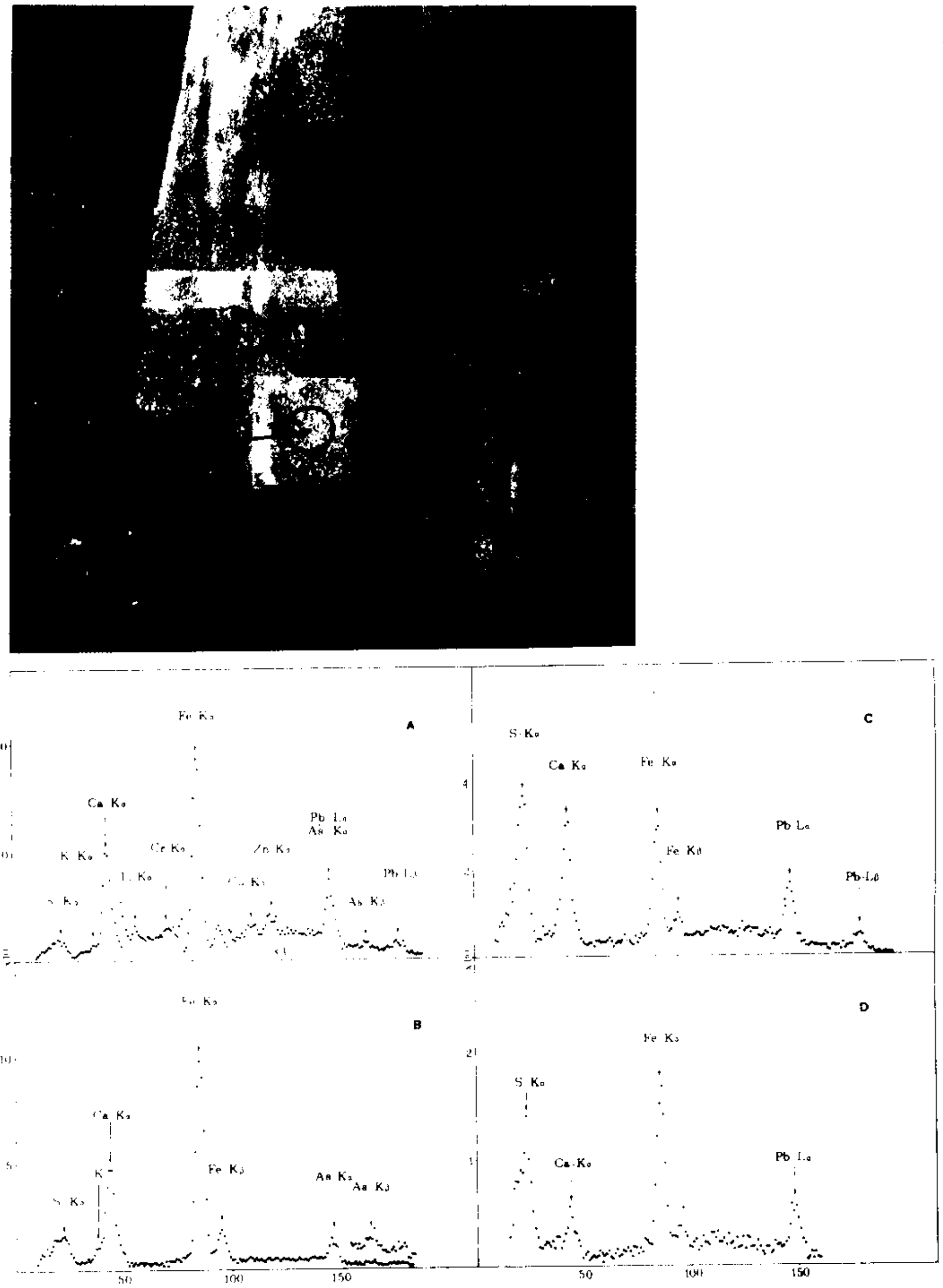


Fig. 6.1 - Giudizio di S. Lucia of L. Lotto. An area of the monk mantle was analyzed during the restauration, after removing layers due to previous restauration processes.

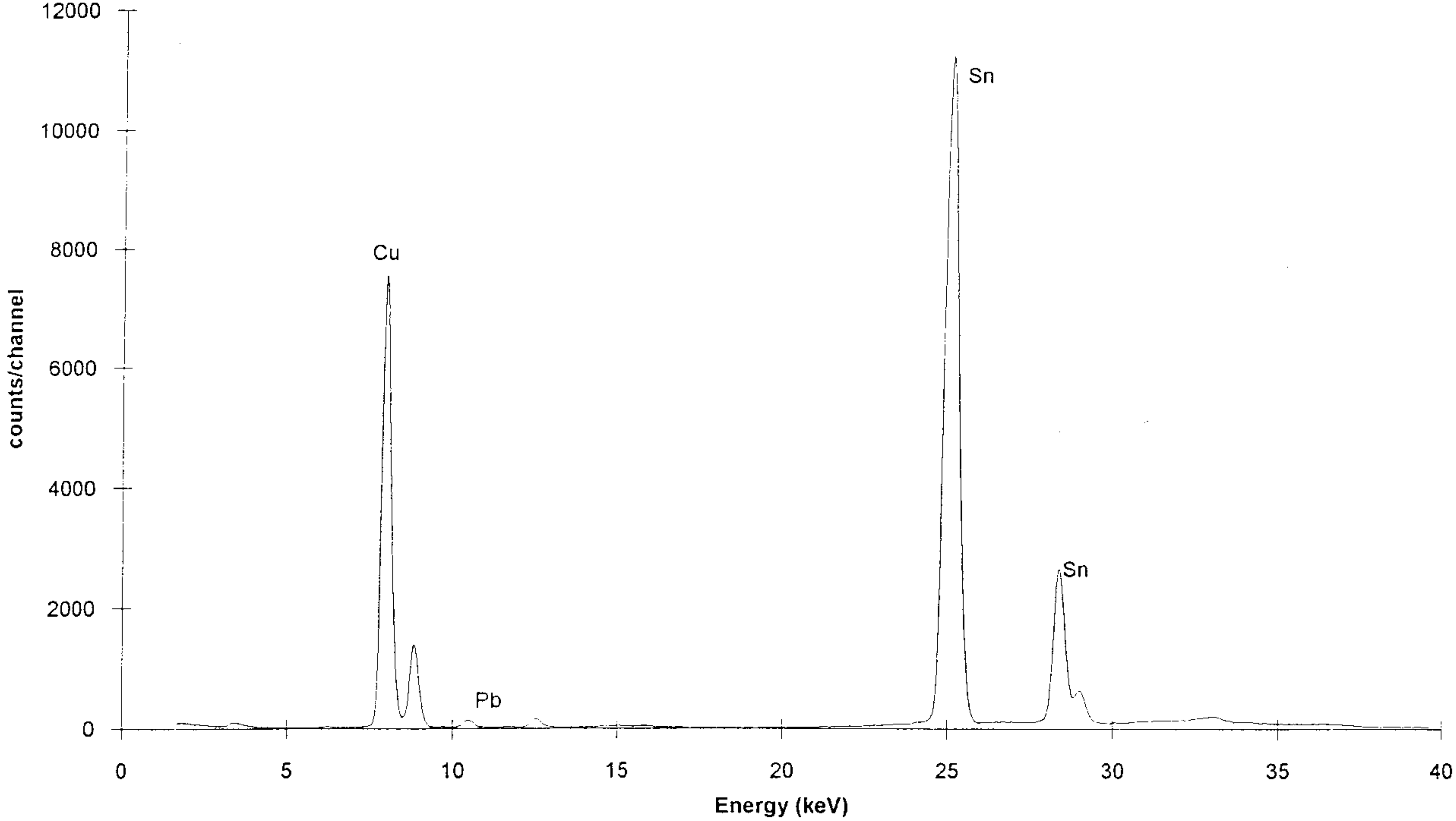


Fig. 6.2 - Typical spectrum of a nuragic bronze. The presence of lead was determined at levels lower than 1%, in accord with the general conclusions of Section 6.2.

6.4 Silver objects

Also in the case of silver alloys the "patina" and surface enrichment processes plays an important role. For this reason, silver objects should be cleaned in the analyzed area. That is generally not possible. We have therefore developed, in addition to EDXRF analysis, a method based on the transmission of monoenergetic X-and gamma rays. This method, non-destructive and representative of the whole volume, is especially suited for analysis of silver coins and of plane objects having a thickness not exceeding 2-3 mm. (13).
Typical results are summarized in Table 3.

6.5 Other objects

Also other objects of different type were analyzed, such as potteries, enamels, illuminated manuscripts, parchments and so on.

Table 1 - Half value of the layer of various materials penetrated by incident photons versus energy (in mm)

E (keV)	wood	concrete	copper	silver	gold
20	8.7	1.0	0.02	0.04	0.005
40	26	5.8	0.15	0.04	0.027
60	35	12	0.46	0.1	0.08
80	38.5	17	1	0.3	0.16
100	41	19	1.6	0.5	0.065
150	46	25	3.3	1.4	0.2
200	50	27	5	2.3	0.4

Table 2 - Energy values of K_α, K_β, L_α and L_β -lines, and energy of the photoelectric discontinuity E_{dis} of the most important elements

Element	K_α	K_β	K_{dis}	L_α	L_β
Ca	3.7	4.0	4.04		
Fe	6.4	7.0	7.1	too low energies for detection	
Cu	8.0	8.9	9.0		
Zn	8.6	9.6	9.7		
Ag	22.0	25.2	25.5	3.0	3.2
Sn	25.2	28.8	29.2	3.4	3.7
Au	67.9	79.1	80.7	9.7	11.5
Hg	69.9	81.4	83.1	10.0	11.9
Pb	73.9	86.1	88.0	10.5	12.7

Table 3 - Ag and Pb content (and Cu as difference from 100) in coins from the XVIII Century by means of attenuation measurements of X-rays.

Coin N.	thickness (cm)	transmission measurur. % Ag	% Pb	densitometry % Ag
1	0.173	31.5	0.9	33.7
2	0.175	30.0	0.8	29.8
3	0.177	29.6	1.2	32.3
4	0.170	31.0	1.1	32.6
6	0.170	30.5	1.0	35.2
7	0.158	30.2	1.0	32.9
11	0.157	13.5	0.2	14.1
17	0.174	29.7	0.8	32.5
18	0.099	30.5	0.9	31.7
19	0.099	18.5	0.5	20.5
20	0.103	26.4	2.5	29.1
21	0.104	29.0	1.0	33.2

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