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NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH
Section A

The use of a mercuric iodide detector for X-ray fluorescence analysis in archaeometry

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For about two decades, energy dispersive X-ray fluorescence (EDXRF) has been employed in Rome for the analysis of works of art. A short history of the applications of EDXRF to paintings and alloys is presented. Finally, the usefulness of mercuric iodide room-temperature semiconductor detectors in this field is shown.

1. Introduction

In the field of works of art there is a great need for nondestructive analytical techniques, and in particular for portable instruments for in situ analysis. Energy dispersive X-ray fluorescence (EDXRF) induced by photons is an ideal technique for the analysis of painting composition, because it is a surface analysis, completely nondestructive, multielemental, simple and relatively cheap. EDXRF can be also used for the analysis of alloys, when the surface is clean or where it can be cleaned at the site of analysis. In the case of paintings the analysis involves a thickness of hundreds of micrometers to millimeters, depending on the energy of the incident radiation and on the composition of the irradiated surface. Using photon sources of different energies, different colour layers can be analyzed.

Analysis of major elements in paintings can give important information like the identification of the painter through the colours he used as determined by the analyzed elements, and the identification of previous restoration areas or even of fakes; colours made up of titanium, chromium, zinc and barium can, for example, be dated.

In the field of alloys, the situation is much more complicated. In this case, the penetration of the incident and secondary radiation is of the order of micrometers to tens of micrometers. The analysis is therefore related to the surface, and all phenomena of surface enrichment or patina will completely alter the composition at the surface with respect to the mean composition of the alloy, and will therefore give wrong results. In the case of bronzes, brasses and silver, where the surface could be nonrepresentative of the whole sample, the surface should be, if possible, carefully cleaned in the analyzed area, which can be of the order of 1 mm^2. On the contrary, in the case of gold alloys, the surface is, in general, representative of the volume composition of the sample.

Analysis of alloys of all types can be very useful for studies of connections between composition and epoch of manufacturing, geographical location and, if trace elements could be detected, origin of the raw material.

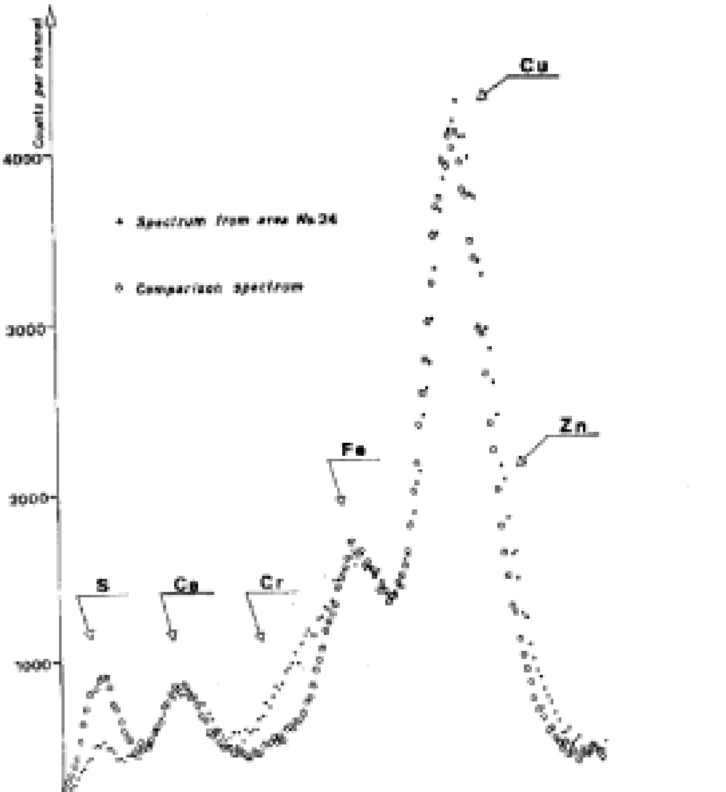
A reach program was started in 1971 as a cooperation between the Institute of Physics of the Faculty of Engineering (at present Department of Energetics) of the University of Rome "La Sapienza" and the Central Restoration Institute of Rome (ICR), in order to explore the potential of the EDXRF technique in the field of works of art. The program included analysis of paintings and alloys at the ICR, and analysis of bronzes and gold alloys in museums and bronze doors around Italy with a portable instrument.

2. Experimental setup and results

When the program "EDXRF in archaeometry" was started, in 1971, the "Laboratory" apparatus for EDXRF analysis was characterized by (fig. 1):

- radioactive sources like ^{3}H and ^{147}Pm bremsstrahlung sources, ^{238}Pu (12-18 keV), ^{241}Am (59.6 keV) X- and gamma ray sources;
- a ($Xe + 5\%\ CH_4$) gas proportional counter, with about 18% energy resolution at 6 keV;
- a 400 channels pulse-height analyzer.

In the portable version, the multichannel analyzer was substituted with a modified single channel analyzer, with four prefixed and precalibrated windows,


Counts per channel
4000
3000
2000
1000
+ Spectrum from area No.34
○ Comparison spectrum
Cu
Zn
Fe
S
Ca
Cr
50
100
150
200
Channel number

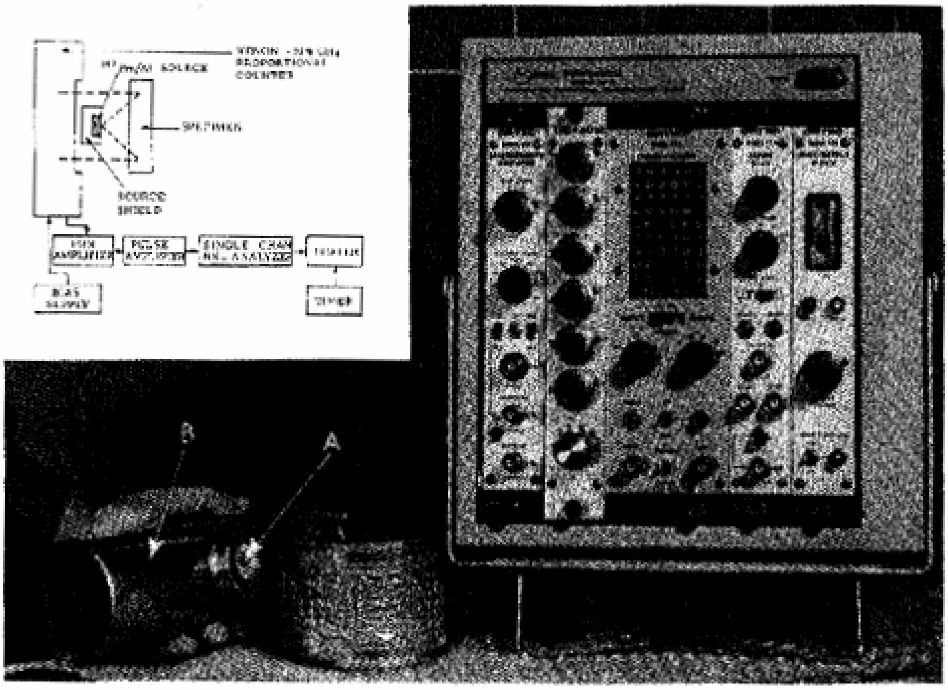


Fig. 2. Portable EDXRF unit using radionuclides as excitation sources. (A) ^{147}Pm source; (B) Xe gas proportional counter. Top left: block diagram of the unit (after ref. [4]).

corresponding, in the analysis of bronzes, to Cu, Zn, Pb and Sn, in the analysis of gold samples, to Cu, Au and Ag (fig. 2).

It is important to note, however, that for the gas proportional X-ray detectors, the energy resolution is not adequate, and in many cases a large overlap occurs between X-ray peaks (fig. 1 bottom).

Several works of art were analyzed, at the ICR, like:

- Raffaello Sanzio: Deposizione, Galleria Borghese, Rome (1507) [1] and Etruscan, Greek and Roman bronzes [2].
- Ghiberti: door of the Battistero called "del Paradiso", Florence 1425–1452.

Results concerning bronzes could be summarized in the following manner:

- Etruscan bronzes are typically two components alloys, characterized by about 85–90% Cu and 10–15% Sn; only traces of Pb are present.
- Greek and old Roman bronzes (approximately BC) are typically three components alloys, containing also between 2% and 10% Pb;
- Oriental bronzes contain also percent concentration of As and Sb.

In the same period, in cooperation with the German archaeological Institute of Rome, a large number of Etruscan gold alloys of the 7th century BC were analyzed [4], with the portable instrument described above, at the Vatican and at the Villa Giulia Museum in Rome, and at the National Museum of Tarquinia.

Etruscan gold alloys are characterized, besides Au, by (fig. 3):

- 20–35% Ag;
- 2–4% Cu.

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

Fig. 1. Top: Experimental setup for the analysis of paintings by means of EDXRF-analysis in 1972. (1) Measuring head (Xe-gas proportional counter); (2) preamplifier; (3) second measuring head for excitation of heavy elements, using NaI(Tl) detector; (4) amplifier; (5) multichannel analyzer (after ref. [1]). Bottom: Typical EDXRF spectrum of an area of the painting "Deposizione" by Raffaello, collected with the gas proportional counter, showing the partial overlap between the peaks (after ref. [1]).

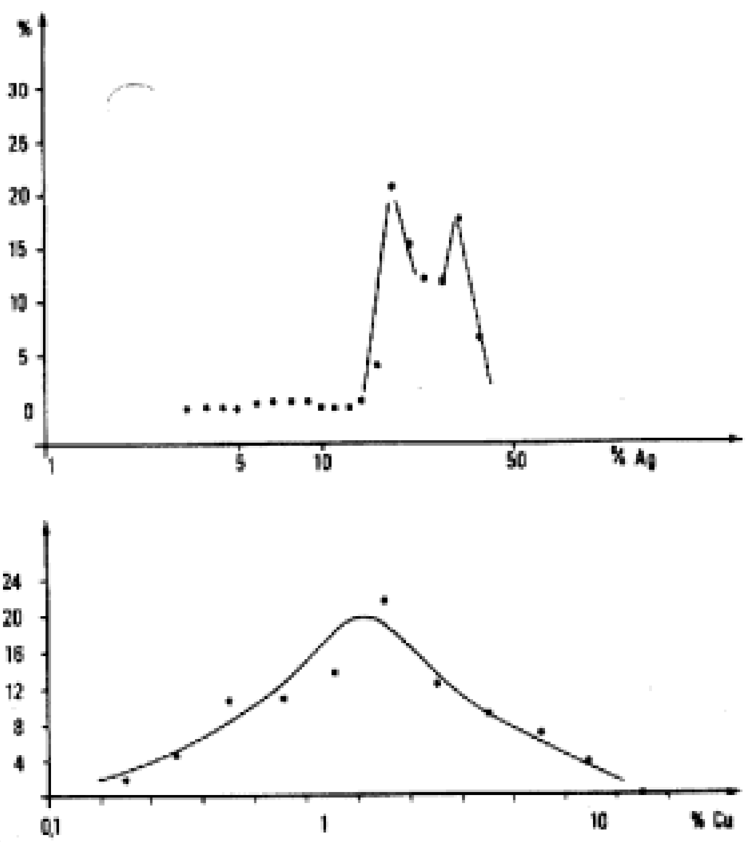


Fig. 3. Distribution of 7th century BC Etruscan gold objects versus Ag and Cu concentration.

detectors. By using a Si(Li)-detector, during 1972 were analyzed:

- Lorenzo Lotto: Giudizio di S. Lucia, Museo Civico di Jesi, 1523–1532 [5];
- A fragment of an Etruscan "pettorale" from the Walters Art Gallery of Baltimore.

A typical result of the EDXRF analysis on a particular of the Lotto's painting during the restoration process is shown in fig. 4.

At the beginning of the 1980s, 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 [6,7]. Concerning the last point, it should be observed that the use of the X-ray tube, with or without absorbers or secondary targets, allows the irradiation of very small areas (typically 0.1 × 0.1 mm).

A multidisciplinary group was constituted at that time, composed by physicists, chemists and art historians for performing a systematic research work on ancient paintings, in particular of Caravaggio and his school, devoted to the interconnections between elemental analysis of pigments and sematometric evaluations of optical parameters [8].

A systematic study on 18 paintings was performed, in situ, including:

- Michelangelo: Holy Family, Galleria degli Uffizi, Firenze, 1504;
- Raffaello: La Fornarina, Galleria dell'Accademia, Venezia, 1520;
- Caravaggio: Boy with a basket of fruits, Galleria Borghese, Rome, 1953.

The equipment which was employed is shown in fig. 5.

A successive important technological improvement was given by the introduction of the room-temperature HgI_2 semiconductor detectors having an energy resolution comparable to that of the cooled Si or Ge detectors [9–13]. The small dimensions of the measuring head (fig. 6) makes this detector ideal for in situ analysis, either combined with a very small radioactive source, or with small portable X-ray tubes. In fact, recently, very small and battery equipped X-ray tubes (20–50 kV, 0.1 mA) have become available, which can be used directly, employing the bremsstrahlung radiation, or filtered, selecting a small gap of energies, or with external, secondary targets, monochromatizing the beam.

Such equipment can be used everywhere, also in places in which no liquid nitrogen is available like excavation areas.

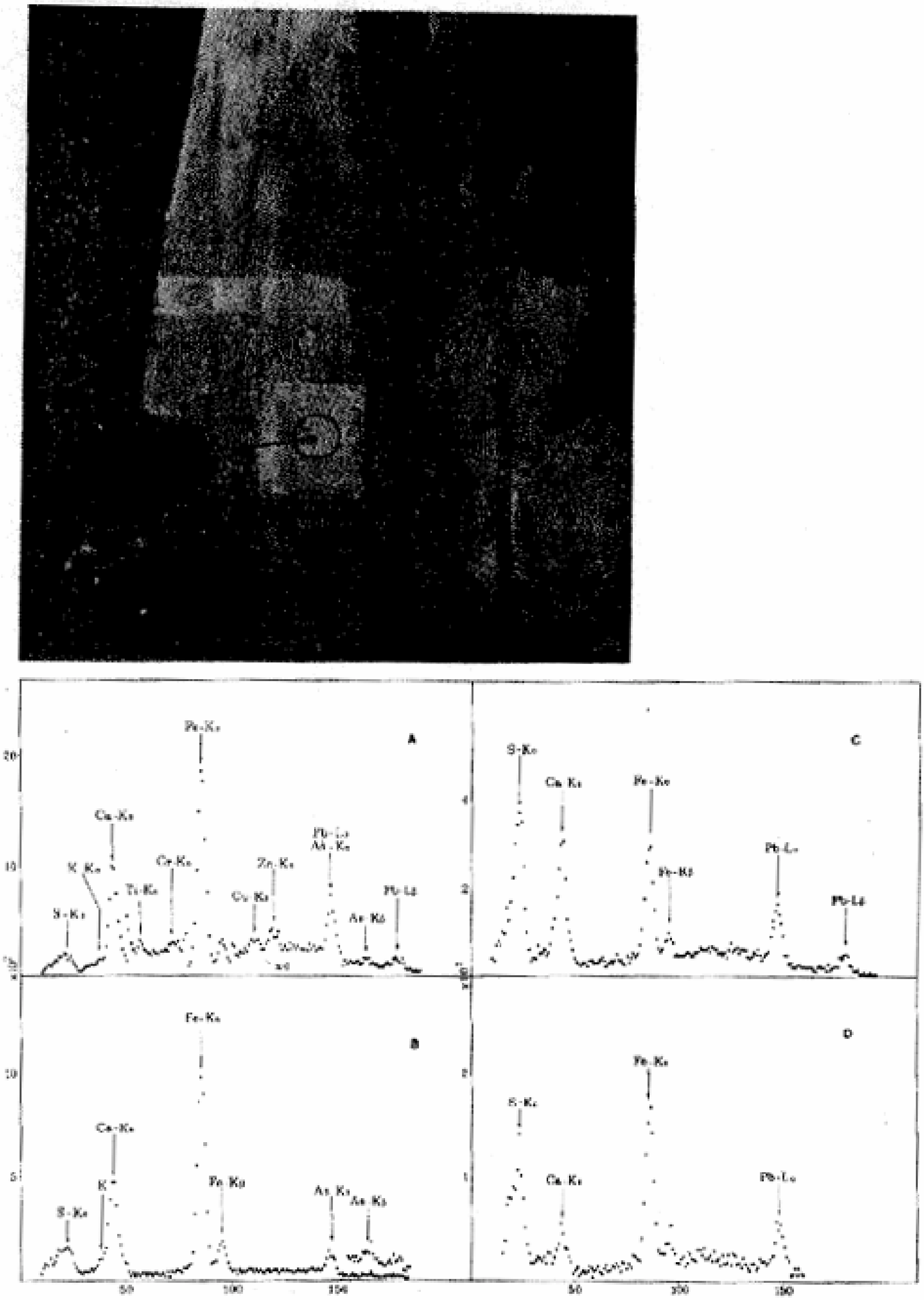


Fig. 4. Lorenzo Lotto's "Giudizio di S. Lucia"; detail of the mantle of the monk, in which the superimposition of three layers of paint was observed by EDXRF-analysis and relative X-ray spectra. The analyzed area is indicated by an arrow (after ref. [5]). (A) EDXRF analysis before any cleaning process; the presence of "modern" elements like Ti and Zn is evident; (B), (C) and (D) after successive cleanings; the spectrum (D) was supposed to be corresponding to the original paint of L. Lotto.

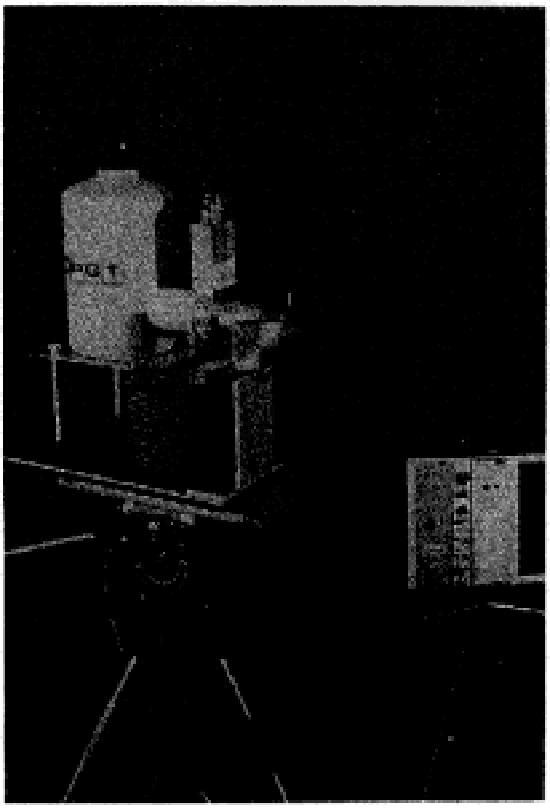


Fig. 5. Experimental setup for the analysis of paintings by EDXRF during the 1980s. The setup is characterized by a portable X-ray tube, by a Ge semiconductor detector with corresponding electronics, and a multichannel card (after ref. [7]).

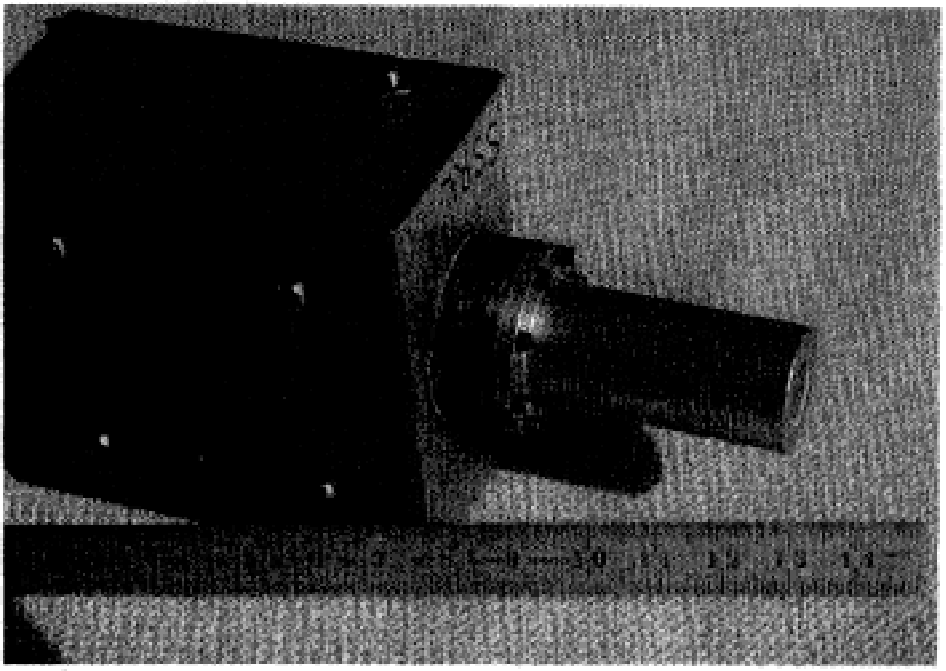
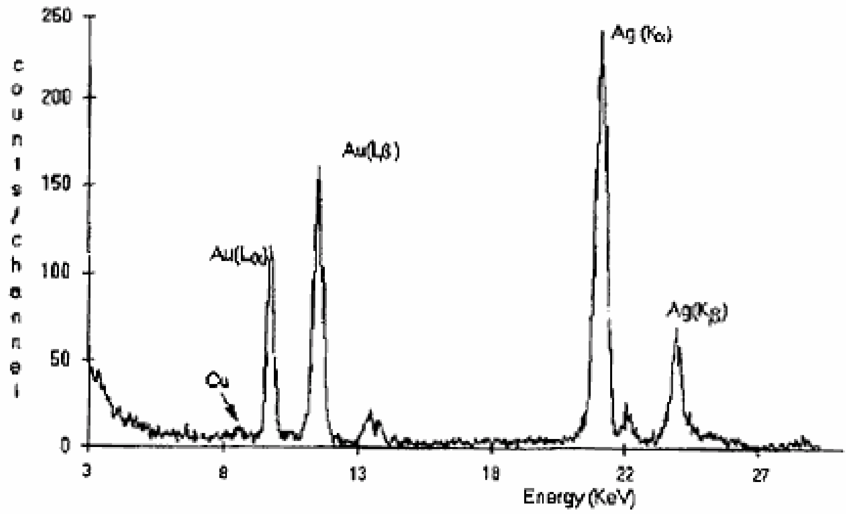


Fig. 6. Room-temperature HgI_2 semiconductor detector. The detector can be partially cooled by the Peltier effect. In this case, a second box of the same dimensions of the detector is needed.



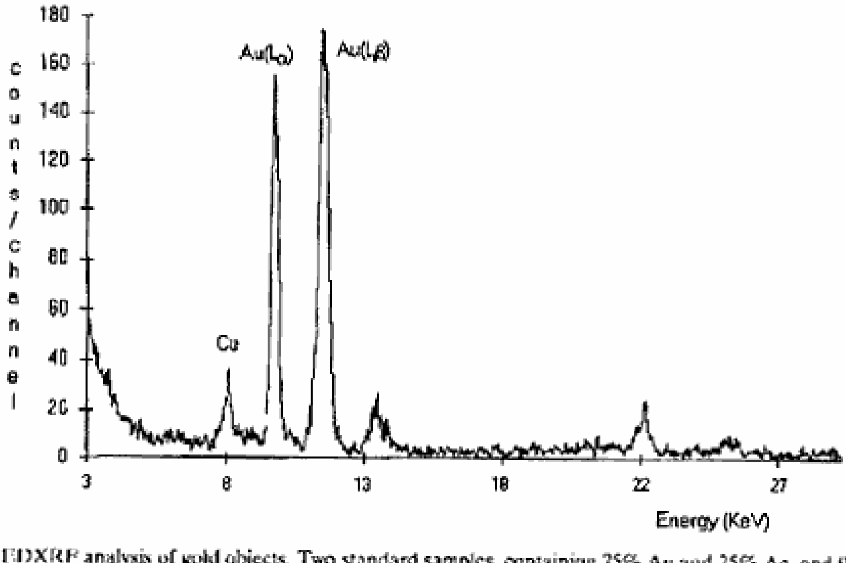


Fig. 7. Example of EDXRF analysis of gold objects. Two standard samples, containing 75% Au and 25% Ag, and 90% Au and 10% Cu respectively have been analyzed with a partially cooled HgI_2 semiconductor detector. A resolution of about 250 eV at 6.4 keV has been measured.

We plan to use the HgI_2-detector associated with sealed-off radioisotopic sources, for systematic analysis of ancient gold objects from Mexico and Latin America, in order to compare the gold composition of these golds with the Etruscan ones [4]. X-ray spectra of a standard gold objects, analyzed with a HgI_2 detector and with a Si(Li) detector are shown in fig. 7.

Acknowledgement

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