NUCLEAR ANALYSES OF SOME ENEOLITHIC GOLD ARTIFACTS DISCOVERED IN THE CĂLĂRAȘI DISTRICT, ROMANIA

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INTRODUCTION

In the rich collections from the Aeneolithic belonging to the Museum of Archaeology, Olteniţa (M.A.O.), Călăraşi district there are some gold artifacts, some of them already known in the literature, others waiting to be published. These objects have not been so far analyzed in order to put in evidence the elements associated with gold and to establish, on this ground, the provenance of the gold used by prehistoric people of the Gumelniţa culture, in its different phases of evolution. The objects that were analyzed are:

1. Stylized gold anthropomorphous figurine of a round form and a central hole, with a trapezoid prolongation. The figurine was discovered in 1960 by Vladimir Dumitrescu on the Gumelniţa Tell in Olteniţa, in the layer of culture belonging to the Gumelniţa culture phase A 2, early stage[1] (1.5 cm long, 1.2 cm diameter, 1 g weight; inventory No. M.A.O.1166, fig. 1a).

2. Aeneolithic treasure from Sultana, Mânăstirea commune, Călăraşi district, made of 11 pieces, discovered by C. Hălcescu, in the known location from the "Malu Roşu" point[2]. The treasure discovered in a sanctuary, near to a sacred hearth, was put away as an offering to divinity into a miniature of the sanctuary.[3] The composition of the treasure is:

a. Gold stylized idol with a discoid concave-convex shape, with a central orifice and a trapezoidal lateral prolongation equipped with two orifices (4.5 cm in diameter, 9.43 g weight, inventory No. M.A.O. 8651, fig. 1d).

b. Stylized idol (anthropomorphic figurine), identical with 2a (4.0 cm in diameter, 10.25 g weight; inventory No. M.A.O. 8652, fig.1e).

c. Idem, but the lateral prolongation was torn in ancient times on the line of the orifices (2.2-3.1 cm in diameter, 2.6 g weight; inventory No. M.A.O. 8653, fig.1c).

d. Discoid gold idol, concave-convex, with two lateral orifices, without central orifice and trapezoidal prolongation. This idol of small dimensions differs typologically from the above-mentioned idols (1.4 cm in diameter, 0.44 g weight; inventory No. M.A.O. 8654, fig. 1b).

e. Discoid idol, broken at harvest into 36 small pieces (0.49 g weight; inventory No. M.A.O. 8658).

f. Four fragments of *saltaleone* manufactured of gold flat band twisted spiral (14.10 cm total length, 3-4.5 cm in diameter, 7.35 g weight; inventory No. M.A.O. 8656, fig. 1f).

g. Chain of seven gold wire links (7 cm length, 5.32 g weight; inventory No. M.A.O. 8655, fig. 1g).

h. Gold link of small size, made of flat band (7 mm in diameter, 2 mm width, 0.4 mm thickness, 0.23 g weight; inventory No. M.A.O. 8657, fig. 1h).

3. Gold bracelet[4], manufactured from flat band by hammering. It has a convex-concave cross section, is polished outside and mat inside. The artifact was discovered in the Neolithic tell from Vlădiceasca, Valea Argovei commune, Călăraşi district, in the dwelling No. 12 belonging to the Gumelniţa culture, phase A 2, early stage (outside maximum diameter 8.5-8.8 cm, inside minimum diameter 7.1-7.5 cm, 2.2 cm width, 1 mm thickness, 79.200 g weight; inventory No. M.A.O. 7654, fig. 2g). The bracelet finds itself analogies in the Aeneolithic necropolis from Varna, Bulgaria researched by Ivan Ivanov[5].

4. Five small tubular beads, made by gold leaf, discovered in 1988 in two graves belonging to the Gumelniţa culture, phase A 2, in the Aeneolithic necropolis investigated at Chirnogi, Călăraşi district, in the point named "Şuviţa Iorgulescu"[6]. The five beads

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have a length between 1.4 and 2.3 mm, the diameter between 2.3 and 2.8 mm and the weight between 62 and 103 mg (fig. 2a - 2e).

5. Gold tubular bead that was a piece of a string consisted of limestone, talc, clay and quartz beads (2.3 mm length, 3.2 mm in diameter, 143 mg weight: inventory No. M.A.O. 4811, fig. 2f). The bead was discovered in a grave of a child, on the high terrace of Danube, between the Chirnogi and Căscioarele communes, Călăraşi district, in the point named by natives "Şuviţa lui Ghiţan"[7]. Beads made by gold leaf have analogies in the Aeneolithic necropolis of Varna, Bulgaria[8].

All the presented gold artifacts belong to the Gumelniţa culture, phase A 2, some of them from the early stage, the other from later stage, and chronologically can be framed in the second half of the 5th millenium Cal. B. C.[9], to the end of it. Drawings of the studied artifacts are given in figs. 1 and 2.

EXPERIMENTAL TECHNIQUES

The analytical method used for all the artifacts was energy-disperse Xray fluorescence (EDXRF). Two radioactive sources: ^{238}Pu (30 mCi, with beryllium window) and ^{241}Am (10 mCi, with nickel window for absorption of soft Xrays) were used for excitation. The plutonium source is convenient for Fe, Cu, Au and Pb detection, and americium source is proper for detection of Ag, Sn and possible other elements with atomic number Z around 50. A Ge(HP) detector was used for the detection of Xrays emitted by the investigated object. The resolution of the spectrometer was 160 eV for the 8.047 keV (Cu-K_α) Xray but it depends of the counting rate.

In order to determine the concentration of elements a computational program[10] that takes into account the Xray cross sections, absorption coefficients and secondary fluorescence was used. The program was strictly tested by means of some standard alloys with gold concentration between 58.30 % and 99.99 %. For instance, by this method, a composition Au/Ag/Cu = 58.6(4)/7.6(1)/33.8(2) % was obtained for an item with certified values Au/Ag/Cu = 58.3/7.7/34 %. The statistical errors are given in brackets.

An artifact was also analyzed by proton activation (PAA) in order to put in evidence trace elements that could define, in principle, the gold provenance. It was bombarded 2.5 h with a proton beam of 15 nA intensity and 11 MeV energy, provided by NIPNE - Bucharest Tandem accelerator. After a cooling time between half an hour and 17 days the piece was counted five times in order to find the energy and the half-life of gamma rays emitted by the activated elements. The detection was made by a spectrometric system with Ge(Li) detector and a pulse high analyzer with 4000 channels. The system resolution was 2.1 keV for the 1332 keV (^{60}Co) gamma ray.

RESULTS AND DISCUSSION

A partial Xray spectrum is shown in fig. 3 in which the processing method is seen: the spectrum from which the background was subtracted is used to calculate the surface of the interested peaks, either by integration or by means of the program *Origin* considering that peaks are Gaussian. The results of EDXRF analysis are listed in table 1. Since the result for iron concentration strongly depends on the cleanliness of the object surface (no cleansing has been done by us), it is preferable to omit the Fe concentration value when it is less than 0.2 %. Even when Fe is reported, it must be treated with some caution.

Firstly pointed out must the unusual high lead concentration of some pieces (Nos. 2e, 2g, 2d, 2a, 1). In the Tylecote's tables[11] on the native gold composition, lead is an element found less than 200 mg/kg (ppm) and, exceptionally 0.8 % (Britain). Since the artifacts analyzed here are from the Aeneolithic, therefore made without doubt from native gold, it must be supposed that there was a source of native gold (at the South of Danube) with such a high Pb concentration. It is also to notice the relatively high concentration of copper and small concentration of silver, at least in comparison with Romanian gold (for which the averaged concentrations are: Ag - 16.8 ± 7.3 %, Cu - 185 ppm, Pb - 153 ppm, Sn - not detected)[12, 13].

The Bulgarian researcher[13] found for similar objects the concentrations 92.3% for gold and 7.50 % for silver. The average values found in this work, without the artifact No. 4, are practically identical: (91.2 ± 2.6) % Au and (7.58 ± 2.35) % Ag. The five beads (the object No. 4) have been omitted since them, and only them, are similar with Romanian native gold (high Ag and low Cu concentrations).

The bracelet from Vlădiceasca could be manufactured of gold flat band with the soldered ends. According to the literature, the ancient solders could be achieved by means of an alloy of gold and copper with a lower melting point. In order to put in evidence such a possibility the Cu/Au concentrations ratio was measured along of the bracelet circle, but, in the limit of the statistical error limits, no variation was detected. This suggests that the artifact has been manufactured of a molten tore, which, by hammering has been widen to the wanted dimension, afterwards its edges have been cut and the piece has been brought at the convex form.

In connection with this bracelet one can notice that its composition, as far as it was here determined, resembles very well with the composition of the alloy from which the Geto-Dacian king Cotiso/Coson struck the coins of Koson type with complex monogram[14]. One can ask himself if these famous and strange coins have not somehow been made of native gold from the same source with gold used for the Vlădiceasca bracelet.

The gold little bead (artifact No. 5) has been analyzed both on the internal face and on the outside one (see table 1). The depletion of the less noble components of the outside face, where the attack of the acids and the wear were probably important, is obvious, even if the title of gold is high (about 88 %).

Finally, it is worth to notice that some analyzed pieces are friable. But it is more interesting that the friable degree seems to be correlated with the led concentration. The most friable piece is 2b, which could not be whole taken out from the earth. It has also the highest lead concentration (4.4 %). The pieces which have around 1 % lead and have a well defined shape, are also affected, although, less by the phenomenon. Thus the piece 2d has a ground edge, and the piece 2a is broken. About the piece 2g (chain of seven links) is difficult to say something, but it was probably originally longer.

Proton activation analysis revealed, besides the minor elements - Cu and Ag - few trace elements: Fe - 57(6) ppm, Pd - 20(6) ppm, Pb - 330(65) ppm, Sn $\leq$ 70 ppm. But a lot of trace elements seen usually by PAA in native Romanian gold [15] (As, Hg, Pt, Sb, Te, Ti, Zr) have not been detected in this artifact. The reason does not consist only in the low sensitivity - due to the low integrated proton current - but also to a special kind of native gold poorer in trace elements.

In order to define the exact provenance of the metal the proton activation analysis for all the artifacts studied in this work should be accomplished, but a data bank with the composition of native gold from this part of Europe would also be necessary.

NOTES

1. Vl. Dumitrescu, *Gumelniţa. Sondajul stratigrafic din 1960*, SCIV, 17, 1966, 1, p. 63, fig. 9; H. Dumitrescu, *Connections between the Cucuteni -Tripolie Cultural Complex and the Neighbouring Aeneolithic Cultures in the Light of the Utilization of Golden Pendants*, Dacia, N. S., V, 1961, p. 79, fig. 7, p. 80 - 81.
2. C. Hălcescu, *Tezaurul de la Sultana*, CCDJ, XIII - XIV, 1995, p. 11-18.
3. D. Şerbănescu, *Modele de locuinţe şi sanctuare eneolitice*, CCDJ, XV, 1997, p. 234-235.
4. Discovered in 1980 by D. Şerbănescu.
5. I. S. Ivanov, *Săkrovištata na Varnenskija halkoliten nekropol*, Sofia, 1978.
6. Discovered by D. Şerbănescu.
7. S. Morintz, B. Ionescu, *Cercetări arheologice în împrejurimile oraşului Olteniţa*, SCIV, 19, 1968, 1, p. 103 - 105.
8. See ref. 5.
9. C. Lichter, *Untersuchungen zu den Bestattungssitten des südosteuropäischen Neolithikums und Chalkolithikums*, Verlag Phillipp von Zabern, Mainz am Rhein, 2001, S. 30, Abb. 2.
10. V. Cojocaru, N. Mărgineanu, C. Rusu, *The relief effect consideration in coin XRF analyses*, 3rd General Conference of the Balkan Physycal Union, 2-5 Sept. 1997, Cluj-Napoca, Abstracts, p. 450; *Inhomogeneous sample analysis using XRF and -ray transmition*, Proceeding Supplement of Balkan Physics Letters, 5, 1997, p. 2171.
11. R. F. Tylecote, *The early history of metallurgy in Europe*, Longman, London, 1987.
12. V. Cojocaru, T. Bădică, I. Popescu, *Romanian Natural Gold Analysis for Provenance Studies*, Proceeding Supplement of Balkan Physics Letters, 5, 1997, p. 2171-2174.
13. Idem, *Natural gold composition studied by proton activation analysis*, (to be published in Journal of Radioanalytical and Nuclear Chemistry).
14. V. Cojocaru, B. Constantinescu, I. Ştefănescu, C. M. Petolescu, *DXRF and PPA analyses of Dacian gold coins of Coson type*, Journal of Radioanalytical and Nuclear Chemistry, 246, 2000, p. 185-190.
15. See ref. 13.

Tabel 1. Composition of the gold Aeneolithic artifacts (Gumelniţa A2) belonging to the Museum of Archaeology, Olteniţa.

Number of object	Inventory	Cu (%)	Ag (%)	Au (%)	Pb (%)	Other elements
1	1166	0.55(2)	8.50(3)	90.3(3)	0.63(18)	
2a	8651	0.19(2)	8.20(1)	90.9(1)	0.74(11)	Sn ≤ 58 ppm
2b	8652	0.63(2)	5.33(2)	93.8(2)	0.11(6)	Sn: 75(25) ppm
2c	8653	0.23(1)	6.12(1)	93.6(3)	n.d.	Sn: 48(22)ppm
2d	8654	0.67(5)	5.45(2)	92.8(2)	1.03(14)	Fe ≅ 0.7 %
2e	8658	0.39(2)	8.16(4)	87.0(5)	4.4(2)	
2f	8656	0.15(3)	12.19(5)	87.2(1)	0.41(8)	
2g	8655	1.21(1)	5.23(2)	92.5(5)	1.05(12)	Sn: 200(80) ppm
2h	8657	0.6(3)	7.40(1)	93.0(5)	n.m.	
3	7654	0.19(1)	5.30(3)	94.5(3)	n.d.	
4	-	0.09(5)	22.03(6)	77.9(5)	n.d.	
5(exterior)	4811	0.19(6)	11.3(1)	88.5(3)	0.05(2)	
5(interior)	4811	0.34(7)	11.5(1)	88.0(4)	0.25(6)	

n. m. = not measured

n. d. = not detecte

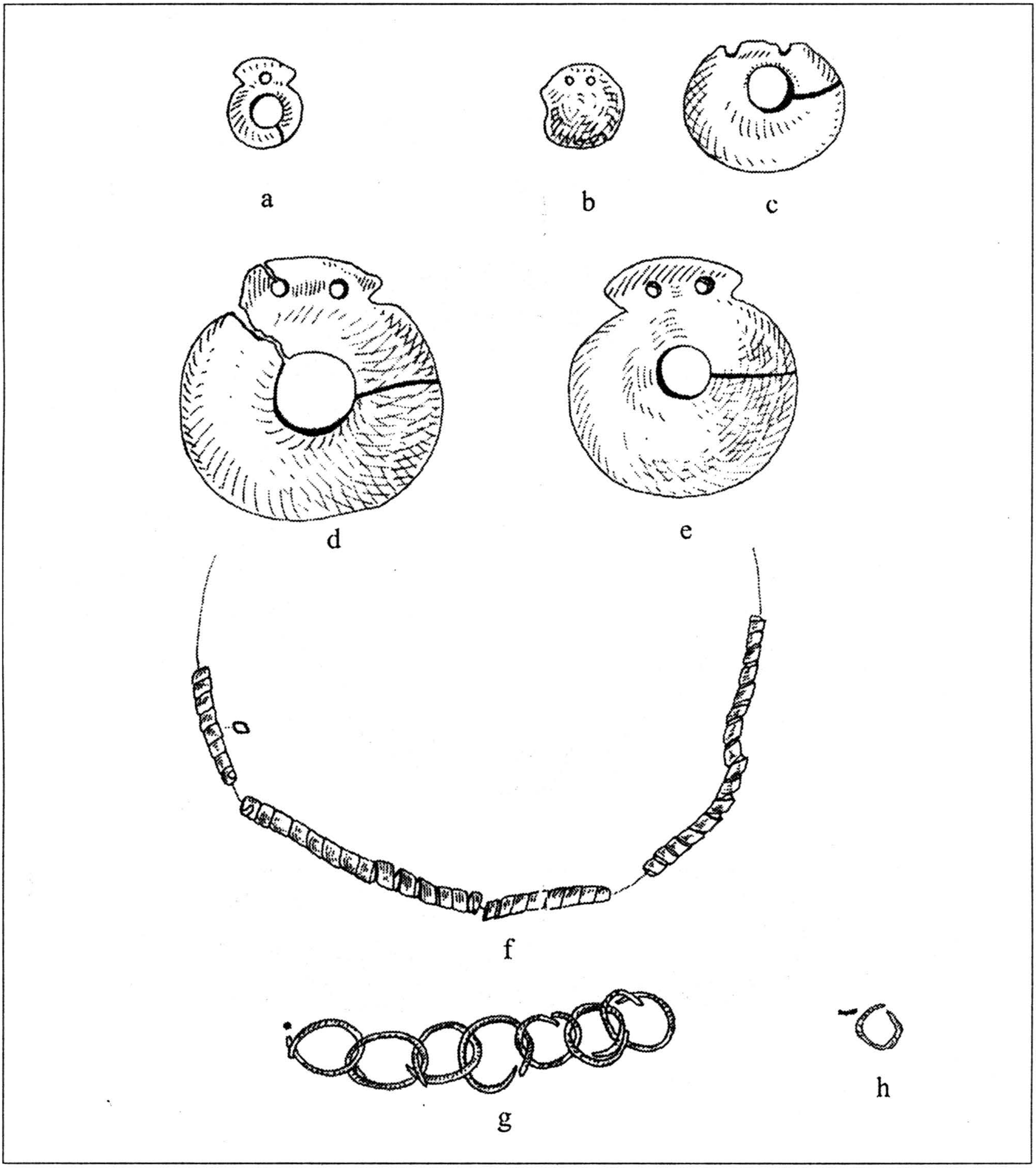

Fig. 1. a. Gold idol from Gumelnița; b-h. gold Neolithic hoard from Sultana
(b-e: gold idols, f - *saltaleone;* g - gold chain, h - gold link).

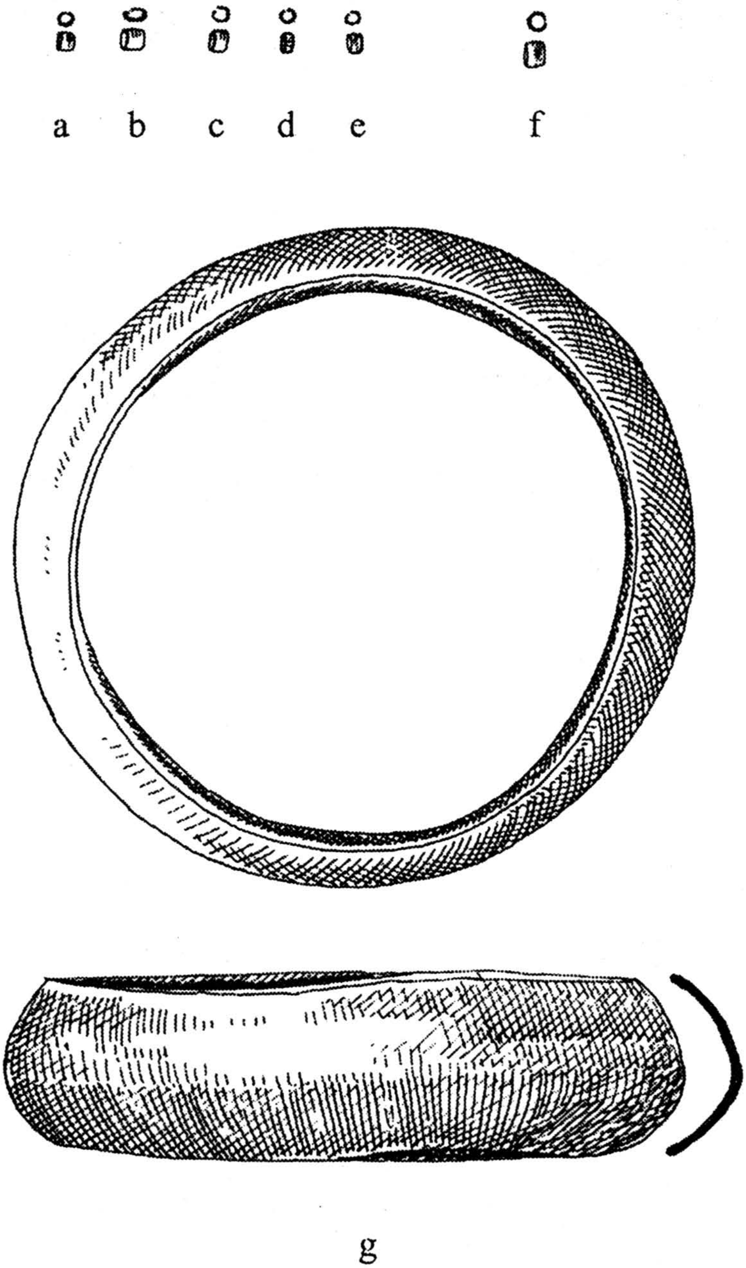

Fig. 2. a-f. Gold beads discovered in the Neolithic burial graves at Chirnogi; g) gold bracelet from Vlădiceasca.

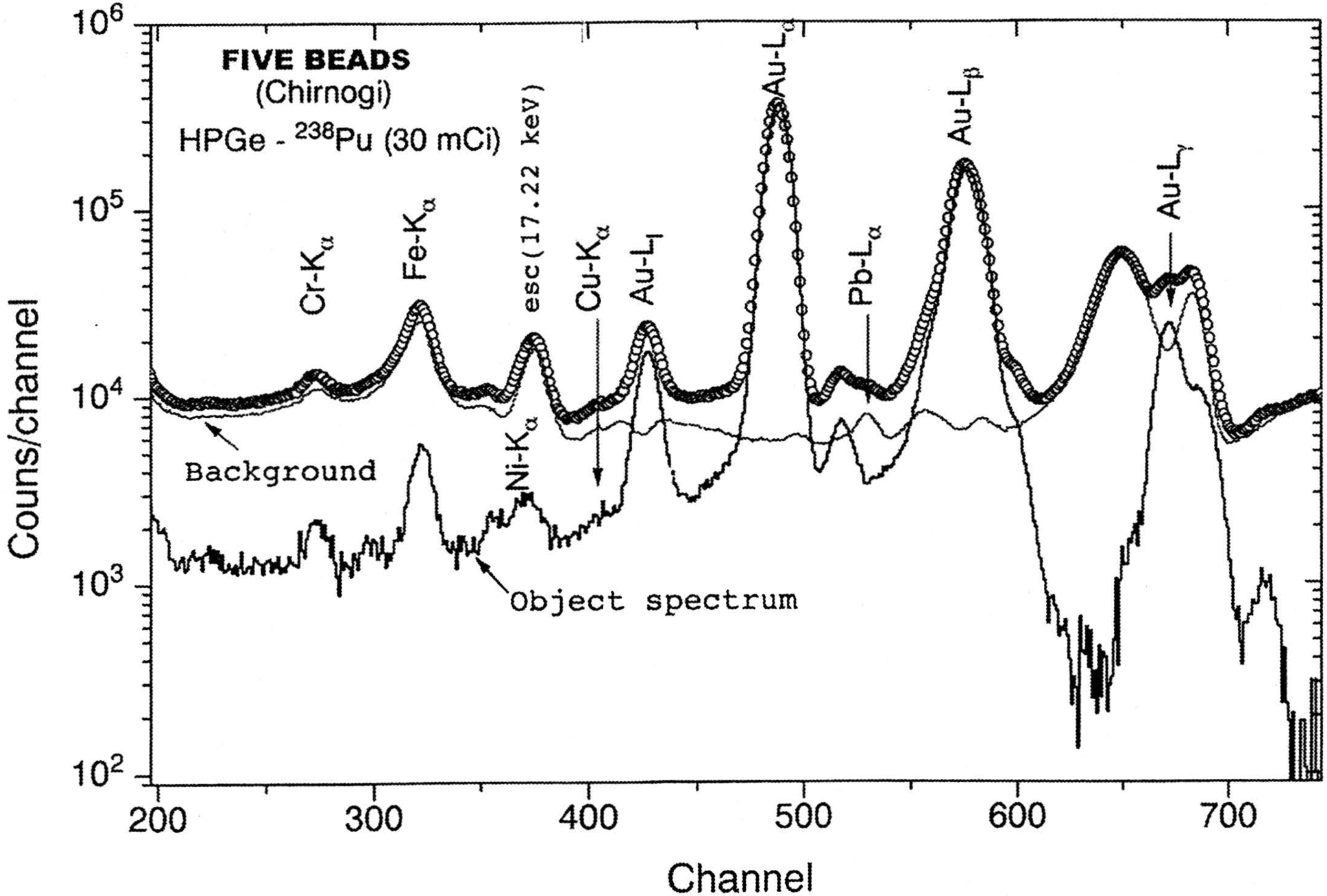

Fig. 3. A partial Xray spectrum of the five gold beads got by the EDXRF method.