

Auger and pike microanalysis of intrauterine devices (IUDs)

A. FOTI (*) - A. M. FOTI (**) - L. TORRISI (**)

Summary: Auger Emission Spectroscopy (AES) and Particle Induced X-ray Emission (PIXE) analysis were employed in a study on the calcification and oxidation processes of the copper wires used in Intra-Uterine Device (IUDs) contraceptives.

A strong copper release ($\sim 50 \mu\text{g/day}$) has been observed in the first year of IUDs application, during the high device antifertility effect. The copper release is reduced with the IUD-use time, because of the calcification process on the surface by organic liquids. This effect produces a drastic reduction in the contraceptive efficiency, and a new IUDs replacement is needed after about 2 years of use.

Auger, X-ray spectrometry and scanning electron microscopy (SEM) have been used to investigate the lifetime and efficiency of IUDs in order to understand the surface modification of copper wire during its permanence in the intrauterine environment.

INTRODUCTION

It has been demonstrated by Zipper *et al.* (1) that copper ion release in the uterine environment produces an antifertility effect. The copper release from intrauterine devices has been studied by Tatum (2) and the rate of pregnancy has been valued during its contraceptive use. Gynaecological research has demonstrated that using the copper IUDs the pregnancy rate, very low in the first year, became higher after 2-3 years use (Hagenfeldt (3)) testifying the poor antifertility efficiency over long periods. The data in literature on the percentage of pregnancy yield versus copper-IUDs use-time indicates a pregnancy yield of the order of 5% at 3 years (1, 4, 5).

The suggestion that contraceptive efficiency is reduced when there is a low critical amount of copper release due to the corrosion and/or calcification of the device in the uterus was proposed by Kosonen (6) and Gosden *et al.* (7) about ten years ago. Gupta *et al.* (8), instead, have described the finely granular and irregular surface of used copper IUDs as due to the effects of copper erosion and to the presence of macrophages, spindle cells, fibroblast, giant cells and mast cells (9).

The aim of this work is to investigate, with the Auger technique and X-ray microprobe analysis, the oxidation and calcification processes involved in the IUDs copper surface to explain the time-dependence of the pregnancy yield in the first years of its use.

MATERIAL AND METHODS

A set of intrauterine devices in copper metal, kindly furnished by the Gynaecological Service

(*) Divisione di Ginecologia - Stabilimento Ospedaliero di Monselice, Padova (Italy)

(**) Istituto di Fisica, Università di Catania (Italy)

of the Monselice (Padua) Hospital, was investigated.

The copper coils analysed, 7-T-200 intrauterine model are wound on a polypropylene support 0.2 mm in diameter and 32 cm in length they have an exposed surface to the uterine environment of about 200 mm². In this work a set of used IUDs (2-34 months), removed from patients 30-40 years old during routine visits to family planning clinics, and new IUDs were analysed. Before each analysis IUD copper wires were cut at 1 cm length, washed with distilled water in an ultrasonic bath, dried in nitrogen flux and put in the analysis chamber at high vacuum pressure.

Using the laboratories of the Physics Department of Catania University three types of investigations were performed on this subject: AES (Auger Electron Spectroscopy), PIXE (Particle Inducing X-ray Emission) and SEM (Scanning Electron Microscopy) analysis, as reported in Fig. 1, for an IUDs used for one year. The first analysis was used to investigate the metal surface modification of superficial layers (~50 Å) during the first period of IUDs use in the intrauterine environment; the second analysis was used to study the composition of the thick film of organic material deposited on the metal surface after a long period of IUDs use, and the third analysis was used to observe the morphology of the IUD surface deposited as a function of its permanence-time in the uterus.

AES spectroscopy for surface elemental analysis is based on the Auger radiationless process: when the core level of a surface atom is ionized by an impinging electron beam, the atom may decay to a lower energy state through an electronic rearrangement which leaves the atom in a doubly ionized state; the energy difference between these two states is given to the ejected Auger electron which will have a kinetic energy characteristic of the parent atom. When the Auger transition occurs within a few angstroms of the surface (depth escape) the Auger electrons may be ejected from the surface without energy loss and give rise to characteristic peaks in the distribution function of the secondary electron energy. Knowing the electron bonding energy in the cell structures, the energy and shape of Auger peaks can be used for the unambiguous identification of the solid surface composition (middle section of Fig. 1).

To calculate the absolute concentration of an element in a given matrix we will consider the Auger yield $Y_a(t)$, produced from a thin surface layer of sample, Δt , according to the following relationship⁽¹⁰⁾:

$$Y_a(t) = (N \cdot \Delta t) \cdot I(t) \cdot \sigma_A(t) \cdot e^{-t/\cos\theta \lambda} \cdot T \cdot \Delta \Omega; \quad (1)$$

where: $(N \cdot \Delta t)$ represents the number of interest atoms per cm²; $I(t)$ is the current of incident electrons; $\sigma_A(t)$ is the Auger emission-probability of the interest peak (cross section) at t depth; θ and $\Delta \Omega$ represent the detector analysis angle and the solid angle subtended by the analyser, respectively; λ is the electron escape depth and T is the transmission of the used analyser. The exponential term represents the Auger electron escape probability from the surface of the target. Auger depth escapes are of the order of 10-50 Å depending on the electron energy and matrix composition.

AES analysis was carried out using 3 KeV electron beams with currents of 1 µA (spot 10 µm in diameter) in a vacuum chamber at 10⁻¹⁰ Torr. To obtain element depth profiles we used together the electron probe, an ion beam to spatter the sample surface, i.e. inducing erosion and analysing depth layers. An argon beam, 4.5 KeV in energy and 100 nA current was sweep onto the sample surface (spot 4 mm²), for time intervals ranging from 1 to 60 minutes, to sputter the sample surface and to obtain controllable depth profiles of more important elements. Knowing the sputtering yield of argon ions in copper (~5 atoms per incident ion), in carbon (~0.5 atoms/ion) and in calcium (~0.5 atoms/ion) it was possible to correlate the element contents with the target depth.

X-ray microprobe analysis and scanning electron microscopy investigations were carried out by using a SEM with an electron microprobe. Electron induced X-ray emission (PIXE) analysis is based on the following effect: after a vacancy is created, an electron can make a transition from another cell to fill the vacancy with the emission of a photon. The excited atoms can release their energy in a radiation process with the emission of characteristic X-rays. The identification of atoms by values of the electron binding energies in the cell locations can be reached by using Moseley's law⁽¹¹⁾.

In our investigation 20 KeV electron beam was used to hit the sample and to induce X-ray emission. A Si(Li) detector (FWHM = 170 eV at 6 KeV) was used to detect characteristic X-rays with energy ranging between 1-30 KeV in a vacuum pressure of about 10⁻⁷ torr (lower section of Fig. 1).

In this case the quantitative analysis of the interest elements will be given by the following relationship⁽¹⁰⁾:

$$Y_x(t) = (N \Delta t) \cdot I(t) \cdot \sigma_x(t) \cdot e^{-\mu t / \cos\theta} \cdot \epsilon \Delta \Omega; \quad (2)$$

where: Y_x is the X-ray yield for the interest peak; $\sigma_x(t)$ is the probability of X-ray emission of the characteristic peak at t depth; μ is the photon-absorption coefficient (cm⁻¹) of produced

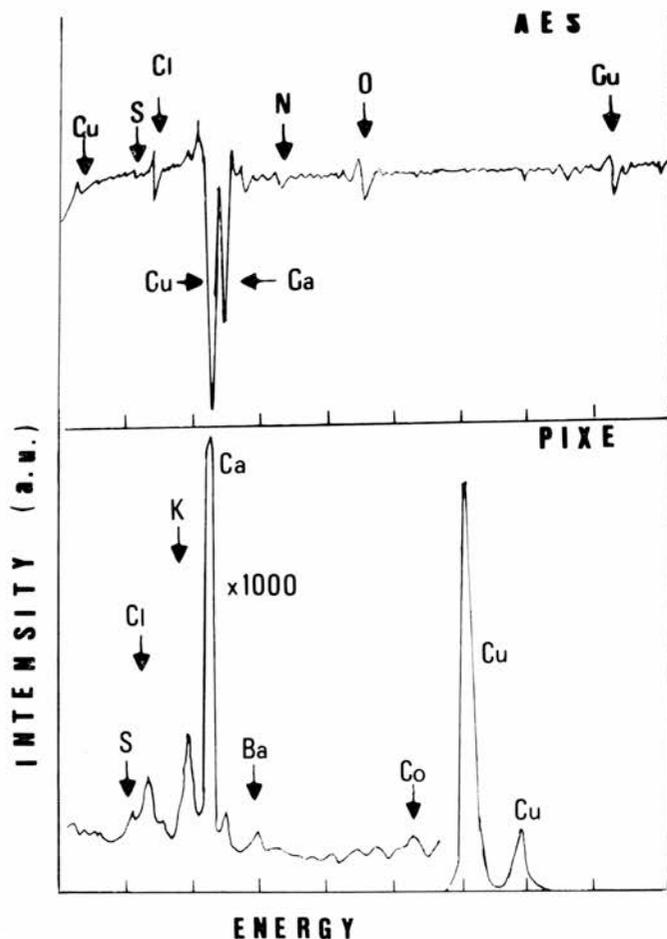
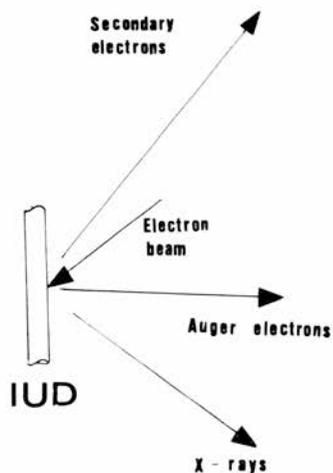


Fig. 1. — Scanning Electron Microscopy (SEM), Auger Electron Spectroscopy (AES) and Particle Inducing X-ray Emission (PIXE) as typical analysis obtained by bombarding with an electron beam the copper wire of a 1 year old IUDs.

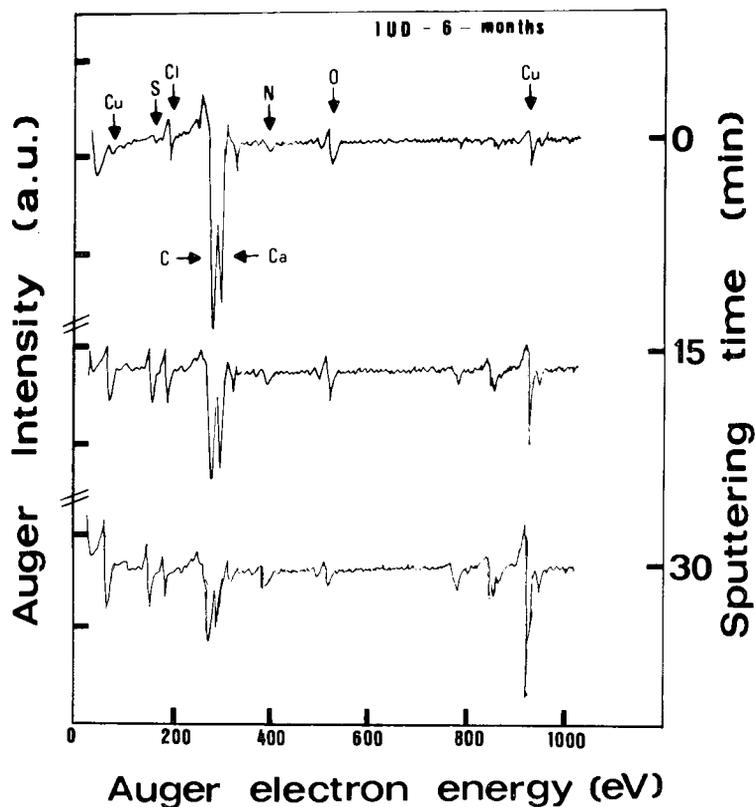


Fig. 2. — AES spectra of a 6 months old IUDs at the beginning (upper section) and during the surface ion sputtering (middle and lower sections).

photons in the matrix, and $\epsilon\Delta\Omega$ is the detection-efficiency for the X-rays of interest. The exponential term represents the X-ray transmission from t sample depth towards the detection direction. Because the range of 20 KeV electrons in calcium and copper is about $7\ \mu\text{m}$ and $2\ \mu\text{m}$ respectively, and the X-rays are produced with different probabilities along the electron paths, the emitted X-ray spectra will give the average elemental composition in the depth probed.

In both AES and PIXE spectrographies, the quantitative analysis were executed comparing, in the same experimental conditions the characteristic Auger or X-ray peaks coming from the analysed sample with those coming from pure standard samples as references. To compare results from AES and PIXE, the sensitivity between the two techniques was considered: AES sensitivity is of the order of 0.1%, while PIXE is about three order magnitudes higher.

Together with electron bombardment to induce X-ray emission the secondary electron produced emission was used to observe the surface morphology as a function of the thickness of the deposited organic material on IUDs surfaces (upper section of Fig. 1).

RESULTS

Auger analysis

By the identification of characteristic Auger peaks, the spectra of the unused 7 IUDs have shown a surface structure formed by some monolayers of copper oxide and a bulk matrix in pure copper. AES analysis on used IUDs (1-2 years) show, instead, a very different surface, rich in

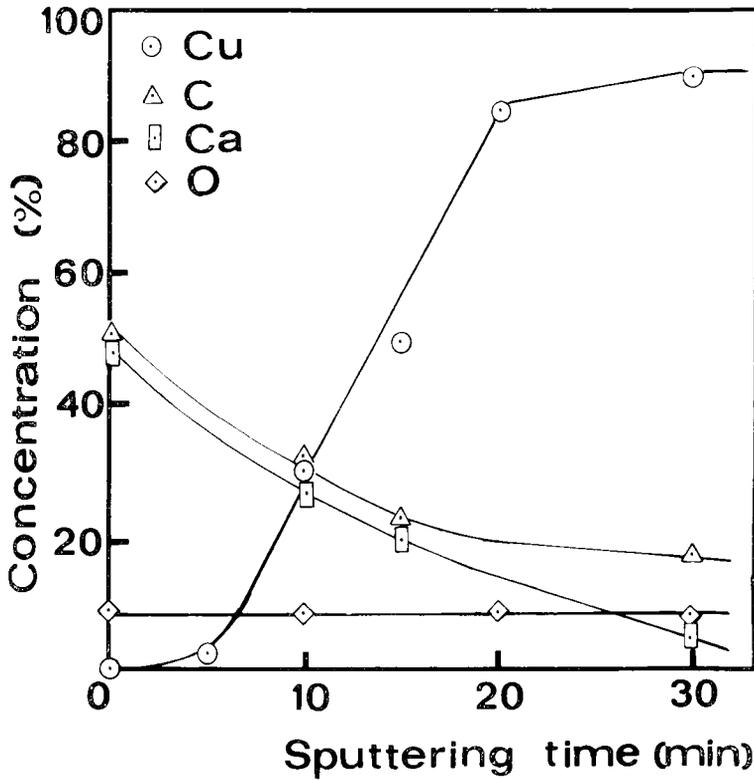


Fig. 3. — The main elements content in a 6 months old IUDs during surface ion sputtering. After 30 min sputtering (300 Å depth) the organic deposit is almost fully eroded.

calcium and carbon, with traces of other elements such as oxygen, chlorine, potassium and sulphur.

In very old IUDs (2-3 years old) no copper signal was detected from sample surfaces, indicating that a thick deposit of organic material overlaps the metal surface, masking the copper; in this case high calcium and carbon signals are detected in the overlap layers.

Fig. 2, upper section, shows a typical AES spectrum of a 6 months old IUD; a little signal coming from copper is evident, indicating that at this stage a copper release is still possible. The erosion of this sample with 4.5 KeV argon beam

shows that the carbon and calcium in the organic deposit film decrease with the sputtering time, as reported in the sequence spectra of fig. 2; the middle and lower sections correspond to about 150 and 300 Å depth, respectively. The oxygen, which is in the copper layers, remains about constant during the ion sputtering and is not correlated to copper and calcium.

These results, summarized in fig. 3 for elements versus sputtering time, indicate that no significant copper oxide growth with IUDs permanence time in the uterus occurs, but that the device surface is submitted, in time, to a strong calci-

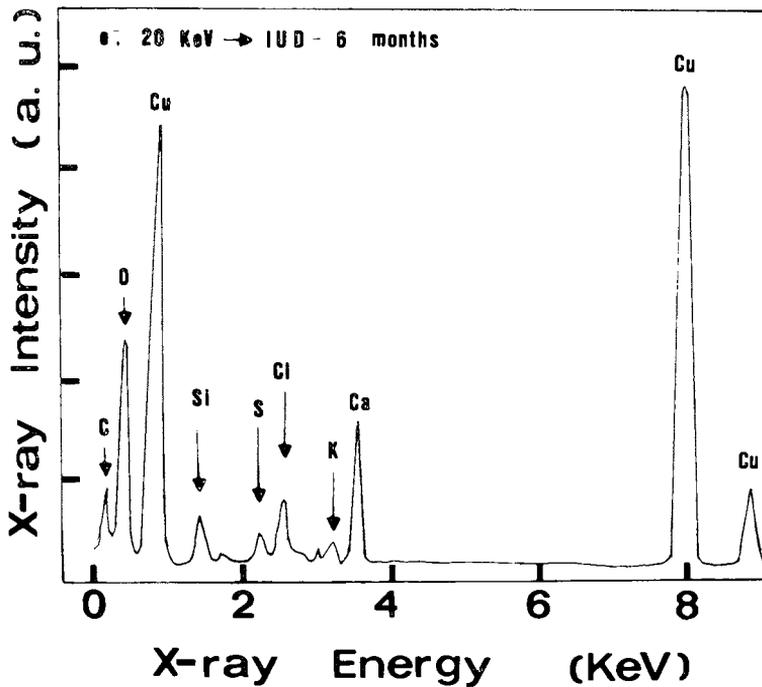


Fig. 4. — Typical PIXE spectrum of 1 year old IUD obtained bombarding the sample with 20 KeV electron beam.

fication. This means that in used IUDs is not the copper oxidation which inhibits the metal release in the uterus; it is instead, the calcium deposit which, by isolating the copper wire completely from the environment prevents further copper release.

Sulphur, chlorine potassium and nitrogen, are present in the organic deposit only in low concentrations of the order of 1 - 5%.

Analysing the different areas of the target the elemental quantitative analysis became reproducible only within the 20-30% due to non-uniform material deposit on the wire surface, according SEM morphology investigations.

X-ray Microprobe analysis

X-ray energy spectroscopy of the elements in the copper-IUDs surface was applied to IUDs of different use times, and results were correlated to the target surface topography.

The elemental X-ray yields, according to AES results, showed a considerable variation in calcium during the use of the IUDs: in the coils used for less than one year, the calcium yield was very low and the film of organic deposit was not uniform, showing areas with uncovered copper; instead, in coils used for 2-3 years a very thick deposited film was found, 1-8 μm in thickness, with a high calcium yield.

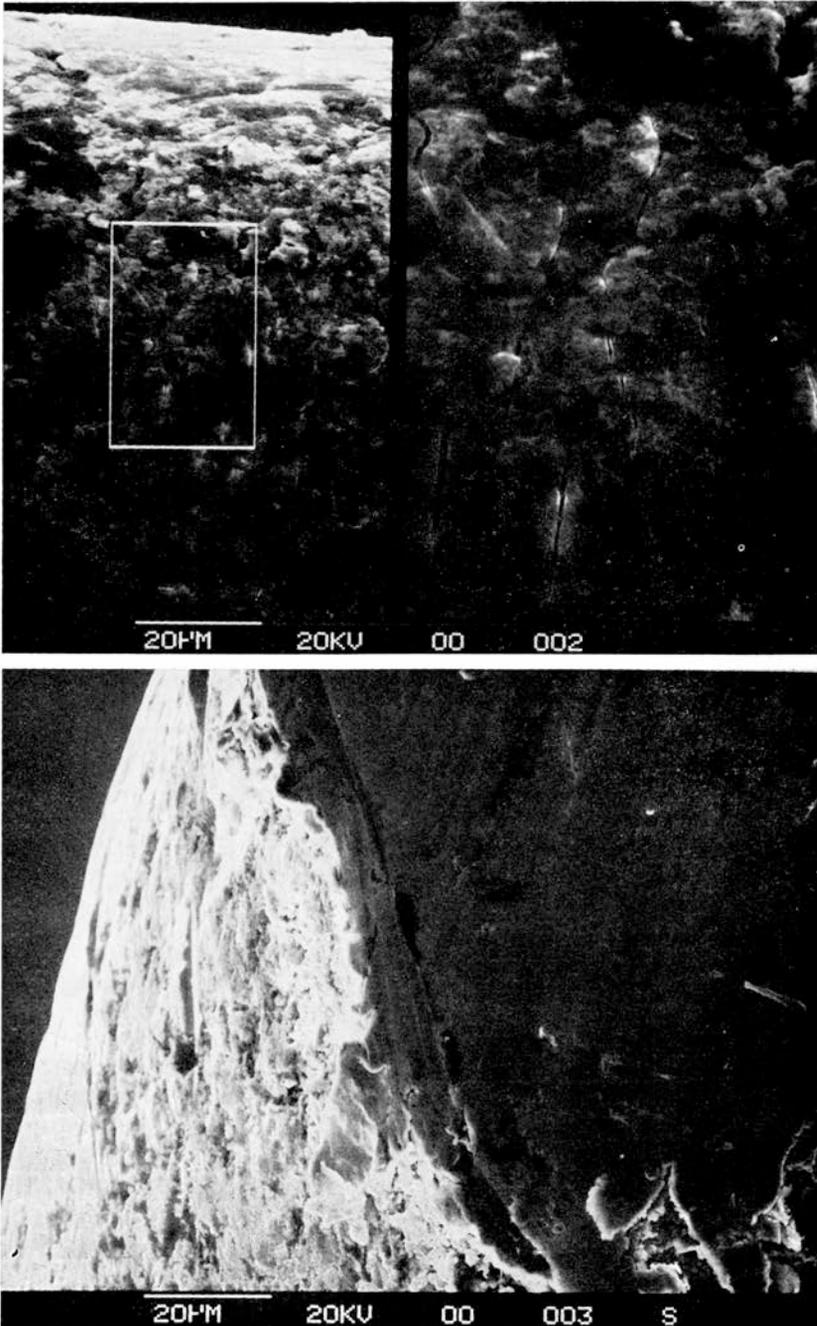


Fig. 5. — SEM photo of organic material on the IUD surfaces deposited during 1 year of use (upper section) and cross section view showing about 5 µm calcareous deposit thickness (lower section).

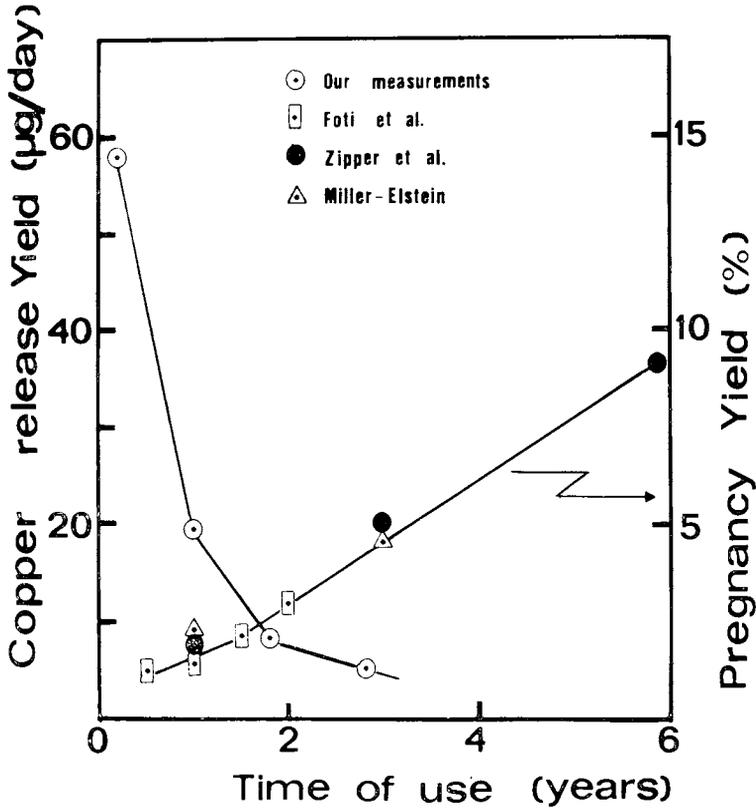


Fig. 6. — Copper release yield ($\mu\text{m}/\text{day}$) as a function of IUD use time (years). Our measurements and data literature show that there is high IUD efficiency in the first year of use.

Besides, investigation on 0.52 KeV oxygen X-ray emission, which is detectable without a detector Be window, demonstrated that, on average, oxygen in the full calcareous layer increases slowly with the use-time of IUDs devices.

Fig. 4 shows a PIXE spectra obtained by bombarding a 1 year-old IUDs with an electron beam of 20 KeV energy. The probe depth, which is of about $7 \mu\text{m}$, detects the copper signal under the thick organic deposit layer. Quantitative results on the detected elements at the same depth agree with the Auger investigations.

A cross section electron probe analysis, point by point, along a diameter of the copper wire, as shown in the SEM photo of fig. 5, lower section, indicates that the maximum oxygen concentration is located in the organic material deposit.

Only low oxygen contents, comparable with those of copper oxide of new IUDs, locate at the copper-calcium interface.

IUDs devices with a thick layer of calcium, analysed in cross section view, had central cores of copper with diameter of about $200 \mu\text{m}$, which is almost the same as that of the unused copper wire.

Our results show that calcification occurs progressively and no copper is pre-

sent in the calcium layers. This indicates that the calcium layer prevents copper outdiffusion in the uterine environment.

The presence of other elements such as chlorine, sulphur, phosphorus and potassium, detected only at low concentrations, indicates that these elements are brought to the metal surface by organic liquid deposited on the wire.

SEM Analysis

The surface morphology in new and used IUDs was investigated by using the SEM technique.

Fig. 5 shows surface views of IUDs copper wire after different times of use. The devices show a considerable incrustation proceeding in which thickness increases with time, giving an irregular calcareous deposit, easily splitting. SEM analysis showed that when the used devices were subjected to a mechanical force, such as bending, cracking and flaking occurred in the brittle corroded portion. By using high magnifications an average grain deposit size, of the order of $0.5 \mu\text{m}$ was observed.

Fig. 5, lower section, shows a cross section view of the copper wire of very old devices, indicating that the calcium thickness deposit in 2 year-old IUDs reaches about $5 \mu\text{m}$. In IUDs used for longer periods (2-3 years) the investigation showed that the deposit thickness is not uniform.

Generally the organic material deposit thickness is high in the areas most exposed to uterine the environment, and low in the areas in contact with the polymeric holder; the maximum calcareous deposit thickness, measured through a wire cross section view, ranged between 1-2 μm .

The results on calcium quantitative analysis versus IUDs used-time indicate contents comparable with other literature data.

A set of coils drawn out the from uterus at different time intervals of use (less than three years) were weighed before and after use so that the copper release yield was valued statistically as in previous data (^{6, 12}).

Fig. 6 shows the measured copper release rate in IUDs used during 3 years; copper release is about $60 \mu\text{g/day}$ in the first month and decrease to $20 \mu\text{g/day}$ at 12 months. The results are in agreement with data in literature which give a release rate between $16.5 - 43.8 \mu\text{d/day}$ (^{6, 12, 13}) (about 10.3 mg/year), a copper-rate in the endometrial fluid of about $1.4 \mu\text{g/g}$ and a release in the cervical mucus of $2,2 \mu\text{m/g}$. Fig 6 shows also the correlation between the experimentally measured copper release yields and the pregnancy yield valued by data in literature.

CONCLUSIONS

The efficiency of the IUDs is related to the copper release into the uterine environment. For a high copper release of about $50 \mu\text{g/day}$ the pregnancy yield is below 2%, while for very low release yields of about $5 \mu\text{g/day}$ the pregnancy yield reaches a value of about 8%.

Our results indicate that oxidation on the copper wire is always negligible and only involves the submicron surface region. The calcification process seems to be the most important in inhibiting the copper release from the IUDs.

Surface morphology analysis combined with X-ray microprobe investigation shows surface layers rich in calcium, carbon, oxygen, sulphur, chlorine and potassium, probably brought by organic liquids.

In conclusion results confirm the data in literature that report high contraceptive efficiency only in the first years of use.

Adequate amounts of copper, in fact, are still present in the device used for less than two years, but after this period

the replacement of the copper coil is needed to maintain the antifertility efficiency high.

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Address reprint requests to:

Dr. L. TORRISI

Istituto di Fisica Università

Corso Italia, 57 - 95100 Catania (Italy)