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Rosie Grayburn[1,2], Pieter-Jan Sabbe[1], Mark Dowsett[2], Michel De Keersmaecker[1], Victoria Flexer[1], Annemie Adriaens[1]

[1]Department of Analytical Chemistry, Universiteit Gent, Gent, 9000 BELGIUM
[2]Department of Physics, Warwick University, Coventry, CV4 7AL UNITED KINGDOM

Background. A new spectroelectrochemical cell (the peCell) was tested using a copper-based biomaterial system: Copper-bearing intrauterine devices (IUDs) are a very popular method for long-acting reversible contraception (LARC). The primary contraceptive effect of the IUD is the prevention of fertilization and implantation through the release of copper ions into the fluid medium of the uterus and their reaction with the endometrium [1,2]. It has been stated that the primary source of these ions is cuprite (Cu_2O) formed on the device surface through *in utero* reactions with the uterine environment [3–5]. However since Cu_2O is almost insoluble[6] at the pH and temperature involved, the reasoning seems spurious in the likely presence of more soluble copper compounds such as cupric sulphate and chloride. Therefore studying the reactions *in situ* plays an essential role in determining what surface reactions give rise to the release of significant quantities of copper ions. Moreover, previous results have found that the treatment and storage of *in utero* samples after removal can provide misleading results during *ex situ* analysis [7]. Therefore there is a strong motivation for the study of this system using the peCell.
A new generation of frameless IUDs (Gynefix®, Contrel Research, Ghent, Belgium) aims to reduce the side effects of conventional IUDs such as bleeding, pain and expulsion [5]. A reversed cathodic protection effect is created by adding more noble gold to these devices, hence creating facilitated galvanic corrosion of the copper[8,9] and therefore improve anticonception rates for a smaller device and possibly provide protection against STDs [10–13]. Samples modelling this Cu/Au system resided within the peCell for one week while *in situ* spectroelectrochemical data was collected at the XMaS beamline.

Experiments. Three samples with varying ratios of Cu/Au were made by sputter-coating ⌀12.5 mm Cu coupons – one sample recreated the Cu/Au surface area ratio of the IUD (⌀2.83 mm Au, Sample 1), and the remaining samples recreated Cu/Au surface area ratios higher (⌀6.25 mm Au, Sample 3) and lower (⌀1.5 mm Au, Sample 2) than the Gynefix®. Samples were mounted within the peCell (Figure 1) two days prior to beamtime as the most interesting behaviour is said to occur in the 1st week [14,15]. The cell body was flooded with electrolyte modelling interuterine fluid [3] (SUF) and a cartridge heater was used to keep samples at body temperature during transportation. SUF contains calcium, potassium and sodium chlorides, urea, glucose, monosodium phosphate, sodium bicarbonate (all < 1 g/l) and albumin (35 g/l) - SUF has no associated biological hazard and was set at a pH = 6.2.

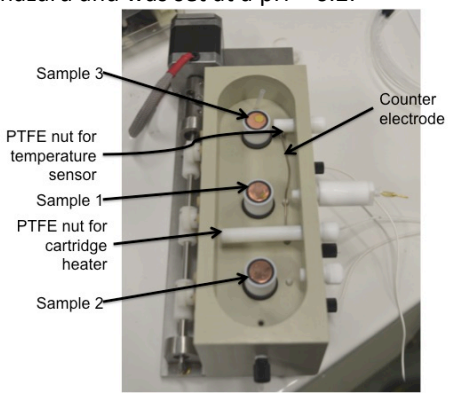

Figure 1 Cu/Au samples mounted within the peCell prior to filling with simulated uterine solution (SUS). A sensor records the electrolyte temperature closest to the electrolyte outlet port. The cartridge heater heats the electrolyte between Samples 1 and 2, across the width of the cell.

During the experiment (including transport to and from the beamline), the corrosion potential of Sample 1 was constantly monitored using a custom voltage logger thus completing the spectroelectrochemical dataset for the sample.

SR-XRD patterns were obtained from these samples *in situ* at time intervals of approximately 24 hours for 5 days using a Mar CCD 165 2D detector. Nine images (exposure time 10 s) were recorded at 9 positions within a range of ± 2 mm from the centre of each sample. If there was a volume of electrolyte between the sample and the window, 10 images per position were taken to improve sensitivity. In addition, using a separate spectroelectrochemical cell (the eCell) time-lapse SR-XRD patterns were collected over a 24-hour period to study the initial corrosion after implantation of these devices in SUS. Data processing was carried out using the esaProject software [16].

Results and conclusions. This work highlights the importance of techniques which monitor corrosion processes *in situ*. The insoluble copper compounds, which do not provide the Cu^{2+} -ions important for anti-conception, were identified and monitored during the course of a 9-day experiment, which included 5-days of beam time at the XMaS beamline.

Using the peCell, we were able to record SR-XRD patterns from three different samples every 24 hours for 5 consecutive days during which time the E_{corr} and temperature of the cell were also monitored. The samples were copper coupons with different surface areas of gold. The sample with the highest surface area of gold showed the least amount of insoluble deposit on the surface but could have corroded to an unknown extent to form soluble corrosion products. The sample with the least amount of gold demonstrated a range of corrosion products during the experiment – copper sulphides were formed initially but the final pattern showed just nantokite. The sample which was modelling the 'real' ratio of Cu/Au in the Gynefix® IUD formed cuprite before sulphides appeared, and these species coexisted until the end of the experiment.

On a separate note, extra clarification regarding post-removal rinsing of in utero corroded IUDs was obtained during the experiments. Previous XRD data recorded from in utero corroded frameless IUDs revealed the presence of solely cuprite as a corrosion product, whereas literature mentions the presence of chlorides, sulphides and calcium crystallites in Cu-bearing IUDs. During a time-lapse experiment it was shown now that the observed corrosion products, different than cuprite, dissolve or convert rapidly into cuprite upon rinsing with water, a post-removal treatment which has been done on the previously measured IUDs.

This work is now being written up for publication (target journal *Analytical Chemistry*) and forms part of two PhD theses (RG, P-JS).

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