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Test of the equipment

In order to check the mass and the concentration sensitivities of the "Eureka" instrument two different electrochemical systems have been used: electrodeposition and electrodisolution processes have been carried out to detect Silver and copper in acidic media (W. Koh, W. Kutner, M.T. Jones and K.M. Kadish, *Electroanalysis*, 5, 1993).

Silver determination

A silver electrodeposition/electrodisolution experiment has been performed by means of a staircase normal cyclic voltammetry. The voltammogram and the frequency-potential plot are recorded simultaneously, as shown in the figure 1.

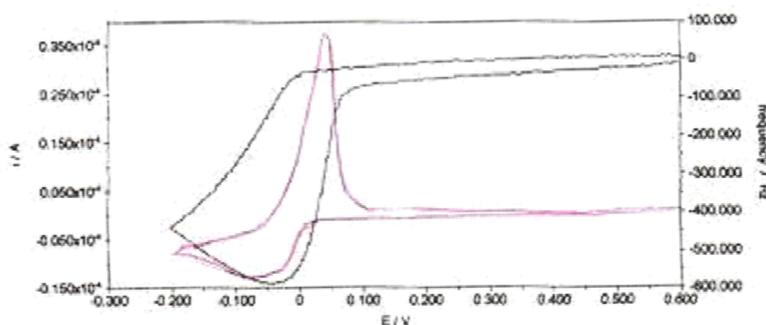


Fig. 1 Simultaneous cyclic voltammetry (red curve) and EQCM response (black curve) in 1 mM AgNO_3 , 0.1 M HClO_4 at a 0.229 cm^2 Au/quartz electrode of 10 MHz fundamental frequency; the potential scan rate was 5 mV/s.

The cathodic current increase resulting for silver electrodeposition onto the electrode surface is accompanied by a frequency decrease due to mass gain. The frequency begins to increase when the potential for anodic stripping of the silver is reached.

The measurement was carried out with a 30 ml static measuring chamber in 0.1 M HClO_4 over a AgNO_3 concentration range of 0.25 to 1.7 mM. The working electrode was a 10 MHz Au quartz crystal (area 0.229 cm^2), the counter electrode was a Pt ring, while an Ag rod was used as a pseudo-reference electrode.

A linear dependence of Δf vs Q was found for both Ag^+ electrodeposition (correlation coefficient $R=0.997$) and Ag^0 electrodisolution ($R=0.998$), as shown in the figure 2.



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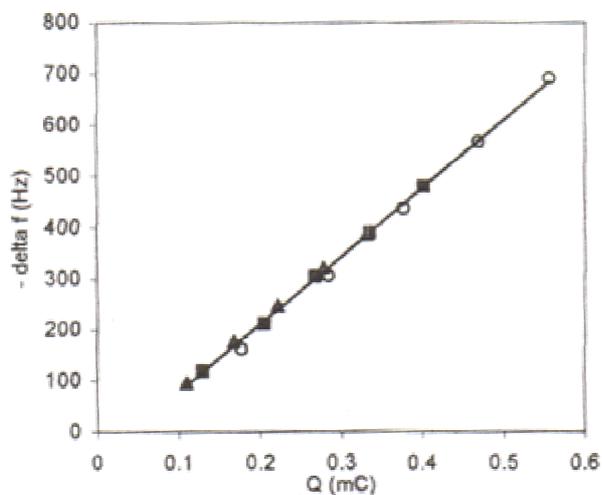


Fig. 2 Frequency change versus charge of the oxidation stripping peak of silver over a 0.25 to 1.7 mM AgNO₃ concentration range and potential scan rate range of 10 to 30 mV/s.

The charges passed upon electrodeposition and electrodisolution were calculated by integration of the electroreduction and electrooxidation peak respectively, and the resulted values were compared to the measured mass charges, Δm , which were calculated with Faraday's law.

The mass sensitivities determined by CV for Ag electrodeposition and electrodisolution at a 10 MHz crystal oscillator were 4.6 ± 0.2 and 3.5 ± 0.1 ng/Hz cm² respectively.

These values are close to the theoretical sensitivity of 4.4 ng/Hz cm², which can be calculated by means of the Sauerbrey equation for the fundamental resonance.

The Sauerbrey equation describes the frequency changes in vacuum due to mass changes of rigid deposition uniformly spread on the active electrode area.

The frequency-concentration plots of the silver anodic stripping peaks are presented in figure 3.

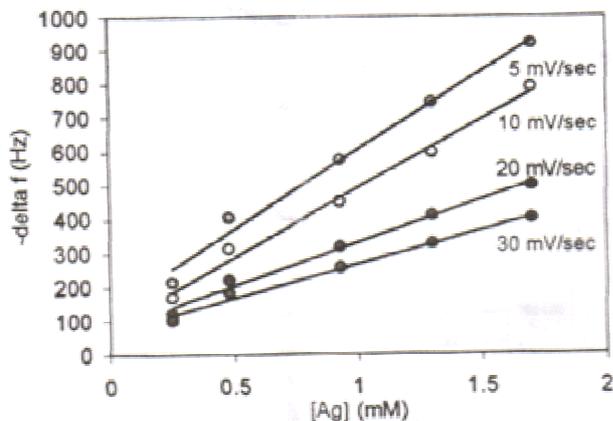


Fig. 3 Dependence of frequency change on the Ag⁺ concentration in 0.1 M HClO₄ upon CV electrodisolution of Ag⁰ at a 0.229 cm² Au/quartz electrode of a 10 MHz fundamental frequency. The potential scan rates were 5, 10, 20, 30 mV/s.



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In the following table the concentration sensitivities at different potential scan rates are shown.

Scan rate (mV/sec)	Ag concentration sensitivity ($\mu\text{M}/\text{Hzcm}^2$)
5	9.39
10	11.10
20	17.42
30	22.05

Table 1. Concentration sensitivities for Ag^0 electrodisolution at different potential scan rates.

Copper determination

Simultaneous CV and Δf vs E are shown in the figure 4. The measurement was carried out with a static measuring chamber in 0.5 M NaCl (pH₂) over a CuCl_2 concentration range of 1 to 4 mM. The working electrode was a 10 MHz Au quartz crystal (the projected electrode area was 0.229 cm^2), the counter electrode was a Pt sheet and the reference electrode was an Ag/AgCl.

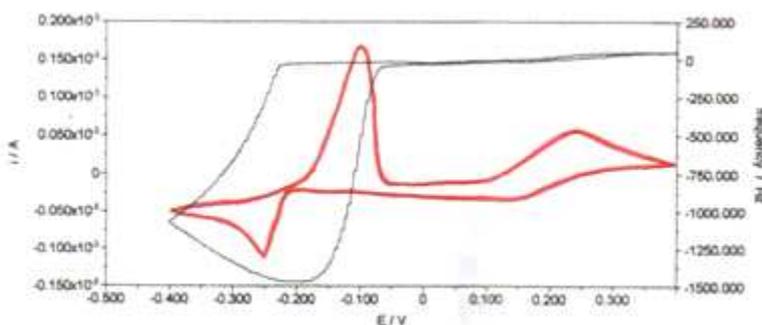


Fig. 4 Simultaneous cyclic voltammetry (red curve) and EQCM response (black curve) in 0.5 M NaCl (pH 2) containing 4 mM CuCl_2 ; the potential scan rate was 5 mV/s.

Two distinct redox couples are shown in the voltammogram, but only the couple at more negative potentials involves a mass change at the electrode. This couple corresponds to the Cu^+/Cu^0 electrodeposition/electrodissolution process.

The couple at more positive potential corresponds to the $\text{Cu}^{2+}/\text{Cu}^+$ anodic peak and a corresponding minor step on the Δf .

However a slight splitting of the $\text{Cu}^{2+}/\text{Cu}^+$ anodic peak and a corresponding minor step on the Δf vs E curve is also observed. This may indicate some precipitation of Cu^+ hydrolysis products.

A linear dependence of Δf vs Q was found for both Cu^+ electrodeposition ($R=0.9994$) and Cu^0 electrodisolution ($R=0.997$).

The mass sensitivities determined by CV for Cu electrodeposition and electrodisolution at a 10 MHz crystal oscillator were 7.47 and 12.64 ng/Hz cm^2 respectively.