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# Solutions to the tasks: Chapter 6 – Combined methods

### Task 6.1 (Rotating ring disk electrode – collection efficiency)

The collection efficiency of an RRDE depends on geometrical parameters only, assuming stable reaction products. The radii are $r_1 = 2.5\,\text{mm}$ for the disk, $r_2 = 3\,\text{mm}$ the inner and $r_3 = 4\,\text{mm}$ the outer of the ring.

The gap between the disk and the ring electrode is:

$$r_2 - r_1 = 0.5\,\text{mm}$$

For the collection efficiency $N$, Albery and Bruckenstein [1] proposed a generally accepted solution:

$$N = 1 - F\left(\frac{a}{b}\right) + b^{\frac{2}{3}}\left(1 - F(a)\right) - (1 + a + b)^{\frac{2}{3}}\left(1 - F\left(\frac{a}{b}(1 + a + b)\right)\right)$$

$$a = \left(\frac{r_2}{r_1}\right)^3 - 1 \qquad \text{and} \qquad b = \left(\frac{r_3}{r_1}\right)^3 - \left(\frac{r_2}{r_1}\right)^3$$

$$F(x) = \frac{\sqrt{3}}{4\pi} \cdot \ln \frac{(1 - x^{\frac{1}{3}})^3}{1 + x} + \frac{3}{2\pi} \cdot \arctan\left(\frac{2x^{\frac{1}{3}} - 1}{\sqrt{3}}\right) + \frac{1}{4}$$

Inserting the radii in the equations and careful evaluation leads to the collection efficiency:

$$N = 0.40$$

You may avoid the cumbersome calculation by using the provided Jupyter notebook.

### Task 6.2 (Electrochemical quartz crystal microbalance)

1. The minimum charge an EQCM can resolve directly links to the frequency resolution. For the fundamental mode of a 6 MHz crystal, the sensitivity factor in the Sauerbrey equation is $C_\text{f} = 81.5\,\text{Hz}\,\mu\text{g}^{-1}\,\text{cm}^2$. With a frequency resolution of $\Delta f_\text{min} = 0.07\,\text{Hz}$, the minimally resolvable mass change is:

$$\Delta m_\text{min} = \frac{\Delta f_\text{min}}{C_\text{f}} = 0.86\,\text{ng}\,\text{cm}^{-2}$$

In comparison, a monolayer of lead on gold translates into a substantial higher mass change:

$$\Delta m_{\mathrm{Pb,ML}} = \frac{M}{nF} \cdot q = \frac{207.2\,\mathrm{g\,mol^{-1}}}{2F} \cdot 300 \times 10^{-6}\,\mathrm{A\,s\,cm^{-2}} = 322\,\mathrm{ng\,cm^{-2}}$$

That means this EQCM ideally allows resolving a fraction of 0.003 of a monolayer lead on gold.

2. For the upper limit of the Sauerbrey equation's applicability, we have a look at silver deposition. We rely on the rule of thumb $\Delta f_{\mathrm{max}} = 0.02 f_0$. The Sauerbrey equation for this EQCM is valid up to:

$$\Delta m_{\mathrm{max}} = \frac{\Delta f_{\mathrm{max}}}{C_{\mathrm{f}}} = 245\,\mathrm{\mu g\,cm^{-2}}$$

This value translates into a maximal thickness $t_{\mathrm{max}}$ using the density of silver ($\rho = 10.49\,\mathrm{g\,cm^{-3}}$) and considering a one-electron deposition process:

$$t_{\mathrm{max}} = \frac{\Delta m_{\mathrm{max}}}{\rho} = 234\,\mathrm{nm}$$

The two parts of this task illustrate the wide range of the EQCM, starting from a tiny fraction of a monolayer to metal thin-films up to several hundreds of nanometers. For higher film thickness, EQCM measurements are also possible, requiring considering the deposited film's properties, e.g., using the Z-match method.

## References


[1] W. J. Albery, S. Bruckenstein, "Ring-disc electrodes. Part 2. – Theoretical and experimental collection effciencies," *Transactions of the Faraday Society* **1966**, 62, 1920–1931, DOI 10.1039/tf9666201920.


Last update: 02/21/22 (jk)