

Q

QCM → quartz crystal microbalance

QCN → quartz crystal microbalance

Quadratic mean → root mean square

Quantitation limit → limit of quantitation

Quartz crystal microbalance — The quartz crystal microbalance (QCM) or nanobalance (QCN) is a thickness-shear-mode acoustic wave mass-sensitive detector based on the effect of an attached foreign mass on the resonant frequency of an oscillating quartz crystal. The QCM responds to any interfacial mass change. The response of a QCM is also extremely sensitive to the mass (density) and viscoelastic changes at the solid-solution interface [i–vi].

It is a piezoelectric (→ *piezoelectricity*) sensing device that consist of an oscillator circuit and a crystal which is incorporated into the feedback loop of the circuit. The crystal is the frequency-determining element, as its quality factor is very high.

The piezoelectric crystals are patterned with two excitation electrodes (electronic surface films) on their opposite sides. Due to the converse piezoelectricity phenomenon, when → *alternating voltage* is applied to the attached electrodes mechanical oscillations occur within the crystal lattice. These oscillations are stable only at the natural resonant frequency of the crystal.

The crystal cut determines the mode of oscillations. Shear vibrations are generated if one large crystal face moves parallel with respect to the underlying planes as in QCMs with AT-cut α -quartz crystals. This crystal wafer is prepared by cutting the quartz at approximately 35.17° from its Z-axis. A typical crystal plate is a cylindrical disk of a diameter 10 mm and thickness about 0.7 to 0.1 mm for resonant operation in the 2 to 15 MHz frequency range. This type of crystals shows weak dependence of the resonant frequency on the temperature and stress for room temperature operation.

The fundamental resonant frequency (f_o) shifts when a thin film is deposited on the surface of the quartz crystal. Under the assumption that the density and the shear modulus of the film are the same as those of quartz and that the film is uniform (constant density and thickness) and covering the acoustically active area of the whole

crystal, the **Sauerbrey equation** [iv] describes the relationship between the resonant frequency shift (Δf) and the added mass (ΔM):

$$\Delta f = f_c - f_o = -\frac{2f_o^2 \Delta M}{A(\rho_q \mu_q)^{1/2}} = -C_f \Delta m, \quad (1)$$

where f_c is the resonant frequency of the composite oscillator formed from the crystal and the film at the surface, A is the acoustically active surface area, $\rho_q = 2.648 \text{ g cm}^{-3}$ and $\mu_q = 2.947 \times 10^{10} \text{ N m}^{-2}$ are the density and the shear modulus of quartz, respectively, Δm the change of the surface mass density, and C_f is the integral mass sensitivity.

Since

$$f_o = \frac{v_q}{2L_q}, \quad (2)$$

where $v_q = \left(\frac{\mu_q}{\rho_q}\right)^{1/2}$ is the wave speed for quartz ($v_q = 3336 \text{ m s}^{-1}$) and L_q is the thickness of the quartz, in this case the only difference between the film-coated and uncoated quartz is the added thickness (ΔL_f). The film should not be too thick, the mass loading should be lower than 2% of the mass of the quartz plate, i.e., typically lower than $20 \mu\text{g cm}^{-2}$. There may be non-mass-related frequency changes due to stress (e.g., caused by an improper mounting) and temperature effects [i, iii].

The values of the integral mass sensitivity for the most frequently used $f_o = 5 \text{ MHz}$ and 10 MHz crystals are $C_f = 5.66 \times 10^7$ and $2.264 \times 10^8 \text{ Hz cm}^2 \text{ g}^{-1}$, respectively. It follows that by using a crystal with $A = 0.3 \text{ cm}^2$ surface area 1 Hz change – which can be measured easily and accurately – corresponds to 6 ng and 1.4 ng, respectively. The uniform distribution of the mass over the active area of the quartz plate is of importance since the differential mass sensitivity (c_f) varies across this area. For typically used round-shape crystals [i, vii]:

$$C_f = 2\pi \int_0^r c_f(r) r dr. \quad (3)$$

The resonant frequency also depends on the density and the viscosity of the contacting media. The frequency shift for measurement in air vs. vacuum is smaller than 10 Hz. However, the frequency shift from air to water or aqueous solution, for a 10 MHz crystal is about 4–12 kHz. The magnitude of this shift can be calculated by using the following relationship:

$$\Delta f = -f_o^{3/2} \left(\frac{\rho_L \eta_L}{\pi \rho_q \mu_q} \right)^{1/2} \quad (4)$$

where ρ_L and η_L are the density and viscosity of the liquid contacting one side of the crystal.

The additional surface mass change can be measured and calculated by using the Sauerbrey equation even in the case when the crystal is in contact with a liquid. It makes the in-situ detection of the surface mass changes possible in the course of electrochemical experiments by using an \rightarrow *electrochemical quartz crystal microbalance (EQCM)*. A lack of conformance with the Sauerbrey equation may be traced back to high-mass loading, surface roughness, surface stress, interfacial slippage, nonuniform mass distribution, and viscoelastic effects. In the latter case the film does not behave as a rigid layer, i.e., the deformation is not purely elastic. It happens when the film is thick and its morphology changes due to, e.g., its swelling.

The frequency can be measured by the help of a frequency counter with an accuracy of 0.1 Hz and sampling time 0.1–1 s.

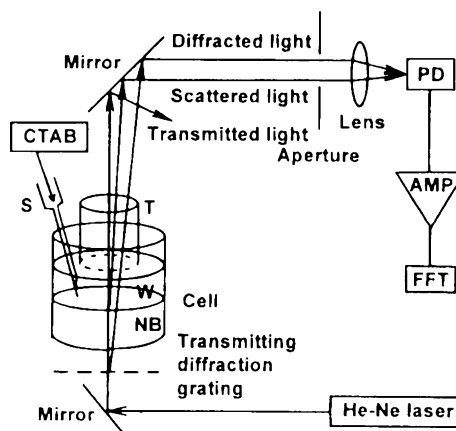
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Refs.: [i] Lu C, Czanderna AW (eds) (1984) *Applications of piezoelectric quartz crystal microbalances*. Elsevier, New York; [ii] Buttry DA (1991) *Applications of the quartz crystal microbalance to electrochemistry*. In: Bard AJ (ed) *Electroanalytical chemistry*, vol. 17. Marcel Dekker, New York, pp 1–85; [iii] Buck RP, Lindner E, Kutner W, Inzelt G (2004) *Pure Appl Chem* 76:1139; [iv] Sauerbrey G (1959) *Z Phys* 155:206; [v] Buttry DA, Ward MD (1992) *Chem Rev* 92:1355; [vi] O'Sullivan CK, Guibault (1999) *Biosens Bioelectron* 14:663; [vii] Bácskai J, Láng G, Inzelt G (1991) *J Electroanal Chem* 319:55

GI

Quasielastic light scattering (QELS) — from thermally excited \rightarrow *capillary waves* provides a useful insight into dynamics of liquid surfaces [i] and \rightarrow *interfaces* [ii]. Essentially, this approach allows investigating the dispersion relationship, which relates the complex angular frequency $\omega = \omega_0 + i\Delta\omega$ ($i = \sqrt{-1}$) of the capillary wave to the capillary wavelength Λ (wavenumber $k = 2\pi/\Lambda$) [iii]. Experimentally, the correlation function $G(t)$ (t is time) [iv] or the power spectrum of the scattered light can be measured by using the optical heterodyne technique for a selected wavenumber k [i]. The power spectrum is approximately lorentzian in form, and is characterized by a peak frequency $f_0 = \omega_0/2\pi$ and a linewidth $\Delta f = \Delta\omega/2\pi$ [iii]. To a first approximation, the peak frequency f_0 of the capillary wave on a water–organic solvent interface can be described by the Lamb's equation [v],

$$f_0 = \frac{1}{2\pi} \left(\frac{\gamma k^3}{\rho^w + \rho^o} \right)^{1/2},$$



Quasielastic light scattering (QELS) — **Figure.** Scheme of the experimental set up for QELS measurements: w – aqueous solution, NB – organic solvent solution, S – microsyringe, T – glass tube, PD – photodiode, AMP – pre-amplifier, FFT analyzer. Reprinted with permission from [vi]. © 1997 American Chemical Society

where γ is the \rightarrow *surface tension*, ρ^w and ρ^o are the densities of the aqueous (w) and the organic solvent (o) phase, respectively. The linewidth Δf reflects the damping of the capillary waves due to the bulk viscosities of the two phases [iii]. Application of the QELS method has been extended to study of dynamics of nonpolarizable [vi] and ideally polarizable [vii] ITIES (\rightarrow *interface of two immiscible electrolyte solutions*). Following the simplified description of the method [vi], the incident beam normal to the interface is quasielastically scattered by the thermally excited capillary wave with a Doppler shift at an angle determined by the ratio of the wavenumbers of the incident beam and the capillary wave (Figure). The scattered beam is optically mixed with the incident beam at the selected angle by means of a transmission diffraction grating, which yields an optical beat detected at the same frequency as the Doppler shift (capillary wave frequency).

Refs.: [i] Hard S, Hamnerius Y, Nilsson O (1976) *J Appl Phys* 47:2433; [ii] Löfgren H, Neuman RD, Scriven LE, Davis HT (1984) *J Colloid Interface Sci* 98:175; [iii] Laudon R (1984) *Ripples on liquid interfaces*. In: Agranovich VM, Laudon R (eds) *Surface excitations*. North Holland, Amsterdam, pp 591–638; [iv] Byrne D, Earnshaw JC (1977) *J Phys D Appl Phys* 10:L207; [v] Lamb H (1945) *Hydrodynamics*. Dover, New York, p 348; [vi] Zhang Z, Tsuyumoto I, Takahashi S, Kitamori T, Sawada T (1997) *J Phys Chem A* 101:4163; [vii] Samec Z, Trojének A, Krtil (2005) *Faraday Discuss* 129:301

ZSam

Quasi-Fermi level — The quasi-Fermi level is a hypothetical energy level introduced by W. Shockley to de-

scribe the behavior of charge carriers under nonequilibrium conditions in \rightarrow *semiconductors*. It correctly predicts the concentration of charge carriers, electrons in the \rightarrow *conduction band*, or holes in the \rightarrow *valence band*, if these are assumed to be in thermal equilibrium at the lattice temperature and if the quasi-Fermi level is used in the Fermi–Dirac distribution function (\rightarrow *Fermi–Dirac statistics*) in substitution to the \rightarrow *Fermi level*. In the case of nonequilibrium conditions, no single Fermi-level exists and the quasi-Fermi levels for \rightarrow *electrons* and \rightarrow *holes* serve the purpose for which the Fermi level alone was adequate at thermal equilibrium. The quasi-Fermi levels essentially are \rightarrow *electrochemical potentials* for electrons and holes, in a different terminology, because it is widespread practice, in semiconductor physics, to refer to the chemical potential of a semiconductor as the Fermi level.

Refs.: [i] Shockley W (1950) *Electrons and holes in semiconductors*. Van Nostrand, New York; [ii] Blakemore JS (1987) *Semiconductor statistics*. Dover, New York; [iii] Rhoderick EH (1978) *Metal-semiconductor contacts*. Clarendon Press, Oxford; [iv] Ashcroft W, Mermin ND (1976) *Solid state physics*. Saunders College, Philadelphia; [v] Seeger K (1991) *Semiconductor physics – an introduction*. Springer, Berlin

IH

Quasireference electrode (QRE) — (\rightarrow *reference electrode*, pseudoreference electrode). An electrode that maintains a given, but generally not well-defined, potential during the course of a series of electrochemical experiments. It has the advantage of not contaminating the test solution by solvent or ions that a conventional reference electrode might contain and transfer. Thus in studies in aprotic solvents, like acetonitrile, a silver wire can behave as a QRE. It must be calibrated with respect to a true reference electrode or reference redox couple that is added at the end of the experiments to obtain meaningful potential values.

Refs.: [i] Bard AJ, Faulkner LR (2001) *Electrochemical methods*, 2nd edn. Wiley, New York, p 53; [ii] Ghilane J, Hapiot P, Bard AJ (2006) *Anal Chem* 78:6868

AJB

Quasireversibility \rightarrow *reversibility*

Quasireversible maximum — is a feature of the square-wave voltammetric response (see \rightarrow *square-wave voltammetry*) of a kinetically controlled \rightarrow *electrode reaction* in which at least one component of the \rightarrow *redox couple* is immobilized on the \rightarrow *electrode surface* [i] and kinetically controlled electrode reaction occurring in a restricted diffusion space [ii] (see \rightarrow *thin-film electrode* and

\rightarrow *thin-layer*). The quasireversible maximum is manifested as a parabola-like dependence of the ratio $\frac{\Delta I_p}{\sqrt{f}}$ (or $\frac{\Delta I_p}{f}$) versus f , where ΔI_p is the \rightarrow *peak current* of the net SW peak and f is the frequency of the square-wave potential modulation (see \rightarrow *square-wave voltammetry*). The maximum of the parabolic curve is positioned within the quasireversible kinetic region of the electrode reaction. The quasireversible maximum arises as a consequence of the current sampling procedure used in \rightarrow *square-wave voltammetry* and chronoamperometric characteristics (see \rightarrow *chronoamperometry*) of the surface-confined electrode reactions, or reactions confined within a thin film. Under conditions of the quasireversible maximum the rate of the electrode reaction is synchronized with the frequency of the square-wave potential modulation. Hence, the position of the maximum is dictated by the \rightarrow *standard rate constant* of the electrode reaction. The position of the quasireversible maximum can be theoretically predicted on the basis of numerical simulations of the electrode reaction. The standard rate constant of the electrode reaction can be readily estimated by comparing the position of the theoretically predicted and experimentally measured quasireversible maximum. Although primarily typical for square-wave voltammetry, the quasireversible maximum can be also observed with other pulse-nature voltammetric techniques (see \rightarrow *pulse voltammetry*).

Refs.: [i] Lovrić M (2002) *Square-wave voltammetry*. In: Scholz F (ed) *Electroanalytical methods. Guide to experiments and applications*. Springer, Berlin, p 111; [ii] Mirčeski V (2004) *J Phys Chem B* 108:13719; [iii] Mirčeski V, Komorsky-Lovrić Š, Lovrić M (2007) *Square-wave voltammetry*. In: Scholz F (ed) *Monographs in Electrochemistry*. Springer, Berlin

VM

Quincke, Georg Hermann



(Reproduced from [i])

(Nov. 19, 1834, Frankfurt an der Oder, Germany – Jan. 13, 1924, Heidelberg, Germany) German physicist who

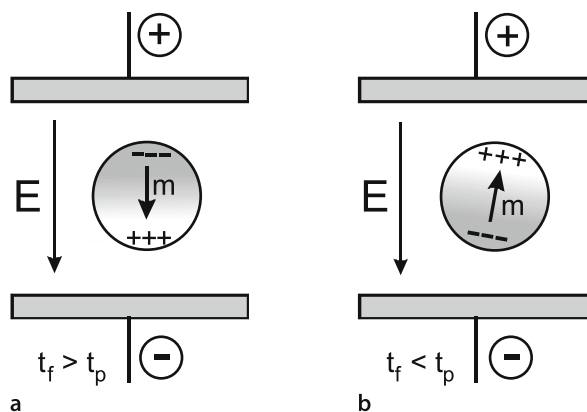
studied in Berlin, Königsberg, and Heidelberg. In 1865 he became Professor in Berlin, in 1872 in Würzburg, and in 1875 in Heidelberg [i]. Q. contributed to the fields of acoustics, optics, electricity, and magnetic susceptibility measurement. In relation to electrochemistry he is remembered for his studies of \rightarrow *electrokinetic effects*, particularly \rightarrow *Quincke rotation* [ii–vii].

Refs.: [i] König W (1924) *Naturwissenschaften* 12:621; [ii] Quincke G (1859) *Pogg Ann Phys* 107:1; [iii] Quincke G (1860) *Pogg Ann Phys* 110:38; [iv] Quincke G (1861) *Pogg Ann Phys* 113:513; [v] Quincke G (1869) *Pogg Ann Phys* 137:402; [vi] Quincke G (1871) *Pogg Ann Phys* 144:1; [vii] Quincke G (1871) *Pogg Ann Phys* 144:161

FS

Quincke rotation — An effect where a particle, suspended in a fluid and subjected to a strong \rightarrow *electrostatic field*, spontaneously rotates [i]. \rightarrow *Quincke rotation* is thus a particular example of \rightarrow *electrorotation*. The onset of Quincke rotation occurs at a threshold value of the electrostatic field, which depends on such factors as the fluid viscosity and the dielectric charge relaxation times of the particle and the fluid (\rightarrow *dielectric relaxation*). Spontaneous rotation will occur only for the case where the charge relaxation time of the particle exceeds that of the surrounding fluid. The charge relaxation time of a material is given by the ratio of its permittivity and electrical conductivity, and so in general spontaneous rotation can occur if the particle is more polarizable than the surrounding fluid.

A simple phenomenological explanation of Quincke rotation is given in the Figure below. In (a) the case is shown where the charge relaxation time of the particle is lower than that of the fluid ($t_f > t_p$). The electric dipole moment (\rightarrow *dipole moment*) induced in the particle, as a result of the build-up of surface free charges, has the same orientation as the applied electric field E [ii, iii]. If the particle is given a slight, random, rotational displacement the resulting electric torque will restore the particle's orientation. On the other hand, if we have the case shown in (b) where the charge relaxation time inequality is reversed ($t_f < t_p$), the induced dipole moment opposes the applied field. A small rotational displacement of the particle produces a torque which tends to further push the particle away from its original orientation, and full rotational motion can be initiated if the electrical torque overcomes the viscous drag imposed by the fluid. The axis of rotation will always be perpendicular to the applied field, but the sense of rotation (clockwise or anti-clockwise) is dictated by the random nature of the initial displacement [iv] and may even exhibit chaotic behavior [v].

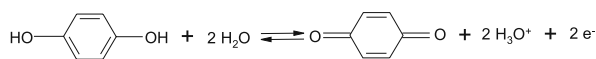


Quincke rotation — Figure

Refs.: [i] Quincke G (1896) *Ann Phys Chem* 59:417; [ii] Melcher JR (1974) *IEEE Trans Educ E-17*:100; [iii] Jones TB (1984) *IEEE Trans Ind Appl IA-20*:845; [iv] Turcu I (1987) *J Phys Math Gen* 20:3301; [v] Lamaire E, Lobry L (2002) *Physica A* 314:663

RP

Quinhydrone electrode — introduced by \rightarrow *Biilmann* in 1921 [i–vi] is a \rightarrow *redox electrode* for \rightarrow *pH* measurements [vii, viii]. Quinhydrone is a sparingly soluble charge-transfer complex consisting of quinone and hydroquinone in 1:1 ratio. At an inert electron conductor (e.g., \rightarrow *platinum* wire or modified \rightarrow *graphite*) the following electrochemical equilibrium is established:



Quinhydrone electrode — Figure

The \rightarrow *potential* of this \rightarrow *redox electrode* (platinum, quinhydrone solution) depends on the ratio quinone to hydroquinone and on the pH of the solution:

$$E = E_{\text{Q/Q}^{2-}}^{\ominus} + (RT/2F) \ln(a_{\text{Q}}/a_{\text{Red}}) - (RT/2F) \ln(K_{a1}K_{a2}) + (RT/2F) \ln(a_{\text{H}_3\text{O}^+}^2 + K_{a1}a_{\text{H}_3\text{O}^+} + K_{a1}K_{a2})$$

($E_{\text{Q/Q}^{2-}}^{\ominus}$ is the standard potential of the system quinone (Q) and the dianion of hydroquinone (Q^{2-}), a_{Red} is the sum of the activities of all hydroquinone forms: $a_{\text{Red}} = a_{\text{H}_2\text{Q}} + a_{\text{HQ}^-} + a_{\text{Q}^{2-}}$, $K_{a1} = 1.75 \times 10^{-10}$ and $K_{a2} = 4 \times 10^{-12}$ are the \rightarrow *acidity constants* of hydroquinone, R is the \rightarrow *gas constant*, T is the absolute temperature, F is the \rightarrow *Faraday constant*). The ratio of quinone concentration to the sum of concentrations of all hydroquinone

forms is unity because of the composition of quinhydrone; however, strong oxidants or reductants may change that ratio; also, in emulsions a preferential dissolution of the quinone in the oil droplets may affect that ratio in the aqueous phase. For $\text{pH} < 9.5$ (i.e., at $\text{pH} < \text{p}K_{\text{a1}}$) the potential of the quinhydrone electrode follows the equation: $E(25^\circ\text{C}) = E_c^{\ominus'}(\text{quinhydrone}) - 0.059\text{pH}$ ($E_c^{\ominus'}(\text{quinhydrone})$ is the \rightarrow formal potential of the quinhydrone electrode at $\text{pH} < 9.5$. At 25°C the formal potential is 0.6995 V vs. SHE [ix]). The classic quinhydrone electrode requires to spoil the solution with some quinhydrone powder and to measure the potential of a platinum electrode in that solution versus a reference electrode [viii]. Recently it has been shown that composite electrodes containing modified graphite and quinhydrone can perform as well as the classical electrodes without spoiling the solutions

and additionally offering various new applications [x–xii].

Refs.: [i] Biilmann E (1921) *Ann Chim* 15:109; [ii] Biilmann E, Lund H (1921) *Ann Chim* 16:321; [iii] Biilmann E, Krarup I (1924) *J Chem Soc* 125:1954; [iv] Biilmann E, Jensen AL (1927) *Bull Soc Chim* 41:147; [v] Biilmann E, Jensen AL (1927) *Bull Soc Chim* 41:151; [vi] Biilmann E (1927) *Bull Soc Chim* 41:213; [vii] Galster H (1991) *pH-measurement: fundamentals, methods, applications, instrumentation*. Wiley-VCH, Weinheim; [viii] Clark WM (1928) *The determination of hydrogen ions*. Williams and Wilkins, Baltimore; [ix] Janz GJ, Ives DJG (1961) *The quinhydrone electrode*. In: Ives DJG, Janz GJ (eds) *Reference electrodes*. Academic Press, New York, pp 270; [x] Kahlert H, Steinhardt T, Behnert J, Scholz F (2004) *Electroanalysis* 16:2058; [xi] Scholz F, Steinhardt T, Kahlert H, Pörksen JR, Behnert J (2005) *J Chem Educ* 82:782; [xii] Kahlert H, Pörksen JR, Behnert J, Scholz F (2005) *Anal Bioanal Chem* 382:1981

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