Pure Appl. Chem., Vol. 76, No. 6, pp. 1139–1160, 2004.
© 2004 IUPAC

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION*

PIEZOELECTRIC CHEMICAL SENSORS

(IUPAC Technical Report)

Prepared for publication by
RICHARD P. BUCK[1], ERNŐ LINDNER[2,‡], WLODZIMIERZ KUTNER[3], AND GYÖRGY INZELT[4]

[1]Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290, USA; [2]Department of Biomedical Engineering, The University of Memphis, Herff College of Engineering, Memphis, TN 38512, USA; [3]Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, PL-01 224 Warszawa, Poland; [4]Department of Physical Chemistry, Eötvös Loránd University, Budapest, Pázmány Péter sétány 1/A, H-1117, Hungary

*Membership of the Analytical Chemistry Division during the final preparation of this report (2002–2003) was as follows:

***President*:** D. Moore (USA); ***Titular Members*:** F. Ingman (Sweden); K. J. Powell (New Zealand); R. Lobinski (France); G. G. Gauglitz (Germany); V. P. Kolotov (Russia); K. Matsumoto (Japan); R. M. Smith (UK); Y. Umezawa (Japan); Y. Vlasov (Russia); ***Associate Members*:** A. Fajgelj (Slovenia); H. Gamsjäger (Austria); D. B. Hibbert (Australia); W. Kutner (Poland); K. Wang (China); ***National Representatives*:** E. A. G. Zagatto (Brazil); M.-L. Riekkola (Finland); H. Kim (Korea); A. Sanz-Medel (Spain); T. Ast (Yugoslavia).

[‡]Corresponding author

Republication or reproduction of this report or its storage and/or dissemination by electronic means is permitted without the need for formal IUPAC permission on condition that an acknowledgment, with full reference to the source, along with use of the copyright symbol ©, the name IUPAC, and the year of publication, are prominently visible. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

Piezoelectric chemical sensors

(IUPAC Technical Report)

Abstract: Piezoelectric chemical and electrochemical sensors are classified. Basic terms and definitions related to piezoelectric materials and sensing devices, electric transducers, and analytical measurements with piezoelectric chemical sensors are provided. In addition, the more essential response equations are presented.

CONTENTS

1. INTRODUCTION
2. MEASUREMENTS WITH CHEMICAL SENSORS: GENERAL RECOMMENDATIONS WITH RESPECT TO PIEZOELECTRIC SENSING DEVICES
   - 2.1 Basic terms and definitions
   - 2.2 Terms and definitions related to analytical measurements
   - 2.3 Basic terms and definitions related to piezoelectric sensing devices
3. BASIC TERMINOLOGY OF PIEZOELECTRIC MATERIALS
   - 3.1 Materials-related terms
   - 3.2 Transducer-related terms
4. CLASSIFICATION OF PIEZOELECTRIC CHEMICAL SENSORS
   - 4.1 Shear-wave or thickness-shear-mode acoustic wave sensors
   - 4.2 Surface wave, surface elastic wave, or surface acoustic wave (SAW) sensors
   - 4.3 Two-port sensors in thin-plate mode
5. FREQUENCY RESPONSE EQUATIONS FOR QUARTZ CRYSTAL MICROBALANCES
   - 5.1 Resonant frequency shift vs. added mass equations for low-mass loading in vacuum
   - 5.2 Resonant frequency shift vs. added mass equations for low-mass loading in gas atmosphere
   - 5.3 Resonant frequency shift vs. added mass equations for low-mass loading in solutions
6. CONCLUDING REMARKS
7. LIST OF SYMBOLS AND ACRONYMS
8. REFERENCES

1. INTRODUCTION

The rapid expansion of the field of piezoelectric sensing devices, within the larger area of chemical sensors and biosensors, requires improved classification and characterization of relevant concepts and principles. The present report addresses mostly the application of piezoelectric sensing devices in electroanalytical chemistry based on the quartz crystal microbalance (QCM) technology, and it has been coordinated with relevant documents of physics and electrical engineering [1–13].

The piezoelectric effect arises when pressure applied to a dielectric material deforms its crystal lattice which causes separation of centers of opposite charges giving rise to dipole moments of molecules. The piezoelectric properties of crystals can be predicted from their crystallographic structures. Piezoelectricity occurs in crystals with no symmetry centers. If electrical contacts (electrodes, electron-conducting metal films) are applied to the sides of a thin slab or rod of a piezoelectric material, current will flow through an external circuit when stress is applied to the crystal. When the stress is released, then the current flows in the opposite direction. The converse piezoelectric effect is experienced when alternating voltage is applied to the attached electrodes. Then, mechanical oscillations occur within the

crystal lattice. These oscillations are stable only at the natural resonant frequency of the crystal. At that frequency, impedance of the crystal to the exciting voltage is low. If the crystal is incorporated into the feedback loop of an oscillator circuit, it becomes the frequency-determining element of the circuit, as its quality factor, Q, is very high. The quality factor is inversely proportional to the resonance bandwidth, which makes the precise determination of the resonance frequency possible.

The crystal cut determines the mode of oscillations. For instance, the AT-cut quartz crystals, vibrating in a thickness shear mode, are used for the majority of piezoelectric work in analytical chemistry in liquids and gas phase. The oscillation frequency decreases when the crystal is loaded with mass. The resonant frequency depends on the viscoelastic properties of the crystal and that of the adjacent phase, as determined by the coupling boundary conditions. Selective surface films can deliberately be applied over the oscillator, such as the quartz crystal, in order to enhance selectivity, i.e., the specific mass response caused by adsorption or absorption of an analyte.

The piezoelectric crystals patterned with electrodes (electronic surface films) on their opposite sides are often referred to as piezoelectric vibrators. A piezoelectric vibrator in combination with the oscillator circuit is called a piezoelectric oscillator. A piezoelectric chemical sensor is a piezoelectric oscillator that responds to changes in the chemical composition of its environment with changes of the resonant frequency, or wave speed. Piezoelectric chemical sensors are generally selective surface film-coated piezoelectric crystal oscillators. The surface film coating boosts selectivity through selective adsorption or absorption. Piezoelectric biosensors apply layers with biocatalytic or bioaffinity functions as selective surface layers over the oscillator surface.

2. MEASUREMENTS WITH CHEMICAL SENSORS: GENERAL RECOMMENDATIONS WITH RESPECT TO PIEZOELECTRIC SENSING DEVICES

2.1 Basic terms and definitions

2.1.1 Activity, activity coefficient, concentration (liquid and solid phases), pressure (gas phase)

Refer to *Manual of Symbols and Terminology for Physicochemical Quantities and Units* (Butterworths, London, 1973).

2.1.2 Measured variables and output signals

Variable values, measured with piezoelectric sensing devices, are usually digital quantities. Resonant frequency (fundamental, f_0, or harmonic, f_n), resonant frequency change (Δf), phase angle (φ), acoustic wave speed (v), acoustic wave speed change (Δv), or relative changes of these quantities with respect to some reference values ($\Delta f/f$ or $\Delta v/v$) are measured depending on the type of a piezoelectric sensing device used. A frequency counter or a phase matching circuit is often used for that purpose.

2.1.3 Intrinsic calibration plot

This is a plot of the measured variable (see Section 2.1.2), vs. the apparent mass, M, of the analyte. Generally, the plot is monotonic. The slope of the calibration plot is predicted theoretically from the Sauerbrey equation (see Section 5.1). A theoretical (linear with constant slope) calibration plot is expected in the low-mass loaded, acoustically thin (rigid) film regime when the material adsorbed or deposited on the surface is uniformly distributed (see Section 2.2.1). Thin, rigid films have very small acoustic phase shift, i.e., they are considered "acoustically thin" films. In "acoustically thin" films, the shear deformation is negligible. The film behaves as an ideal mass layer that moves synchronously with the resonator surface. However, when the film is thicker or more compliant (e.g., a viscoelastic polymer coating), the displacement applied by a piezoelectric resonator (quartz) can undergo a significant phase shift in propagating across the layer. As the acoustic phase shift becomes significant, so do the interference effects. When the phase shift approaches $\pi/2$ rad, the interference becomes constructive

and there are sharp variations in the resonant frequency [14,15]. This condition is called film resonance [16,17].

2.1.4 Extrinsic calibration plot

This is a plot of the measured variable (see Section 2.1.2), vs. concentration (or activity) of the analyte in the ambient (external) phase. This plot depends both on the adsorption isotherm (or extraction properties of a selective surface film; see Section 2.3.3) and on the intrinsic calibration plot (see Section 2.1.3).

2.2 Terms and definitions related to analytical measurements

2.2.1 Sensitivity

In case of low-mass loading and absence of non-mass-related frequency changes, the intrinsic calibration plot is linear, $\Delta f = -C_f(\Delta M/A)$. The slope of the plot, i.e., the measured frequency change per unit mass change, $\Delta f/\Delta M$, represents the integral mass sensitivity, C_f, typically, expressed in Hz cm^2 ng^{-1}. The differential mass sensitivity, $c_f = df/dm$, describes the frequency change due to a change of local mass, m, on acoustically active area, A, of the quartz crystal (see also Section 3.1.5). The differential mass sensitivity varies across this area. The integral mass sensitivity is defined by the integral of the differential mass sensitivity over the acoustically active area [2,3,18–21]. For the typically used round shape, thickness shear wave piezoelectric oscillators, C_f is expressed as:

$$C_f = 2\pi \int_0^{r_e} c_f(r) r \mathrm{d}r \quad (1a)$$

C_f for rectangular shape oscillator is expressed as:

$$C_f = \iint c_f(x, y) \mathrm{d}x \, \mathrm{d}y \quad (1b)$$

Expressions for other geometrical shapes can be found in [20].

A calibration plot is expected to be linear if the analyte coating is uniformly distributed over the acoustically active area at low values of mass loading, typically lower than 2 % of the quartz crystal mass and is typically lower than 20 μg/cm^2.

2.2.2 Limits of detection and linear concentration range

A typical calibration plot is shown in Fig. 1. By analogy to other metrological definitions [22], the *lower detection limit* is defined as the concentration (or activity) of the analyte for which the measured signal (e.g., frequency or frequency change) deviates from the average signal value in Region I by a multiple of the standard deviation of a single measurement of the limiting low concentration (or activity) in Region I. The selected multiple value depends on the adopted statistical significance level.

Certain other metrological simplifications used in other areas of analytical chemistry cannot be recommended here because, generally, the functional relation of the measured variable and concentration is unknown, and if it is known, then it is not necessarily linear. However, extrapolations of linearized, mid-range responses on a linear concentration scale (Region II in Fig. 1) may be possible. The latter intersection defines the *lower detection limit*. Similarly, an *upper detection limit* is defined for devices that become insensitive to high concentrations (or activities). The upper detection limit is the concentration (or activity) of the analyte for which the measured signal deviates from the limiting high-concentration (or activity) response by a multiple of the standard deviation of a single measurement in the limiting high-concentration range (Region III in Fig. 1). Again, the selected multiple value depends on the adopted statistical significance level. Accordingly, the linear concentration range is defined as the concentration range between the lower and upper detection limits.

Since many factors affect the detection limits, the experimental conditions used, such as composition of the gas, vapor, or solution analyzed as well as composition of the selective surface film, its his-

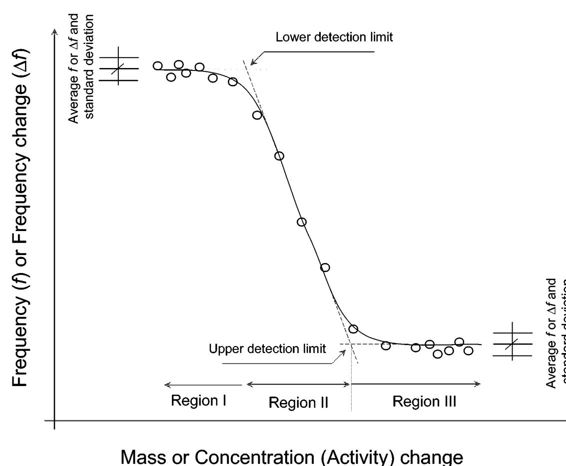

Fig. 1 Calibration plot of a quartz crystal microbalance (QCM) or electrochemical quartz crystal microbalance (EQCM).

tory and preconditioning should be reported. Moreover, parameters like flow rate, stirring rate, temperature, pressure, etc. should be given.

2.2.3 Drift, standard deviation, hysteresis, and reproducibility: Terms related to short- and long-term stability

2.2.3.1 Drift

Drift is a slow, nonrandom change of the measured signal of a piezoelectric sensing device under unaltered experimental conditions. The drift is determined by fitting a linear function to the data set collected in a given period of time. The slope of the line of the measured variable vs. time is called drift. The random deviation of the measured variable around the fitted line defines the *standard deviation* of the measured variable.

2.2.3.2 Hysteresis

Hysteresis is defined by the failure of the measured signal that has been altered through changes in the ambient conditions (e.g., concentration) to return to its original value when the alteration is removed. Usually, hysteresis has kinetic origins. Therefore, reversible values of the measured signals are expected if sufficient time is allowed for the system to return to its initial condition.

2.2.3.3 Repeatability

Repeatability of the measured signal with the piezoelectric chemical sensor is determined similarly to other sensing devices [23] in repeated experiments under the same ambient conditions (e.g., concentration), but following diverse preceding ambient conditions. The standard deviation of the measured signal (e.g., frequency) in these repeated experiments is called *repeatability*. If hysteresis of the piezoelectric device is distinct, then the repeatability will be poor.

Repeatability is defined by the International Organization for Standardization (ISO) as the precision under repeatability conditions, i.e., conditions where independent test results are obtained with the same method on identical items in the same laboratory by the same operator using the same equipment within short intervals of time (ISO 3534-1) [24]. Repeatability of results of measurements is defined by IUPAC as the closeness of the agreement between the results of successive measurement of the same measurand and carried out under the same conditions of measurement [22].

2.2.3.4 Reproducibility

Reproducibility of the signal measured with the piezoelectric chemical sensor is determined in repeated experiments under the same conditions in different laboratories. Reproducibility is defined by the International Organization for Standardization (ISO) as the precision under reproducibility conditions, i.e., conditions where test results are obtained with the same method on identical items in different laboratories by different operators using different equipment (ISO 3534-1) [24].

2.2.4 Interfering substance and selectivity

2.2.4.1 Interfering substance

Interfering substance is any substance, other than analyte, whose presence in the sample affects the measured signal of a *piezoelectric sensing device*. Interfering substances fall into two categories, i.e., *"device" interfering substances* and *"method" interfering substances*.

"Device" interfering substances induce a device response (measured signal or measured signal change) similar to that generated by the analyte. The presence of interfering substances falling into this category generally results in an apparent increase in the concentration (or activity) of the analytes. These interfering substances interact with the selective surface film (see Section 2.3.3) in a similar way as the analytes. At high solution concentrations, even highly discriminated substances may induce "device" interference as they are absorbed into the selective surface films in appreciable concentrations by ion exchange, extraction, etc.

"Method" interfering substances interact with the analyte generating *"method" interference*. The presence of interfering substances falling into this category decreases the apparent activity (or concentrations) of the analytes.

2.2.4.2 Selectivity

The *selectivity* of a piezoelectric device refers to the degree to which it is free from interference by other species contained in the sample matrix. Selectivity is a measure of the relative contribution of the measurand to the changes in the measured variables (e.g., to the mass increase of a selective surface film), compared to the contributions of similar substances. Piezoelectric devices are not substance selective. Typically, selectivity is induced by both a selective surface film and the chemical properties of analytes. Selectivity can be improved by the deconvolution of the total change of the measured signal into contributions of individual substances via concentration and time dependencies under thermodynamically and kinetically controlled conditions. In fact, an apparent mass increase may be caused by processes other than the mass increase of the surface film due to uptake of the analyte.

2.2.5 Response time

2.2.5.1 Short- and long-time constants

The *short-time constant* is the shortest time required to establish a measured apparent mass point. This time is typically about 2.5 cycles of the mass indicating frequency, being roughly of the order of $1/f_0$. In practice, the time needed to achieve readings of the frequency counter stable within 0.1 Hz, is determined by the counter.

The *long-time constant* is determined by the time elapsed after a change of external concentration (or activity) of the analyte and the establishment of a new stable reading of the frequency counter. The long-time constant is controlled by the rate of mass transport to the oscillator surface and/or into the film deposited onto it. If the transport rate is controlled by diffusion then, generally, the long-time constant is in the order of d^2/D where d is a diffusion boundary layer or film thickness and D is the apparent diffusion coefficient. In polymeric selective surface films, "polymer reconfiguration", i.e., mass reorganization, may occur over an extremely large time span, i.e., from milliseconds to months. In such cases, the long-time constant can be viewed as the time required for establishing coupling between the quartz crystal and the adjacent film. Its magnitude is of the order of $Q/\pi f_0$.

2.2.5.2 Practical response time

Practical response time is defined as the time which elapses between the instant at which a piezoelectric sensor is brought into contact with a sample (solution or gas) or at which the concentration of the substance of interest in the sample is changed and the first instant at which the slope of the time dependence of the measured variable (e.g., $\Delta f/\Delta t$) becomes equal to a preliminary determined threshold value, characteristic for the piezoelectric crystal. The selection of the threshold value determines the practical response time and influences the precision and accuracy of the determination. This definition invokes ideal and desirable, span-independent conditions.

> *Comment:* The use of the practical response time, defined as the time elapsing between the instant at which the environment of the piezoelectric sensor is changed and the first instant at which the measured signal of the piezoelectric sensor becomes equal to a fixed value (t^*) or reaches a given fraction of the total expected change of the measured variable (e.g., 95 %, t_{95}), requires initial knowledge of a new steady-state value which, however, may not be available. Nevertheless, specific values of $\Delta f/\Delta t$ can be related to t_{95} or t^* through mathematical models, provided that long-term frequency or phase-determining processes have been identified. However, it seems doubtful that relationships fully describing practical response times can be derived, in view of different functional dependencies that characterize responses of the piezoelectric sensors, both at short- and long-time domains.

2.3 Basic terms and definitions related to piezoelectric sensing devices

2.3.1 Piezoelectric sensor

A piezoelectric sensor is a device that responds to changes occurring in its environment with changes of the resonant (fundamental or harmonic) frequency, or wave (phase) speed. Bulk and surface acoustic wave piezoelectric sensors are distinguished depending on the way of the wave propagation. The resonant frequency primarily depends on thickness of the piezoelectric crystal and the attached layer, on the viscoelastic properties of the crystal and that of the adjacent phase, as determined by the coupling boundary conditions. Mass loading, ambient viscosity, and electric permittivity, compression or extension stresses, local electric fields, charge, film conductivity, and surface tension affect the coupling conditions.

2.3.2 Electronic surface film

Electronic surface films are electron-conducting coatings (partial or complete) over the faces of piezoelectric crystals. They are used to stimulate oscillations, measure resonance parameters, and/or provide a surface layer for adsorption, absorption and chemical or electrochemical reactions of substances of interest. One or several purposes may be served simultaneously. Typical coatings are the 100-nm-thick Pt, Ag, or Au films. An underlayer used to increase the film adhesion (e.g., a 20-nm-thick Cr or Ti film) and its preparation procedure should be specified along with the design of the electronic surface film (continuous rather than interdigitated, IDT, see Section 4.2). The mode of oscillation and the type of the sensor is determined by the nature of the electronic surface film or films. The electronic surface film is often a part of an electrochemical cell. In that case, a reference electrode and, most often, an auxiliary electrode are required to complete the circuit (see Section 3.2.2).

2.3.3 Selective surface film or coating

Selective surface films and/or coatings are thin layers of material attached to one or both sides of the crystal, or one region (channel) of an oscillator to provide selectivity through adsorption or absorption of substances of interest from a complex sample matrix. Absorption usually involves partitioning, extraction, or ion exchange. General guidelines used in chromatography apply in choosing materials for selective surface films. The films of adsorbed or absorbed substances may be conductive or nonconductive. In case of conducting films, the measured variables are more attenuated and they contribute to

frequency shifts that reciprocally correspond to the space charge relaxation times. The effect of charge contributes to the resistance and capacitance values in the extended impedance model (see Section 3.2.3). The surface coverage of molecules in the surface film should be specified.

2.3.4 Quartz crystal microbalance (QCM)

Quartz crystal microbalance (QCM) 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. Initially, QCM has been used as a mass sensor in the vacuum and gas-phase experiments. However, the response of QCM is also extremely sensitive to mass and viscoelastic changes at the solid-solution interface. In order to boost selectivity, selective surface films are applied. In contrast to the inherent oscillator material, such as quartz, these films may suffer, however, changes in their elastic constants by virtue of absorption of ambient substances (e.g., parameters of a deposited palladium surface film change after absorption of hydrogen).

> *Comment*: In view of a broad interest in selective surface films and the determination of the mass and mass changes of these films, generally, the "apparent" mass or "apparent" mass changes are insufficient for documenting experimental results. Also, other parameters (see Sections 2.3.1–2.3.3) should be reported.

2.3.5 Electrochemical piezoelectric sensor assembly

An electrochemical piezoelectric sensor assembly is a combination of the piezoelectric sensor and an electrochemical cell containing the sample electrolyte solution, the reference electrode, as well as other electrodes as required, driving oscillator, amplifiers, and readout unit(s). In most electrochemical experiments, the piezoelectric crystal (e.g., quartz crystal) with the attached electronic and selective surface films (piezoelectric sensor) is clamped between two O-rings. Generally, only one crystal face and one oscillator electrode, which serves both as a part of the oscillator circuit and as the working (indicator) electrode in the electrochemical cell, are in contact with the sample solution. The ac excitation voltage can be easily separated electronically from the electrochemical dc potential. The assembly may have its special name, such as electrochemical quartz crystal microbalance (EQCM). Most often, AT-cut (thickness shear mode) quartz crystals are used. Various examples of applications of EQCM in electrochemistry and electroanalytical chemistry, particularly in sensor applications, are reported in numerous review articles [5,7–13,18,25,26].

3. BASIC TERMINOLOGY OF PIEZOELECTRIC MATERIALS

3.1 Materials-related terms

3.1.1 Piezoelectricity

Piezoelectricity is a property of certain classes of material including natural crystals of quartz. In piezoelectric materials, mechanical strain is generated by application of an electric field or, conversely, an electrical polarization is generated by application of mechanical stress.

3.1.2 Piezoelectric materials

Piezoelectric materials are found in 20 out of 21 crystal space groups with no symmetry centers. Piezoelectric materials may be organic or inorganic solids. They may contain intrinsic electric fields, especially if unequally charged substances are present in their structures. Piezoelectric materials should be specified, although α-quartz is most commonly used for presently constructed sensors. Ferroelectrics are materials, initially isotropic, that are subsequently polarized above their Curie temperature by application of a strong electric field to induce anisotropy (poling) and strong piezoelectric properties. Prepolarized crystals have a preferred direction, the poling direction, called "z".

3.1.3 Transducer-oscillator material configurations

Among the many piezoelectric materials, α-quartz is most commonly studied and used as piezoelectric oscillator, because desired features can be achieved through various cuts of its native crystals [2,3,27–29]:

(i) small temperature dependence of the resonant frequency for room temperature operation or for low temperature operation, and
(ii) small dependence of the resonant frequency on built-in stress from applied contacts or surface films.

A typical "thick" 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. Most commonly used plate oscillators are cut to exhibit longitudinal (thickness expander) modes or thickness shear modes. For quartz, cuts across the *X*-axis, *Y*-axis, or so-called rotated Y-cuts are used. Various designations of cuts appear in the literature: X-cut (thickness expander), AC, AT (thickness shear), DT (plate shear), BT, ST (horizontal shear), SC (stress compensated), etc. Symbol T specifies a cut with minimal temperature dependence of the resonant frequency. Within these general cuts, there are subgroups (e.g., planar, plano-convex, and others). These cuts should be specified, as their properties are very important for the piezoelectric sensor performance. Electronic surface films and electrical contacts are usually accomplished by vacuum deposition, sputtering or electroplating of metal films on both crystal faces [3,8].

3.1.4 Modes of oscillation

The typical formats of piezoelectric devices and the corresponding particle motions and crystal deformations are summarized in Fig. 2. A rectangular solid bar may exhibit three types of vibrations, i.e., longitudinal (bulk extension and compression), lateral (flextural and shear), and torsion along each three axes. Vibrations of a rectangular sheet (with two large dimensions and one small dimension) are of the same type, but their coupling is characteristic. The characteristic sheet vibrations are afforded by placing the electrical stimulation constant on opposite faces or on the same face. Most importantly:

(i) *Shear vibrations* are generated if one large crystal face moves parallel with respect to the underlying planes as, e.g., in QCMs with AT-cut crystals. This crystal wafer is prepared by cutting the quartz at approximately 35.17° from its *Z*-axis. If ac voltage is applied across the crystal, by means of two excitation electrodes deposited on its opposite faces, then shear vibration is generated in the *X*-axis parallel to the electric field, i.e., one face displacing parallel to the other without thickness change.
(ii) *Bulk expander vibrations* change the crystal dimensions in one direction.
(iii) *Surface elastic waves* propagate along a crystal surface by moving surface particles both in and out of the plane (normal to the surface) and along the surface (in the plane). These waves were analyzed by Lord Rayleigh and are characteristic of many materials, not necessarily piezoelectric ones. The crystal is affected to the depth of only a few wavelengths, i.e., about 100 µm for the typical wavelength of about 30 µm. Then, particles are displaced by a few tenths of nanometer.

    Bulk and surface waves propagating through semi-infinite media are usually nondispersive, i.e., wave speed is independent of frequency. However, the presence of interfaces, especially in layered structures, and the use of thin plate oscillators of one dimension comparable with the wavelength, introduces dispersion.
(iv) *Complex bulk waves*, such as *horizontal shear waves*, are often dispersive in oscillators of thickness comparable to the wavelength. There are various acoustic plate modes. They are called by various names: Lamb, generalized Lamb, Love, Sezawa and others. Usually, a thin transducer is layered with a second material whose properties change with the ambient. Figure 2 illustrates some of these oscillators in relation to devices built from them.

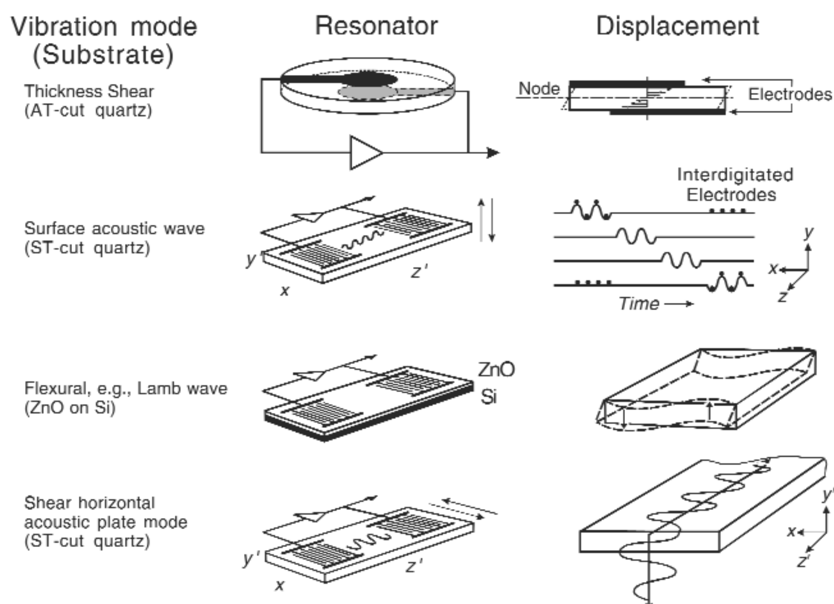

Fig. 2 Typical formats of piezoelectric devices and the corresponding particle motions/deformations. For the surface acoustic wave and shear horizontal mode, arrows indicate the direction of particle motion. (Adapted from [6].)

3.1.5 Clamps and edges

There are three regions of a quartz crystal oscillator:

(i) the outer edge of the crystal that may (or may not) be clamped to a rigid support;
(ii) the central portion of the crystal lying between the electronic surface films (oscillator electrodes); and
(iii) the remaining region between the electronic surface film region and the edges.

The central part of the crystal between the oscillator electrodes is driven into oscillations of the largest amplitude, i.e., the differential mass sensitivity reaches maximum at the center of the plate. The amplitudes of the oscillations decrease with the increase of the distance from the near-resonant regions and certain frequencies are severely damped. Finally, at the edges, the oscillations are not permitted. Usually, the sizes of the two excitation electrodes are slightly different in order to decrease the capacitance effect. The smaller electrode determines the piezoelectrically active area.

3.2 Transducer-related terms

3.2.1 Narrow- and broad-band piezoelectric sensors

Applications of piezoelectric sensors have focused on narrow-band transducers, e.g., crystalline oscillators, notably quartz, because of their low electromechanical coupling factors and high mechanical Q values, i.e., low mechanical energy losses. For piezoelectric sensors, materials are chosen whose intrinsic energy losses are small, unless mechanically coupled to another layer of a material whose properties are expected to dominate the change in the oscillator frequency. For the *LRC* oscillator circuits, the Q factor is the measure of freedom from energy loss or effectiveness of energy storage, as measured by the number of cycles, N, per decay time: $Q = \pi N$ or $Q = R(C/L)^{1/2} = (1/2k_d)$. The Q factor is inversely proportional to the damping factor, k_d, [$k_d = (1/2R)(L/C)^{1/2}$] and reflects the frequency distribution around the resonant frequency of the oscillator. For quartz, this loss is insignificant. Quartz

shows low attenuation, i.e., high Q value and low electromechanical coupling. That is, Q is in the range 10^6 to 10^8 in air or vacuum and 1000 to 3000 in contact with a liquid phase. Narrow-band resonators feature sharp resonant frequency values with a few percent bandwidth. Precise measurement of the frequency, attenuation, and phase speed values is possible. Ceramic piezoelectric materials are most often found in broad-band, non-sensor applications.

3.2.2 Impedance characteristics of quartz oscillator circuits

3.2.2.1 Impedance analog

A quartz crystal, coated with electronic surface film and connected to an oscillator circuit (piezoelectric oscillator), such as that presented in Fig. 2, is driven into oscillations by an applied ac voltage. Of course, the "resonant" frequency can be experimentally determined by noting a large Q value of the crystal and corresponding low energy loss. This characteristic response suggests the properties of the low-resistive-loss "tank" circuit, i.e., a series *LRC* circuit. It further suggests that there must be similarities between other oscillating systems that obey second-order linear equations with constant coefficients. Indeed, the quartz oscillator circuit is analogous to a weight on a spring, a pendulum, and a plucked string. The latter is particularly appropriate, as illustrated in Fig. 3. All of these masses that can move, convert energy from stored (potential) to motion (kinetic), and have some small damping (energy loss). In addition, charges move and opposite charges separate in space for piezoelectric crystals. These factors lead to the electrical equivalent shown in Fig. 4.

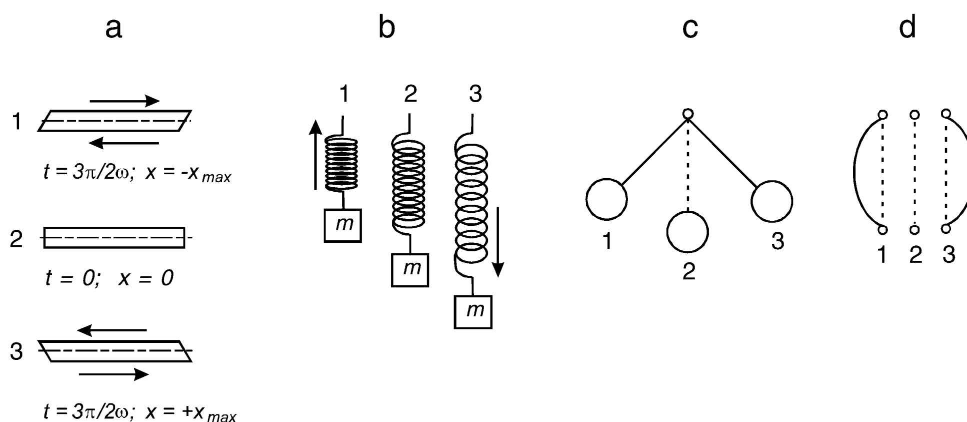

Fig. 3 Schemes of oscillator systems: (a) shear mode AT-cut quartz crystal, (b) mass on a spring, (c) swinging pendulum, (d) a stressed string. The numbered positions correspond to equivalent states of oscillation in each system. (Adapted from [7].)

3.2.2.2 Equivalent circuit of quartz crystal and quartz crystal with electronic surface films

A normal series "tank" circuit mentioned above, without the parallel capacitor, is shown in Fig. 4. The electronic surface films add their own parallel "geometric" capacitance. The correspondence between mechanical and electrical circuit parameters can be written by comparing the coefficients in the equations of motion [7,30–32]. The impedance of the "tank" circuit is simply a circle in the complex impedance plane plot of negative imaginary impedance, $-Z_{\mathrm{Im}}$, as ordinate, and real impedance, Z_{Re}, as abscissa with zero at the intersection. The frequency of the applied perturbation is parametric variable running counterclockwise around the plot. The impedance is zero both for zero and for infinite frequency. The second zero value of Z_{Im} corresponds to the resonant frequency.

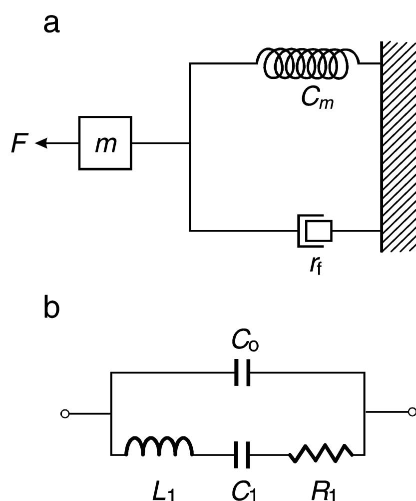

Fig. 4 Electroacoustical system (a) mechanical model and (b) its corresponding electrical equivalent. (Adapted from [7].)

The corresponding admittance plane plot is a closely related circle when Y_{Im} is plotted against Y_{Re}. However, the frequency variable runs clockwise around the semicircle. The admittance planes are plotted for circuits with the "tank" alone as well as with "tank" and a parallel capacitor, in Figs. 5a and 5b, respectively. Note that two resonant frequency values are possible, i.e., f_p and f_s, as it is discussed in Section 3.2.4 (eqs. 3 and 4).

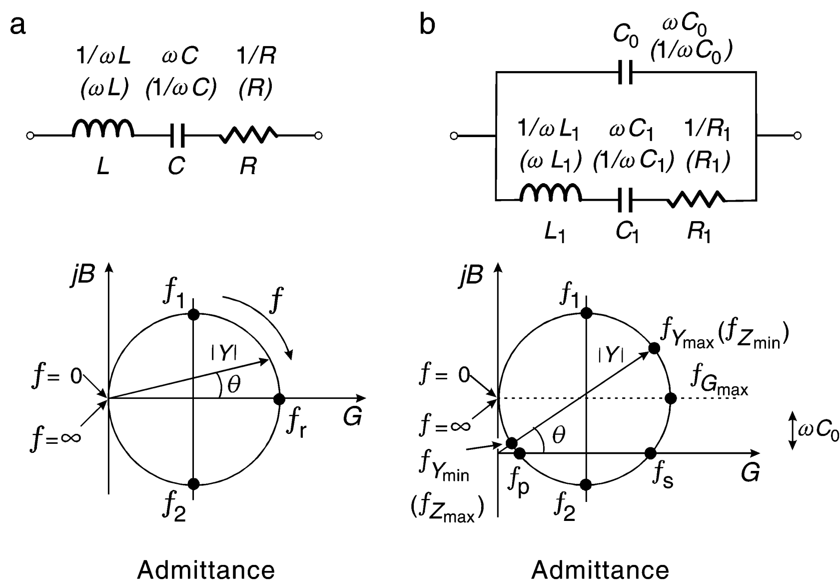

Fig. 5 Admittance locus for (a) series *LCR* circuit and (b) the equivalent circuit of a quartz oscillator. The admittance (impedance) of each component is also shown. (Adapted from [7].)

3.2.3 Selective surface films of a transmission line character

An oscillator coated with a thick film may approach infinite transmission line behavior. A thin film may be equivalent to finite transmission lines. These conjectures are based on extension of the wave propagation theory for two contacting phases with different densities and shear moduli to a series of phases.

Each phase should contribute different values of resistance, capacitance, inductance, and shunt resistance, and capacitance per unit length. Figure 6 shows a simple equivalent circuit (without shunts) that is deduced from impedance measurements. The various *R*, *L*, and *C* quantities correspond to quartz (subscript q for the quartz), electrolyte (subscript L for the liquid) and selective surface film (subscript f for the film).

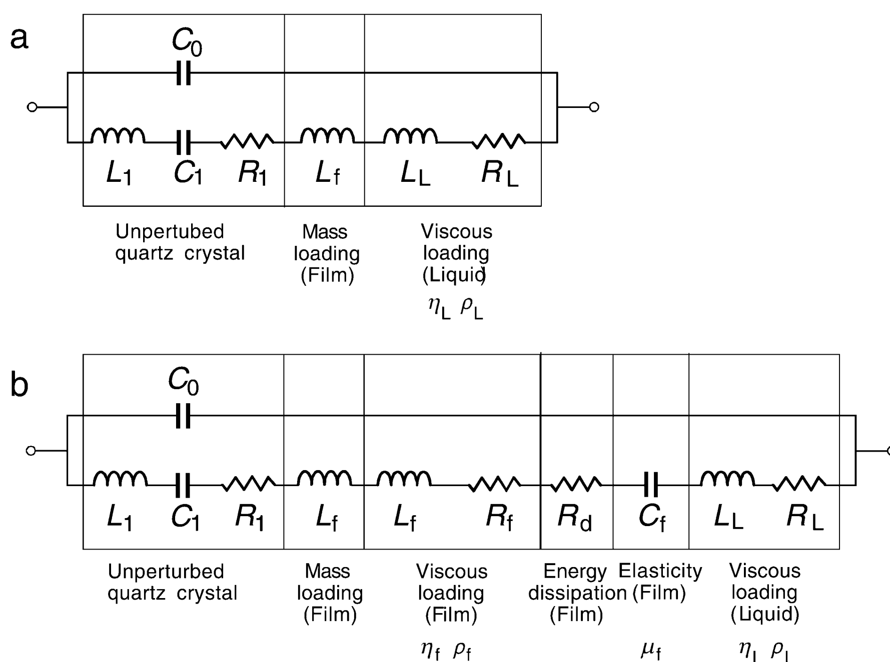

Fig. 6 (a) The general equivalent circuit representation for an AT-cut quartz resonator with contributions from the mass of a rigid film and the viscosity and density of a liquid in contact with one face of the quartz oscillator. (b) One possible equivalent circuit representation for an AT-cut quartz resonator with a viscoelastic selective surface film immersed in a liquid. (Adapted from [7].)

The composite oscillator should not lose much energy to the measuring circuit if sensors are to be used to monitor or determine mechanical properties of a specimen. That is, the electrical measuring circuit should be deliberately mismatched so that the circuit *Q* value is much larger than the resonator specimen *Q* value.

Bulk and surface waves propagating through semi-infinite media are usually nondispersive, i.e., wave speed is independent of frequency. However, the presence of interfaces, especially in layered structures, and the use of thin plate oscillators of one dimension comparable with the wavelength introduces dispersion.

3.2.4 Equivalent electrical constants and symbols

Oscillations of the piezoelectric crystal, induced by an external electric circuit, correspond to electrical circuit elements, such as capacitance, *C*, inductance, *L*, and resistance, *R*, in series, as shown in Figs. 4a and 4b. The capacitance can be viewed as connected with symmetric vibrations that separate charge, although it is the net uncompensated charges on the surface that are important. The inductance may be connected with vibrations that move net (uncompensated) charge in space while the resistance is related to the energy loss mainly through external phases and surface films.

Since the crystal is mounted and coated with electronic surface films, there may be stray resistance and capacitance to ground from wires as well as geometric capacitance of the crystal itself, i.e., a

dielectric contained between electronic surface films, C_0. The latter is the important parallel quantity and along with other quantities has "clamped" values. The C_1, L_1, and R_1 quantities are related to mechanical properties, i.e., C_1 to elastic constants, L_1 to system mass including the electronic surface films and selective surface film, and R_1 to external (acoustic) load. There are two resonant frequencies, i.e., f_s corresponding to the series combination of C_1, L_1, and R_1 and f_p for the whole parallel circuit arrangement.

Whereas the resonant frequency of an ideal loss-free quartz crystal would be:

$$f_r = 1/[2\pi(LC)^{1/2}] \tag{2}$$

the modified resonance occurs at:

$$f_p = (1/2\pi)[1/L_1C_1+1/L_1C_0]^{1/2} \tag{3}$$

and

$$f_s = (1/2\pi)[1/L_1C_1]^{1/2} \tag{4}$$

3.2.5 Further definitions

A number of publications cover the relevant principles and definitions [1–5,7–11].

4. CLASSIFICATION OF PIEZOELECTRIC CHEMICAL SENSORS

Device assemblies and the included transducer should be described, first, in terms of the mode of oscillation. The common categories are designated by capital letters. The secondary description refers to the transduction method, which may involve continuous, interdigitated, or wedge electronic surface films, optical contacts rather than electrical, and indirect contacts through space. The position of the electronic surface films, which may be placed on the same or opposite faces of the oscillator, and the position of a selective surface film with respect to the electronic surface film, should be specified. Also, the contacting external phases, i.e., gases or liquids, and the symmetry of their placement against the oscillator crystal should be defined.

4.1 Shear-wave or thickness-shear-mode acoustic wave sensors

These are single-port sensors, called quartz crystal microbalances (QCMs) if the resonators are made from quartz (see Section 2.3.4). Usually, a cylindrical, about 100 µm thick, AT-cut quartz crystal disk is used with electronic surface films patterned on its opposite sides. The pattern is roughly circular and centered with lead or pad contacts running to the disk edge. The electronic surface film area is usually a fraction, about 0.1, of the quartz surface area. The crystals operate at relatively low frequency, typically 3 to 15 MHz. There are three types of QCMs:

4.1.1 Sensor with both oscillator sides contacting ambient gas

4.1.2 Sensor with one oscillator side contacting a solution and the other side contacting ambient gas

4.1.3 Sensor with both oscillator sides contacting a solution

4.2 Surface wave, surface elastic wave, or surface acoustic wave (SAW) sensors

Surface acoustic wave sensors are two-port devices. Two sets of IDT electrodes, i.e., "finger" patterned electronic surface films, are deposited on the "top" side of a piezoelectric crystal as transmitter and receiver. This surface, patterned with the electronic surface film, is exposed to ambient gas or solution or is coated with a selective surface film. Radiowave frequencies applied to the transmitter electrodes pro-

duce a synchronous mechanical stress in the crystal which, in turn, produces an acoustic wave with both longitudinal and vertical shear components. This surface wave propagates along the surface of the piezoelectric crystal and is received at the second set of electrodes, where the mechanical vibrations are translated to a voltage. Surface acoustic wave sensors generally operate at higher frequencies than QCMs.

4.2.1 Single evenly spaced IDT sensors

The spacing of the "fingers" is repeated at a distance, l, in a single evenly spaced IDT sensor. It launches waves of wavelength, λ, in both directions. Close to the resonance frequency or to an odd harmonic of it, the amplitude approaches maximum.

4.2.2 Single oddly spaced IDT sensors

Single odd spaced IDT sensors launch broad-band waves.

4.2.3 Filter or delay line

Filter or delay lines use two sets of evenly spaced fingers. One of them serves to launch and the other to receive diminished amplitude waves, and/or to determine the delay time by using pulses.

4.2.4 Surface wave resonator

Surface wave resonators use two sets of evenly spaced fingers. They are connected together and resonate at frequencies determined by the spacing between the launching and receiving fingers.

4.2.5 Surface wave resonator with high Q

Surface wave resonators with high Q use two sets of evenly spaced fingers. They are spaced to match to the natural resonant frequency of the quartz.

4.2.6 Two-channel sensors

In two-channel sensors, one channel is coated with a selective surface film. Differences are measured in the resonant frequency and delay time values of two channels.

4.2.7 Wedge bulk wave transducer

A wedge bulk wave transducer couples into the surface wave and provides an alternate method for generating surface waves without the IDT pattern.

4.3 Two-port sensors in thin-plate mode

4.3.1 Acoustic plate (bulk wave) mode

These sensors often operate at higher frequencies than QCMs and are thus more sensitive to apparent mass changes. The bulk wave resonator includes IDT patterns launching and receiving electronic surface films to generate and detect shear horizontal plate modes. The IDT films are located on the face of the thin quartz plate opposite to the face exposed to solution or coated with a gas-sensitive selective surface film. Plates are typically 0.5 mm thick, and 25 to 75 fingers are patterned.

4.3.2 Acoustic plate (Lamb wave) mode

In acoustic plate devices, the thickness of the oscillator is infinitely larger than the wavelength of the propagating wave λ. When the thickness of the SAW oscillator is reduced, so that it becomes comparable to λ, the whole plate becomes involved in the periodic motion and a symmetric and antisymmetric Lamb wave is created. This happens in plate-mode oscillators with thicknesses of a few micrometers.

5. FREQUENCY RESPONSE EQUATIONS FOR QUARTZ CRYSTAL MICROBALANCES

Symbols, as well as dimensional, mechanical, and electrical constants, are listed in Section 8. Subscripts q, f, g, and L refer to quartz, surface film and ambient gas or liquid, respectively.

5.1 Resonant frequency shift vs. added mass equations for low-mass loading in vacuum

5.1.1 Sauerbrey limiting equation

The Sauerbrey limiting equation for a quartz crystal oscillator with uniform (constant density and thickness) surface film covering the acoustically active area of the whole crystal [1–5,7–11]:

$$\frac{\Delta f}{f_0} = \frac{f_c - f_0}{f_0} = -\frac{\Delta t_f}{t_q} = -\frac{\Delta M}{A \rho_q t_q} \tag{5}$$

$$\Delta f = -\frac{2 f_0^2 \Delta M}{A\left(\rho_q \mu_q\right)^{1/2}} = -C_f \Delta m \tag{6}$$

follows from

$$f_0 = \frac{v_q}{2 t_q} \tag{7}$$

and

$$v_q = \left(\frac{\mu_q}{\rho_q}\right)^{1/2} \tag{8}$$

under the assumption that the film density and shear modulus are the same as those of quartz. The only difference between the film-coated and uncoated quartz is then the added thickness, Δt_f. There may be non-mass-related frequency changes due to stress [18] and temperature effects. The mechanical stress is due to the deposition of materials with high compressive stress. Materials with high compressive stress tend to bend the crystal and influence the radial sensitivity of the resonating quartz. Bending can also occur by improper mounting of the crystal in the holder, which tends to promote spurious secondary modes of oscillation. The frequency shift due to the stress effect can be separated from the mass effect by using the double resonator technique. The origin of the stress effects are explained and described in detail in [3]. The variation of the frequency as a function of temperature is very low in the case of standard AT-cut crystal (35.17°) between –10 °C and +50 °C [3].

5.2 Resonant frequency shift vs. added mass equations for low-mass loading in gas atmosphere

$$\frac{\Delta f}{f_c} = \frac{\left(f_c - f_0\right)}{f_c} = -Ap - B\left(\pi f_c \rho_g \eta_g\right)^{1/2} - C_f \Delta m_f \tag{9}$$

Where p is the gas pressure; ρ_g and η_g are gas density and viscosity, respectively [33]. Hence, the frequency shift, for instance for measurement in air vs. vacuum is smaller than 10 Hz.

5.3 Resonant frequency shift vs. added mass equations for low-mass loading in solutions

5.3.1 Quartz oscillator contacting a viscous solution with one face only

The solution of the boundary value problem for the quartz oscillator contacting a viscous solution (subscript L) with one side only is:

$$\Delta f = -f_0^{3/2}\left(\frac{\rho_L \eta_L}{\pi \rho_q \mu_q}\right)^{1/2} \tag{10}$$

Hence, the theoretically expected frequency shift from air to water or aqueous solution, for instance, for a 10 MHz crystal, is about 2 to 4 kHz. However, this value is usually underestimated. The observed frequency shift is often 1.5 to 3 times higher. This discrepancy is ascribed to the differences between the surface and bulk values of viscosity and density, hydrophilic or hydrophobic nature of the surface, intermolecular forces, electric double layer structure, etc. If the solution is in contact with both oscillator faces, then the frequency change is multiplied by a factor of two.

A lack of conformance with the Sauerbrey equation may be traced back to viscoelastic effects, high-mass loadings, surface roughness, surface stress, interfacial slippage, nonuniform mass distribution, and changes in the ambient temperature [3,7]. These non-mass-related changes in the measured frequency are related to changes in the morphology of the selective surface film (viscoelastic effects), decreasing sensitivity of the QCM (high-mass loading), trapping of liquid in surface cavities (surface roughness) [5,41], asymmetrical cell arrangement (surface stress), and the coupling between the oscillator surface and the adjacent solution (interfacial slippage). Some of these "non-mass" related frequency shifts are taken into consideration in advanced models [31,38].

5.3.2 Quartz oscillator coated with a selective surface film of the same mechanical properties as quartz

An additional frequency shift is expected in the presence of a selective surface film of the same mechanical properties as those of quartz. Relative to vacuum, the total frequency shift is then the sum of terms, i.e., when the crystal oscillator is placed into a viscous medium and when mass is added [7]:

$$\Delta f = \left(f_c - f_0\right) = -\left[\frac{2 f_0^2}{\left(\rho_q \mu_q\right)^{1/2}}\right]\left[\left(\frac{\Delta M}{A}\right) + \left(\frac{\rho_L \mu_L}{4\pi f_0}\right)^{1/2}\right] \tag{11}$$

5.3.3 Quartz oscillator coated with a viscous surface

If a selective surface film is viscous, then its behavior is expected to be "non-ideal". In such a case, the apparent mass changes calculated from the Sauerbrey equation may be erroneous. However, impedance measurements and QCM studies of systematic thickness variations can help to interpret the observed frequency shifts [7,15,29–32,34–40,42–44].

6. CONCLUDING REMARKS

Piezoelectric microgravimetry using EQCM has become a widely used technique in several areas of electrochemistry, electroanalytical chemistry, bioelectrochemistry, etc. because detecting mass changes, which accompany electrochemical reactions, is helpful for elucidation of mechanisms of various important physicochemical processes. In recent years, automatic, microprocessor-controlled instruments have been introduced, which satisfy most requirements of fundamental and applied research, although their commercial availability is still limited. The majority of investigations have been devoted to ion and solvent transport associated with the electrode reactions and synthesis of electrochemically active polymer modified electrodes [45–79]. In these papers, many fundamental problems, e.g., viscoelastic be-

havior, plastic changes of the surface layer during the break-in phenomenon, film nonuniformity, and temperature effects have been addressed. EQCM has been applied in diverse fields of science and technology, such as membrane research [80], metal deposition [81], electroplating [82], electrosorption [83–87], underpotential deposition [88,89], adsorption of biologically active materials [90], biofilms [91], layered nanostructures [92], drug delivery [93], analytical determination of small ions and biomolecules [12,95], self-assembling monolayers [12,96–98], electrochemical oscillations [99–102], conducting salts [103], semiconductors [104], batteries [105], and corrosion [106–109]. EQCM has been combined with rotating disc electrode [110], probe beam deflection [111], scanning electrochemical microscopy [111], or differential electrochemical mass spectrometry [112]. A phase-controlled microbalance for double layer studies [113] and the ac EQCM apparatus [114] have also been developed. Moreover, EQCM has been applied successfully for the surface stress measurements [115–118]. Simultaneous measurements of impedance and mass loading for the determination of the Q value and validation of the Sauerbrey equation are being now routinely carried out [14].

7. LIST OF SYMBOLS AND ACRONYMS

Subscripts q, f, and L refer to quartz, film, and liquid, respectively.

A — acoustically active surface area; cm^2
B — susceptance
C — capacitance; F
C_0 — capacitance of quartz oscillator; F
C_1 — capacitance; F
c_f — differential mass sensitivity; Hz ng^{-1}
C_f — integral mass sensitivity; Hz cm^2 ng^{-1}
d — diffusion boundary layer thickness; cm
D — diffusion coefficient; cm^2 s^{-1}
ΔE — applied potential difference; V
f — frequency measured after contacting the oscillator with ambient; Hz
f_c — resonant frequency of the composite oscillator formed from the crystal and the film(s) at the surface; Hz
f_0 — fundamental resonant frequency of the oscillator in vacuum, before contacting with ambient or before modifying its surface films; Hz
f_p — resonant frequency corresponding to a parallel equivalent circuit arrangement; Hz
f_n — normal frequencies of a free AT-cut quartz oscillator of the thickness t_q with neither interface clamped, $f_n = (n + 1)v/2t_q = (n + 1)(\mu/\rho)^{1/2}/2t_q$; Hz
f_r — resonant frequency of ideal oscillator (energy-loss free); Hz
f_s — resonant frequency corresponding to a serial equivalent circuit arrangement; Hz
Δf — frequency difference; Hz
G — conductance; $S = \Omega^{-1}$
k_d — damping factor, $k_d = (1/2R)(L/C)^{1/2}$
k — wave number or propagation constant, $k = 2\pi/\lambda$; cm^{-1}
k_T — electromechanical coupling efficiency
l — length; cm
L — inductance; Ω s
M — mass; g
m — surface mass density (mass/area); g cm^{-2}
n — harmonic number (e.g., $n = 1$ for the fundamental or first harmonic frequency, $n = 2$ for the second harmonic, and $n = 3$ for the third harmonic, etc.)
N — number of cycles of resonant oscillations
Q — mechanical or electrical quality factor of the resonator

p	pressure; bar
R	resistance; Ω
r_e	electrode radius; cm
t_f	film thickness; cm
t_q	quartz thickness; cm
t	time; s
u	particle speed; m s^{-1}
x	displacement
x_{max}	maximal displacement
Y	admittance; S = Ω^{-1}
Y_{Im}	imaginary component of admittance; S = Ω^{-1}
Y_{Re}	real component of admittance; S = Ω^{-1}
Z	mechanical impedance, $Z = \rho v = (\rho\mu)^{1/2}$; kg $m^{-2}s^{-1}$
Z_{Im}	imaginary component of impedance; Ω
Z_{Re}	real component of impedance; Ω
ε	electric permittivity
φ	phase angle; rad
λ	wavelength, $\lambda = 2t_q$; cm
μ	shear modulus; kg m^{-1} s^{-2}, or N m^{-2}, or dyn cm^{-2}
μ_q	shear modulus of quartz, $\mu_q = 2.947 \times 10^{10}$ N m^{-2} or 2.947×10^{11} dyn cm^{-2}
η	dynamic viscosity; g cm^{-1} s^{-1}
η_f	dynamic viscosity of film; g cm^{-1} s^{-1}
η_L	dynamic viscosity of liquid; g cm^{-1} s^{-1}
v	acoustic wave propagation speed, also called transverse speed or phase speed, $v = (\mu/\rho)^{1/2} = 2t_q f_0$; m s^{-1}
v_q	wave speed for quartz, $v_q = 3336$ m s^{-1}
ρ	density (mass/volume); g cm^{-3}
ρ_f	density of film; g cm^{-3}
ρ_L	density of liquid; g cm^{-3}
ρ_q	density of quartz, $\rho_q = 2.648$ g cm^{-3}
ρ_m	density of material deposited on resonator; g cm^{-3}
w	width; cm
ω	angular frequency, $\omega = 2\pi f$; Hz
ac	alternating current
EQCM	electrochemical quartz crystal microbalance
IDT	interdigitated
QCM	quartz crystal microbalance
SAW	surface acoustic wave

8. REFERENCES

1. R. M. White. In *Methods of Experimental Physics*, Vol. 19, Chap. 10, p. 495, Academic Press, New York (1981).
2. G. Sauerbrey. *Z. Phys. Chem*. **155**, 206 (1959).
3. C. Lu and A. W. Czanderna. *Applications of Piezoelectric Quartz Crystal Microbalances*, Elsevier, Amsterdam (1984).
4. M. O'Donnel, L. J. Bousse, J. G. Miller. In *Methods of Experimental Physics*, Vol. 19, Chap. 1, p. 29, Academic Press, New York (1981).
5. R. Schumacher. *Angew. Chem., Int. Ed. Engl.* **29**, 329 (1990).
6. M. D. Ward and D. A. Buttry. *Science (Washington, D.C.)* **249**, 1000 (1990).
7. D. A. Buttry and M. D. Ward. *Chem. Rev.* **92**, 1355 (1992).
8. D. A. Buttry. In *Electroanalytical Chemistry*, Vol. 17, A. J. Bard (Ed.), p. 1, Marcel Dekker, New York (1991).
9. M. R. Deakin and D. A. Buttry. *Anal. Chem*. **61**, 1147A (1989).
10. J. W. Grate, S. J. Martin, R. M. White. *Anal. Chem*. **65**, 940A (1993).
11. A. J. Ricco. *Interface (ECS)* **3**, 38 (1994).
12. C. K. O'Sullivan and G. G. Guilbault. *Biosens. Bioelectron*. **14**, 663 (1999).
13. J. F. Alder and J. J. McCallum. *Analyst* **108**, 1169 (1983).
14. R. Saraswathi, A. R. Hillman, S. J. Martin. *J. Electroanal. Chem*. **460**, 267 (1999).
15. S. J. Martin, H. L. Bandey, R. W. Cernosek, A. R. Hillman, M. J. Brown. *Anal. Chem*. **72**, 141 (2000).
16. S. J. Martin, G. C. Frye, S. D. Senturia. *Anal. Chem.* **66**, 2201 (1994).
17. R. Lucklum, C. Behling, R. W. Cernosek, S. J. Martin. *J. Phys. D: Appl. Phys.* **30**, 346 (1997).
18. D. M. Ullevig, J. F. Evans, M. G. Albrecht. *Anal. Chem*. **54**, 2341 (1982).
19. M. D. Ward and E. J. Delawski. *Anal. Chem.* **63**, 886 (1991).
20. J. Bácskai, G. Láng, G. Inzelt. *J. Electroanal. Chem*. **319**, 55 (1991).
21. P. J. Cumpson and M. P. Seah. *Meas. Sci. Technol*. **1**, 544 (1990).
22. J. Inczedy, T. Lengyel, A. M. Ure. *Compendium of Analytical Nomenclature* (the "Orange Book"), 3rd ed., Blackwell Science, Oxford (1998).
23. R. P. Buck and E. Lindner. *Pure Appl. Chem*. **66**, 2527 (1994).
24. ISO 3534-1 Statistics -Vocabulary and Symbols. Part I: Probability and General Statistics Terms (1993).
25. A. D'Amico and E. Verona. *Microfabricated Chem. Sensors Prog. Solid. St. Chem.* **18**, 177 (1998).
26. J. Janata and A. Bezegh. *Anal. Chem.* **60**, 62R (1988).
27. D. E. Henderson, M. B. DiTaranto, W. G. Tonkin, D. J. Ahlgreen, D. A. Gatenby, T. W. Shum. *Anal. Chem*. **54**, 2067 (1982).
28. G. Inzelt and J. Bácskai. *J. Electroanal. Chem.* **308**, 225 (1991).
29. R. Beck, U. Pitterman, K. G. Weil. *Ber. Bunsenges. Phys. Chem*. **92**, 1363 (1988).
30. H. L. Bandey, M. Gonsalves, A. R. Hillman, A. Glidle, S. Bruckenstein. *J. Electroanal. Chem.* **410**, 219 (1996).
31. D. M. Soares, M. A. Tenan, S. Wasle. *Electrochim. Acta* **44**, 263 (1998).
32. R. A. Etchenique and E. J. Calvo. *Electrochem. Commun*. **1**, 167 (1999).
33. G. C. Dunham, N. H. Benson, D. Petelenz, J. Janata. *Anal. Chem*. **67**, 267 (1995).
34. S. Bruckenstein and M. Shay. *Electrochim. Acta* **30**, 1295 (1985).
35. T. Nomura and M. Okuhara. *Anal. Chim. Acta* **142**, 281 (1982).
36. K. K. Kanazawa and J. G. Gordon II. *Anal. Chim. Acta* **175**, 99 (1985).
37. B. A. Martin and H. E. Hager. *J. Appl. Phys.* **65**, 2630 (1989).
38. G. Hayward. *Anal. Chim. Acta* **264**, 23 (1992).

39. M. Yang and M. Thompson. *Anal. Chem*. **65**, 3591 (1993).
40. V. Tsionsky, L. Daikhin, E. Gileadi. *J. Electrochem. Soc*. **143**, 2240 (1996).
41. L. Daikhin, E. Gileadi, G. Katz, V. Tsionsky, M. Urbakh, D. Zagidulin. *Anal. Chem*. **74**, 554 (2002).
42. S. J. Martin, V. E. Granstaff, G. C. Frye. *Anal. Chem*. **63**, 2272 (1991).
43. A. R. Hillman, A. Jackson, S. J. Martin. *Anal. Chem*. **73**, 540 (2001).
44. H. L. Bandey, S. J. Martin, R. W. Cernosek, A. R. Hillman. *Anal. Chem*. **71**, 2205 (1999).
45. D. Orata and D. A. Buttry. *J. Am. Chem. Soc*. **109**, 3574 (1987).
46. R. Borjas and D. A. Buttry. *J. Electroanal. Chem.* **280**, 73 (1990).
47. S. Bruckenstein and A. R. Hillman. *J. Phys. Chem.* **92**, 4837 (1988).
48. A. R. Hillman, D. C. Loveday, M. J. Swann, R. M. Eales, A. Hamnett, S. J. Higgins, S. Bruckenstein, C. P. Wilde. *Faraday Discuss. Chem. Soc*. **88**, 151 (1989).
49. A. Glidle, A. R. Hillman, S. Bruckenstein. *J. Electroanal. Chem*. **318**, 411 (1991).
50. A. P. Clarke, J. G. Vos, A. R. Hillman, A. Glidle. *J. Electroanal. Chem*. **389**, 129 (1995).
51. E. Pater, S. Bruckenstein, A. R. Hillman. *J. Chem. Soc., Faraday Trans.* **92**, 4087 (1996).
52. M. Skompska and A. R. Hillman. *J. Electroanal. Chem*. **433**, 127 (1997).
53. M. J. Henderson, A. R. Hillman, E. Vieil. *J. Phys. Chem*. **103**, 8899 (1999).
54. S. Bruckenstein, K. Brzezinska, A. R. Hillman. *Phys. Chem*. **2**, 1221 (2000).
55. C. Barbero, M. C. Miras, R. Kötz, O. Haas. *Synth. Met.* **55–57**, 1539 (1993).
56. M. C. Miras, C. Barbero, R. Kötz, O. Haas. *J. Electroanal. Chem.* **338**, 279 (1992).
57. T. Tjarnhage and M. Sharp. *Electrochim. Acta* **39**, 623 (1994).
58. G. Inzelt. *J. Electroanal. Chem.* **287**, 171 (1990).
59. G. Inzelt and J. Bácskai. *J. Electroanal. Chem.* **308**, 255 (1991).
60. J. Bácskai and G. Inzelt. *J. Electroanal. Chem.* **310**, 379 (1991).
61. G. Inzelt and J. Bácskai. *Electrochim. Acta* **37**, 647 (1992).
62. K. Martinusz, E. Czirók, G. Inzelt. *J. Electroanal. Chem*. **379**, 437 (1994).
63. G. Inzelt. In *Electroanalytical Chemistry*, Vol. 18, A. J. Bard (Ed.), p. 89A, Marcel Dekker, New York (1994).
64. S. Pruneanu, E. Csahók, V. Kertész, G. Inzelt. *Electrochim. Acta* **43**, 2305 (1998).
65. M. A. Malik, G. Horányi, P. J. Kulesza, G. Inzelt, V. Kertész, R. Schmidt, E. Csahók. *J. Electroanal. Chem.* **452**, 57 (1998).
66. G. Inzelt and E. Csahók. *Electroanalysis* **11**, 744 (1999).
67. M. D. Ward. *J. Electrochem. Soc.* **135**, 2748 (1988).
68. S. Basak, C. S. C. Bose, K. Rajeshwar. *Anal. Chem.* **64**, 1813 (1992).
69. E. Sabatani, A. Redondo, J. Risphon, A. Rudge, I. Rubinstein, S. Gottesfeld. *J. Chem. Soc., Faraday Trans.* **89**, 287 (1993).
70. A. J. Kelly and N. Oyama. *J. Phys. Chem*. **95**, 9579 (1991).
71. A. J. Kelly, T. Ohsaka, N. Oyama, R. J. Foster, J. G. Vos. *J. Electroanal. Chem*. **287**, 185 (1990).
72. W. Kutner and K. Doblhofer. *J. Electroanal. Chem*. **326**, 139 (1992).
73. C. K. Baker and J. R. Reynolds. *J. Electroanal. Chem*. **251**, 307 (1988).
74. Y. Wang, G. Zhu, E. Wang. *J. Electroanal. Chem*. **430**, 127 (1997).
75. H. Lee, H. Yang, J. Kwak. *J. Electroanal. Chem*. **468**, 104 (1999).
76. M. Shin, E. Y. Kim, J. Kwak, I. C. Jeon. *J. Electroanal. Chem*. **394**, 87 (1995).
77. H. N. Dinh and V. I. Birss. *J. Electroanal. Chem*. **443**, 63 (1998).
78. H. P. Dai, Q. H. Wu, S. G. Sun, K. K. Shin. *J. Electroanal. Chem*. **456**, 47 (1998).
79. W. Kutner, J. Wang, M. L'Her; R. P. Buck. *Pure Appl. Chem*. **70**, 1301 (1998).
80. W. Kutner. *Electrochim. Acta* **37**, 1109 (1992).
81. B. K. Niece and A. A. Gewirth. *Langmuir* **13**, 6302 (1997).
82. E. Gileadi and V. Tsionsky. *J. Electrochem. Soc*. **147**, 567 (2000).
83. C. P. Wilde and M. Zhang. *J. Chem. Soc., Faraday Trans*. **89**, 385 (1993).

84. C. P. Wilde and M. Zhang. *Electrochim. Acta* **38**, 2725 (1993).
85. A. Zhon and N. Xie. *J. Colloid Interface Sci.* **220**, 281 (1999).
86. K. Shimazu and H. Kita. *J. Electroanal. Chem*. **341**, 361 (1992).
87. T. Nomura and T. Kanazawa. *Anal. Chim. Acta* **245**, 71 (1991).
88. M. R. Deakin, T. T. Li, O. R. Melroy. *J. Electroanal. Chem*. **243**, 343 (1988).
89. S. Bruckenstein and S. Swathirajan. *Electrochim. Acta* **30**, 851 (1985).
90. F. Lacour, R. Torresi, C. Gabrielli, A. Caprani. *J. Electrochem. Soc.* **139**, 1619 (1992).
91. D. E. Nivens, J. Q. Chambers, T. R. Anderson, D. C. White. *Anal. Chem*. **65**, 65 (1993).
92. E. W. Bohannan, L. Y. Huang, H. F. Miller, M. G. Shumsky, J. A. Switzer. *Langmuir* **15**, 813 (1999).
93. K. Kontturi, P. Pennti, G. Sundholm. *J. Electroanal. Chem*. **453**, 231 (1998).
94. T. Nomura and T. Nagamune. *Anal. Chim. Acta* **155**, 231 (1993).
95. M. Muratsugu, F. Ohta, Y. Miya, T. Hosokawa, S. Kurosawa, N. Kamo, H. Ikeda. *Anal. Chem.* **65**, 2933 (1993).
96. L. L. Nordyke and D. A. Buttry. *Langmuir* **7**, 380 (1991).
97. J. Wang, L. M. Frostman, M. D. Ward. *J. Phys. Chem*. **96**, 5224 (1992).
98. K. Shimazu, I. Yagi, Y. Sato, K. Hosaki. *Langmuir* **8**, 1385 (1992).
99. G. Inzelt. *J. Electroanal. Chem*. **348**, 465 (1993).
100. G. Inzelt and V. Kertész. *Electrochim. Acta* **42**, 229 (1997).
101. G. Inzelt and V. Kertész. *Electrochim. Acta* **40**, 221 (1995).
102. G. Inzelt, V. Kertész, G. Láng. *J. Phys. Chem*. **97**, 6104 (1993).
103. M. S. Freund, A. Brajter-Toth, M. D. Ward. *J. Electroanal. Chem*. **289**, 127 (1990).
104. C. Wei, C. S. C. Bose, K. Rajeshwar. *J. Electroanal. Chem*. **327**, 331 (1992).
105. J. Desilvestro, W. Scheifele, O. Haas. *J. Electrochem. Soc*. **139**, 2727 (1992).
106. S. Zakipour, C. Leygraf, G. Portnoff. *J. Electrochem. Soc*. **133**, 873 (1986).
107. R. Schumacher, A. Müller, W. Stöckel. *J. Electroanal. Chem*. **219**, 311 (1987).
108. A. Jardy, A. L. Lasalle-Molin, M. Keddam, H. Takenouti. *Electrochim. Acta* **37**, 2195 (1992).
109. W. A. Smyrl and M. A. Butler. *Interface (ECS)* **2**, 35 (1993).
110. P. Kern and D. Landolt. *J. Electrochem. Soc*. **147**, 318 (2000).
111. B. Gollas, P. N. Bartlett, G. Denuault. *Anal. Chem*. **72**, 349 (2000).
112. Z. Jusys, H. Massong, Baltruschat. *J. Electrochem. Soc*. **146**, 1093 (1999).
113. W. Kautek, M. Sahre, D. M. Soares. *Ber. Bunsenges. Phys. Chem*. **99**, 667 (1995).
114. S. Cordoba-Torresi, C. Gabrielli, M. Keddam, H. Takenouti, R. Torresi. *J. Electroanal. Chem.* **290**, 269 (1990).
115. T. R. Beck and K. F. Lin. *J. Electrochem. Soc*. **126**, 252 (1979).
116. M. Seo, X. C. Jiang, N. Sato. *J. Electrochem. Soc*. **134**, 3094 (1987).
117. X. C. Jiang, M. Seo, N. Sato. *J. Electrochem. Soc.* **137**, 3804 (1990).
118. L. Jaeckel, G. Láng, K. E. Heusler. *Electrochim. Acta* **39**, 1031 (1994).