

Quartz crystal microgravimetry – fifty years of application and new challenges

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This review paper is devoted to the semicentenary of the publication of Sauerbrey's theory which laid the foundation of quartz crystal microgravimetry (QCM) – a method that has gained an exceptional importance in various fields of science and technology, in particular electrochemistry, materials science and biosensors. The paper provides a brief historical overview of QCM development as well as recent trends in several innovative fields: anticorrosive stability of PVD alloys, adhesion of microorganisms, long-term effects in the atmosphere, and biosensors including piezo-immuno ones. The review covers also several important QCM modifications – the nanobalance with foil and oxide electrodes as well as energy dissipation control. The advantages of the QCM method are summarised as a possibility to observe the bio-electro-chemical events non-invasively *in situ* and in real time and in both gaseous and liquid environments.

Key words: QCM review, corrosion, PVD, alloys, biosensors, piezoimmunosensors

INTRODUCTION

It was 1959 when G. Sauerbrey published his work devoted to the dependence of quartz oscillation frequency on the change in surface mass. The study appeared in the journal *Zeitschrift für Physik*, its title in German being *Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung* [1]. So, this year (2009) marks a semicentenary of quartz crystal microgravimetry (QCM) – a method that has gained an exceptional importance in various fields of science and technology, especially in mass sensing at electrochemical interfaces and bio-molecular systems. The QCM applications encompass today large areas of science and technology, where different scientific fields interplay: physics, chemistry, materials science and biology. The scope of QCM investigations ranges from single metals in vacuum to detection of HIV infectivity factors, cancer cells and antithrombogenic drugs.

Application of quartz crystal micro- or nano-balance (QCM, QCN) underwent an explosive development during the recent two decades. The QCM expansion was largest into electrochemistry, e. g. underpotential deposition (UPD), corrosion, conducting polymers, passive layers, bioelectrochemical sensors, etc. With the development of the electrochemical quartz crystal microbalance (EQCM), electrochemists re-

ceived a perfect tool for obtaining sensitive mass information *in situ* and in real time (e. g. parts of the atomic monolayer of a metallic electrode), which complemented conventional voltammetry or impedance data including those obtained with the use of a ring-disc electrode system.

The newly emerged fields of microgravimetric approaches are electrochemical materials science and bioelectrochemistry. Of particular importance are such subjects as multifunctional alloys, biofilm sensors, drug delivery, cell immobilization and molecular recognition. There is a niche in the review literature of these newly emerged fields. So, this paper attempts to fill several gaps by focusing on such subjects as stability evaluation of PVD alloys, oxide-based QCM, immunosensors and biofilm development.

HISTORY

The QCM development route falls into several stages: 1) metals in vacuum and gases (adsorption, oxidation, corrosion, thin films, detection in gas chromatography); 2) metals in solutions (electrochemistry of systems with rigidly attached mass); 3) energy dissipating systems (viscoelastic films) and 4) complex biochemical and biomimetic systems (protein, nucleic acid and living cell biosensors, drug discovery). These developmental stages were documented in review papers [2–11].

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The basic principle of QCM is given by Sauerbrey's equation [1]:

$$\Delta f = -2\Delta m n f_0^2 / (A \sqrt{\mu_Q \rho_Q}). \quad (1)$$

In this formula, Δf stands for the frequency change, Δm is the added or removed mass, n is the overtone number, f_0 is the fundamental frequency of the quartz oscillator, A is the surface area, μ_Q is a shear modulus ($\mu_Q = 2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$) and ρ_Q is the density of quartz ($\rho_Q = 2.648 \text{ g cm}^{-3}$). The equation predicts how the oscillation frequency of a quartz resonator depends on foreign mass added to (or removed from) the oscillator surface. It should be noted that the ratio (1) is valid only for a relatively small mass rigidly bound to the quartz surface (elastic mass change). It becomes inaccurate when the mass change exceeds ca. 2% of the crystal mass.

Soon after invention, QCM attracted attention of corrosion researchers. B. Littler was the first to use QCM for corrosion studies and patented the approach in 1966 [12]. As is commonly known, corrosion is an electrochemical process of metal degradation, which is accompanied by mass changes due to metal conversion into oxidized species. The mass of a corroding sample increases if the oxidized species remain on the surface, and it decreases if they leave the surface. The QCM method was, therefore, of great promise in corrosion science due to its capability to sensitively detect the mass change of corroding electrodes. The kinetics of the initial stages of oxide film formation was studied on aluminium [13–19], iron [20], tantalum [21], permalloy ($\text{Ni}_{0.8}\text{Fe}_{0.2}$) [22], copper [23, 24], silver [24], potassium [25], titanium [26], cobalt [27], zinc [28, 29], nickel [29, 30] and tin [30]. Other important fields of early stages of QCM development included applications to study the adsorption of gases, water and organic compounds, detection in gas chromatography, measurement of air humidity and the concentration of pollutants, control of the thickness and composition of sputtered materials.

It was a belief for a rather long time that Sauerbrey's ratio is inapplicable to solutions, as it assumes that the oscillator surface does not undergo any shear deformations during the oscillation, which is true for thin rigid films, e. g. metal coatings. In 1980, studies appeared to show that QCM is applicable also to liquids [31–35]. Bruckenstein with co-workers used QCM for electroanalytical purposes *in situ*, in particular to weigh monolayer amounts of materials deposited on electrodes [33, 34]. Soon after these works, more papers appeared on QCM application in liquids [36–41].

When in electrolyte, the metal coating on quartz may play two roles – of an excitation electrode of the resonator and of electrochemical one, to which conventional electrochemical means such as voltammetry, impedance spectroscopy may be applied. The possibility to perform simultaneously QCM and electrochemical measurements provided great opportunities to expand electrochemical horizons. The microbalance transformed into electrochemical QCM (EQCM), which provided a vast amount of new electrochemical information in vari-

ous fields, to name just a few: underpotential metal deposition (UPD), formation of oxides and metal layers, dissolution (corrosion) process, polymer films including conductive ones, ion transport and adsorption, metal passivation phenomena, complex biomolecular systems and adhesion of whole cells, energy dissipation properties of visco-elastic films, etc. The QCM principles and application were comprehensively reviewed by Schumacher [6], Ward [8], Hillman [9] Tsionsky et al. [10] and Marx [11].

Lithuanian electrochemists have started EQCM experiments in the early 1990s. The studies have dealt with cadmium corrosion in solutions and the dynamics of the formation of barely soluble layers at different pH [42, 43] and EQCM studies of Pt electrodes [44, 45].

BASIC PRINCIPLES OF MICRO-WEIGHING

The QCM oscillator is designed from a quartz disc sliced from a single crystal, usually AT plane, $35^\circ 10'$ angle from the Z-axis (Fig. 1). The AT cut is used as it has minor temperature fluctuation in frequency at room temperature. Both sides of the quartz are coated with metal electrodes, typically inert ones, such as Pt or Au. The quartz disc, being a piezoelectric material, deforms when the electric field is applied by the electrodes. The disc starts to oscillate with a characteristic fundamental frequency when connected to the oscillator circuit with some inductivity (Fig. 1). Most of the QCM operate in the thickness shear mode of oscillation, i.e. the lateral surface motion is explored. The lateral amplitude of the oscillating quartz crystal is in the order of several nanometers. The linear dependence between the mass and the frequency change was verified by many researchers for rigid samples in vacuum or under atmospheric pressure, and the results are well surveyed in the literature [6–9].

Kanazawa et al. derived the ratio for the oscillator frequency shift exerted by an electrode contact with a liquid [35]:

$$\Delta f = f_0^{3/2} (\eta \rho / \pi \mu_Q \rho_Q)^{1/2}, \quad (2)$$

where ρ and η are the density and viscosity of a liquid, and μ_Q and ρ_Q are the density and shear modulus of quartz. The equation was found to be in good agreement with the sucrose concentration reported by Nomura [32]. It has been shown in [35] that the penetration of the lateral wave into solution is 250 nm.

The microbalance based on a torsional resonator has also been reported [46]. The sensitivity of these resonators is about 100 times less as compared to that of a conventional thickness-shear resonator, but an advantage is that the torsional mass device can probe rather thick layers. i.e. in the range of hundreds of microns, which is impossible by conventional QCM. Torsional QCM is important when viscoelastic effects are of interest, for instance, coatings, biofouling, etc.

Sauerbrey's equation (1) predicts calculation of the mass change of so-called elastic subjects which during

oscillation dissipate no energy. Metallic coatings, thin adsorbed layers, metal oxides belong to such subjects. Polymer films, biomolacular systems or whole cells represent so-called inelastic subjects [11]. Mass oscillation is said to be inelastic if there is energy loss (viscous damping) during the oscillation process.

To evaluate the viscoelastic properties of films, the concept of resonant resistance (R) was proposed by Muramatsu et al. [47, 48]. A decrease in f and an increase in R are observed in case of viscoelastic energy dissipation. In case of pure elastic mass attachment, the frequency change will follow Sauerbrey's equation with no changes in R . The change in R for a quartz crystal in contact with a liquid was derived [47]:

$$\Delta R = (2\pi f \rho \eta)^{1/2} A / k^2, \quad (3)$$

where k stands for the electrochemical coupling factor.

A modification of microbalance with dissipation monitoring was developed by Rodahl and co-authors [49]. This technique, called QCM-D, was shown to be suitable to measure energy dissipation in biological samples, e. g. adhesion of *Escherichia coli* [50–52] or biofilm formation of *Streptococcus mutans* [53]. According to the calculations in [35], a shear wave caused by a crystal / liquid contact penetrates the liquid to a depth of approximately 250 nm. Due to the attachment of cells, the oscillation amplitude decays much faster than in a pristine surface, and this can be measured as the dissipation factor.

To summarize, the experimentally observed frequency change may be caused by three main phenomena: 1) rigid (pure elastic) attachment of the mass to the oscillator surface; 2) a viscous contact with solution and a change in its viscosity and density; 3) energy dissipation due to inelastic attachment of the mass.

The EQCM method has also a serious limitation: the materials to be studied are limited to those electroplated, evaporated or sputtered. Bulk materials may be studied only in the form of thin foils, provided these can be sliced and glued to a quartz wafer [54, 55]. Most of the authors limited their investigations to Au or Pt coatings on quartz.

PVD ALLOY SENSORS

Physical vapour deposition (PVD), especially magnetron-sputtering (MS), has attracted considerable attention in recent years as an effective approach to obtain corrosion-resistant coatings. The MS technique for alloy deposition usually employs a set of single metal targets or a single target

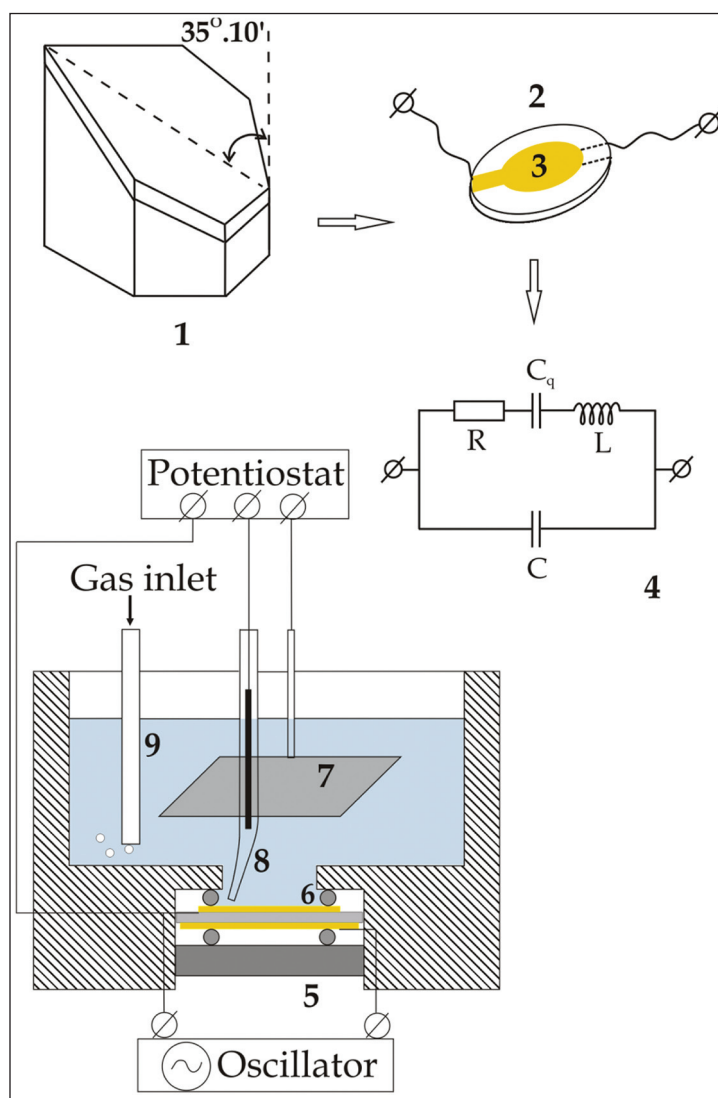


Fig. 1. Configuration of QCM: quartz crystal with AT section (1), quartz wafer (2) coated with metallic electrodes (3), oscillation equivalent circuit with quartz resonator (C_q), inductivity (L), resistance (R) and conductivity (C). The electrochemical cell comprises quartz resonator (2) mounted between two rubber rings (6, sections) and a jig (5), supporting (7) and reference electrodes (8), gas inlet (9) and solution

made of an alloy of interest. Sputtering is performed in an inert working gas, usually Ar. Due to interaction of the ionized argon with the target (cathode), the atoms are released from the metal surface and travel to a substrate, which is placed vertically or horizontally in front of the target. It is possible to form an alloy at different deposition rates and temperatures which influence the structure and, in turn, the properties of the alloy, e. g. corrosion resistance. To obtain a high degree of alloy purity, efforts should be given to avoid oxygen contamination. For instance, the oxidised target surface should be pre-cleaned and the sputtering chamber should be pre-treated at high temperatures prior to alloy deposition.

The superior anticorrosive stability of the sputtered alloys was attributed mainly to chemical homogeneity and the amor-

phous properties. Such alloys are free from crystallographic defects, e. g. dislocations, crystal imperfections, distortions, grain boundaries, second-phase elements, etc. As a result, the passive films formed spontaneously on amorphous alloys are more uniform and contain less “weak” sites as compared to films on crystalline counterparts. Such interpretation, however, is not unambiguous. Li et al. studied amorphous alloys and came to a conclusion that crystallization effects caused deterioration of the corrosion resistance [56]. It has also been shown that precipitation of nanocrystallites with dimensions less than 20 nm could increase corrosion resistance [56, 57].

The sputtering procedure makes it possible to obtain compositions with refractory metals, i. e. when the metal has a melting point higher than the boiling point of other alloy components. Examples are co-deposition of Al and Al–Mg with Zr, Mo, W, Ti, Nb, Ta [60–64] or Ta with Fe–Cr–Ni [65]. The corrosion rates of the latter were found in a highly acidic medium (12 M HCl) to be more than six orders of magnitude lower than those of a Ta-free counterpart. Amorphous Al–refractory–metal alloys also exhibited a higher electrochemical passivity than that of crystalline Al.

To evaluate the corrosion resistance of sputtered alloys, electrochemical methods are usually employed. However, the selection and application of electrochemical criteria are often quite complicated, as the electrochemical approaches have serious limitations. The electrochemical methods relate to solutions in which the conditions are quite different from those in the atmosphere (where alloys are usually explored). The commonly used evaluation of passive alloys is based on determination of breakdown potentials. This means, however, obtaining information from a highly exerted system, which is not necessarily adequate to that under open circuit conditions (under which alloys are usually explored in a liquid environment). The capabilities of voltammetric curves are also limited as they often fail to exhibit clear Tafel regions from which the corrosion current could be obtained by extrapolation procedures. When making a decision from Tafel curves, care should be taken to separate the corrosion current from the exchange current (at a thermodynamic equilibrium). The impedance spectra are widely employed to characterize the corrosion behaviour, using charge transfer resistance (or polarization resistance) as a criterion. Multicomponent alloys, however, sometimes do not exhibit a clear resistive behaviour in a low frequency domain. It is necessary to derive charge transfer resistance from data fitting, which is associated, as a rule, with modelling ambiguities.

An advantage in corrosion investigations of sputtered alloys is provided by the QCM method, a sensitive mass detector in both gaseous and liquid environments. The approach is attributed to non-invasive measurements, as during evaluation a sputtered alloy does not undergo any chemical or physical intervention, except of that due to corrosion.

QCM has been used for *in-situ* corrosion studies of magnetron-sputtered Co–Cr–Mo and Ni–Cr–Mo alloys [66]. These alloy compositions are of importance in various tech-

nical and medical applications. Studies have been performed in an oxygen-containing atmosphere and NaCl solutions. A limit of water adsorption was detected to be as high as ca. $1 \mu\text{g cm}^{-2}$ in a humid inert atmosphere (Ar gas). After achieving a steady state of water adsorption, corrosion was initiated by oxygen gas, and the microbalance indicated an increase in sample mass, which was due to oxygen bonding by the corroding surface.

The mass gain rate at any time interval is obtained from the dm / dt slope of the mass curve. The corrosion rate determined from mass data can be expressed in electric units (A cm^{-2}) according to the ratio [66]

$$j_{\text{corr}} = -(nFC / \Delta M) (df / dt), \quad (3)$$

where j_{corr} stands for corrosion current density (A cm^{-2}), df / dt is the rate of change of the quartz oscillation frequency, F is the Faraday constant, n is the number of electrons in the corrosion reaction, ΔM is the molar mass of the group responsible for the mass gain during corrosion (O, OH, OOH, etc.) and C is the proportion coefficient between the frequency and the mass change (e. g. $C = 18 \text{ ng Hz}^{-1} \text{ cm}^{-2}$ when the main resonance frequency is $f_0 = 5 \text{ MHz}$). Assuming the mass change rate $dm / dt = 1 \text{ ng s}^{-1}$ and the above C value, we can simplify the ratio (3) to

$$j_{\text{corr}} = -9.65 \times 10^{-5} (n / \Delta M). \quad (4)$$

The corrosion density calculations according to (4) give the same value of $j_{\text{corr}} = 12 \mu\text{A cm}^{-2}$ for different oxides (M_2O , MO , M_2O_3 , MO_2 , MO_3) because of the same ratio $n / \Delta M$. Thus, the corrosion current calculation does not require knowing what oxides and in which proportion are formed during atmospheric corrosion; it is only necessary to know that the corrosion products are oxides. The analogous testing in solutions is complicated due to a possibility of the corrosion product to pass into a liquid phase. Thus, to evaluate corrosion currents, data on the concentration of elements in the solution are necessary. This means extra procedures, which are usually time- and labour-consuming ones.

Corrosion resistance of light metal alloys was also investigated by QCM [67, 68]. Magnesium as the lightest metal is attractive in a variety of technical applications where weight reduction is of importance (aerospace, automotive, computers, mobile phones, etc.). However, magnesium alloys are susceptible to pitting corrosion due to a low protective capacity of the magnesium hydroxide film. Valve metals such as Al and Zr may promote formation of barrier-type films and improve the performance of magnesium alloys. Zirconium has also an exceptional grain-refining effect when added to magnesium.

Nanocrystalline Mg–Al–Zr alloys with a grain size of the order of 30–50 nm have been deposited by MS on quartz substrates [68–70]. The sequence of corrosion resistance depending on Zr content was established by QCM. The measurements were performed both in humid air and NaCl solutions.

Corrosion properties of MS stainless steel (Fe–Cr–Ni) and that with a Ta additive have been studied by QCN in a NaCl solution and a highly aggressive medium – 10 M HCl [71]. A distinctive mass change behaviour indicated that the corrosion resistance of a Ta-containing alloy was about two orders of magnitude higher as compared to that of the Ta-free counterpart.

The corrosion behaviour of highly stable Au–Pd–In alloys was studied by QCM in simulated physiological solutions [72, 73]. QCM was used in these studies to characterize the corrosivity of simulated physiological solutions, such as artificial saliva, Ringer's solution and lactic acid. An essential role of dissolved oxygen in the corrosivity of these media was clearly shown.

OXIDE-BASED QCM

Oxide-based QCM represents a modification of conventional microbalance where metal electrodes are replaced by conductive oxides. Two cases of oxide-based QCM have been reported: indium tin oxide (ITO) and ruthenium dioxide (RuO_2) [74, 75]. Kim et al. applied ITO electrodes to study polypyrrole films by combining QCM with UV-visual spectroscopy. An oxide instead of metal was chosen because of its transparency, which enables to perform optical measurements. The designed experimental system was capable of providing information about the charge, frequency, resistance and optical absorbance of the electrochemical interface. Rich analytical information was obtained about the electric, optical and viscoelastic properties of polypyrrole.

A new type of quartz crystal nano-balance (QCN) has been designed using crystalline RuO_2 which exhibits a metallic-like conductivity and, therefore, was used as a substitute for metallic electrodes [75]. Conductive RuO_2 electrodes with the electrical resistance $R < 70 \mu\Omega \text{ cm}$ were deposited on quartz by reactive magnetron sputtering. The operation of the oxide-based resonator was stable in both gaseous and liquid environments as was demonstrated by prolonged experiments of water adsorption – absorption in humid air and electrochemical copper deposition–dissolution. The sensor opens new opportunities to study thin films of RuO_2 , which are of great practical importance. RuO_2 is used in microelectronics to fabricate precise thin-film resistors, interconnections, gate electrodes, diffusion barriers, electrochromic materials, hydrocarbon sensors. In electrochemical industry, RuO_2 -based electrodes have been used for many years in chlorine and alkali production due to the possibility to run hydrogen and chlorine evolution reactions at low overpotentials. The catalytic activity of RuO_2 in electro-oxidation of alcohols, hydrogen, CO and ammonia makes it applicable in fuel cells. Ruthenium oxide has also extremely large pseudocapacitances which make it promising as an electrode material for supercapacitor applications. The designed RuO_2 mass nano-sensor provides an opportunity to study nano-scale mass effects which are of interest in the various RuO_2 appli-

cation fields mentioned above. The sensor also makes it possible to avoid galvanic effects which may occur when using conventional QCM with metallic electrodes.

QCM CELL ADHESION SENSORS

Expanding QCM application to liquids laid also the basis for studies of biological subjects, as QCM operation in liquids rather than in gases is desirable for biological systems. First studies in the QCM-sensing of bacterial adhesion appeared in the early 1990s [76–78], i. e. some ten years after the first applications of QCM to solutions [31–33]. Several reviews on the application of QCM in biology and medicine are found in [11, 79–81]. The microgravimetric approach was regarded in the recent review by Marcotte and Tabrizian as “a new avenue” in the field of cell adhesion on biomaterials [81].

QCM appeared to be particularly useful for microbial biofilms as this approach made it possible to observe adhesion events non-invasively, label-free, *in situ* and in real time. Nivens et al. performed the first long-term monitoring of microbial biofilms by conventional QCM [77]. A monitoring of *Pseudomonas capacia* formation in a flow cell during two days was performed. The detection limit of the used technique was determined to be 3×10^5 cells per square centimetre. Other examples of bacterial adhesion are *Staphylococcus epidermidis* [82], *Streptococcus mutans* [79, 80], *Escherichia coli* [77, 85–89], microbial-mixed culture from drinking water [90], *Pseudomonas aeruginosa* [91], *Aspergillus niger* [92]. From this diversity, *Escherichia coli* was most widely studied. First QCM studies of microbial populations relate to this species [77], and it still attracts the attention of researchers [89].

Redepenning et al. studied by QCM adhesion of cells in neonatal rat calvaria osteoblast [78]. The frequency change was found in proportion to the electrode coverage by the osteoblast. It has been concluded that the surface coverage determined by QCM is a more informative parameter when compared to the cell number, as osteoblasts during adhesion undergo morphological changes. Other examples of cell adhesion studies by QCM include different mammalian cell lines [93], human platelets [94] and the endothelial cells [95–97].

Cell adhesion is determined by numerous surface characteristics of biomaterial: chemical composition, wettability, surface roughness, topography and charge [81]. It has been shown, for instance, that *A. niger* fungi colonize on aluminium preferentially the sites of local corrosion attack (defects, micro-pores, micro-cracks) where accumulation of moisture is favoured [98]. Such localized colonization promoted microbiological healing effect on these “weak” sites and increase in corrosion resistance of aluminium.

There is a limited choice of biomaterials available for cell adhesion and other biomedical investigations by QCM. The metallic materials are restricted by those electroplated, evaporated or sputtered. Most of the authors, therefore, studied adhesion of microorganisms on a gold surface, which is a common material used to fabricate microbalance electrodes.

Glued foil resonators provide some extension in assortment of biomaterials [54, 55, 99]. Bucur et al. [54] were the first who proposed glued foil electrodes and verified that such a microbalance operates in accordance with Sauerbrey's equation. Later on, this approach was used to study the anodic dissolution of stainless steel [99].

Glued foil electrodes made of aluminium were used to demonstrate a possibility to sense by QCM the activity of microorganisms on a metal surface under atmospheric conditions *in situ* and in real time [55]. Other innovative aspects of QCM application included a long-term monitoring (over a month) and taking into account the influence of atmospheric pressure. The research subject was *Aspergillus niger*, a filamentous ascomycete fungus (Fig. 2). The difference between the QCM data for abiotic and biotic samples reflected microbiological activity which resulted in an exponential mass gain during exposure. Numerous phenomena take place when microorganisms colonise a metal surface, e. g. production of corrosive metabolites (inorganic and organic acids, sulphide, ammonia, carbon dioxide, nitrogen oxides, etc.), chelation of metal cations, production of organic solvents (ethanol, propanol, butanol), etc. Due to non-uniform surface colonisation, microorganisms may cause localised corrosion, which is also affected by favoured water uptake by the biofilm.

The increase in mass, registered by QCM during a two-month colonization (Fig. 2), was due to various phenomena such as development of biomass, secretion of metabolites, water uptake by the colony and microbially induced corrosion with formation of barely soluble corrosion products. The biomass development is an inelastic process because the mass

is not rigidly coupled to the surface. Conversely, formation of insoluble compounds represents an elastic attachment of mass, which does not dissipate energy. The foil method demonstrated a possibility to expand the scope of materials to be studied by QCM.

FUTURE PERSPECTIVES: PIEZOIMMUNOSENSORS

The development of QCM systems in electrochemistry has triggered the development of piezoimmunosensors – a new category of QCM sensors. They are designed by immobilization of specific antibodies on a metal substrate (QCM electrode), which capture target bacteria, viruses, or pathogenic cells in a corresponding medium. The formation of an immune complex (specific antibody–cell binding) results in a shift in QCM resonant frequency and, thus, an opportunity appears to follow the process *in situ* non-invasively (without instrumental interfering with the system) and in real time. The QCM method is less time- and labour-consuming, cost-effective and rather simple when compared to other immunoassay methods. The piezoimmunosensors are now under active development. Such sensors have been developed for detection of the HIV1 virion infectivity factor [96], immunoassay of prostate specific antigen [101], ovarian cancer cells on protein surfaces [102], early detection of molecular cancer biomarkers, i.e. mesothelin – a protein linked to pancreatic and ovarian cancer [103], pellicle formation on a human fibronectin coated titanium [104]. A very promising QCM development is also as a sensor of chemical bonding of drug molecules. For instance, a QCM sensor of heparin adsorption on titanium immobilised by 3-(trimethoxysilyl)-propylamine has been recently demonstrated [105]. The sensor helps in developing non-thrombogenic coatings for metallic coronary stents, e. g. stainless steel and titanium alloys.

CONCLUDING REMARK

The historical route of QCM has started in applied physics as an attempt to study metals in vacuum. The application has progressed subsequently to chemistry, biology and medicine. Thus, the QCM application route witnessed a global trend in research: from physics *via* chemistry to biology and medicine with increasing complexity of metal (M) interfaces: M/vacuum → M/gas → M/solution → M/organics / solution → M/biofilm / solution-air → M/antibody / cell / solution.

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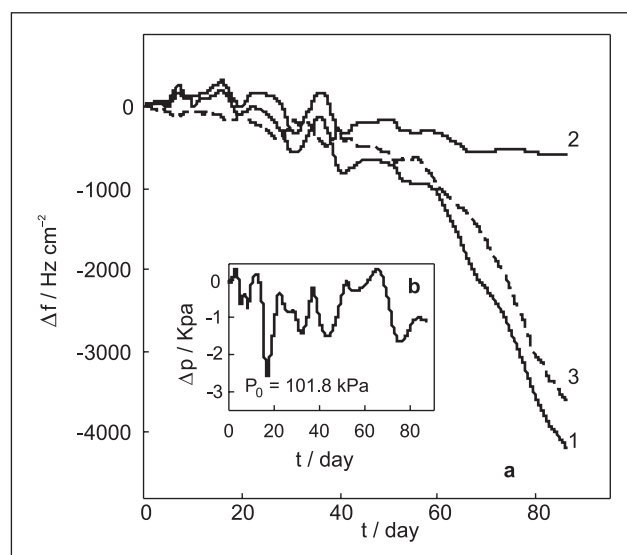


Fig. 2. Long-term QCM measurement with Al glued foil electrodes subjected to influence of *Aspergillus niger* fungi under atmospheric conditions (1) and analogous data for sterile sample (2). Curve 3 indicates microbiologically induced increase of mass obtained when subtracting (2) from (1). Insertion shows atmospheric pressure variation relatively to the initial pressure. (Authors: K. Leinartas, P. Miečinskas, E. Juzeliūnas)

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KVARCO KRISTALO MIKROGRAVIMETRIJA – PENKIASDEŠIMT TAIKYMO METŲ IR NAUJI IŠŠŪKIAI

Santrauka

Apžvalga yra skiriama Sauerbey teorijos, kurios pagrindu buvo sukurta kvarco kristalo mikrogravimetrija (KKM), penkiasdešimtmečiui. Šis metodas ypač svarbus įvairiose mokslo ir technologijų srityse: elektrochemijoje, medžiagų moksle ir biojutikliuose. Straipsnyje glaustai pateikiama KKM istorinė plėtra, taip pat pastarųjų metų taikymo tendencijos keliose naujausiose tyrimų srityse: PVD lydinių antikorozinis stabilumas, mikroorganizmų adhezija, ilgos trukmės matavimai atmosferoje, pjezoimuniniai jutikliai. Apžvelgiamos kelios svarbios KKM modifikacijos: nanosvarstyklės su klijuotų plėvelių ir oksidų elektrodais bei energijos sklaidos kontrolė. KKM privalumai apibūdinti keletu aspektų, tai – galimybė tirti kompleksinius bio-elektro-cheminius reiškinius, nedarant destruktinio poveikio tiriamiesiems pavyzdžiams, be to, *in situ*, realiame laike ir tiek dujų, tiek skysčių aplinkoje.