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SURVEY ON MASS DETERMINATION WITH OSCILLATING SYSTEMS
Part III. Acoustic wave mass sensors for chemical and biological sensing

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Abstract

We will review the application of acoustic wave mass sensors in chemical and biological sensing with focus on quartz crystal microbalance and surface acoustic wave devices. In chemical sensing, it is unlikely that a single sensor will display a selective and reversible response to a given analyte in a mixture. Alternative strategies such as use of sensor arrays and sampling devices will be discussed to improve performance. We will also discuss applications of quartz crystal microbalance as biosensor in the liquid phase.

Keywords: biosensor, gravimetry, oscillator, quartz balance

Introduction

Quartz crystal microbalance (QCM), also known as thickness shear mode or piezoelectric quartz crystals, and surface acoustic wave devices (SAW) are the main devices that have been employed as transducer elements in chemical and biological sensing. In chemical or biological sensing, a layer is added to the device surface that can recognise and bind the analyte. Binding transfers the analyte from the medium being analysed to the device surface where it alters some property of the acoustic wave. A wide range of selective layers including bioreceptors and polymer films can be employed for sensor applications [1]. The addition of the film alters the resonant frequency of the sensor.

In both QCM and SAW devices the sensitivity is dependent on the square of the resonant frequency. SAW devices operate at a higher frequency and therefore have higher predicted sensitivities although this is not necessarily realised. SAW devices have the advantage that they can be miniaturised with precise and reproducible char-

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acteristics using photo-lithographic techniques. In addition, lithographic fabrication capability permits a complex circuit to be present on the substrate surface. The major advantage of the quartz crystal microbalance is that they have higher mechanical Q and therefore have higher stability. More recently there has been increasing interest in miniaturisation of quartz crystal microbalances using microfabrication techniques.

Acoustic wave devices have been most widely used for gas or vapour phase sensing. Owing to wide applicability there has been increasing interest in the use of these devices for the liquid phase. SAW devices have been little used in the liquid phase since liquid-phase operation is precluded in devices which have surface normal particle displacements.

Vapour sensing

Vapour sensing requires a chemical layer to collect and concentrate vapour molecules from the gas phase to the device surface. If the chemical layer is rigid, then the frequency change of a piezoelectric quartz crystal is described by the Sauerbrey relation [2].

$$\Delta f = -2.3 \cdot 10^{6} f_{\mathrm{o}}^{2} \frac{\Delta M_{\mathrm{s}}}{A} \tag{1}$$

where Δf is the change in frequency of the quartz crystal in Hz, f_{o} is the fundamental frequency of the quartz crystal in MHz, ΔM_{s} is the mass of material deposited or sorbed onto the crystal in g and A is the area coated in cm^2.

The factors which influence sensitivity of the sensor include (i) strength with which the chemical layer sorbs the vapour (higher K higher sensitivity), (ii) thickness of polymer film and (iii) dielectric effects. When the chemical layer is conducting then interaction of analyte and chemical layer will, in the case of SAW devices, lead to changes in propagation of the Rayleigh wave and the associated electric potential wave. An enhanced response will thus be observed due to changes in both mass and dielectric effects.

The selectivity and reversibility of acoustic wave devices is entirely dependent on the chemical coating. If the analyte and chemical interface have very high bonding strength then the device will be highly selective but have poor reversibility. Conversely if the bonding strength of the analyte material interface is very low then the selectivity will be very low but the reversibility will be very good. Selectivity and reversibility are thus mutually exclusive properties. Two major approaches have been proposed to overcome this problem. In the first approach, a sampling device, such as a denuder tube, is introduced prior to the detection system. The walls of the denuder tube act as a perfect sink for the analyte. The sample passes through the sampling device with the analyte becoming bound to the walls of the tube. Analysis is then performed by thermal desorption of the analyte in a reference stream which is directed to the detector. Selectivity is thus primarily carried out by the denuder tube and the detector is only required to be partially selective and therefore has good reversibility [3].

The second method of overcoming problems of selectivity and reversibility involves the use an array of coated sensors with each sensor element only having partial selectivity for the analyte. The sensors are reversible since they are only partial selective. The specificity is obtained from the pattern of responses that act as a fingerprint for the analyte. Pattern recognition can be performed using a variety of standard statistical and soft computing based methods. In general, data from the sensor array can be analysed using supervised or unsupervised methods. Unsupervised learning methods such as principal component analysis (PCA) are used in exploratory data analysis, they attempt to identify a gas mixture without prior information. PCA is a commonly used multivariate technique that acts unsupervised, it finds an alternative set of axes (principal components) about which a data set may be represented. The axes are orthogonal to one another and are designed to provide the best possible view of variability in the independent variables of a multivariate data set. If the principal component scores are plotted they may reveal natural clustering in the data and outlier samples. PCA provides an insight into how effective the pattern recognition system will be at classifying the data. Plotting the load data enables the factors (original data columns) to be compared to one another, if two factors show little separation then it is likely that the measurements are correlated and are not truly independent.

Supervised learning techniques classify a vapour sample by developing a mathematical model relating training data. A neural network is an example of a supervised method that is able to solve non-linear problems, it is dynamic and self-adapting. Neural networks are based on the cognitive processes of the human brain and are efficient in comparing unknown samples to a number of known references. A neural network is a collection of units that are connected in some pattern. A unit is a simple processor which has a rule for combining the inputs and an activation function that takes the combined input to calculate an output. A weight is specified by (i) unit the weights connect from (ii) unit the weight connects to and (iii) number that denotes weight value. A negative weight value will inhibit activity of the connected to unit and a positive value will strength connected to unit. The pattern of connectivity refers to which units connect, direction of connection and the connection weights. The task that a network is required to perform is coded in the connection weights i.e. the connection weights represent the memory of the network. Fuzzy set theory is capable of dealing with vague and uncertain data and has been used for pattern recognition [4]. Fuzzy sets differ from classical sets in that they allow for an object to be a partial member of a set. A fuzzy set is fully defined by its membership function.

Liquid sensing

The Sauerbrey relation is not appropriate for description of the shear vibration of the quartz crystal in contact with liquid. Kanazawa and Gordon have described the resonant frequency change in liquid [5] as:

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

where ρ_L, ρ_Q are respectively the density of liquid and quartz crystal, μ is the shear modulus and η is the viscosity of the liquid. The resonant resistance of the quartz crystal reflects its mechanical resistance and is given by:

$$R = \frac{(2\pi f \rho_L \eta)^{1/2} A}{k^2} \tag{3}$$

where k is the electro-mechanical coupling factor. In the case of liquid operation, the measurement of dissipation (lost energy per oscillation divided by the total energy stored in the system) is crucial. Simultaneously, the change of the resonance frequency and the dissipation factor for up to four different resonance frequencies e.g. basic frequency plus 3rd, 5th and 7th harmonic overtone are measured. Dissipation factor measurement of the oscillation allows accurate thickness estimations and viscoelastic properties of floppy films such as polymer multilayers, cell and bacteria adhered to functionalised surfaces, elongated proteins or polymers with no specific structure adsorbed to solid surfaces. It is possible to observe structural changes e.g. phase changes, creation of networks, absorption of water.

In contact with a liquid the resonance frequency is influenced by the fluid. For small-sized immersed colloidal particles (∅ 10 nm) a change of the resonance frequency with concentration is observed. Large particles (∅ 400 or 1000 nm) have no influence on the resonance frequency which is equal to that of the pure liquid [6]. A double arrangement of quartz crystals is able to detect density and viscosity of fluid [7, 8].

Immunosensors based on QCM have been developed [9, 10]. An AT cut quartz coated with gold electrodes positioned in a special flow through system detects a mass accumulation caused by immobilisation of synthetic peptides. With this system antibodies against HIV have been detected. Advantage is in situ measurement avoiding complicated equipment and procedures.

Measurements in liquids were improved by design and experiment of horizontally polarised shear wave devices. The shear wave is only propagating along the surface and not coupled with compression wave [11]. Hence cross sensitivities were remarkably reduced. A wide variety of bioactive components, either affinity or catalytic, can be employed including enzyme/enzyme substrate, antigen/antibody (more selective than enzymes), DNA/complementary strand and DNA/RNA. Immobilisation of the bioactive component can be carried out by physical adsorption, covalent bonding and polymer entrapment. Physical adsorption is easy but because the bonding is weak the bioactive component can be easily washed away. In the case of covalent bonding the bioactive component is more strongly held and the direction of the bioactive component can be more easily controlled. Polymer entrapment is a simple method of immobilisation but thick films will adversely effect the kinetics of mass transfer of analytes.

Vibrating band

Bahner and Gast reported on measurement of solid particles in water by means of a transversally oscillating ribbon [12]. After loading in water the ribbon was dried and then the mass change measured. Dust concentration measurements in liquids may be performed in situ by means of a longitudinally vibrating ribbon [13, 14]. In order to measure viscosity of liquids and elasticity of layers the longitudinally vibrating ribbon should be placed between walls in short distance.

Conclusions

Applications for acoustic wave mass sensors will increase. It is also clear that further development of devices will take place including mode of operation, microfabrication of devices and type and method of attachment of active layer.

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