

# Determination of coupled solvent mass in quartz crystal microbalance measurements using deuterated solvents

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## Abstract

A simple method is described for determining of the contribution of hydrodynamically coupled solvent to the adsorbed film mass determined in a quartz crystal microbalance (QCM) when operated in liquid. The method requires no additional apparatus and utilizes the change in QCM resonant frequency response between measurements made in nondeuterated and deuterated solvents. The mass of coupled water in a polymer film has been determined and is found to agree with that determined by XPS analysis of the dried polymer film.  
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## 1. Introduction

The quartz crystal microbalance (QCM) is frequently used to investigate the mass of a film adsorbing to a surface immersed in a solution [1–9]. The adsorbed mass is usually calculated from the change in resonance frequency,  $\Delta f$ , upon adsorption of the film using the Sauerbrey equation [10],

$$\Delta f = -\frac{2f_0^2}{\rho_q v_q} \Delta m = -\frac{f_0}{\rho_q t_q} \Delta m = -C \Delta m, \quad (1)$$

where  $f_0$  is the resonant frequency in the solvent before adsorption of the film,  $\Delta m$  is the mass of the adsorbed film,  $\rho_q$  and  $v_q$  are the specific density and shear wave velocity in quartz, and  $t_q$  is the thickness of the quartz plate. The Sauerbrey equation was developed to describe the QCM response to the adsorption of a film in vacuum and does not strictly hold when applied to adsorbed films in liquids, particularly when the adsorbed film is thick and viscoelastic [5,11]. However, experimental evidence suggests that the response of the resonant frequency to film mass is indeed linear [12], supporting common practice. The mass measured in this manner includes a contribution due to solvent mole-

cules that are bound or hydrodynamically coupled to the adsorbed film. Therefore, mass determinations made using the QCM in liquid exceed those of optical techniques, where the mass of the film alone is determined. This complicates comparison of QCM measurements with measurements using other methods and prevents direct determination of the adsorbed film mass. If the mass of the “trapped” solvent could be determined in a QCM measurement this would be of considerable utility, as it would enable the mass of the adsorbed film alone to be determined and reveal the solvency state, of the film which cannot easily be determined using other methods. This is of particular importance in biochemical applications and is important where the structure of adsorbed polymer films is of interest.

Deuterated solvents differ considerably in physical properties but very little in chemical properties from the non-deuterated equivalent. It is the change in density that is important here. It is assumed that the altered chemical properties of the deuterated solvent have an insignificant effect on the mass or conformation of the adsorbed film. We note that this is a reasonable assumption that is often employed in other studies such as neutron scattering [13], whilst acknowledging that there is evidence that the D-bond is stronger than the H-bond [14]. This may be important in some systems such as surfactants at concentrations near the CMC or polymers in conditions near an abrupt solubil-

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ity change. Here we describe a simple method whereby the solvent contribution to the measured mass by QCM can be determined by employing deuterated solvents. The method involves measurement and comparison of frequency shifts performed in the presence of standard and deuterated solvents.

## 2. Materials and methods

A commercial (*q*-sense) quartz crystal microbalance (QCM-D) was used and is described elsewhere [15]. Circular discs of AT-cut quartz crystals, 14 mm in diameter, with a fundamental frequency of  $\sim 5$  MHz were used. A 5-nm-thick chromium adherent layer was first evaporated onto the quartz crystal, followed by the active surface, an evaporated gold electrode ( $\sim 100$  nm thick). During operation, the crystal is excited to oscillate with an amplitude of  $\sim 1$  nm in the thickness shear mode [16]. Results are presented using data from the third overtone ( $\sim 15$  MHz). These data are less affected by the mechanical mounting of the cell and are therefore more reliable. This is primarily a result of superior “energy trapping” for the third overtone compared to the fundamental frequency [17]. The Sauerbrey constant for the third overtone is  $C = 167 \text{ cm}^2 \mu\text{g}^{-1} \text{ s}^{-1}$ . This was calculated using Eq. (1), the measured value of  $f_0 = 4948170.6 \text{ Hz}$ , and literature values [18] of  $\rho_q = 2648 \text{ kg m}^{-3}$  and  $\nu_q = 3340 \text{ m s}^{-1}$ .

The deuterated water used in the experiments was supplied by Aldrich and used without further purification. The normal water used was purified using a Milli-Q system. The cationic polyelectrolyte used was a random copolymer of uncharged acrylamide (AM) and positively charged [3-(2-methylpropionamide)propyl]trimethylammonium (MAPTAC) with a MWT of  $\sim 900$  KDa and a degree of polymerization of 12,200. The relative number of charged monomers was 1%; hence, in line with previous reports, the polymer is referred to as AM-MAPTAC-1%. This polymer was kindly supplied as a gift from the Laboratoire de Physico-Chemie Macromoleculaire, Université Pierre et Marie Curie, Paris. Prior to an experiment, the gold surface of the crystal was cleaned with bichromic acid and rinsed in water and ethanol, to remove contamination. This procedure was identical to that followed in previous measurements on the same polymer [19] allowing direct comparisons to be made to previous results. In addition, the same polymer solution electrolyte concentration, 0.1 mM KBr, was used for adsorption of the polymer; this was followed by rinsing in water. This resulted in a minor change in resonant frequency. Solvent measurements used in the calculations were made using solutions without added electrolyte. Experiments were conducted at a constant temperature of  $25.5 \pm 0.05$  °C, as temperature changes influence the resonance frequency response. In the initial setup it was necessary to allow several hours of equilibration time to obtain a stable signal free from influences of the mechanical mounting. These drifts are presumed to

be induced by the relaxation of the O-ring against which the quartz crystal is placed. As the effects of the mechanical mounting vary each time a crystal is mounted in the cell it is necessary to make all the measurements required for the determination of solvent mass on a single crystal without altering or disturbing the cell mounting.

## 3. Results and discussion

The approach employed to determine the contribution of solvent to the measured mass is simple when a polymer that irreversibly adsorbs to the surface is employed. The resonance frequency of a single quartz crystal is measured in solvent and deuterated solvent. Then the film of interest is adsorbed to the surface of the QCM and the resonance frequency of the quartz crystal is again measured in solvent and in deuterated solvent. Note that in this case, only one polymer solution need be prepared and it is not necessary to prepare a solution in deuterated solvent. If the film material does not irreversibly adsorb, but rather is in equilibrium with the solution, the material must be added to both the deuterated and nondeuterated systems for the second set of measurements. Measured values of the resonant frequency for the AM-MAPTAC-1% system studied here are shown in Table 1 and the experimental data are presented in Fig. 1. Additionally, the calculated drift in each measurement is listed in Table 1, as this is the dominant contributor to the measurement error.

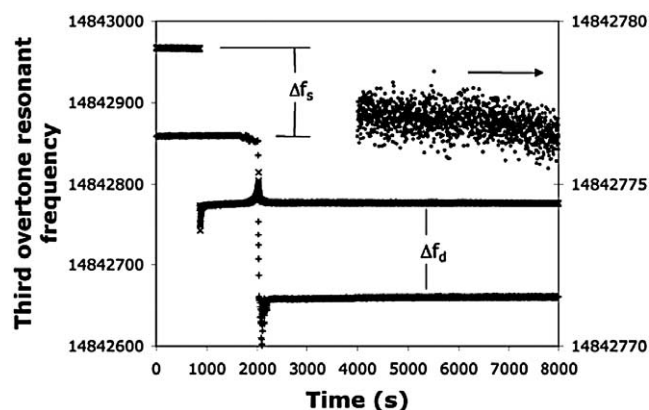


Fig. 1. Raw QCM data required to determine the mass of coupled solvent. In the upper trace (crosses) the third overtone of the resonant frequency of a bare crystal is measured in water. A stable value is obtained until approximately 1000 s have passed. At this time  $\text{H}_2\text{O}$  was exchanged for  $\text{D}_2\text{O}$  and the resonant frequency dropped rapidly before settling to a stable value. This stability was interrupted at  $\sim 1900$  s when fresh  $\text{D}_2\text{O}$  was passed into the cell. The value then stabilized and was thereafter stable throughout the measurement. The last 4000 s of this trace (triangles) is shown on an expanded scale indicated on the right hand axis. The lower trace (pluses) also follows the exchange of  $\text{H}_2\text{O}$  for  $\text{D}_2\text{O}$  but in this case the polymer film was present on the crystal surface. At  $\sim 1800$  s the stability of the cell was disturbed by temperature changes associated with preparations for the injection of  $\text{D}_2\text{O}$ . After injection at  $\sim 2000$  s the signal rapidly changed before re-stabilizing. The experimentally determined values of  $\Delta f_s$  and  $\Delta f_d$  required in Eq. (2) are indicated on the figure.

Table 1  
Hydrodynamically coupled mass determination

System	Third overtone $f_0$ (Hz)	$\Delta f$ (Hz)	Drift <sup>a</sup>	$\Delta m$ (mg m <sup>-2</sup> )	Film mass (mg m <sup>-2</sup> )	Solvent mass (mg m <sup>-2</sup> )	$S_{\text{fraction}}$
H <sub>2</sub> O	14842966.7		0.16				
D <sub>2</sub> O	14842777.0		0.08				
H <sub>2</sub> O + AMPTAC1	14842859.3	-107.4	0.32	6.47	1.26	5.21	0.81 <sup>b</sup>
D <sub>2</sub> O + AMPTAC1	14842660.3	-116.7	0.15	7.02	1.26	5.76	0.82

<sup>a</sup> Drift in Hz per 600 s, determined from data treated with a boxcar average of 20 points. The difference in the maximum and minimum measured values of the frequency over a time interval exceeding 600 s was used to compute the drift.

<sup>b</sup> This compares favorably with the  $S_{\text{fraction}}$  of 0.78 determined by comparison of measurements done with QCM and XPS on the dry film [19].

Table 2  
Evaluation of solvent systems for coupled mass determination

Solvent	Density at 20 °C [20]	Density of deuterated form at 20 °C <sup>a</sup>	Density ratio deuterated/hydrogenated	Relative sensitivity <sup>b</sup>
Water	0.997	1.104	1.107	1.00
Cyclohexane	0.7790	0.893	1.146	1.37
Ethanol	0.7893	0.901	1.142	1.32
Methanol	0.7914	0.888	1.122	1.14
Acetone	0.7845	0.872	1.111	1.04
Benzene	0.8765	0.950	1.084	0.78
Pyridine	0.9819	1.050	1.069	0.65
Toluene	0.8996	0.943	1.048	0.45

<sup>a</sup> The precise density is dependent upon the level of nondeuterated solvent present. These data were obtained from the Apollo Scientific deuterated compound catalog for solvents with the highest available level of deuterium.

<sup>b</sup> The relative sensitivity compares the performance of the different solvent systems for determination of coupled mass of solvent relative to the H<sub>2</sub>O/D<sub>2</sub>O system. A higher value will result in a greater difference in frequency response to coupled solvent and therefore will give a reduced error in the measurement of solvent mass. The relative sensitivity is determined from  $(1 - \text{density ratio})_{\text{solvent system}} / (1 - \text{density ratio})_{\text{water-deuterated water}}$ .

The difference in density of the deuterated ( $\rho_d$ ) and standard solvents ( $\rho_s$ ) leads to a difference in the measured  $\Delta f$  values between the solvents. This allows  $S_{\text{fraction}}$ , the fraction of the total mass due to solvent, to be calculated using

$$S_{\text{fraction}} = \frac{\Delta f_s - \Delta f_d}{\Delta f_s (1 - \rho_d / \rho_s)}, \quad (2)$$

where  $\Delta f_d$  is the resonant frequency difference between the bare crystal surface in D<sub>2</sub>O and the crystal with adsorbed polymer film in D<sub>2</sub>O and will have a negative sign. Similarly,  $\Delta f_s$  is the resonant frequency difference between the bare surface in H<sub>2</sub>O and the polymer film in H<sub>2</sub>O. The mass of the (dry) polymer film,  $F_{\text{mass}}$ , and the coupled water,  $S_{\text{mass}}$ , can then be calculated using

$$F_{\text{mass}} = \frac{\Delta f_s}{-C} (1 - S_{\text{fraction}}) \quad (3)$$

and

$$S_{\text{mass}} = \frac{\Delta f_s}{-C} S_{\text{fraction}}, \quad (4)$$

where  $C$  is the Sauerbrey constant for the crystal (see Eq. (1)).

Small measurement errors can adversely affect the determination of coupled solvent. The major contribution to this error is instrumental drift due to temperature variations and mechanical influences of the cell mounting. We estimate that this introduces an uncertainty of less than  $\pm 1$  Hz in our measurements, though it is difficult to determine the true uncertainty due to drift. Although this represents a small error

in the mass determination it becomes significant in the determination of the solvent contribution to the measured mass, as the difference in the frequency changes determined in the numerator of Eq. (2) is not large. Thus the accuracy of the measurement is very important for this determination. With an uncertainty in measurement of  $\pm 1$  Hz the percentage of the total mass attributed to the solvent is conservatively expressed as  $80 \pm 20\%$ , though the uncertainty in the measurement is perhaps somewhat less than this. The accuracy of this technique will improve with expected advances in the measurement electronics and cell design of the instrument. The polymer that we have used here has previously been investigated using QCM and XPS [19]. The XPS technique was performed on the dry polymer film and therefore comparison of the results was able to yield the mass of the film and the mass of the coupled water. The percentage mass of the coupled water was determined to be  $\sim 78\%$ . This is in close agreement with our calculation of the coupled mass using the deuterated solvent method ( $\sim 80\%$ ).

The value of the numerator in Eq. (2) is dependent upon the density change of the solvent upon deuteration. Thus solvents with large changes in density will give proportionally larger differences in response and therefore reduce the error in the technique. We have evaluated a number of solvent systems and calculated the sensitivity relative to the H<sub>2</sub>O/D<sub>2</sub>O system. This is presented in Table 2. We note that an ethanol system will give enhanced sensitivity (32%), as will cyclohexane (37%), while other common solvents will give a similar or reduced sensitivity compared to the aqueous system.

Note that the change in viscosity that accompanies a change in solvent does not enter the calculation of  $S_{\text{fraction}}$  as the  $\Delta f$  values refer to the change in frequency upon adsorption of a film in a given solvent.

The exchange of solvent with deuterated solvent in QCM measurements has been reported previously as a simple check on the applicability of using a viscoelastic Voight model of the adsorbed film [5]. This more complex and complete analysis, which required several overtones to be measured and optical measurements to be made on the film, showed that the mass and viscoelastic changes were consistent with the change in solvent properties on going from H<sub>2</sub>O to D<sub>2</sub>O. Additionally, calculation of the solvent contribution was made by comparison with optical techniques. The simple method described here is less precise than comparative measurements by optical techniques but requires only a basic QCM apparatus. An alternative isotopic substitution approach that may be applied to films with little entrained water, such as tightly packed surfactant layers, is to deuterate the adsorbing material and compare the measured frequency change with that for nondeuterated material.

#### 4. Summary

A simple method utilizing the density difference between a deuterated and a nondeuterated solvent has been described and demonstrated for determination of the mass of coupled solvent in QCM measurements. The method allows the contribution of the film and solvent to the total measured mass to be determined and does not require any additional instrumentation.

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