**White Paper**
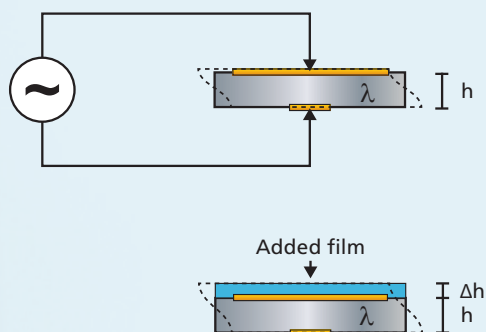
# QCM-D in relation to other QCMs

What are the differences, and does it matter which one is used?

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# QCM-D in relation to other QCMs
## What are the differences, and does it matter which one is used?



**[Figure 1]**
*Top:* Schematic illustration of a quartz crystal,
of thickness **h**, excited to resonance.
*Bottom:* A crystal with added mass of thickness **h** + Δh

**Surveying the market for QCMs, it becomes apparent that there is a vast range of different QCM versions in addition to the traditional one. Extended versions such as the QCM-A, QCM-D, QCM-I and QCM-R are but a few examples, and they all seem to provide similar information. What do these abbreviations mean, and is there any difference between these different QCM versions or are they equivalent? This white paper will introduce the necessary background theory of the oscillator concepts and terminology, and then clarify what the different QCMs signify, as well as how they are distinct from one another. The key takeaways, including a side-by-side comparison of instrument strengths, weaknesses and application suitability, are summarized in an overview, presented at the end of paper.**

## A balance for very small masses

QCM is short for Quartz Crystal Microbalance. As the name suggests, this technology was first used as a balance for very small masses. Originating from Sauerbrey's discovery back in 1959 [1], this real-time technology enables the monitoring and characterization of surface mass changes at the nanoscale. The Sauerbrey equation,

$$\Delta m = -C \cdot \Delta f \qquad (1)$$

which relates the QCM frequency change, $\Delta f$, to a surface mass change, $\Delta m$, through a simple multiplication with a constant, $C$, allowed for the monitoring and characterization of thin film deposition in vacuum and coating applications. The equation assumes that the thin layer, deposited on top of the oscillating crystal, can be approximated to be a part of the crystal itself, **Figure 1**. Hence, the propagation of the sound wave in the added material is assumed to be the same as that in the quartz. This means that the sound wave travels with the same velocity in the added material as in the quartz, and a thicker crystal, of thickness $h + \Delta h$, will only result in longer wavelength, λ, in accordance with the resonance condition below (Eq. 2). In the equation, $n$ is the overtone number and $v_q$ is the speed of sound in quartz. The overtones refer to the different crystal harmonics that can be excited to resonance, and $n = 1, 3, 5…$ This means that the crystal can oscillate not only at the fundamental mode but also at the odd overtones. The information from these overtones is essential, as we shall soon see.

$$f = \frac{nv_q}{2h} = \frac{nv_q}{\lambda} \qquad (2)$$

The approximation of the added material behaving like quartz is good enough for thin and rigid films and where the mass is small (film mass < 2% of total crystal mass), rigidly attached and homogeneously distributed over the crystal surface. When fulfilled, the change in resonance frequency as a function of added mass is linearly related via the Sauerbrey equation (Eq. 1), where $C$ is the mass sensitivity.

A QCM is often referred to as an acoustic sensor since it relies on an acoustic wave to sense mass changes. However, the frequency of this wave is typically several MHz and will therefore be rather hard to hear.

## The breakdown of the Sauerbrey equation

As the thickness of the added layer increases, the material properties of the film will start to gain significance and influence the accuracy of the mass determination. The point when this happens depends on the acoustic properties of the added material, i.e., the different characteristics demonstrated by the acoustic wave as it travels in the added film compared to in the quartz crystal. This discrepancy was soon discovered in the early era of vacuum technology applications, where the QCM was used as a film thickness monitor in vacuum and gas phase environments. For thicker films, the estimated thickness would deviate from the true one. By developing new equations that also took the density and acoustic impedance of the added material into account, the accuracy of the mass determination was much improved. The deposition rate of thick films could also thereby be monitored [2-4].

## Energy loss – when and why is this important to measure?

For even thicker films, or for soft viscous or viscoelastic films, an approach different from that of Sauerbrey's must be taken [5-7]. The wave propagation in these materials will be very different from that of quartz, **Figure 2**, and the energy losses (dampening of the acoustic wave) in the film can be significant. To calculate the thickness and mass of such films, information about the energy losses must be collected. This can be done in different ways, which we will soon discuss in more detail. The measurement of the energy losses is not only necessary in order to determine what equation to use for the mass and thickness quantifications, but it is also necessary for viscoelastic modelling. In the viscoelastic models, both frequency and energy loss information at multiple harmonics are needed as input into the model to solve for the multiple unknowns [7].

## The energy loss describes the damping of the oscillator

We have concluded that information about the energy loss is needed, but what energy loss are we talking about? The QCM is a damped harmonic oscillator. One property of a damped harmonic oscillator is that, if it is not forced to oscillate by an external power, it will gradually lose energy and the oscillation will die out. It is this damping that we are referring to when we talk about the energy loss.

An important parameter describing the characteristics of the oscillator is the quality factor, or $Q$ factor. This is a dimensionless parameter that describes the damping of the oscillation at resonance by relating the amount of energy stored in the oscillation to the amount of energy lost.

$$Q = 2\pi \times \frac{energy\ stored}{energy\ lost\ per\ cycle} = \frac{1}{D} \qquad (4)$$

The energy loss, or the dissipation, $D$, is the inverse of the $Q$ factor. Hence, a high $Q$ factor indicates that the energy loss during the oscillation cycle is small and that the oscillation will persist for a longer time. The higher the $Q$ factor, the lower the damping and the longer the oscillation will keep on going.

Another way to describe the $Q$ factor is to look at the resonance peak of the oscillator, **Figure 3**, where the $Q$ factor equals the center frequency, $f_0$ over the bandwidth, $BW$. The bandwidth, $BW = \Delta f = f_2 - f_1$ of the resonance peak is defined as frequency span over which the power of the peak is greater than half the power at the center frequency, $f_0$. See **Figure 3**.
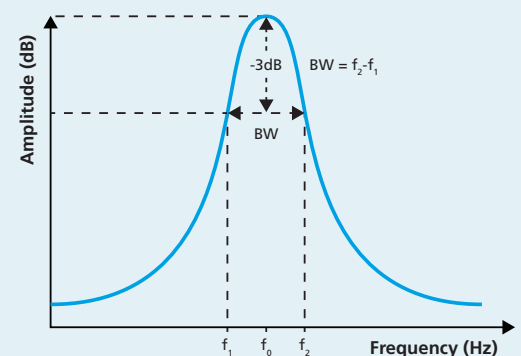
$$Q = \frac{f_0}{f_2 - f_1} = \frac{f_0}{\Delta f} = \frac{f_0}{BW} \qquad (5)$$
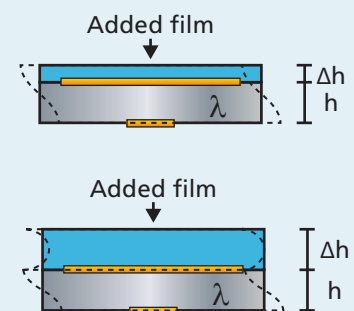


[Figure 2] *Schematic illustration of a quartz crystal, of thickness $h + \Delta h$, excited to resonance.*
*Top: The added layer is thin and rigid and follows the oscillation of the crystal.*
*Bottom: The added material does not follow the oscillation of the quartz and cannot be approximated to be a part of the crystal.*



[Figure 3] *A schematic illustration of the resonance peak, showing the center frequency $f_0$, and the bandwidth ($BW$), which gives the $Q$ factor.*

**Signal**
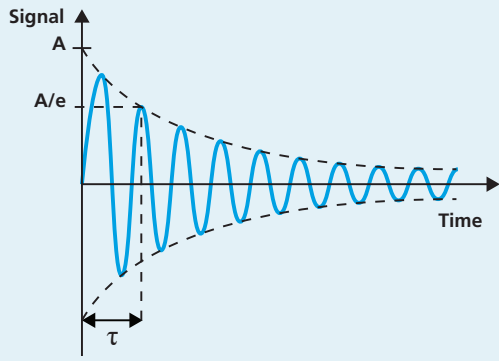


[Figure 4] *A damped oscillation with maximum amplitude A and decay time τ. τ is the time it takes for the amplitude to decay by a factor of **1/e, i.e**. about 37%.*
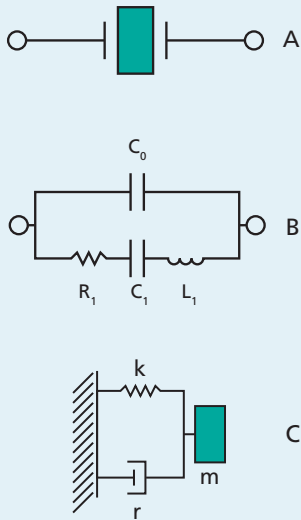


[Figure 5]
*A. Quartz crystal sandwiched between two electrodes.*
*B. Equivalent electrical circuit.*
*C. Equivalent mechanical resonator model.*

Yet another way to describe the $Q$ factor is to relate it to the decay time, $\tau$, of the oscillation, **Figure 4**, where the decay time is the time it takes for the oscillation to decay to $1/e$ of the maximum amplitude.

$$A(t) = A \cdot e^{-t/\tau} \tag{6}$$

$$Q = \pi f \tau \tag{7}$$

## Resonator model systems

To describe the behavior of the resonator system, it can, for example, be represented via a mechanical or an electrical model [8-14], **Figure 5**. The two lumped element models that we use here are coupled via the piezoelectric effect and are inter-changeable. The two models will help us describe the behavior of the resonator system under certain conditions.

In the acoustic domain, we use a mechanical model which represents the oscillating quartz (**Figure 5a**), as a mass connected to a spring and damper, **Figure 5c**. In the electrical domain we use an equivalent circuit with two arms, **Figure 5b**. The circuit is called a *Butterworth-Van Dyke circuit*, abbreviated to BVD. The LCR arm in the electrical circuit is referred to as the motional arm, as this represents the oscillating quartz crystal. The static shunt capacitance in parallel with the motional arm represents the electrode capacitance of the crystal.

## The components in the mechanical model

In the mechanical model [7, 15] (**Figure 5c**), $m$ corresponds to the oscillating mass, the spring corresponds to the stiffness (elastic modulus) of the quartz and the dashpot represents the damping, i.e., the energy losses in the oscillator.

## The components in the electrical model

The physical equivalents of the components in the BVD electrical model [16-18] (**Figure 5b**), the inductor $L_1$, the capacitor $C_1$, the resistor $R_1$, are the displaced mass, the ability to store energy, and the energy losses, respectively. $C_0$ is the static capacitance arising from the electrodes on the quartz.

## The Q factor in the acoustic and electrical domains

The acoustic and electrical equivalent circuit models both describe a damped harmonic oscillator for which the equations of motions can be described. Without going into the details of the equations, the damping, or the Q factor, can of course be described in the respective domain using the mass and energy loss parameters. The equivalent energy storing parameters are not needed in the calculations of $Q$.

$$Q = \frac{2\pi f L_1}{R_1} \tag{8}$$

$$Q = \frac{2\pi f m}{r} \tag{9}$$

## Different ways to measure the energy losses

To evaluate viscoelastic materials, both the frequency and damping at multiple harmonics are needed. As discussed in the previous section, the $Q$ factor describes the damping of the oscillator at resonance, and the damping, $D$, is the inverse of $Q$ (Eq. 4). There are many ways to measure or extract the $Q$ factor and hence there are different ways to obtain the information about the energy loss in the system. For example, we can measure the bandwidth, the oscillation decay time or the equivalent electrical circuit components, and use one of the equations listed above to extract the $Q$ factor and then the $D$ value.

## 1. Impedance and admittance measurements

One way to assess the $Q$ factor / $D$ value is to use impedance or admittance spectroscopy [8, 10]. A sinusoidal voltage, V, is applied over the crystal and the resulting current, $I$, is measured as a function of the frequency of the applied voltage. The ratio of the voltage and current will then give the frequency dependent impedance, $Z$. The admittance, $Y$, which is the reciprocal of the impedance, can also be extracted. This result can then be used to quantify the parameters of the electrical equivalent circuit, of which $L_1$ and $R_1$ are needed to calculate $Q$ or $D$ according to Eq. 8.

The Q factor can also be obtained by measuring the bandwidth, or half bandwidth at half maximum, $\Gamma$, of the resonance peak, and then using Eq. 5.

*Pros and cons of impedance and admittance measurements*
A benefit of impedance measurements is that they contain enough information to extract the $D$ value. It is also possible to measure several harmonics of the crystal oscillator. These are two prerequisites for viscoelastic modelling.
A drawback with this method is that the frequency sweeps are lengthy, which makes the measurements slow and limits the maximum time resolution. Another drawback is that the measurement is sensitive to small variations in the shunt capacitance, which can influence the accuracy and/or noise of the measurement.

## 2. Decay time measurement, pinging

Another approach is to measure the decay time, $\tau$, of the crystal oscillation[19-20]. Using this so-called pinging approach, the crystal is rapidly excited to resonance, the driving voltage is turned off, and then the decay time of the oscillation is monitored. $Q$ and $D$ can then be extracted along with the resonant frequency of the sensor.

*Pros and cons of decay time measurements*
There are several benefits to this method. As with the impedance frequency sweep method, pinging allows for overtone measurements which makes viscoelastic modelling possible. The pinging principle is also very fast, which enables a high time resolution. Additionally, the short circuit mode practically eliminates the interference from the shunt and stray capacitance, which greatly improves measurement stability.

## 3. Resistance measurements

The resistance, $R$, which is essentially equivalent to the resistor in the motional arm in the circuit in **Figure 5b**, can be measured, for example, via an advanced oscillator circuit[18].

*Pros and cons of resistance measurements*
The R parameter alone cannot be used to calculate the $Q$ factor. Also, when letting the QCM sensor be a part of an oscillator circuit, only one resonance frequency is measured. Hence, this method does not allow for viscoelastic modelling and $R$ can only be used as an indicator of the energy losses in the system. The oscillator circuits are generally sensitive to changes in stray capacitance, making it hard to obtain a stable measurement.

## Different QCMs in terms of parameters and principles

The different versions of QCMs that may be encountered in the instrument arena are similar, yet different. Except for the standard QCM, which only measures the resonant frequency, all the others also measure, in addition to f, parameters related to the energy loss. Although there are only three main ways to measure the energy loss; via 1) impedance spectroscopy, via 2) the decay time of the oscillation or via 3) the resistance, the technology names out there suggest that there are many more ways to do so. For example, the abbreviations QCM-A, QCM-D, QCM-I, QCM-R, and QCM-Z give little information on the actual measurement principle, and what information that the respective technology offers. **Table 1** below shows an overview description of six common QCM versions.

| QCM ABBREVIATION | PARAMETERS MEASURED | METHOD TO MEASURE ENERGY LOSS | COMMENT |
|---|---|---|---|
| QCM | Resonance frequency, $f$ | - | Energy loss is not measured. |
| QCM-I | $f$ and impedance, $I$ | Impedance | The energy loss is obtained either via the fitted equivalent circuit parameters or via the bandwidth of the resonance peak. |
| QCM-A | $f$ and admittance, $A$ | Admittance | Similar to QCM-I, as the admittance is the reciprocal of the impedance. |
| QCM-D | $f$ and Dissipation, $D$ | Impedance or pinging | The dissipation can be obtained in different ways, for example via the bandwidth (i.e. an impedance measurement) or via the decay time (pinging). Currently, QCM-Ds based on both the impedance approach and the pinging approach exist. |
| QCM-R | $f$ and resistance, $R$ | Resistance | The resistance is obtained from the oscillator circuit. |
| QCM-Z | $f$ and impedance, $Z$ | Impedance | See above |

**[Table 1]** *Overview of six common QCM abbreviations, including their method approach to measure the energy losses*

## Concluding remarks on what QCM to choose

So, which of the discussed QCM setups should be chosen? The answer to this question depends on the intended use of the instrument. Will measurements be taken in the gas phase or in the liquid phase? Will viscoelastic layers be studied? Will the processes studied be fast or slow? And is quantitative information needed, or will qualitative information be sufficient?

### Viscoelastic films and/or films in liquid?

Essentially, if there is the intent to study anything other than rigid films in vacuum, then a QCM is needed that also monitors the energy losses in addition to the frequency. As shown in this whitepaper, even though there is seemingly a large range of different QCM types available which all measure the energy loss, there are only three principle ways to measure it - via i) impedance spectroscopy, via ii) the oscillation decay time or via the iii) resistance of the equivalent circuit. It is important to note that these three method approaches are not equivalent in terms of information content, and which method to go for depends on the intended application and information needs. Although perhaps obvious, it is worth mentioning that, in order to characterize an unknown system, the information quality has to be sufficient to allow for the film properties to be resolved. I.e. if you are not 100% sure that the film on your QCM sensor is solid, the measurement result will be in doubt if only the resonant frequency is used to estimate the mass of the film. If only frequency and dissipation of one harmonic is measured and it is detected that the film causes a change in dissipation, then you are at loss since you have no way of estimating what type of film you have on your sensor (more than that it is not solid).

## Qualitative or quantitative information?

If only a qualitative measure of the layers is of interest, then information from one harmonic might be sufficient. If, however, the information on the viscoelastic films is to be quantified, information about f and D at multiple harmonics is needed. From a theoretical perspective, this information extraction is only possible with the impedance method and the decay time method. These two methods are therefore the only ones that enable viscoelastic modelling. The third method, the resistance approach, can only offer a qualitative estimate of the energy losses in the system. Note, however, that even though an instrument may be based on the impedance or decay time method, this is not a guarantee for overtone capabilities, as not all instruments may have this functionality implemented. If an evaluation of viscoelastic films is of interest, overtone capabilities are thus something to look for.

## Fast or slow processes?

Another feature to consider is the rate with which measurements are possible, i.e., the measurement time resolution. If slow processes are being studied, such as films that take a long time to form or slow layer restructuring events, or if the buildup is not of interest but only the final equilibration values, then the time resolution may not be so important. If, however, the interest is in following fast processes and surface changes, then the time resolution is a specification to keep an eye on. Again, in order to characterize an unknown system, the information content has to be sufficient to allow for the process characteristics to be resolved. I.e. if it is not known beforehand whether any fast processes are to be dealt with, then an instrument with high time resolution will be needed in order to reveal whether this is the case or not. The time resolution will, to some extent, be limited by the technical principle on which the QCM is based. For example, the decay time method which is based on pinging is a lot faster than the impedance method, which captures slow spectrum sweeps.

## The technical principle says a lot, but not everything

We have here shown that the technical principle on which the QCM is based largely determines the capabilities in terms of data quality and time resolution, see overview in Table 2. However, as already mentioned, there is a lot more to a well-functioning and useful piece of equipment than just the method that it is based on. The method is a good start, but then the supplier must make the most of the inherent capabilities and design a robust and well-functioning instrument suited for the purpose. For example, not all impedance based QCMs will have overtone capabilities. Other parameters that are important to keep an eye on from a QCM perspective are, for example, the temperature stability and the mechanical design. Two aspects of utmost importance for stable and reproducible QCM measurements.

| METHOD | QCM | QCM + IMPEDANCE MEASUREMENT | QCM + DECAY TIME MEASUREMENT | QCM + RESISTANCE MEASUREMENT |
|---|---|---|---|---|
| Output parameters | $f$ | $f, R_1, L_1$ (also gives $C_0, C_1$, but these are not needed for the film characterization) or $f, BW$ (alternatively $\Gamma$) | $f, D$ | $f, R$ |
| Viscoelastic film analysis possible | No | Yes, if overtones are measured | Yes, if overtones are measured | No |
| Aquisition rate | Fast | Slow | Fast | Fast |
| Suitable for | Thin and rigid films with no viscoelastic component. | If overtones available, then suitable for all films, from thin to thick, and for rigid as well as viscoelastic films. Limitations in acquisition rate make this best suitable for slow processes. | If overtones available, then suitable for all films, from thin to thick, and for rigid as well as viscoelastic films. High kinetic resolution makes this suitable for both fast and slow processes. | Thin and rigid films. The R output provides some relative information about viscoelastic properties, but quantification not possible. |

[Table 2] *Overview of the four principle QCM methods, including parameters measured and application suitability.*

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# QCM-D vs. other QCMs

What are the differences, and does it matter which one I use?

There is a vast range of QCM versions in the market; QCM, QCM-D, QCM-I and QCM-R being but a few examples. Here, we present an overview of the measurement principles that these instruments are based on, and what the different methods signify in terms of pros, cons and application suitability.

## What QCM should I choose?

As summarized in **Table 1**, the QCMs available in the market are based on three different measurement principles. The technical solution and the parameters measured varies to some extent between the instruments, which in turn affects the information content and the time resolution of the measurement. Which QCM to choose depends on the intended use of the instrument; will measurements be taken in the gas phase or in the liquid phase? Will viscoelastic layers be studied? Is quantitative information needed, or will qualitative information be sufficient? And will the processes studied be fast or slow?

**A**. Viscoelastic films and/or films in liquid?

Unless it is known beforehand that the film is rigid, the measurement result will be in doubt if only the resonant frequency is used to estimate the film mass. Hence, except for studies of rigid films in vacuum, **a QCM that monitors the energy losses will be needed to know whether the film is viscoelastic or not.** QCMs that measure the energy loss are based on either i) impedance spectroscopy, ii) oscillation decay time measurement or iii) resistance of the equivalent circuit. Each of these methods has its pros and cons in terms of quantification and time resolution, **Table 2**.

| QCM ABBREVIATION | PARAMETERS MEASURED | METHOD TO MEASURE ENERGY LOSS | COMMENT |
|---|---|---|---|
| **QCM** | Resonance frequency, $f$ | - | Energy loss is not measured. |
| **QCM-I** | $f$ and impedance, $I$ | Impedance | The energy loss is obtained either via the fitted equivalent circuit parameters or via the bandwidth of the resonance peak. |
| **QCM-A** | $f$ and admittance, $A$ | Admittance | Similar to QCM-I, as the admittance is the reciprocal of the impedance. |
| **QCM-D** | $f$ and Dissipation, $D$ | Impedance or pinging | The dissipation can be obtained in different ways, for example via the bandwidth (i.e. an impedance measurement) or via the decay time (pinging). Currently, QCM-Ds based on both the impedance approach and the pinging approach exist. |
| **QCM-R** | $f$ and resistance, $R$ | Resistance | The resistance is obtained from the oscillator circuit. |
| **QCM-Z** | $f$ and impedance, Z | Impedance | See above |

**[Table 1]** *Overview of six common QCM abbreviations, including their method approach to measure the energy losses.*

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# Overview

**B.** **Qualitative or quantitative information?**

If only a qualitative measure of the film is of interest, then information from a single harmonic might be sufficient. If, however, viscoelastic films are to be *quantified,* information about $f$ and $D$ at *multiple* harmonics is needed. This information extraction is only possible with the impedance and the decay time methods. These are hence the only methods that enable viscoelastic modelling. Not all impedance or decay time-based methods will have overtone functionality implemented however. *If quantitative evaluation of viscoelastic films is of interest, overtone capabilities are something to look for.*

**C.** **Fast or slow processes?**

Another feature to consider is the measurement time resolution. If the process rate is not known beforehand, then an instrument with high time resolution will be needed to reveal whether any fast processes are indeed involved. The time resolution will, to some extent, be limited by the technical principle on which the QCM is based. For example, *the decay time method which is based on pinging is a lot faster than the impedance method,* which captures slow spectrum sweeps.

## Other important aspects to consider

The technical principle on which the QCM is based, determines the capabilities in terms of data quality and time resolution. Additional aspects to keep an eye on are *temperature stability* and the *mechanical design*, both of utmost importance for stable and reproducible measurements.

| METHOD | QCM | QCM + IMPEDANCE MEASUREMENT | QCM + DECAY TIME MEASUREMENT | QCM + RESISTANCE MEASUREMENT |
|---|---|---|---|---|
| **Viscoelastic film analysis possible** | No | Yes, if overtones are measured. | Yes, if overtones are measured. | No |
| **Acquisition rate** | Fast | Slow | Fast | Fast |
| **Suitable for** | Thin and rigid films with no viscoelastic component. | If overtones available, then suitable for all films, from thin to thick, and for rigid as well as viscoelastic films. Limitations in acquisition rate make this best suitable for slow processes. | If overtones available, then suitable for all films, from thin to thick, and for rigid as well as viscoelastic films. High kinetic resolution makes this suitable for both fast and slow processes. | Thin and rigid films. The R output provides some relative information about viscoelastic properties, but quantification not possible. |

**[Table 2]** *Overview of the four principle QCM methods, including parameters measured and application suitability.*

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