Allan L. Smith[1]

Gravimetric Analysis of the Nonvolatile Residue from an Evaporated Droplet, Using the Quartz Crystal Microbalance/ Heat Conduction Calorimeter

ABSTRACT: A quartz crystal microbalance/heat conduction calorimeter (QCM/HCC) has been used to determine the nonvolatile residue at the parts-per-million level in 10 μL droplets of methanol and a 45 μL droplet of water. The QCM was used to measure the mass of the nonvolatile residue, and the calorimeter was used to determine the mass of the solvent by the heat required to evaporate the droplet.

KEYWORDS: gravimetric analysis, nonvolatile residue, quartz crystal microbalance, extractable residue

Introduction

In reality, no liquid is absolutely pure. Even high-purity solvents have some dissolved chemical contaminants at the parts-per-million level or less. In many critical fields such as foods, pharmaceuticals, medical products, plastics, metallurgy, electronics, aerospace, high-purity chemicals, and clean room environments, there is a need for precise measurement of the purity of liquids used. Often, these requirements are formalized in government regulations or accepted ASTM standard practices.

The standard way of determining the nonvolatile residue (NVR) in water or an organic solvent is to evaporate a measured quantity of filtered sample solution to dryness and weigh the residue on an analytical balance. This type of gravimetric analysis is fundamental in the fields of water quality, the environment, and the chemical and pharmaceutical industry. The International Standards Organization (ISO) and the American Society for Testing and Materials (ASTM) have many published standard gravimetric methods for determining NVR. One example is the recently developed ASTM standard test method F 2459-05 for extracting residue from metallic medical components and quantifying via gravimetric analysis.

The present limit of precision of analytical balances routinely used for gravimetric analysis is ± 0.01 mg. To determine the NVR at a level of 1 part per million to a precision of ± 10 % (one part in 10^7) with this balance requires a solvent mass of 0.01 mg $\times 10^7 = 100$ g. Evaporation of this amount of solvent is slow, and determining the difference in mass between the empty vessel and the vessel with residue requires two careful balance measurements.

The object of this study is to investigate the advantages and problems of using the quartz crystal microbalance (QCM) as the gravimetric device for weighing the residue in NVR measurements, coupled with a heat conduction calorimeter (HCC) for determining the volume of the corresponding evaporated solvent. We show here that it is possible to get parts-per-million precision in the determination of NVR from water and methanol using as little as 50 μL of solvent—a thousand times less solvent than needed with an analytical balance. At present there are problems in the reproducibility and accuracy of these measurements, but the causes of these problems are identifiable and solutions are being tested.

Principles of QCM/HCC and Its Application to Gravimetric Nonvolatile Residue Determination in Liquids

We used a Masscal™ G1 quartz crystal microbalance/heat conduction calorimeter to prove the concept that a droplet of liquid can be injected onto the quartz crystal microbalance sensor and analyzed for both

the volume of the droplet and the mass of its nonvolatile residue after evaporation. The quartz crystal microbalance/heat conduction calorimeter (QCM/HCC) was designed to measure simultaneously the heat flow, mass uptake or release, and viscoelastic property changes in a submilligram solid film sample when gases are absorbed or react with the film in an isothermal environment. The measurement principles and a description of the apparatus have been described in a recent review article [1], and only the relevant working equations will be summarized here.

A thin uniform film of density ρ_f and thickness h_f applied to one side of a QCM over a large area compared to the piezoelectrically active area of the crystal produces a frequency shift of the QCM given by the Sauerbrey equation:

$$\Delta f = - C_q \rho_f h_f = - C_q m_f / A_f \qquad (1)$$

Here Δf is the difference in frequency between the coated and bare crystal, m_f and A_f are the film mass and area, and C_q is a constant independent of film properties and dependent only on the properties of quartz. For a 5 MHz QCM used in this work, $C_q = 56.3 \ \mathrm{Hz \ cm^2 / \mu g}$. Notice that a decrease in frequency corresponds to an increase in deposited mass.

The thermopile directly under the QCM in the sample chamber of the G1 acts as a heat flow sensor to measure the instantaneous thermal power $P(t)$ flowing to or from the QCM. When a solvent droplet is injected onto the QCM surface, the heat required to evaporate this droplet is

$$Q = \int P(t)dt = m_s \Delta_{vap} H_s / M_s \qquad (2)$$

where m_s is the mass of the solvent droplet and $\Delta_{vap} H_s$ and M_s are the molar enthalpy of vaporization and the molar mass of the solvent, respectively.

Data and Analysis

Nonvolatile Residue of a Water Droplet

For gravimetric determination of NVR using solvent droplets, the G1 sample chamber was modified so that 10–100 μL droplets of solvent can be deposited onto the QCM mounted inside a temperature-equilibrated sample chamber while acquiring data from all three signal channels. A short vertical 1/16 in. OD tube is positioned above the center of the QCM. Solvent can be deposited on the QCM either via a syringe pump attached to this tube or directly from a syringe inserted through the introduction tube.

Figure 1 shows the results of injecting 45 μm of water from a syringe (Poland Springs Natural Springs Water, total dissolved solids ("TDS") 26–60 ppm) onto a clean, bare QCM equilibrated inside the 250 μL G1 sample chamber at 60°C. The run began with dry nitrogen flowing through the sample cell, but flow was turned off at 400 s. The droplet was injected at 600 s and the nitrogen flow was increased stepwise thereafter to a final value of 4 standard cm^3 per minute (sccm). Notice that the thermal power signal, which measures the evaporation rate, increased proportionally as the gas flow rate increased. The integrated heat signal Q(t) at any time (c) is a direct measure of the mass of water evaporated at that time. Q levels out at 110.1 J after 5200 s, indicating that all of the water has evaporated. The frequency signal (d) does not measure the mass of the water droplet; the amplitude of the QCM shear vibration is damped by the water, rendering the QCM inoperative as a balance as long as the water droplet has not evaporated [2,3]. The motional resistance signal (e) indicates significant viscous damping of the QCM by the liquid droplet, but as the droplet evaporates the damping decreases until at 5200 s the motional resistance is approximately that of the bare QCM at the beginning of the run. Now that the balance is again operative, the decrease in frequency of 27.5 Hz shows that a solid residue remains on the QCM surface. Subsequent examination of the crystal showed an annular deposit ~2 mm in diameter, displaced from the center of the crystal by 3.8 mm.

Using Eq 1 with the piezoelectrically active area of the crystal of 0.312 cm^2 gives the mass of the residue as 0.15 μg. The total integrated heat required to evaporate the droplet is 110.1 J, and from Eq 2 this corresponds to a droplet mass of 46.7 mg of water. Since 45 μL of water weighs 45 mg, the integrated
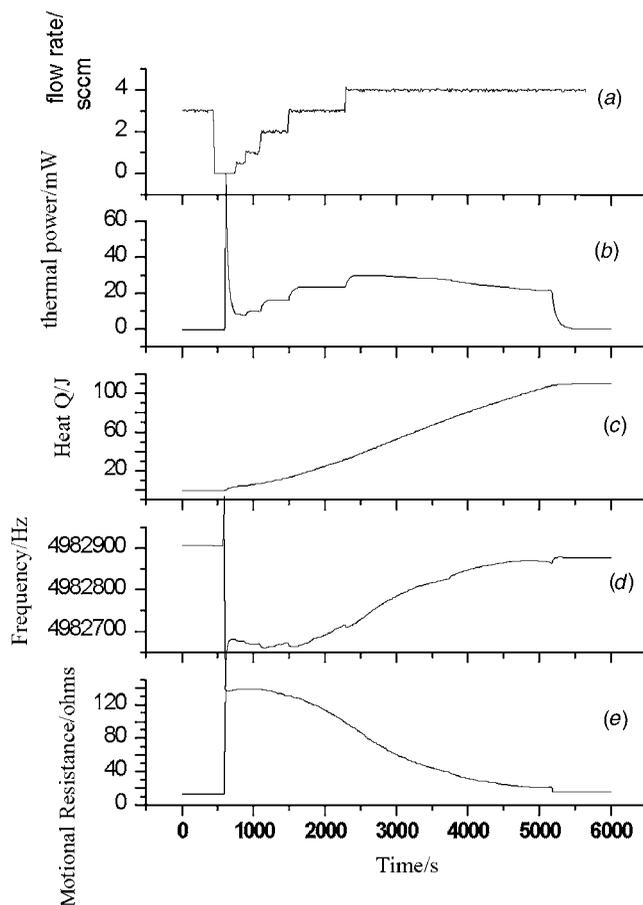
FIG. 1—*Quartz crystal microbalance/heat conduction calorimeter signals from the evaporation of one 45 μL droplet of water at 60°C. (a) Nitrogen flow rate, in standard cm³/min, (b) Thermal power needed to evaporate the droplet, in mW, (c) Integrated heat derived from the thermal power signal by $Q = \int P dt$, (d) QCM frequency in Hz, (e) Motional resistance in ohms. The droplet was introduced at 600 s and evaporated completely at 5200 s.*

heat yields a mass in very good agreement with the deposited volume of water. The calculated residue after evaporation is thus 3.3 ppm, a good deal lower than expected from the TDS specifications of the water given by the manufacturer.

This experiment is the first of a series of studies, the object of which is to determine the dependence of the results on the flow rate of gas and the evaporation temperature. These results will be presented in a subsequent publication.

Nonvolatile Residue of Methanol Droplets

Another bare clean QCM was equilibrated in the G1 at 40°C. Reagent grade methanol was placed in a gas-tight syringe in a syringe pump (Harvard Apparatus) driven at 25 μL/min. In this mode, drops of about 10 μL form and detach from the tube, producing instantaneously large changes in frequency, motional resistance, and thermal power, as shown in Fig. 2. The syringe pump is turned off temporarily when a droplet strikes the QCM and turned on again when the baselines stabilize.

Table 1 presents the results of an experiment in which three droplets are deposited sequentially on the same QCM. Here Δf is the frequency change due to the evaporation of the drop, Q is the heat required to evaporate it, m_r is the mass of the residue in nanograms, m_m is the mass of methanol in the drop in milligrams, NVR is the nonvolatile residue after evaporation of the methanol in ppm, and ΔV_{pred} is the volume of the methanol drop in microlitres predicted from its mass and the density.

Discussion

The microbalance/calorimeter gave much too low a NVR for the Poland Springs water sample. It is well known in the QCM community that the differential mass sensitivity of a QCM varies radially from its
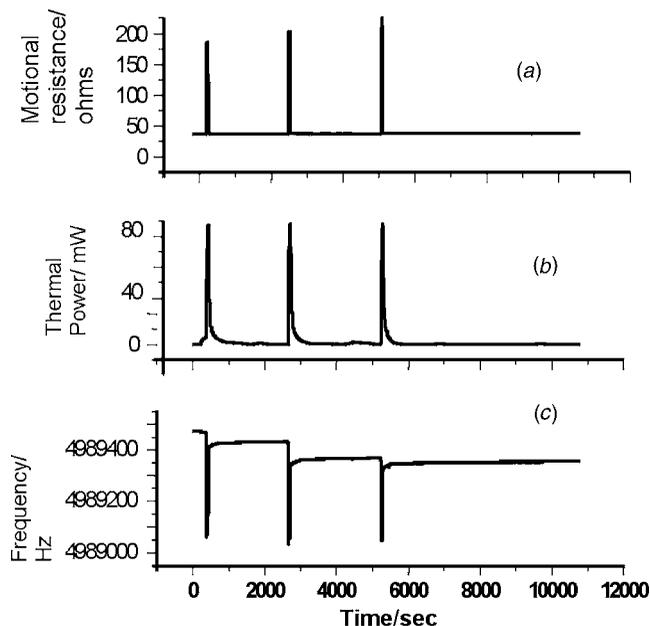
FIG. 2—*Quartz crystal microbalance/heat conduction calorimeter signals from the evaporation of three successive 10 μL droplets of methanol at 40°C. The nitrogen flow rate was 5 sccm. (a) motional resistance, (b) thermal power, (c) frequency.*

maximum value at the center of the crystal to zero somewhere beyond the radius of the smaller electrode, following an approximate Gaussian distribution [4]. From Fig. 3 of Ref [4] we estimate that for the residue spot positioned at the observed radius of 0.38 cm (or $r/r_e \sim 1.2$), the mass sensitivity has decreased by about a factor of ten from its Sauerbrey value. Applying this correction factor to our results, we get a calculated residue after evaporation of ~33 ppm, in better agreement with the value specified by the water supplier.

TABLE 1—*Nonvolatile residue from three 10 μL droplets of methanol.*

Droplet #	Δf/Hz	Q=∫Pdt/J	m_r/ng	m_m/mg	NVR/ppm	ΔV_{pred}/μL
1	−44	9.22	55	8.07	6.8	10.2
2	−63	8.86	79	7.75	10.2	9.8
3	−14	7.97	17	6.98	2.5	8.8
total	−121	26.06	152	22.8	6.5±3.9[a]	29

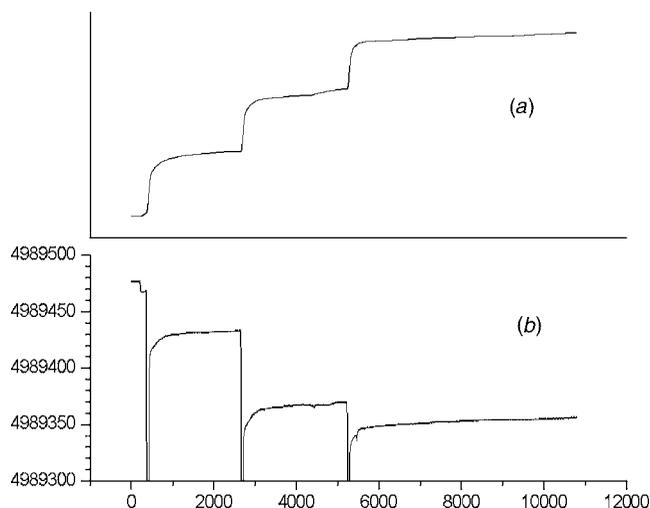[a]Mean and standard deviation for three droplets.

FIG. 3—*Integrated heat and detailed frequency shift from Fig. 2. (a) integrated heat, (b) frequency shift.*

Further experiments have shown that the droplet dried off-axis because electrostatic forces due to inappropriate grounding moved the droplet after it was deposited in the center of the crystal. Clearly, in order for this method to become a reliable gravimetric assay, the position of the residue on the QCM surface must be accurately controlled.

The results for successive droplets of methanol are encouraging, even though the standard deviation of the NVR is unacceptably high. Calculated droplet volumes are very close to that computed from the flow rate of the syringe pump, but the precision of the calorimetric determination of droplet volume is far higher. It is possible to determine the integrated heat to a precision of ±1 mJ; for methanol, this corresponds to a droplet volume precision of ±1 nanolitre, or one part in 10^4.

The residue from the first drop is redissolved and displaced somewhat on the crystal surface when the second droplet is deposited and evaporates. We believe this is the major contribution to the large standard deviation in NVR. We did not determine independently a NVR of the reagent grade methanol used in this experiment.

Conclusion

Using a quartz crystal microbalance/heat conduction calorimeter it is possible to determine gravimetrically the nonvolatile residue in water and high-purity methanol to the parts-per-million level of precision, using between 10 and 50 µL of the solvent. This method, when refined and developed, promises major savings in both time and cost in the present methods used for gravimetric determination of nonvolatile residues of liquids and solutions.

References

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