# Insights Into the Drying Behavior of Capillary Suspensions

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## Introduction

Cracking and particle mobility are a significant problem in the drying of films from hard sphere suspensions. Particle coatings can be found in various applications of which printed electronics have gained massive interest. Screen printed circuits offer access to low cost products such as near field communication (NFC) tags for digital marketing and as user-friendly solution to every day applications. During drying of the conductive pastes, cracking is a well-known problem that has to be suppressed. The conventional way of achieving a crack free surface is to add binders and surfactants to the suspensions in order to modify their printing properties and take up the stresses generated through capillary pressure differences within the film during drying. The downside of this approach is the fact that in order to conduct electricity a particle-particle contact needs to be established. This is accomplished by degrading and burning off the binder and surfactants with a subsequent sintering step. Elevated temperatures are needed which can cause problems with polymeric substrates. Another approach to circumvent these difficulties is using capillary suspensions [1]. The capillary force from a secondary liquid induces a sample-spanning network [2, 3], which limits the degree of particle motion during drying, and also counters the capillary force within pores generated by evaporation. Previous work employing a simultaneous weight and stress measurement technique allowed the correlation of the occurring stresses during drying of capillary suspensions. We found that using capillary suspensions reduces drying stresses. We partially attributed this observation to an increase in film porosity, but mostly to the sample spanning particle network induced by capillary bridges from the secondary fluid. On the one hand, this network leads to a more uniform pore size distribution and thus smaller capillary pressure differences when menisci form in the pores. These formed menisci are responsible for particle movements causing stress increase and eventually lead to cracks. On the other hand, the capillary forces from the bridges act as counter forces to the capillary pressure difference driven particle movement.

The two competing phenomena however, could be questioned, since the secondary liquid used to induce the capillary bridges is often water. Capillary suspensions are comprised of two immiscible fluids. If the secondary liquid is water, then using an oily bulk phase is the obvious choice. This means that the secondary fluid for which it is desirable to stay trapped in the network structure during drying, has a lower boiling temperature than the oil. Thus, the water is prone to evaporate first and therefore not contributing to counter the occurring stresses. This work has the aim of investigating the residual water content and the evaporation of the components.

## Experimental

1. Karl Fischer titration

The Karl Fischer titration is a water specific reaction used to determine the water content in samples. There are two commonly used techniques: the volumetric and the coulometric titration. The latter is generally more exact when determining low water contents, thus making it the first choice for this work. In order to access the bound water in the coatings, an indirect method has to be used because injection of the particles in the titrator is not possible. Therefore, methanol was used to dissolve the trapped water from the film. Samples were dried in a temperature-controlled chamber and the weight loss was recorded via suspended underfloor weighing. At different drying

times, the process was stopped and the particle coating was scraped off the substrate and weighed into a vial. Subsequently, a known amount of methanol was added. Shaking the vial with the particles breaks the coating's structure, making the bound water accessible. A centrifugation step separated the particles from the solvent, which was then ready to be analyzed with the Karl Fischer titration.

2. FTIR- ATR

FTIR equipped with an attenuated total reflectance (ATR) crystal, allows determining the IR absorbance spectra of the samples. The suspensions are coated on the crystal and left to dry. To increase the drying rate, a heat lamp was used. This method gives insight into the composition at the bottom of the coating. In order to prevent overlapping of other IR active groups, the capillary suspension samples were formulated with $D_2O$.

3. TGA- MS

Thermogravimetrical analysis (TGA) is a very accurate weighing scale in which the temperature can be very exactly controlled while measuring the sample's weight loss. When coupled with a mass spectrometer, it provides a tool to monitor and identify the evaporated species. The capillary suspension sample was placed in a crucible and then introduced into TGA. Subsequently, it was exposed to isothermal drying after which a temperature ramp to 500 °C was set to drive the residual fluids out of the film, followed by another isothermal segment. A blank run with the same method provided a correction file to account for buoyancy effects in the TGA, residual gases and overlapping mass to charge ratio (m/z) in the mass spectrometer.

For all experiments capillary suspensions were formulated with $Al_2O_3$ particles, 1-heptanol as the oily bulk phase and water or $D_2O$ as secondary phase.

**Results**

The evaluation of the Karl Fischer titration was inconclusive. We measured unusually high water contents along with a wide variation among the different samples. This suggests that additional water was introduced into the samples, possibly due to a high relative humidity in air.

Figure 1 shows the result for a FTIR- ATR measurement. Wavenumbers were recorded between 4000 cm$^{-1}$ and 1000 cm$^{-1}$. The z-axis was magnified and cut off, visually showing the decrease of the characteristic $D_2O$ peak at $\nu \approx 2750$ cm$^{-1}$ with time. After several minutes the secondary liquid peak has approached zero, while heptanol is still present in the film. This result could be an interplay of several factors. The obvious one is that the higher vapor pressure $D_2O$ readily evaporates and is therefore not available to form capillary bridges. Another possibility could be the occurrence of capillary mass transport, which could drive the heavy water towards the upper film areas. Since the IR beam only penetrates the sample for a few microns the mass transport would show as evaporation rather than just mass transport. A third option could be a combination of effects. Part of the $D_2O$ is evaporated but at some point the concentration is simply below the detection limit of the device showing as evaporated when there is still secondary liquid left to keep the network strength. This is seen as the likeliest case, because tests showed that even when $D_2O$ was initially present it could not be detected.

On the left y- axes, the monitored and corrected mass spectral data for heptanol and $D_2O$ are shown. The recorded intensity peaks were measured for mass to charge ratios of 20 m/z and 56 m/z for $D_2O$ and heptanol, respectively. At the onset of the measurement, the heptanol peak increases rapidly. The following constant rate period shows a near constant concentration of the evaporated

heptanol. When leaving the constant rate period, the heptanol concentration in the atmosphere is gradually decreasing, indicating the first consolidated regions in the film.
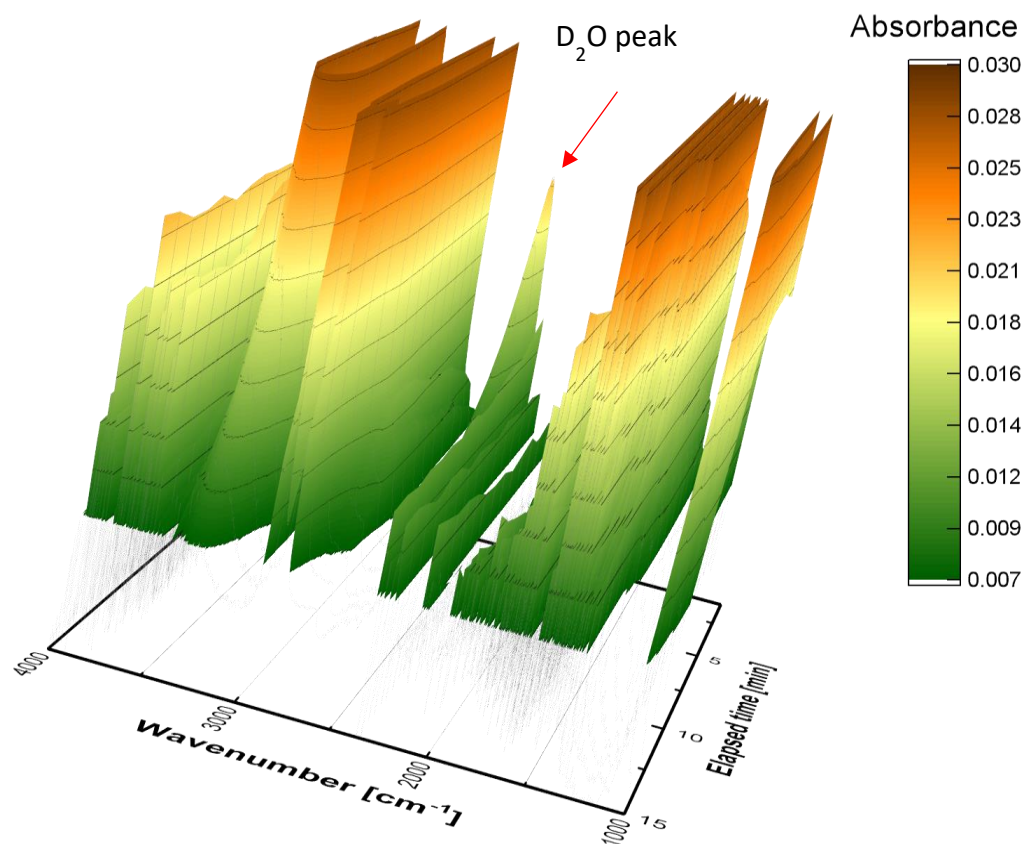


**Figure 1:** FTIR- ATR spectral data of a 2.5% $D_2O$ capillary suspension with its characteristic peak. The wavenumbers are presented on the x-axis within the range of 4000 cm$^{-1}$ to 1000 cm$^{-1}$. In z- direction the absorption intensity is plotted and adjusted to a color map range to visually enhance the peak of interest. The drying starts with a high initial $D_2O$ peak rapidly decreasing and soon approaching zero.

The subsequently observed sharp heptanol drop occurs when most liquid of the film has dried and the liquid level everywhere in the film recedes into the pores. Shortly after the film is getting closer to its equilibrium dry state, the heptanol concentration in the mass spectrum is virtually zero. The constant near zero value stays at the same level of the detection threshold even after ramping up the temperature. This strongly suggests that there is no residual heptanol left in the film.

The $D_2O$ concentration similarly starts to increase at the beginning, though at a lower level. In contrast to heptanol, the heavy water concentration stays higher for longer and thus shifts to the right. The steep decrease that can also be seen occurs about 4 minutes later, when liquid already receded into the film. The concentration drop is additionally relatively not as large as the heptanol one. On the contrary, when heptanol has completely evaporated, the $D_2O$ keeps evaporating in the near sorption equilibrium. The decrease persists even after ramping up the temperature. This finding strongly suggests that the secondary liquid, albeit having the higher bulk vapor pressure, remains longer in the film presumably as capillary bridges.
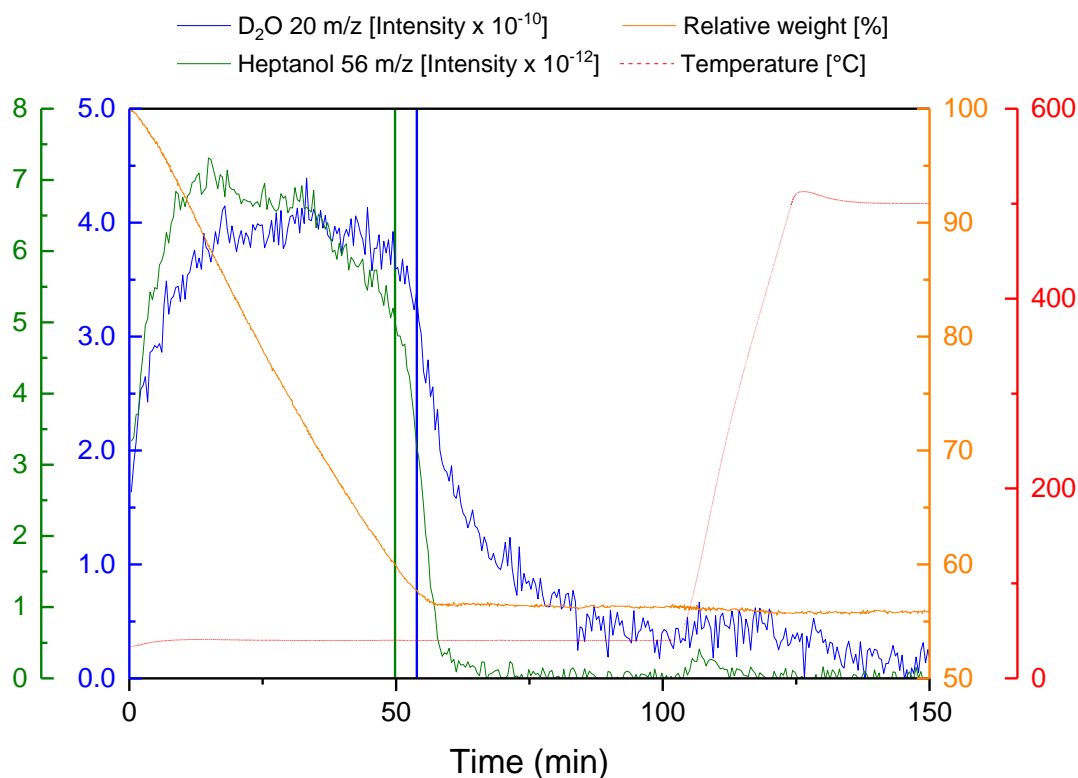
**Figure 2**: TGA- MS measurement of capillary suspensions formulated with $D_2O$. The temperature in red shows the employed temperature ramp and method for the measurement. In orange the relative weight loss is depicted. The blue and green curves show the MS gas phase data for $D_2O$ and heptanol. From the vertical lines it can be seen that the $D_2O$ concentration drops later. Additionally it dries slower and its concentration is higher in the quasi-dry film compared to heptanol.

## Conclusions

We performed several measurements to shed light on the question if the secondary liquid in capillary suspensions stays trapped between the particles longer than the lower bulk vapor pressure. Whereas other water specific measurement such as Karl Fischer could not answer this question, the FTIR- ATR left several possibilities as to when water is evaporating and byf how much. TGA- MS however strongly suggests that although $D_2O$ is evaporating, there is still some left after heptanol has dried.

## Acknowledgements

## References

1. Gubbi J, Buyya R, Marusic S et al. Internet of Things (IoT): A vision, architectural elements, and future directions. Future Generation Computer Systems 2013; 29 (7): 1645–1660

2. Perelaer BJ, Laat AWM de, Hendriks CE et al. Inkjet-printed silver tracks: Low temperature curing and thermal stability investigation. J. Mater. Chem. 2008; 18 (27): 3209

3. Schneider M, Maurath J, Fischer SB et al. Suppressing Crack Formation in Particulate Systems by Utilizing Capillary Forces. ACS Appl Mater Interfaces 2017; 9 (12): 11095–11105