EVAPORATION FROM CARBON NANOTUBE FOREST: ANALYTICAL POSSIBILITIES OF THE MASS MEASUREMENTS

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Abstract
The evaporation of liquids from porous materials is a very complex phenomenon, which can be followed by simultaneous weight monitoring, electric resistance measurement, infrared imaging and contact angel measurement. The appropriate evaluation of these measurement results can carry both quantitative and qualitative analytical information. The aim of our recent work is to demonstrate this opportunity through the example of the evaporation of simple solvents from a carbon nanotube forest. In this work the focus will be on the analytical possibilities of the mass measurements.

Introduction
Recent developments in nanotechnology have highlighted the importance of the classical topics of wetting, droplet spreading and evaporation due to their pronounced effect in technological applications (*e.g.,* air/fuel premixing, micro-fluidics, oil recovery, etc.) [1,2]. Multiple phenomena take place simultaneously when a liquid droplet contacts a porous surface: wetting, spreading, capillary filling, gravity induced convective flow, adsorption, evaporation from the surface, evaporation from the pores, etc. The evaporation of a sessile droplet can be studied by several experimental methods: transmission electron microscopy, environmental scanning electron microscopy, contact angle measurement, high speed camera recordings, thermal imaging, just to name a few. The evaporation of sessile droplets can be followed by an equipment assembled at the Department of Applied and Environmental Chemistry, University of Szeged: this equipment can guide simultaneous weight monitoring, electric resistance measurement and infrared imaging at a controlled temperature (typically at 50 °C). There are several experimental results characteristic for the evaporation process, the most important ones being the total evaporation time, time of evaporation only from the surface, full width at half maximum of the time-dependent mass and resistance curves, evaporation rate, initial area of the droplet, and the wetted area at the moment of total evaporation from the surface, etc. [3-6]. The main goal of this work was to demonstrate the analytical possibilities of the mass measurements through the example of sessile droplet evaporation (water-ethanol mixtures) from a carbon nanotube forest (CNT forest).

Experimental
Materials: The carbon nanotube forest (vertically aligned CNTs) was grown on Si/SiO_2 substrate by 30 minutes of catalytic chemical vapor deposition (CCVD) at 890 °C in a single zone tube furnace from ferrocene/xylene (0.5 g / 25 mL) precursor solution (0.1 mL/min ferrocene/xylene, 44 mL/min Ar).

Methods:
Scanning electron microscopy (SEM) was used for the determination of the general structure and morphology of the prepared carbon nanotube forest. For these measurement a Hitachi S-4700 microscope was used equipped with a field emission gun operated with accelerating voltages of 10 kV.

Liquid droplet evaporation (distilled water - ethanol mixtures) was studied from the CNT forest. The droplets (5 µL, 50 °C) were instilled with an Eppendorf Xplorer electronic pipette on the surface of the solid. The temperature, the electric resistance and weight variations could be simultaneously monitored by the equipment assembled at the Department of Applied and Environmental Chemistry, University of Szeged.

The CNT forest was placed onto a purpose-built sample holder. The setup included a type K thermocouple in contact with the non-wetted part of the solid. The distance between the solid and the heater was 1 cm. Data from the thermocouple was fed back to the temperature controller that maintained a base solid temperature of 50 ± 0.5 °C by continuously adjusting the heater power using fuzzy logic control.

The sample holder was placed on a Sartorius Cubis microbalance with 0.01 mg readability and the weigh variation during droplet evaporation was recorded.

For thermal imaging a FLIR A655sc infrared (IR) camera was used. This unit has a thermal sensitivity of 30 mK, an accuracy of ±2 °C for temperatures up to 650 °C at 640x480 resolution. Its uncooled microbolometer detector has a spectral range of 7.5-14.0 µm. The IR camera is equipped with a 2.9x (50 µm) IR close-up lens, with 32x24 mm field of view and 50 µm spatial resolution. The recorded images are transferred to a PC with FLIR ResearchIR Max software. Sessile droplet evaporation movies were acquired at maximum resolution with 50 Hz frame rate. The CNT forest's emissivity (ε_{film}) was determined by calibration at the initial solid temperature (50 °C) with a black electrical tape ($\varepsilon = 0.95$). During liquid surface evaporation the temperature was determined by taking into account the emissivity of the liquid ($\varepsilon_L = 0.95$); after surface evaporation, the emissivity of the wetted material was calculated as the average between the emissivities of the studied liquid and the CNT forest.

The sample holder plastic plate with the 0.7 cm radius gap in the center was equipped with two copper electrical connections at the opposite edges of the gap on the bottom of the sheet. The copper electrodes were contacted to the source meter by 0.3 mm diameter copper wires. The rigidity of these wires did not affect the balance because of the large inertia of the whole assembly mounted on the balance plate. This was confirmed by independent experiments before the evaporation profile (electrical resistance variation as a function of time) measurements. The computer recorded the electrical resistance of the solid as measured by a Keithley 2612A Source Meter.

Before the measurements, the CNT forest was mounted in the assembly and heating at initial temperature was applied until the sample weight both stabilized. Then all recordings (IR imaging and sample weight) were started a few seconds before dropping. The evaporation was studied by dropping a single droplet of a selected solvent to the center of the solid and simultaneously recording the IR video and the mass until they returned to their original values. The schematics of the equipment is presented in Fig. 1. The ambient air temperature and the relative humidity of the ambient atmosphere were kept constant (at 25 °C and 55 RH%, respectively) [3-6]. In our experiments the weight and IR video were simultaneously monitored, but in this work we will focus only on the results of the mass measurements.
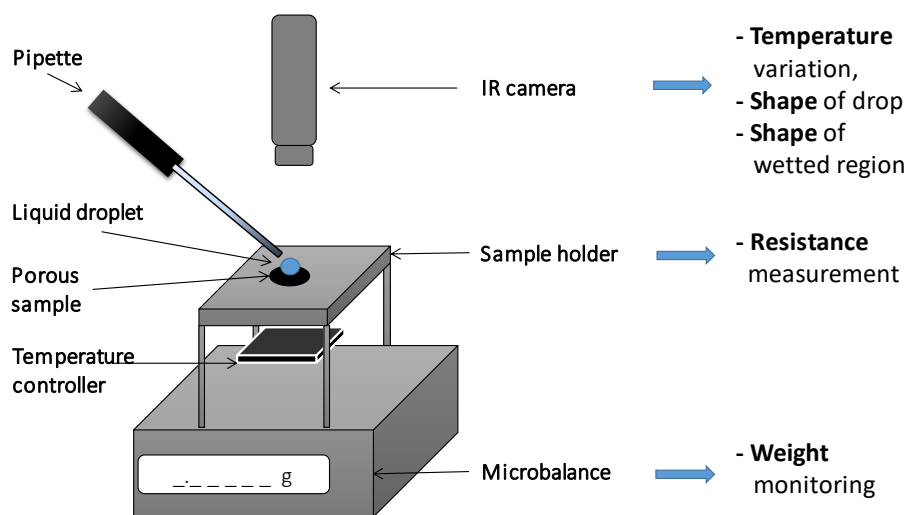
Figure 1. Evaporation monitoring equipment schematic.

Results and discussion

The SEM image of the CNT forest can be seen in Fig. 2. The height of the forest (*i.e.* the length of the vertical alligned carbon nanotubes) is ~1200 μm.
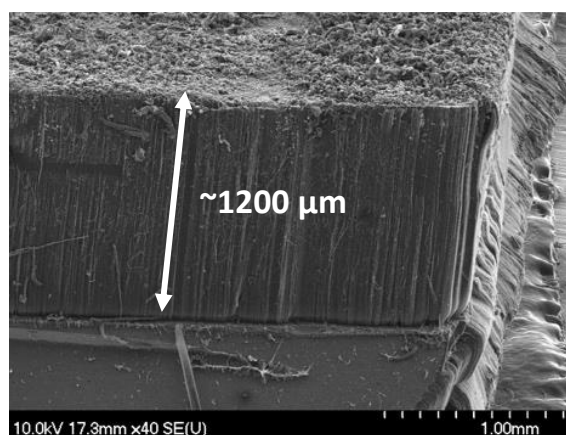

Figure 2. SEM image of the CNT forest.

In general at the moment we drop the liquid on the solid (t_0), the liquid starts to diffuse immediately into the pores, but a part of it remains spread on the surface of the material. The evaporation of this liquid from the surface takes place together with the diffusion. Once all liquid evaporates from the surface, namely the primary surface evaporation is complete (t_s), liquid is left only in the pores. The solvent gradually evaporates from the pores as well. The complete evaporation of the solvent (t_t) was confirmed by the fact that the mass of the solid material returned to the baseline.

One typical mass variation is illustrated in Fig. 3. where t_0 marks the time when the drop was instilled. The mass of the sample increased as soon as the solvent was dropped to the solid and this is followed by a quasi-linear weight decrease. Once the primary surface evaporation is complete (t_s), the mass decreases as linear (within experimental error) functions of time due to the continuous evaporation of the solvent. The total evaporation time (t_t) was at the moment when the mass of the solid returned to the baseline. At the linear weight decreasing ranges, the rate of evaporation (-dm/dt) is constant. The change of -dm/dt value suggests the change of the dominant evaporation process, *e.g.*, evaporation of the droplet sitting on the surface of the solid, evaporation of the condensed water from the porous system or the evaporation of the adsorbed water from the microscopical surface of the porous system (see the linear ranges in Fig. 3.).

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From this type of measurement, the typical experimentally determined data are the shape of the curve: m_{max}, area, FWHM; the t_s and t_t, the evaporation rate $-dm/dt$ and its change. These data are characteristic for the measured system and can be used to identify them [3-6].
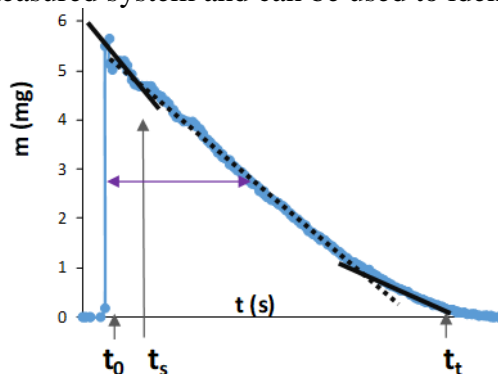

Figure 3. Illustration: weight variation of a representative solid material as a functions of time during the evaporation process.

The evaporation of water-ethanol mixtures from the surface of the CNT forest can be seen in Fig. 4. It is clear that the liquids with ethanol-content evaporate faster than the pure water. Based on the detailed analysis the t_t, the area, the FWHM, the evaporation rate for the condensed water in the porous system and for the adsorbed water can be determined. The t_t and area are plotted as a function of ethanol-content in Fig. 5.

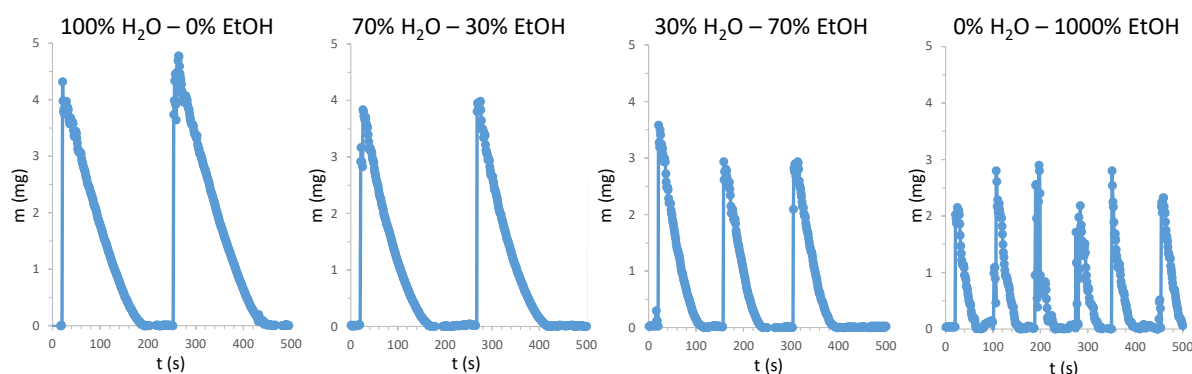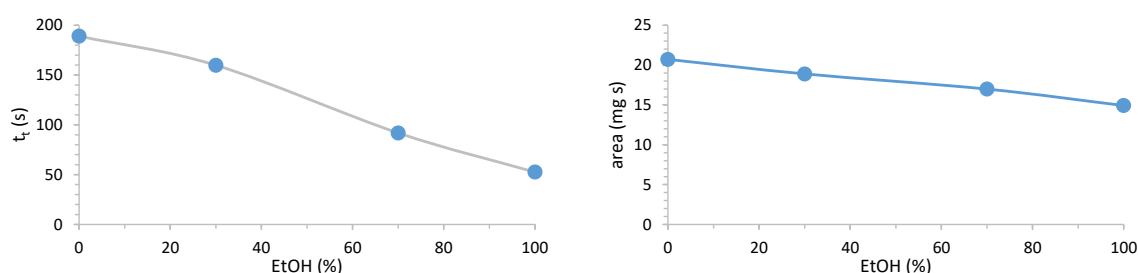Figure 4. Evaporation of water-ethanol mixtures from CNT forest (5 µL, 50°C).

Figure 5. Analytical possibilities of the mass measurements. (Evaporation of water-ethanol mixtures from CNT forest, 5 µL, 50°C.)

Conclusion
The weight monitoring of the evaporation of liquids from porous materials can provide information about the mechanism of wetting and vaporization which is a significant area of the basic researches. Furthermore, it can be proved by using appropriate statistical methods (*e.g.,* matrix of Pearson correlation coefficients, hierarchical cluster analysis, functional analysis,

etc.), that the experimentally determined characteristic values are specific for the physical properties of the solvents, and they are also dependent on the quality of the solid materials, therefore, they can be used for qualitative chemical and quantitative analysis via the estimation of physical properties. The results allow us to presume the possibility of this experimental setup and theoretical approach for a potential future application in the field of analytics.

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