Progress towards traceable microwave moisture measurements

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ABSTRACT

The design and basic principles of an experimental setup comprising a microwave-based moisture measurement system with a humid air generator is described. The combination of these two instruments implements a measurement technique similar in principle to that performed by a dynamic vapor sorption system. This technique enables a rapid determination of adsorption/desorption isotherms of moist samples implementing a secondary standard for on-site moisture measurements. Traceability to primary methods, such as loss-on-drying (LoD) or coulometric Karl Fischer (cKF) titration, can be achieved by preliminary calibration of the microwave resonances of a cylindrical resonator. We report preliminary tests of the performance of the whole system as used to determine the moisture content of tobacco.

Keywords: microwave resonator, moisture, humidity generator

1 INTRODUCTION

In spite of the widespread application and the critical importance of moisture measurements in industrial processing, several issues, including the proliferation of material specific reference standards for each method and the dearth of calibration services and certified reference materials, still limit the dissemination of measurement traceability and, as a consequence, a reliable assessment of the measurement uncertainty. In a cooperative effort to address these issues, the METefnet - Metrology for moisture in materials – a Joint Research Project (JRP) within the European Metrology Research Programme (EMRP) [1] is currently being developed [2]. Within this framework of activities, a specific task aims at the realization of transfer standard instrumentations to improve dissemination traceability from primary laboratory moisture standards to industrial test sites and to favor inter-laboratory comparison.

In the following, we describe the development of a simple, low-cost, portable transfer moisture standard, as implemented at Istituto Nazionale di Ricerca Metrologica (INRiM). This system combines a resonant cavity moisture meter and a compact humid gas generator to provide a stable and traceable humidity reference by conditioning a stable environment for moist samples. The requirements for compactness, ruggedness and versatility guided the design of the microwave moisture meter in the form of a stainless steel cylindrical cavity with small internal volume (83 cm^3) but still capable of precise measurements of resonance parameters, as assessed by the tests described in section 2.1. The design and operating features of the humidity generator are described in section 2.2. Finally, in section 3 we discuss the performance of the whole system in the determination of the moisture content of a test substance (tobacco flakes) as evaluated by calibration of the microwave moisture meter against a LoD analyser and by recording a non-gravimetric absorption isotherm of tobacco near ambient temperature.

2 MEASUREMENT SETUP

2.1 Cylindrical cavity resonator

The application of cavity resonator methods to measure the complex permittivity of dielectric materials is not new [3] and has previously demonstrated to be extremely accurate, suiting the requirements for the

realization of reference permittivity standards [4], [5]. The cavity used in this work (Fig. 1) is a hollow stainless steel right circular cylinder with a wall thickness of 9 mm, nominal internal diameter d = 42 mm and length l = 60 mm, for a total internal volume of 83 cm^3. A total of six holes bored through the cavity sidewall and end-plates allow to select different combinations for positioning probe adapters allowing selective excitation and detection of different subsets within the TM- and TE-mode classes.

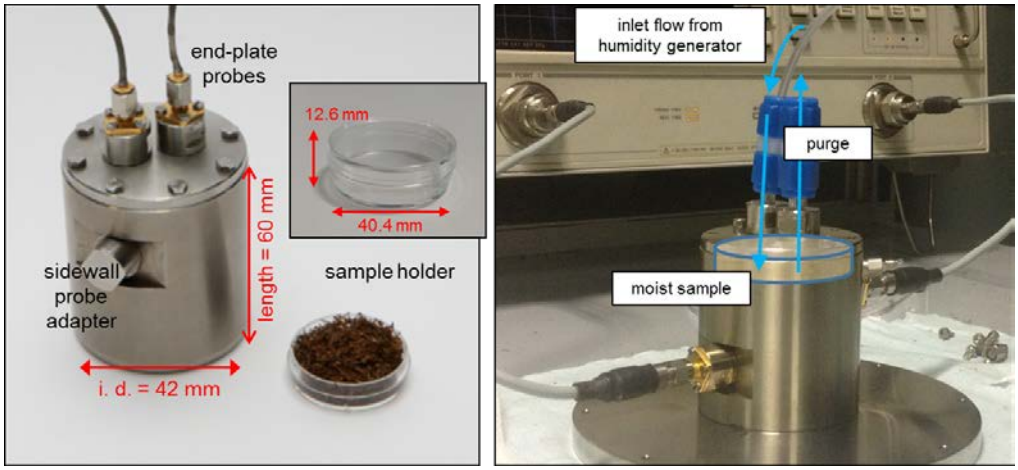

Fig. 1: *(Left) - Cylindrical steel resonator and polystyrene sample holder. Alternative positioning of two straight probes on the sidewall or the end-plates of the cavity allows selection of different classes of microwave modes. (Right) experimental flow-through setup with connection to a humid air generator.*

Within several possible alternative experimental configurations, the combination of mounting two straight probes on the cavity sidewall, the selection of the well isolated mode TE111 within the microwave spectrum (Fig. 2), and the positioning of a polystyrene cylindrical sample holder (o. d. 40.5 mm; thickness 1.0 mm) upon the cavity end-plate, was found to be a convenient choice, driven by the results of preliminary FEM simulations of the small perturbation induced by the insertion of the sample holder onto mode TE111 eigenfrequency.

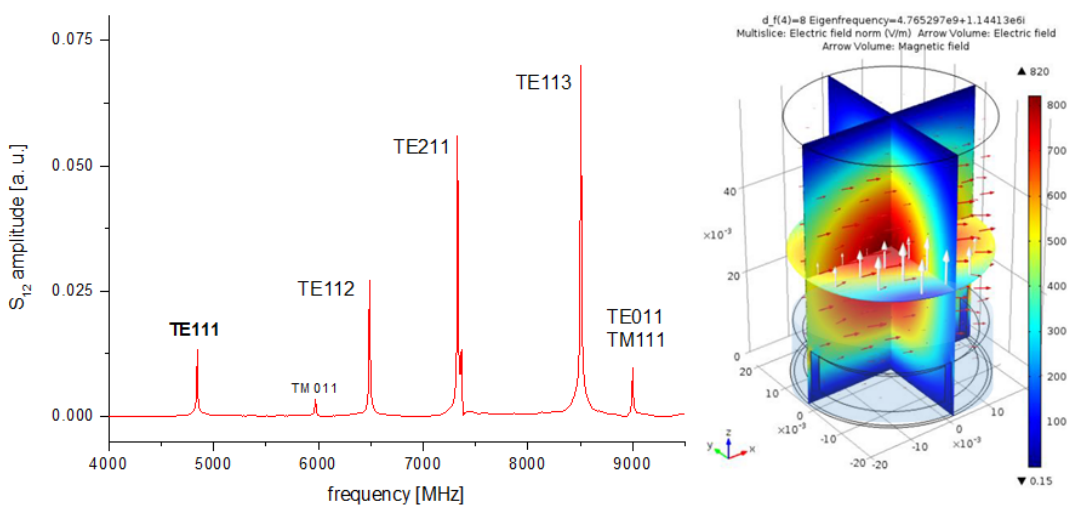

Fig. 2: *(Left) Microwave spectrum selected by two straight probes mounted on the cavity sidewall. (Right) FEM model of TE111 eigenfunction as modified by the presence of a polystyrene sample holder.*

When the resonant cavity is simply filled with air at ambient temperature, with no sample holder inserted, the frequency f and half-width g of the selected TE111 resonance are respectively found at the nominal values f_0 ~ 4.84 GHz and g_0 ~ 1.21 MHz. For the precise determination of these parameters, coaxial lines couple the two antennas to a vector network analyzer set to sweep through 201 frequencies, spanning approximately 5g and centered approximately at f. The analyzer returns values of the complex scattering parameter S_{21}. These data are fitted by a Lorentzian function plus linear complex background terms to account for the slight overlapping with the neighboring modes in the spectrum. This equation, with a total of 8 adjustable parameters, is equivalent to a single term in the sum defined by eq. (15) in [6], as used for precise fitting of the triply-degenerate resonances of a quasi-spherical resonator. With this procedure, the relative precision which characterizes a single fitted scan of the complex eigenfrequency of mode TE111 for the air-filled cavity is $u_r(f_0) \sim 2\cdot10^{-8}$ and $u_r(g_0) \sim 1\cdot10^{-4}$. Incidentally, we remark that a low-cost, portable instrument capable of achieving the same equivalent precision performance of a network analyzer is available for on-line measurements [7]. The insertion of the (empty) polystyrene sample holder within the cavity, coaxially laying in contact with the cavity end-plate, perturbs the TE111 eigenfunction with a major decrease of the resonance frequency by $\Delta f = f - f_0 = -48$ MHz and a minor increase of the halfwidth by only 40 kHz, thus preserving the resonance quality factor and the achievable precision in the determination of the resonance parameters (Fig. 3). With respect to this reference performance, as discussed below in section 3, when a moist sample fills the volume delimited by the holder, the quality factor of the resonances decreases, in proportion to the permittivity and the density of the moist sample, by as much as one order of magnitude, with a corresponding reduction of the S/N ratio. However, even in these operating conditions, the relative precision of a single measurement of the parameters of mode TE111 is typically $u_r(f) < 2\cdot10^{-6}$ and $u_r(g) < 1\cdot10^{-3}$ and hence more than adequate for the application considered here.

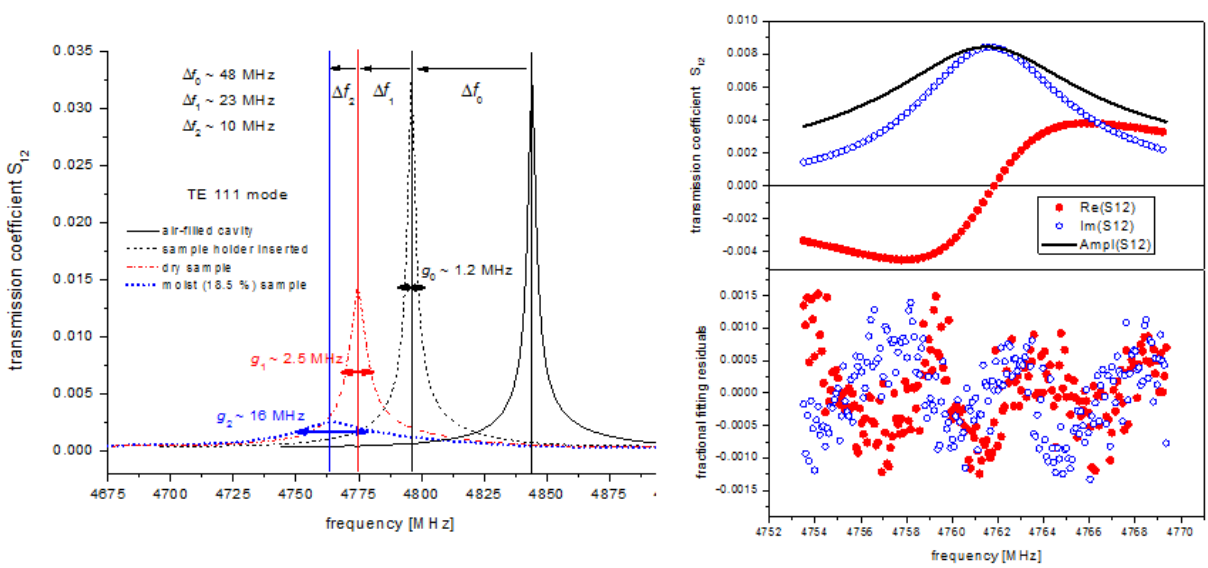

Fig. 3: *(Left) Frequency shifts and halfwidth increase induced onto mode TE111 resonance by the sample holder and a moist sample (tobacco). (Right Top) Complex spectrum in the vicinity of the TE111 mode with a moist sample in the cavity (Right Bottom) residuals from a fit using a Lorentzian function. In this case example, the frequency could be determined with a fractional uncertainty of $2.6\cdot10^{-7}$.*

2.2 Portable humidity generator

To realize a transfer moisture standard by combined use with the microwave moisture meter, a compact, humid gas generator capable of providing an accurate reference dew-point temperature was developed.

The generator is based on an isothermal condenser; it operates between -15 °C and 50 °C, at atmospheric pressure and slightly above (up to 1250 hPa), to produce a continuous humid gas stream with flow rates up to 2 l min^{-1}. The generator works in condensation mode being fed by a pre-saturated gas flow with a dew/frost point temperature higher than the preset saturation temperature (approx. +10 °C). The saturator condenser stage - based on a shell-and-tube heat exchanger (STHE) design – with an outer diameter of 50 mm and a height of 150 mm is shown in Fig. 4. It consists of a bundle of eighteen vertical thin-walled parallel tubes connecting two hollow stainless steel cylinder , the upper plenum operates as a gas collector while the lower one as a reservoir for the condensate. When the inlet humid gas flows through the STHE, condensation occurs and latent heat is released to the surrounding cooling fluid into the bath. The condenser was conceived to be hosted in the thermostatic well of a portable, thermoelectrically-cooled, temperature calibrator. A calibrated industrial platinum resistance thermometer (IPRT) is inserted into a through-hole thermo-well in thermal contact with the condensate reservoir, thus enabling the measurement of the actual condensation temperature of the gas at the saturator outlet. Fig. 4 shows the assembled generator comprising a cylindrical bubbling pre-saturator and the saturator hosted in a liquid bath thermostat unit.

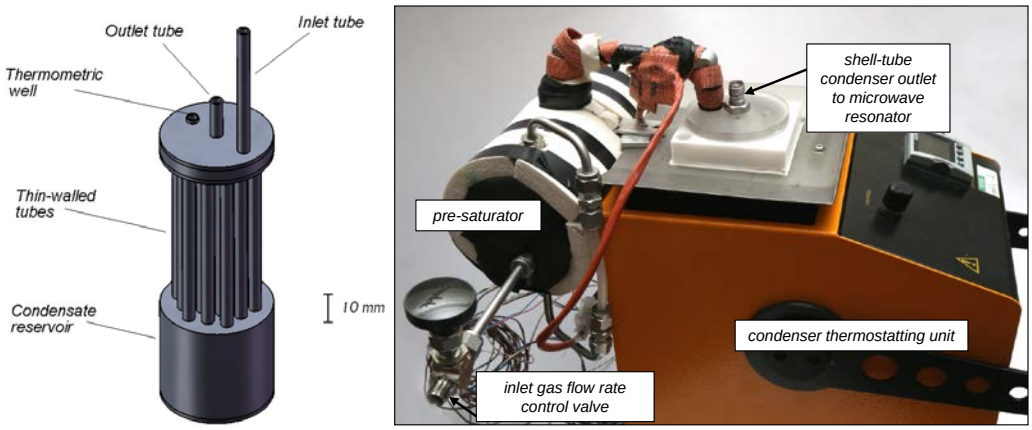

Fig. 4: *(Left) Sketch of the heat exchanger/condenser unit. (Right) Assembled portable humidity generator.*

The generator was validated by comparison against the primary humidity standard maintained at INRIM. A chilled-mirror hygrometer (CMH) was used as the transfer standard for the comparison. The portable humidity generator compared favorably with the primary standard, to better than 0.1 °C, over the dew/frost point temperature range from −15 °C to 50 °C.

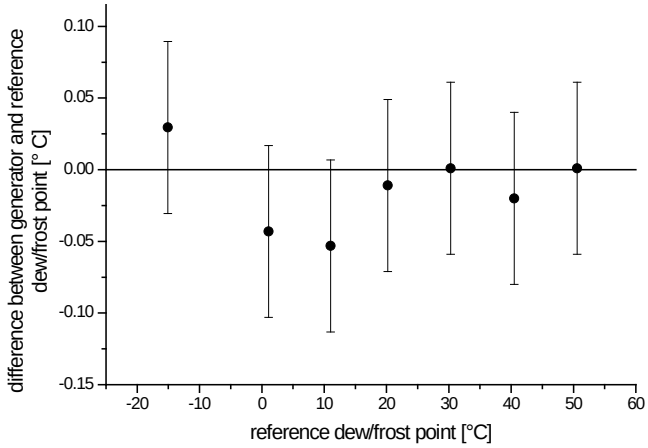

Fig. 5: *Validation of the humidity generator against a primary humidity standard.*

3 EXPERIMENTAL VALIDATION

For a preliminary estimate of the performance of the cavity resonator as a moisture meter, we considered tobacco as a suitable test material, in reason of a rather large variability of its packaging density, its high hygroscopicity leading to a rapid response to induced changes in moisture content, and the availability of reference data of its dielectric constant in the literature [8], [9]. To interpret our experimental results, following the principles outlined in [8], we make the following initial assumptions and approximations: i) at constant temperature and frequency, the dielectric constant ε of a moist sample is a function of the density ρ and the moisture content Ψ; ii) the insertion of the moist sample within the resonator determines a negative frequency shift Δf and an increase of the halfwidth Δg of an observed mode, with respect to some reference condition of the empty cavity, which are respectively proportional to the real and imaginary part of $\varepsilon(\rho, \Psi)$; iii) at constant moisture content, the ratio $\Delta g/\Delta f$ remains constant as a function of the density; iv) as a function of the moisture content, the ratio $\Delta g/\Delta f$ varies as a unique, monotonic function which is characteristic of the material under test and may be used for the purpose of calibrating the response of the microwave moisture meter against a primary humidity reference. To test these assumptions, samples of moist tobacco were prepared with densities varying between 30 mg cm^{-3} and 90 mg cm^{-3} and moisture content between 7.5 % and 25 %. Taking the value of the resonance parameters f and g of mode TE111 when the cavity contains an empty sample holder as a reference, and using the procedure described in section 2.1, the perturbations Δg and Δf induced by filling the volume of the holder with samples of variable mass and nominal constant moisture were recorded, leading to the results displayed in Fig. 6. These data show that for mode TE111 the hypothesis that the ratio $\Delta g/\Delta f$ is proportional to the moisture content of the sample and remains constant as a function of the sample density is indeed a reasonable approximation.

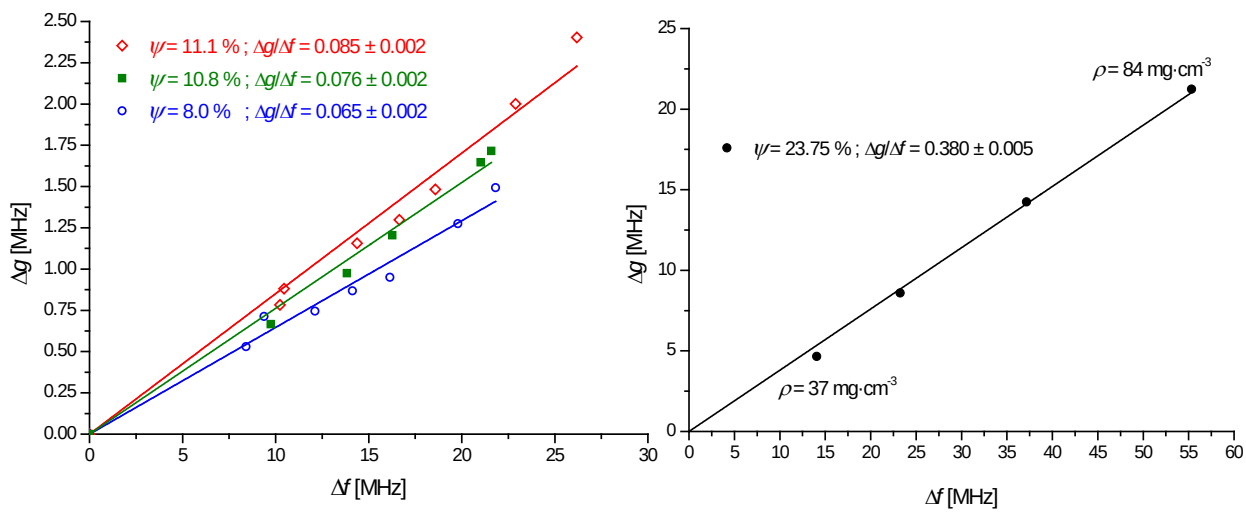

Fig. 6: *Linear interpolation of the density dependence of TE111 resonance parameters as a function of moisture content in tobacco: (Left) 8.0 % < Ψ < 11 % ; (Right) Ψ ~ 24 %.*

The overall precision and repeatability of the microwave technique was subsequently estimated by calibrating the variation of the ratio (" g/" f)$_{TE111}$ as a function of the dry moisture content[1] as determined by transferring the moist samples to a commercial infrared LoD moisture analyzer. From a linear interpolation to these calibration data (Fig. 7) we found that the moisture content varied linearly as an

[1] Percentage moisture content (MC) defined on a dry basis, MC = 100×(mass loss under drying/mass of dry sample).

increasing function of the ratio (” g/” f)$_{TE111}$ indicating that the repeatability of the microwave technique in the determination of MC was in the order of 1.5 % over the whole measurement range considered here. Aliquots of the same samples were also analysed by means of cKF, finding a satisfactory overall agreement with the results previously obtained by LoD.

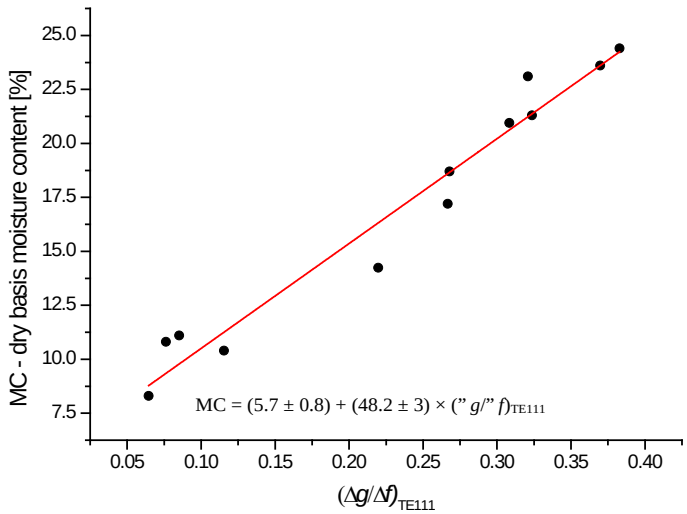

Fig. 7: *Calibration data and linear interpolation of microwave moisture meter response against an infrared LoD moisture analyzer*

Following this preliminary characterization, a manifold was realized to connect a sealed sample holder, enclosed within the resonator, downstream the outlet flow from the humid air generator (see section 2.2). To minimize the impact of the manifold onto the microwave eigenfunctions, 1/8" o. d. PTFE tubing and connectors were inserted flush with the cavity interior embedded in two ports bored through the upper end-plate of the cavity (Fig. 1), providing firm mechanical support to the sample holder and a gas-tight connection to the generator. This simple setup allowed to vary the humidity of the gas flowing through the test samples by controlling the temperature of the saturator stage of the humidity generator. As a first test, the equilibrium moisture content of tobacco was determined by measuring the temperature of the cavity resonator which was not thermostatted but left free to follow the variation of the ambient temperature of the laboratory at about 298 K, with a daily fluctuation of ± 0.5 K. The experiment was started by the determination of the desorption isotherm, by decreasing the dew-point temperature of the saturator in a few steps from 295 K, corresponding to a relative humidity in the sample RH ~ 80 %, down to 274 K, or equivalently RH ~ 21.5 %, with this lower limit imposed by using water as the thermostatting fluid of the generator. Following each temperature variation, the cavity ratio (” g/” f)$_{TE111}$ was recorded as a function of time to monitor its asymptotic approach of a stationary condition as an indicator of thermodynamic equilibrium between the sample and the flowing gas. At a flow rate of 0.8 l min^{-1} this condition could be reached within 2 to 3 hours. After completing data collection near the minimum temperature 274 K, the flow through the sample was diverted to a dry gas (nitrogen) source to check the reference resonance parameters for a correct, updated estimate of ” g and ” f. Each experimental record of the ratio (” g/” f)$_{TE111}$ was then converted to a corresponding estimate of the moisture content of the sample using the calibration curve in Fig. 7. Finally, the dew-point temperature steps were reversed and the temperature ramped up to 295 K to determine the corresponding adsorption function. The resulting sorption isotherm of tobacco (Fig. 8) shows the typical trend of the multilayer and capillary condensation phases of a sigmoid type, in satisfactory qualitative and quantitative agreement with available sources [9], [10].

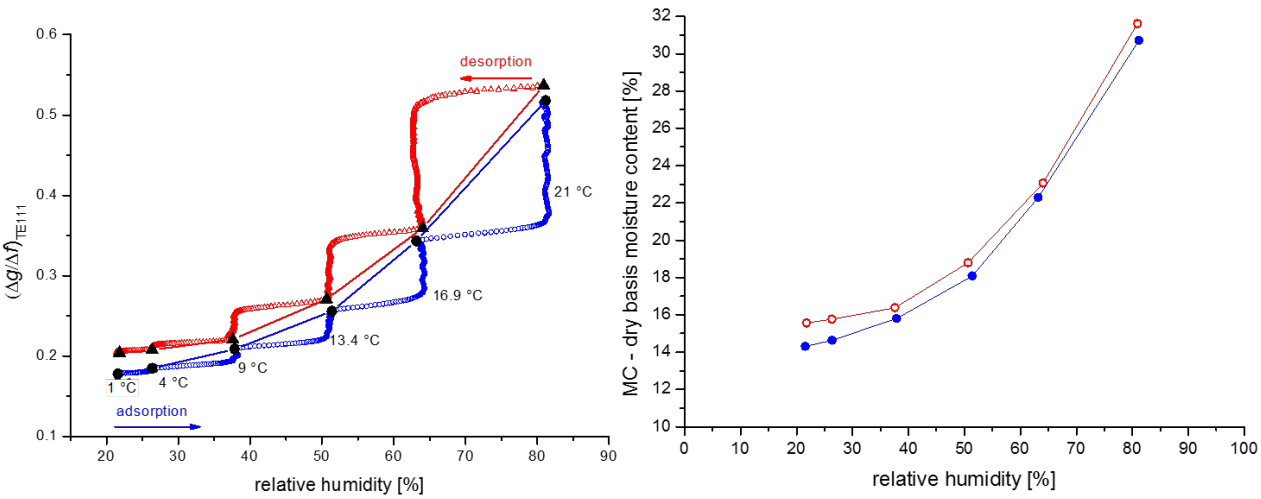

Fig. 8: *(Left) variation of the cavity resonator (" g/" f)$_{TE111}$ response at 25 °C along a desorption (red triangles)-adsorption (blue dots) cycle recorded by varying the dew-point temperature back and forth between 21 °C (RH ~ 80 %) and 1 °C (RH ~ 21.5 %); full symbols mark asymptotic equilibrium conditions at each intermediate temperature .(Right) Sorption isotherm of tobacco at ambient temperature (298 K); full (blue) dots delimit adsorption and hollow (red) dots delimit desorption.*

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