Automatic Scanning Absorptometer (ASA)

1. Introductive notions

A well known measurement method of liquid absorption into porous material was proposed by Bristow in 1967 under the so-called Bristow wheel[1]. The porous material in thin layers is rolled on a wheel with a well-defined radius, which rotates with a constant speed. A liquid container placed above the porous material surface will leave a length of the liquid track as a function of the liquid volume and the speed of the wheel. Increasing the speed, the same amount of liquid will let a longer track, the liquid container will have a shorter contact time with the porous material, and so the liquid depth of penetration into material will be smaller.

The Automatic Scanning Absorptometer (ASA) is a modern version of the Bristow method. Instead of wheel it uses a horizontal rotary disk (turntable) with eccentric. The liquid container is replaced with a nozzle connected via transparent tubes with a glass capillary that measures the amount of liquid transferred to the porous material fixed on the disk. Due to the fix position of the nozzle and rotation abound an eccentric, the track on the porous material is a spiral defined by the radius and pitch (the distance between the two consecutive radiuses at the same polar angle. Varying the speed of the disk and making the measurements for well defined time intervals when the speed is kept constant, the ASA setup bundles within one run the entire series of Bristow wheel measurements.

The ASA device we used in our research is a Kumagai Riki Kogyo (KM 500win) setup schematically represented in Figure 1. It has to be noticed that the glass capillary has an optical sensor that follows the liquid meniscus made at the liquid/air interface. Due to the liquid absorption, the meniscus moves and its position is recorded by the software in order to calculate the absorbed liquid volume as *transferred liquid volume* (TLV).

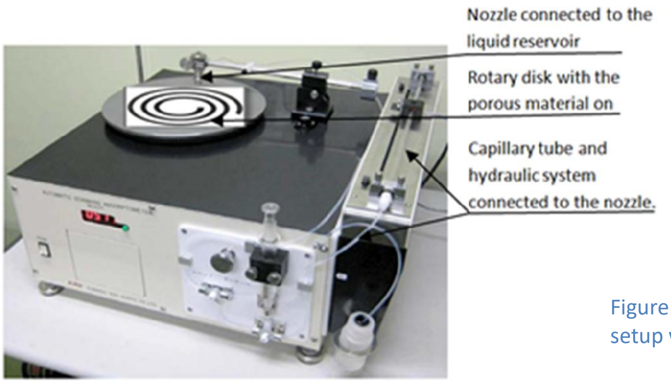

Figure 1. A schematically representation of the ASA setup with the main functional components.

During its movement under the nozzle that delivers the liquid, the rotary disk has well defined by software intervals of time when the speed is constant, when the speed is increased to the next

[1] J. A. Bristow, "Liquid absorption into paper during short time intervals," *Sven. Pap.*, (1967) vol. 70, no. 19, pp. 623–629.

constant value, and of course, at the end of the measurement when the movement is decelerated down to standstill. Only during the constant speed the TLV value is recorded, as well as the *contact time*, t, defined as the time that the nozzle has been in contact with the porous media during the TLV measurement. In this way, the system determines accurately the liquid penetration into porous media on several orders of magnitude timescales: milliseconds to seconds.

Before presenting more detailed measurements, some constructive details about the nozzle are needed. The surface that gets in contact with the porous media is shown in Figure 2 with the main geometrical dimensions: $= 4.9\ \mathrm{mm}$ from $= 6.2\ \mathrm{mm}$ and $= 1.0\ \mathrm{mm}$ from $= 3.0\ \mathrm{mm}$. The area used to supply with liquid is L_{slit} x W_{slit}, but as a function of the physical properties of the liquid and its interactions with the material of nozzle (stainless steel) and porous media, the contact area may be different due to wetting.

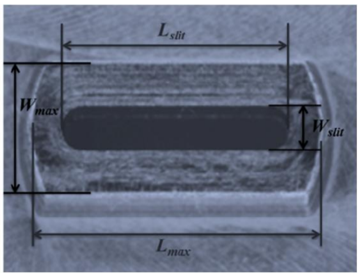

Figure 2. The ASA nozzle with its geometrical dimensions: total length, L_{max}, and wide, W_{max} and the slit dimensions that supplies the liquid.

2. More about the transferred liquid volume (TLV) and the contact time

Supposing a porous material (e.g. porous paper) with porosity $\in$ [-], that absorbs the TLV amount during a section of constant speed of the rotary disk, the liquid depth of penetration into porous material can be simply calculated. As we noticed in the previous section, the TLV is measured by the movement of the capillary sensor with high accuracy. Knowing TLV and $\in$, the penetration depth is :

$$\delta = \frac{TLV}{A \cdot \in} \qquad (1)$$

where A is the contact area defined as the product of the nozzle length (L_{max} for perfect wetting liquid/stainless steel interface or L_{slit} for perfect non-wetting contact interface) with the length of the spiral track made during this time sequence. The latter is well described by the set parameters (internal radius and pitch of the spiral) as software input.

Mathematically the Archimedean spiral, called also arithmetic spiral, can be described in polar coordinates (r, θ) by the equation:

$$r = a + b \cdot \theta \qquad (2)$$

with a and b real numbers.

The arc length of a curve r(θ) is given by:

$$\zeta = \int_{\theta_i}^{\theta_f} \sqrt{r^2 + \left(\frac{dr}{d\theta}\right)^2}\, d\theta =$$

$$= \frac{1}{2b}\cdot\left[(a+b\theta_2)\cdot\sqrt{(a+b\theta_2)^2+b^2} - (a+b\theta_1)\cdot\sqrt{(a+b\theta_1)^2+b^2}\right] + \tag{3}$$

$$+\frac{b}{2}\cdot\left[arcsh\left(\frac{a+b\theta_2}{b}\right) - arcsh\left(\frac{a+b\theta_1}{b}\right)\right]$$

which is a non-simple expression[2] to operate with.
In the first approximation, the method recommended by the ASA software is:

- for each point on the spiral, due to the L dimension of the nozzle, there is an inner radius, r_{in} and an outer radius r_{out} and from here a centre position of the nozzle can be parameterized as:

$$r_c = \frac{r_{out} - r_{in}}{2} = (a + \frac{L}{2}) + b\theta \tag{4}$$

- for each arc- spiral traced during constant speed movement, there is an initial value of θ parameter, θ_{ini} and a final one, θ_{fin}. The length of the arc-spiral is empirically calculated as:

$$\zeta = \frac{1}{2}\left(r_{c,fin} - r_{c,ini}\right)\cdot\left(\theta_{fin} - \theta_{ini}\right) \tag{5}$$

- the area of an arc-spiral traced during constant speed movement by the nozzle with length L, is:

$$A = L\cdot\zeta \tag{6}$$

The contact time can be calculated, according to the ASA manual, using:

$$\mathrm{t} = \frac{\mathrm{W}}{2\cdot\pi\cdot \mathrm{f}_{\mathrm{turntable}}\cdot r_c} \tag{7}$$

with the frequency of the rotary table $f_{turntable}=f_{motor}/(30\cdot 10^{-3})$ and r_c defined by relation (4). The relation liquid / material of the nozzle concerning the wettability defines the real value of W and L parameters.

3. Examples of ASA measurements

In order to ensure a natural transfer of the liquid into the porous media, driven only by the capillary suction, the ASA system must be perfect equilibrated to avoid any extra pressure on the liquid path. Then, prior the measurement start, the experimenter has to make at the bottom of the nozzle that will interact with the media, a very small meniscus with the liquid using the "hydraulic circuit" of the setup. This is crucial for well functioning of the measurement method.

[2] E.W. Weisstein, *Archimedes'spiral*, MathWorld, http://mathworld.wolfram.com/ArchimedesSpiral.html

Because the absorption of the liquid into a porous material is dependent on the environmental conditions (temperature and relative humidity), the porous media (paper) is preconditioned in a climate room at T=23^{0}C and RH=50%.

Once the measurement started, the ASA software will take over and life the TLV/A (the transferred liquid volume normalized to the contact area per measurement) will be displayed as a function of square root of contact time. Such an example is presented in Figure 3, where the results of the measurements of two different liquids (water and a mixture with glycerol to model the ink) on the same type of paper are shown. We have selected these data to emphasize the strong influence on the ASA measurements of the liquid properties and the interaction with porous media. The liquid surface tension, viscosity and the contact angle with the cellulose fibres from the paper play an important role. We mention the fact that not only the values of the liquid absorbance are different, but also the shape of the curve.

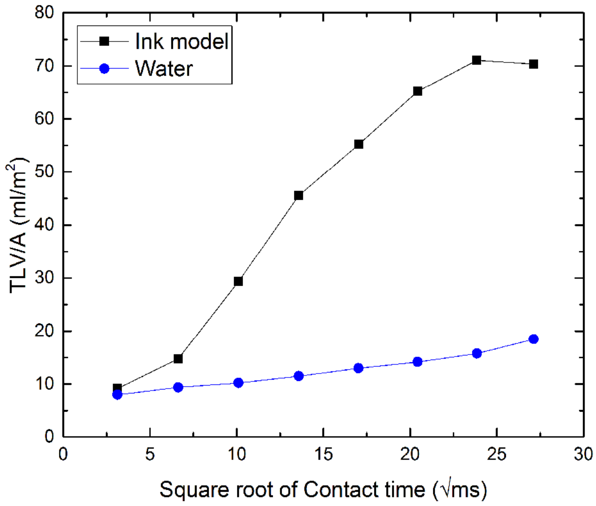

Figure 3. Examples of the ASA measurements for two different liquids (water and a model for ink) absorbed into the same type of paper. The TLV/A is represented against the square root of contact time. *With courtesy of Thijs van Stiphout.*

The slope of the curve TLV/A = f($t^{1/2}$) is an indication for the absorption rate of the liquid into the porous media. In the examples presented in Figure 3 it is clear that the slope for water penetration is smaller than the one for the model of ink (it is about 12 times smaller).

Considering the plot TLV/A= f($t^{1/2}$) as approximated by a linear dependency: $\frac{TLV}{A} = p + q\sqrt{t}$ and taking into account relation (**1**), the speed of the penetration front can be estimated mathematically as:

$$\frac{d\delta}{dt} = \frac{q}{2\cdot\in}\cdot\frac{1}{\sqrt{t}} = \frac{1}{2\cdot\in}\cdot\frac{q^2}{\delta\cdot\in - p} \quad (8)$$

Therefore, the liquid penetration speed in this model is strongly dependent on the depth where the liquid is at the moment t. Both, the porosity of the media as well as the surface roughness (the p parameter represents the TLV/A amount that fill the roughness) play an important role in defining the speed of liquid penetration.

4. From TLV/A to depth of penetration: an experimental approach

The ASA measurement starts in the middle of the spiral, where the relative speed of the nozzle versus the substrate is small. In other words, here contact time is larger. Consequently, the depth of penetration of liquid into porous substrate must be larger when comparing with the depth corresponding to points measured later. In order to experimentally measure the depth of penetration, the cross-section in various positions along the ASA spiral have been investigated using the light microscopy methods. This experiment needs special preparation:

i) porous paper: plain paper from the commercial TopColorZero family;
ii) as liquid, a model of ink with black pigment will be used;
iii) cross-sections of the ASA spiral corresponding to the experimental points of plot TLV/A= f($t^{1/2}$) are made using microtome;
iv) to reveal the ink penetration into paper and avoid reflectance, the dark field microscopy (with or without 1 polarizing filter) is used for investigating the ASA spiral cross-sections.

The results are presented in Figure 4 . It is easy to observe that:
a) the pigment particles have been transported by the liquid component of the ink into the paper;
b) the penetration depth is function of the measurement point (as expected: more liquid – point 2 – means a larger penetration depth).

Having the cross-sections for all points of ASA measurements, the penetration depth for each point is estimated in this manner. Using the ASA experimental data, a plot: the depth of penetration against the TLV/A is immediately and it is shown in Figure 5. As expected a nice linear dependency is revealed: 1.41um/mL/m^2. In the first approximation, considering the relation (1), this value can be related to the paper porosity. We expect that the parameters that influence the paper permeability for the investigated liquid are represented within this slope.

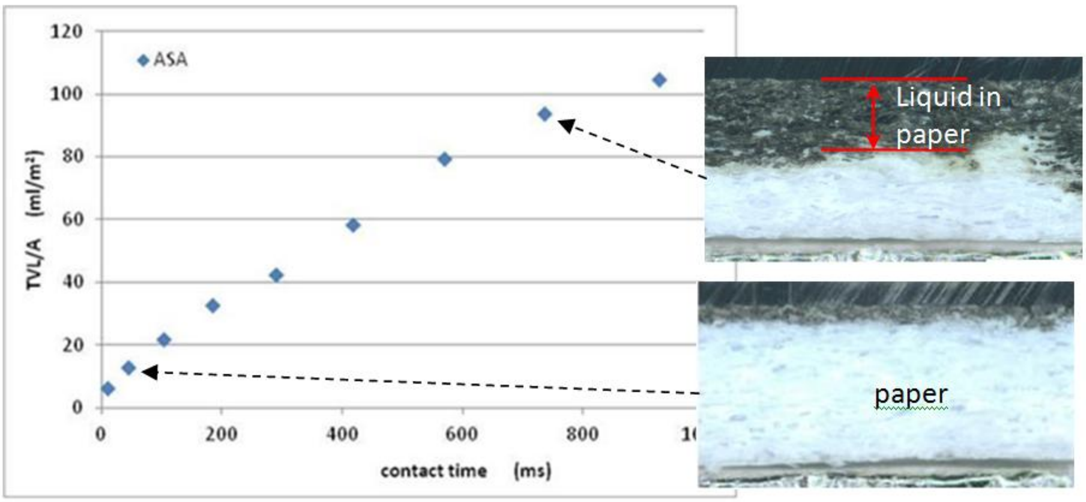

Figure 4. The TLV/A versus the contact time measured by ASA method and the light microscopy on cross-sections realized for measurement points 2 and 8. *The light microscopy photos, with courtesy of Tiny Ritzen.*

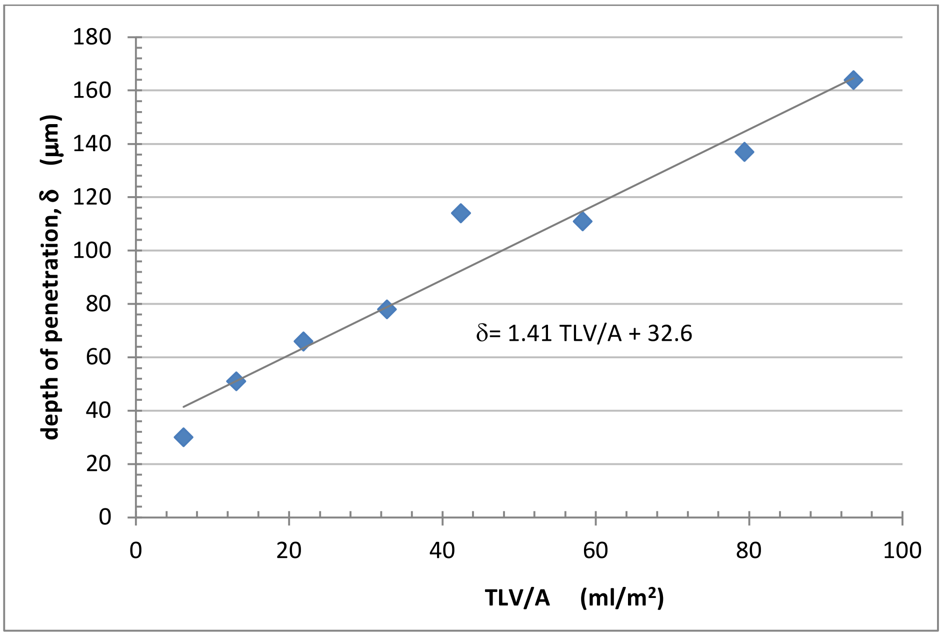

Figure 5. The penetration depth of liquid into porous plain paper as a function of the transferred liquid volume per contact area. This is a combination of ASA measurements, microtome and light microscopy investigation on the ASA spiral cross-sections.