LEAF DIFFUSION RESISTANCE TO WATER VAPOUR AND ITS DIRECT MEASUREMENT

II. DESIGN, CALIBRATION AND PERTINENT THEORY OF AN IMPROVED LEAF DIFFUSION RESISTANCE METER

C. J. STIGTER, J. BIRNIE, B. LAMMERS

Laboratory of Physics and Meteorology,
Agricultural University, Wageningen, The Netherlands

CONTENTS

1. INTRODUCTION

For control and extension of microclimatic submodels in relation to growth models (LEMON, 1970; DE WIT et al., 1970; LEMON et al., 1971; GOUDRIAAN and WAGGONER, 1972) leaf diffusional resistance measurements rank first among the field data to be collected. An introduction and reviews concerning relevant factors (within the plant canopy, near the surface of the leaf and within the leaf) and concerning measuring methods have been given recently (STIGTER, 1972; this paper will be refered to further on as (I)). We discussed there also our choice of a Wallihan leaf diffusion resistance meter. Problems encountered by several workers were preliminary reviewed by going through the existing literature.

The principle of the method is simple. A small room (sensor cup) containing a humidity sensor is clamped onto the leaf. The initial water vapour concentration in the cup is preferably low and spatially constant. The concentration increases after clamping, due to the transpiration of the leaf via stomata and cuticula. To detect the ambient vapour concentration we used an electrical humidity sensor. The time needed for the decrease in electrical resistance of the sensor between two fixed values is taken as a measure for leaf diffusion resistance (I, p. 29). Temperature of the evaporating surface and of cup air (sensor) have to be measured. After measurement the cup air is dried. Absolute measurements in the field can be obtained after calibration in the laboratory with fixed dummy resistances of known value. Recently the visually detected appearance of a condensated drop of water on a cooled surface in the cup has been used alternatively as a more rough indicator for evaporation speed (MORESHET and YOCUM, 1972).

With the equipment used in practice so far, many troubles did show up (e.g. MORROW and SLATYER, 1971a; GEE and FEDERER, 1972; ELFVING et al., 1972; (I)). It appeared to be necessary to carry out further research on these problems and we have applied the results obtained in design, calibration and use of a modified leaf resistance meter.

2. CLASSIFICATION OF PROBLEMS

A first classification of problems can be made by separating:
a. problems occurring already during *calibration* performances with fixed dummy resistances, under controlled temperature conditions;
b. problems encountered in the measurements *on leaves*.

This article describes mainly the first category of troubles. In a following paper (III) we will discuss the independent determination of the resistance of the dummies used, the laboratory test of the measuring strategy applied in the field and measurements with the calibrated instrument in the field (and the greenhouse).

The problems dealt with here can in turn be classified under the following headings:

  i. Materials of the sensor cup and auxiliary equipment (§ 4).
 ii. Diffusional resistance of the sensor cup and transport processes in cup and calibration resistances (§ 5).
iii. Physical properties of the sensor. Influence of cup and evaporating surface temperatures. Resulting calibration procedure (§ 6).
iv. Properties of electrical equipment used (§ 7).

3. THE METHOD OF MEASURING

3.1. The measuring method in theory

Evaporation from a constant-temperature saturated surface to a half-infinite space of constant vapour concentration e_p is described by:

$$I = \frac{e_l - e_p}{R_l + R_p},\tag{1}$$

the equivalent of Ohm's law (I, p. 11). In (1) I is the vapour flux density; e_l and e_p are absolute humidities, e_l being the vapour concentration at the evaporating surface (which for a leaf is underneath the real surface; I, p. 11 etc.); R_l and R_p are internal (e.g. epidermal) and external (e.g. boundary layer) resistances respectively.

If the half-infinite space is replaced by the small volume of a humidity sensor cup, e_p is a function of time, even under isothermal conditions of surface (S) and volume (V). The change in concentration is then given by:

$$\frac{d\,e_p\,(t)}{dt} = \frac{I\,(t)\,S}{V},\tag{2}$$

from which follows with (1):

$$\frac{d\,e_p\,(t)}{dt} = \frac{S}{V}\frac{e_l - e_p\,(t)}{R_l + R_p}.\tag{3}$$

In (3) R_p is now the diffusional resistance of the porometer cup which forms the new 'boundary layer'. This equation was also applied by TURNER and PARLANGE (1970). The formula is valid only when spatial uniformity for $e_p\,(t)$ exists in V. Therefore forced mixing of incoming vapour flux and cup air, by a fan, is an important condition. Integrating (3) from $t = t_i$ to $t = t_f$ (representing the moments of successive indication of the two fixed electrical resistance values of the humidity sensor), we obtain for the measured transient time:

$$t_f - t_i = \Delta t = \frac{V}{S}\,(R_l + R_p)\,\ln\frac{e_l - e_p\,(t_i)}{e_l - e_p\,(t_f)}.\tag{4}$$

This can be written as:

$$\Delta t = K\,(R_l + R_p),\tag{5}$$

with

$$K = \frac{V}{S}\,\ln\frac{e_l - e_p\,(t_i)}{e_l - e_p\,(t_f)}.\tag{6}$$

In calibration practice we use (5) and (6). Bringing the apparatus with porometer resistance R_p, which is originally not known, successively over a series of dummy resistances R_l of known value, a series of transient times Δt is obtained.

Drawing a diagram of used resistances against transient times, a straight line with slope K is acquired (5). Knowing K, S, e_l and the two fixed e_p-values (from the calibration certificate supplied by the manufacturer of the humidity sensors) a value for V may be calculated using (6). Extrapolation to $\Delta t = 0$ gives the value $R_l = -R_p$ at the absciss (Comp. Fig. 9 of § 6). In principle, of course, only two dummy resistances (of which one may be zero) are sufficient to obtain two independent equations (4) for measuring V and R_p (compare also § 6.4.c).

As in principle only e_l, e_p (t_i) and e_p (t_f) are temperature dependent, each combination of temperatures of evaporating surface and cup gives a different K-value. If a fan is applied in the cup and if the sensor does not take up a detectable amount of moisture, nor interferes otherwise, V is constant. It may only differ from the geometrical cup volume as the fan agitated air does not reach to the same extent each corner of this volume. It is clear that measured Δt-values in the field are now directly related to the leaf resistance to be known (R_l) via (5), with known K (via (6) with V being a constant or at least known otherwise) and R_p known from calibration.

3.2. THE MEASURING METHOD IN PRACTICE.

Working at low e_p's and with small difference (Δe_p) between e_p (t_f) and e_p (t_i), we may approximate (3) with:

$$\frac{\Delta e_p}{\Delta t} = \frac{S}{V} \frac{e_l - \bar{e}_p}{R_l + R_p}. \tag{7}$$

This may be written again as:

$$\Delta t = K' (R_l + R_p). \tag{8}$$

We now have:

$$K' = \frac{V}{S} \frac{\Delta e_p}{e_l - \bar{e}_p} \tag{9}$$

with

$$\bar{e}_p = e_p (t_i) + \tfrac{1}{2}\Delta e_p. \tag{10}$$

During all the work done so far we have measured in each calibration measurement and each field measurement two Δt's, with an electronical self-timing equipment (§ 7). For that purpose three fixed electrical resistance values of the humidity sensor have been used. In the laboratory, with constant diffusion resistance, the ratio of the two Δt's of course remains constant. This provided us with a nice check in the field whether and when the stomata were changing their opening during measurements (III). We used for this performance (overlapping) Δe_p's corresponding to 1.5% and 6.5% relative humidity for the short and the long measuring time respectively. For both cases the difference

between K and K' was negligible for all examples (ca. 100) tested. Therefore (7) and (9) may be used for calculations.

The model used up till now, with a constant V, appears to be too simple in practice. The following phenomena are the most important ones responsible for deviations from the simple model.

1. *The sensor takes up water.* This apparent additional volume V_s will influence considerably the measuring time if V_s is not much smaller than the geometrical porometer volume $V = V_p$. If time needed to build up the mean concentration in the *total* (apparent) volume V_t ($= V_p + V_s$) is negligible, the simple model could still be used. Just as in the case with only V_p the time constant of the system might then be disregarded. This however is not the real situation.

2. *The sensor has a noticeable response time (lag time, time constant).* We make use in our measurements of a dynamical method. The two indicated e_p-values don't correspond with steady state conditions of the sensor in equilibrium with the ambient vapour concentration in the cup. However, these e_p-values are taken from calibration diagrams made up in equilibrium situations. So in dynamical use the indication of the sensor does not correspond with the real cup vapour concentration. Under such conditions our simple model would be preserved only in the case the final time lag between cup and sensor has become constant (after the starting effect and before the linearization approximation of (7) has become invalid). The higher the time constant the more unlikely the saving of the model would become. It will be shown that the dynamical response may be incorporated in V_s (or V_t), however, because of other intrinsic properties of the sensor. In the definite form of (7), (8) and (9) V now of course becomes V_t.

3. *The response time is not really constant.* The response time of many humidity sensors is a combination of the effect of several physical phenomena. Therefore the response time is only constant under accurately reproduced circumstances (e.g. KOBAYASHI, 1960).

4. *Temperature exerts influence.* Temperature of the cup is of influence on the time constant of the sensor. This is apart from the influence of temperature on the equilibrium values of $e_p (t_i)$ and $e_p (t_f)$.

5. *Hysteresis effects, ageing and the impact of external agents.* These effects may influence the values of $e_p (t_i)$ and $e_p (t_f)$ as given by the manufacturer and as used in (7). Moreover the time constant may change because of the same effects.

6. *The wall of the cup can adsorp and absorb water vapour.* The process of water ad- and absorption respectively desorption by different materials is complicated and not always very reproducible. Therefore the material of the wall may also contribute an unknown amount of apparent volume to V_t (total volume).

If we want to retain the form of (7) for our measurements, it is clear from the above that we have to determine the value of V_s (V_t) under our specific measuring conditions.

After a description of the design of the sensor cup we will deal below with the wall materials used in several modifications and in our own cup. We were able to eliminate point 6. in our device. Further we will demonstrate how V_s did behave under different conditions. From this it will be shown that using (7), (8) and (9) as a partly empirical but theoretically supported model is much more promising for correct field measurements than the use of (8) only. The latter is common practice of most workers at the moment. Under such conditions V_p must indeed not be susceptible to change because of convection currents in the cup. Thus a fan remains essential. We will show that a simple calibration before and after a day of field measurements and an occasional thorough calibration will yield satisfactory results.

During the preparation of this manuscript we found once more emphasized the objections against this simple diffusion porometer method (BEARDSELL et al., 1972). With our calibration method and other precautions and checks these objections are all met. This is i.a. demonstrated by the proved insensitivity of the apparent calibration volume V_t (or V_s) to leaf temperature (§ 6) and by complete incorporation of sensor ageing effects and dynamical response effects in this calibration volume. These are, together with the cup materials and the calibration procedures used, the major advantages of our set up.

4. DESIGN OF A DIFFUSION POROMETER

4.1. THE SENSOR CUP.

A hollow, horizontal cylinder, flattened (horizontally) at its lower side is used as the sensor cup. A rectangular opening in the bottom forms the entree for water vapour from the leaf. A vertical cross-section is given in Fig. 1.
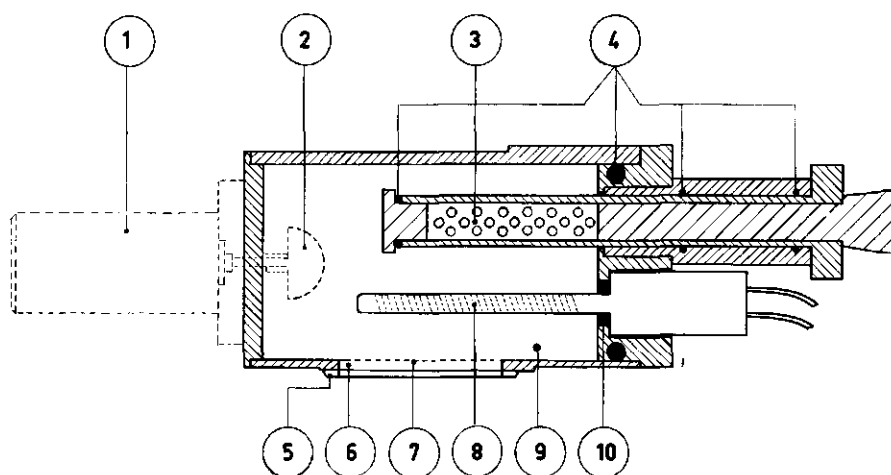

FIG. 1. The porometer used. Cross-section through the central longitudinal axis of the cylindrical cup ($V_p = 39.9 \pm 0.2 \, cm^3$). Material: polypropylene.

One may discern:
1. the motor (Mauthe GmbH, Type 16-35-12).
2. the fan (four mutually perpendicular flat blades).
3. silica gel holder for drying pellets (dust-poor 'Kali-Chemie AG Trockenperlen'). A content of 10 to 15 pellets is enough for about 30 measurements. For refilling, the closing rod of the holder is taken out and the moistened pellets brought into a small container. From a new container with the mentioned amount of pellets the holder is filled by one movement only. The holder may be moved into and out of the cup.
4. O-rings for sealing.
5. rubber sealing fringe around the sensor cup opening. The evaporating surface is in this way sealed off from the surroundings (Saba silicone sealant, Nr. 25, grey; can not be used over thick nerves).
6. sensor cup opening ($2.03 \pm 0.01 \, cm^2$).
7. perforated membrane (VECO–125K, calculated resistance (III): 0.14 s/cm (25 °C), thickness 35 μm, 2800 pores/cm^2, smallest pore diameter 120 μm).
8. sensor (Hygrodynamics Inc., TH 7 15–1284; cylinder of 4 cm length and 3 mm diameter).
9. thermistor (YSI-precision-thermistor, 1 MΩ (25°), Nr. 44015). The bead is held in the ventilation stream by its own streched wires (perpendicular to the given cross-section).
10. luting material to fix the sensor (Bucarid).

The opening to bring a second sensor into the cup has not been drawn. It was situated behind the motor, which in turn was mounted at the viewers side of the central cross-section.

Real shape and several details are shown in Fig. 2, 3 and 4. Apart from the caption of Fig. 1 the following remarks are important:

1. A simple agitating fan system was used for mixing the cup air, in stead of a circulation system as used for example by GRIEVE and WENT (1965, Comp (1) p. 29), BYRNE et al. (1970) and TURNER and PARLANGE (1970). Effectiveness of the agitating system was demonstrated by smoke experiments in perspex dummy sensor cups and confirmed by measurements with and without the fan (§ 5). Influence of the motor-fan system on equilibrium temperature in the cup was less than 0.1 ° C.

2. Cup and sensor dimensions have been chosen such that a second sensor can be brought into the cup (TURNER and PARLANGE, 1970) without making the instrument bulky. The little sieve in the 2 cm² opening effectively suppressed convective currents to pass and prevented (hygroscopic) dust to enter. However, it hardly added resistance to the diffusing water vapour.

3. HANDEGORD et al. (1965) found silica gel to be safe as a drying agent for storing our type of humidity sensor. When not in use our sensor cup was stored in a container with silica gel, with its own drying agent being inside of the cup (MORROW and SLATYER, 1971 a). We preferred a built in silica gel holder for several reasons. Firstly it is now much easier to hold the sensor at a
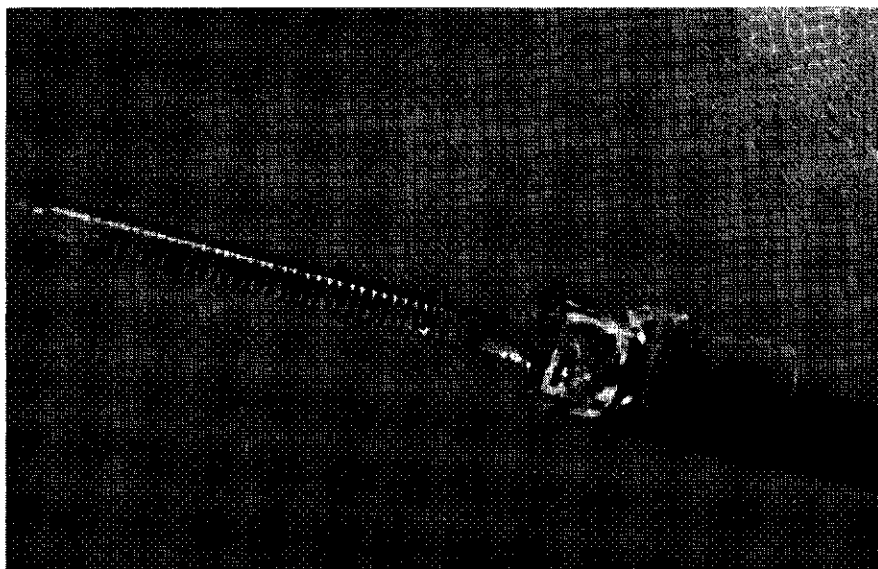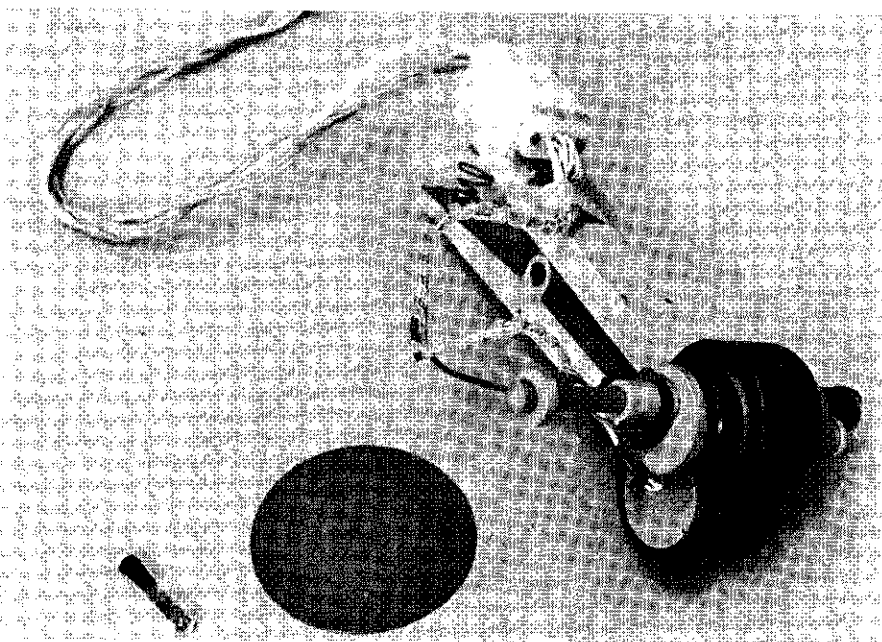

FIG. 2. The sensor used.

Fɪɢ. 3. The leaf diffusion resistance meter (porometer) in its field clamp. At the left side of the cup the silica gel holder, pulled out of the sensor cup. Below this holder the sensor connecting wire head. At the right the opening for the second sensor (closed by a P. P.-rod) and the motor behind. At the upper end of the clamp the sensor wires are connected by an electrical plug onto the electronical circuitry. In the foreground left to the porometer a high resistance perforated membrane and a standard glas container holding drying pellets.

fixed concentration within the cup (§ 6). Secondly the influence of drying can be studied more thoroughly. Finally, the method is less susceptible to silica gel dust deposit onto the sensor (suggested by Mᴏʀʀᴏᴡ and Sʟᴀᴛʏᴇʀ, 1971 a; P. A. M. Hᴏᴘᴍᴀɴs, personal communication, 1972) if the same drying pellets are used again after recycling.
4. Putting the rubber gasket on water repellent material, no leakage was observed. This check was thoroughly facilitated by the use of a wall material with extremely small water adsorption and absorption capability. Additional advantage of the use of this wall material is that influence on V_t is almost completely removed (§ 6, Appendix 1, 2).
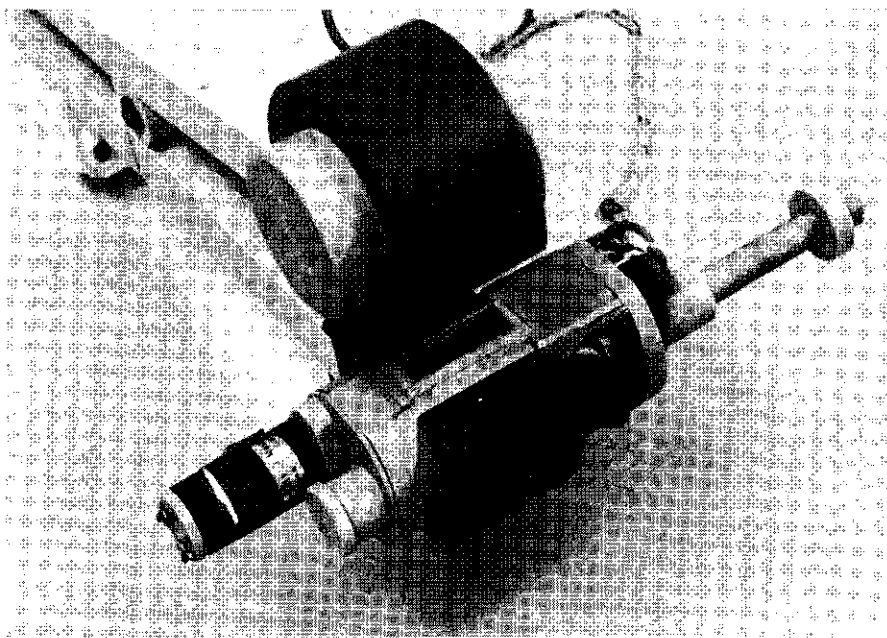
FIG. 4. The porometer upside down. Now the sensor cup opening is shown with rubber sealing fringe and built in anti-convection membrane.

4.2. THE CUP MATERIAL USED.

Perspex (Methyl methacrylate) is able to adsorb and absorb a relatively appreciable quantity of water (vapour). This property is held responsible by some workers for the appreciable drift phenomena observed with perspex diffusion porometers (MORROW and SLATYER, 1971 a; Appendix 1). Several water repellent coatings were tried out by us but they all failed to give any effect worth mentioning.

DJAVANCHIR (1970) has used teflon (Polytetrafluorethylene) as a cup material. This however implies special construction measures as joining by glues is very difficult. To base our choice more quantitatively and to learn more about ad- and absorption, we did some simple experiments, which have been described in Appendix 2. Together with perspex and teflon we used opaque hard P. V. C. (Polivinyl-chloride) and polypropylene (P. P.) (Comp. KLEIN and KLEIN, 1970; JARVIS et al., 1971). They are more easily glued (DAVIDSON, 1966) and more machinable.

From the results obtained in these experiments we drew the conclusion that

10

P.P. could be safely used as the cup material. Long term drift, as far as brought about by translocation of water vapour between sensor and wall, was indeed almost completely absent. A proof of the absence of drift from internal sensor phenomena is given in Appendix 1. The above involves three important consequences comparing P.P. to perspex cups (MORROW and SLATYER, 1971 a):

1. as already mentioned leakage control has become far better which is of importance in relation to earlier experiences (GEE and FEDERER, 1972).

2. extreme drying, before starting a measurement, onto a high value of sensor electrical resistance, where drift apparently has no more influence, is not necessary. The measuring accuracy therefore becomes higher (§ 6).

3. the procedure to reduce drift to a relatively low and stable level before commencing measurements can be omitted. The same applies to measuring of drift at intervals and trying to correct the measurered transient times for the drift determined. It can be shown, moreover, that such corrections are questionable (Appendix 1 and 2).

5. CALIBRATION RESISTANCES AND THE DIFFUSION RESISTANCE OF THE CUP

As was shown in (I, p. 45) tubes with the same cross-sectional area as the cup opening and with different lengths can not be used as dummy calibration resistances. Diffusion processes in such a calibration performance are too different from those through the leaf epidermis. They are not obeying Fick's law for stationary diffusion. Therefore multipore membranes are more appropriate calibration resistances.

Perforated perspex plates – as used for instance with the commercially available porometer types based on the work of KANEMASU et al. (1969) – run the risk, however, of absorbing unknown amounts of water vapour in the pore walls and elsewhere. Therefore P. P. or teflon plates would be preferable. This can not solve, however, the problem of the relatively high resistances of such sieves (from 7 to 45 s/cm in the commercial set) in comparison to the values of 1 to 10 s/cm most frequently occurring on leaves in the field. To avoid interpolation between the lowest calibration plate and a measurement without such a plate we preferred using nickel membranes, that range roughly from 0.1 to 10 s/cm. Such nickel multipore membranes are manufactured by electrolysis (VECO-zeefplatenfabriek, (III), Comp. Lee, 1967; Ting and Loomis, 1963, 1965).

Drawing a calibration diagram (§ 3.1) of measured transient times against such known resistances, extrapolation to $t = 0$ empirically yields a value for the cup diffusion resistance R_p (§ 6). To check our method we tried to obtain also a *theoretical* value of this cup resistance for comparison. As an approximation TURNER and PARLANGE (1970) assumed in their calculations fully developed Poiseuille flow to exist in their circulation type porometer. For our agitation type porometer an estimation by calculation of boundary layer resistances in turbulent flow (near the cup wall and near the cylindrical sensor surface) seems more appropriate.

Two components of R_p are theoretically known. The resistance of the still air below the nickel membrane (Fig. 1, Nr. 7) built in the cup opening, onto the leaf or calibration plate surface can be calculated from simple geometry: 0.95 ± 0.05 s/cm. The resistance of the mentioned nickel membrane is 0.14 ± 0.01 s/cm.

The boundary layer resistance to water vapour flow out of this perforated membrane *into* the cup may in our opinion be approximated most accurately by a formula given in (I, p. 21), for turbulent air flow over leaves (one side):

$$R = 1.3 \sqrt{d/u} \tag{11}$$

This formula was recently confirmed to be a very good approximation by PEARMAN et al. (1972), PARLANGE et al. (1971) and PARLANGE and WAGGONER (1972). Here d is a characteristic length for which we take the mean sensor cup

opening dimension (2 cm). For u, the measured ventilation speed in the cup, we found a mean value of 45 ± 5 cm/s. The value was obtained by a calibrated heated thermistor anemometer (Wilh. Lambrecht KG, Type 641 N), brought into the cup through the opening for the second sensor. Use of the given values in (11) yields a resistance value for this boundary layer of 0.30 ± 0.05 s/cm.

Estimation of the sensor (Fig. 2) boundary layer resistance for turbulent mass exchange is made in the following way. The bulk flow being (almost) a potential flow, heat transfer coefficients from cylindrical wires as measured by HILPERT (e.g. GRIGULL, 1963; KESTIN, 1966) or collected from different sources by VAN DER HEGGE ZIJNEN (1957) can be used. For our wind speed and cylinder diameter (0.3 cm) both sources yield 0.7 s/cm.

The influence on this value of non-uniform bulk flow and turbulence will be difficult to disentangle (VAN DER HEGGE ZIJNEN, 1958). Moreover the influence of the latter depends on intensity as well as scale of turbulence (VAN DER HEGGE ZIJNEN, 1958). Therefore only limits may be given for our situation.

Measurements of COMINGS et al., cited by KESTIN (1966) and VAN DER HEGGE ZIJNEN (1958), reveal that with relatively low wind speed and small diameter turbulence in bulk flow would not enhance the transfer from cylinders. On the other hand measurements were made by PARLANGE et al. (1971) and PARLANGE and WAGGONER (1972) on boundary layers of small leaves in a turbulent fan flow and in turbulent flow encountered outdoors. They found transfer under uniform flux condition enhanced by *at maximum* a factor 2.5. Applied to our cylinder such a factor would yield a minimum resistance of 0.3 s/cm. PEARMAN et al. (1972) found a *mean* raise of heat transfer from metal discs in turbulent fan flow with a factor 1.5. This would result in a cylinder boundary layer resistance of 0.5 s/cm. From the above we accept as a reasonable estimation for our sensor boundary layer resistance 0.5 ± 0.2 s/cm.

Total R_p now becomes: $0.95 + 0.14 + 0.30 + 0.5 \simeq 1.9 \pm 0.3$ s/cm. The mean measured value was 1.9 ± 0.1 s/cm. It is clear that the result by approximation of cup transport phenomena is in fair agreement with the experimental value.

The resistance of the porometer *without* using the fan may be found in two ways. Transient time/resistance diagrams can be made without using the fan. Secondly *one* measurement without fan can be made after a calibration series *with* fan (§ 6). Both methods yielded the value 3.60 ± 0.15 s/cm. With pure one dimensional flux and no deviations from Fick's law the distance between anti-convection membrane and sensor determines the resistance, together with nickel membrane and opening values. The former, 6.8 ± 0.4 mm, adds about 2.7 ± 0.2 s/cm to the latter value of 1.1 s/cm (0.95 + 0.14). So the total resistance in this case is 3.8 ± 0.2 s/cm. Again the result is not unreasonable. It shows nicely the influence of the fan agitation process which reduces the *inner* resistance of the cup with more than 70%. In the field inhomogeneous temperature distribution within the cup can also cause circulation in the cup. As a result the diffusion pattern in a cup without air agitation may easily be disturbed. This will lower the inner resistance incontrollably.

6. CALIBRATION OF THE POROMETER

As said in (I, p. 29) electrical hygrometers hold advantages in simple field equipment. Preparing a choice one may take use of the well known review of humidity sensors in WEXLER (1965). From more recent literature it may be concluded that lately no break-through occurred in this field (LAI and HIDY, 1968; SZULMAYER, 1968; PANDE, 1970). In diffusion porometers sulfonated polystyrene (Pope-) sensors and Lithium Chloride (LiCl-) sensors have been used.

The use of Pope-sensors (PANDE, 1970) is documented by MEIDNER (1970), MONTEITH and BULL (1970) and STILES (1970). Flatness of these sensors is of advantage in unventilated porometers. The fact that their water absorption is negligible should also be an advantage. On the other hand they also suffer heavily from the ever occurring draw backs of humidity sensors. They have a high temperature dependence and very high time constants (e.g. MONTEITH and BULL). Also influence has been observed of the material of electrodes, of changes in calibration and of slowing down of their response time in the course of time (Comp. § 3.2 and e.g. MUSA and SCHNABLE, 1965; VISSCHER and SCHURER, 1972). Therefore no incentives do exist to use these sensors in stead of the LiCl-elements applied most frequently up till now.

On the latter type of elements an acceptable amount of knowledge, theoretical as well as experimental, is gathered (KOBAYASHI, 1960; several articles in WEXLER, 1965). When we started our study not much was known about the particular behaviour of these sensors in diffusion porometer use. A thorough empirical study, as carried out by MONTEITH and BULL (1970) in relation to the Pope-elements, therefore appeared to be necessary. Also TURNER and PARLANGE's study (1970) on the apparently attractive "two sensors – method' was in need of supplementary experiments (I, p. 34). When our research was progressing the earlier mentioned articles of MORROW and SLATYER (1971a, 1971b) were published. They contain a first list of important observations around the behaviour of the commercially available unventilated Perspex diffusion porometer. We succeeded to obtain a series of corresponding and complementary observations concerning the behaviour of the ventilated P.P. porometer. Some surprising results can be theoretically derived from what is known of the LiCl-element properties (Comp. § 3.2, § 6.4.b. and Appendix 3).

Small LiCl-sensors are of importance in the 'two sensors – method' as well as in application in small porometers (STILES, 1970). Examples have been mentioned by STRUNK et al. (1964) and ROGERS (1965), but were not applied in diffusion porometers so far. We preferred a small type 'narrow range sensor' (Fig. 2), which only differs from the big ones used hitherto in its dimensions and its smaller amount of water uptake (Hygrodynamics Inc., Silverspring,

Maryland, private communication, 1971). This choice made it possible to compare our results with those gathered by others on this type of element.

6.2. THE METHODS USED.

Not aware of the factors influencing the behaviour of the LiCl-elements (as described by us in § 3.2. and in Appendix 3) TURNER and PARLANGE (1970) tried to determine V_s by an attractive method. Measurements were done in a reproducible way with one sensor and two sensors in the cup respectively. The second sensor acted as an additional water vapour sink and for the measurements involved one could derive (if the sensors took up negligible space):

$$(\Delta t)' = \frac{2 V_s + V_p}{S} (R_p + R_l) \ln \frac{e_l - e_p (t_i)}{e_l - e_p (t_f)} \tag{12}$$

or

$$(\Delta t)' = \frac{2 V_s + V_p}{S} \frac{\Delta e_p}{e_l - \bar{e}_p} (R_p + R_l). \tag{13}$$

With one sensor our formula (8), combined with (9) in its definite form was $(Vt = V_s + V_p)$:

$$\Delta t = \frac{V_s + V_p}{S} \frac{\Delta e_p}{e_l - \bar{e}_p} (R_p + R_l). \tag{14}$$

Equations (13) and (14) are (during calibration) two independent equations with two unknown variables, V_s and R_p. The mentioned authors did obtain values for V_s at different temperatures, be it with vapour source and porometer at the same temperature and with $R_l = 0$ only.

Because the principle of the method is sound we decided to pay attention to its application (I, p. 34). As the indicating sensor we took one that was already used for a long time before in a series of try-outs. A fresh sensor was taken as the additional vapour sink to obtain the values of equation (13). However, no compatible results were obtained from which R_p and V_s could be estimated unambiguously.

The main assumption underlying the method is that the V_s-values for the two sensors are equal and remain equal. Our inconsistent observations contrarily indicated sensible sensor changes resulting in higher transient times, under identical circumstances, from one day to the other. Appreciable long term slowing down of sensor reactions after storage during several months was already observed by MORROW and SLATYER (1971a).

It is clear that a rapid fall of time constant and/or calibration (Comp. Appendix 4), which is not equal for both sensors, makes the combination of (13) and (14) invalid. Presumably TURNER and PARLANGE worked with fresh sensors, but their inexplicable high coefficient of variation in V_s points also into the

direction of short term sensor changes. As the two sensors are undeniably used in a completely different way in the course of time, such differences in V_s can be expected to grow rapidly. This was confirmed by us in later observations. Therefore the 'two sensors – method' must be disregarded.

Also the temperature correction for K' (in eq. (8) and (9)) as given by KANEMASU et al. (1969) implicitly assumes V_s to be constant in time and moreover independent of temperature. It can be shown that the correction concerned is in fact based on two presumptions. Firstly *total* water absorption was taken constant. Secondly water absorption *partitioning* between geometrical porometer volume and the total volume of sensor and perspex walls was also taken constant in time and independent of temperature. This will be shown to be not justified.

An other calibration method, as described by BYRNE et al. (1970, Comp. (I, p. 34)), also seems to be doubtful under dynamical sensor use and varying sensor response. In the first place the building up of concentration in the cup during calibration is completely different from the situation during measurements. Our experience with influences of the 'starting point' of a measurement on the transient times (Appendix 3) would therefore make this method invalid. Secondly overshoot seriously limits this 'injection method' (I, p. 34). The observed changes in time constant enhance heavily the likeliness of overshoot to take place.

Finally BRAVDO's (1972) calibration method is invalidated by his erroneous use of literature values for LiCl-sensor water absorption. Moreover no allowance is made for the measurement to be dynamical in nature and a few other misinterpretations may be mentioned (Appendix 4). On the contrary his combination of measurement of resistance to CO_2 and water vapour flow is of interest.

Because of the above we tried to take up again the use of (8), *but with the aid of (9) to calculate values for* V_t *(= V_s + V_p) under all temperature conditions.* We decided to follow these values in the course of time. Some experimental details relating the determination of V_t under the measuring procedure are described in Appendix 3. The need for an accurately reproducible measuring strategy in each individual measurement arises from the considerations given there and in § 6.4.

During the preparation of our manuscript a method making use of an Al_2O_3-sensor was published (PARKINSON and LEGG, 1972). The sensor was used as a measuring device in an open flow porometer (I, p. 27) which may also be called a sudorimeter (MONTEITH, 1972). The advantage of this method is the use of the humidity sensor in a steady state measurement. A disadvantage of the method for field work is the use of a nitrous oxide (or an other indifferent gas) supply which has to offer an adjustable, but during the measurements constant, gas flow over the leaf part in the cup.

No information is given on ageing effects of the sensor on its calibration values and its time constant. The latter determines the time necessary to obtain

16

a steady state reading. This period may not be too long, as will be demonstrated from our field experiments (III).

Waiting time is also a draw back of an other recently described variant of the open method (BEARDSELL et al., 1972), mainly constructed for spruce forest canopy measurements. This method uses a dry air supply of which the inlet speed has to be (manually) balanced against transpiration rate to have a constant humidity within the chamber. The humidity is measured by a high time constant sulfonated polystyrene sensor. Moreover with the device described leaf surface must be determined after each measurement, which makes the method unsuitable for canopy profile measurements.

Whether the disadvantage of gas supplies and waiting periods for equilibrium are in field use less serious than the disadvantage of the dynamical sensor use in our method is questioned by the present authors.

6.3. CALIBRATION EQUIPMENT AND PERFORMANCE.

A survey of the equipment used in calibration measurements is given in Fig. 5. In the foreground on the left the porometer, taken out of its field clamp (behind) and set in a special grip, on a teflon base plate. The weight on top imitates clamp pressure as applied in the field. In the foreground at the right a heat source bearing saturated filter paper and a thermojunction (detail in Fig. 6). To prevent direct contact between wet surface and perforated membranes
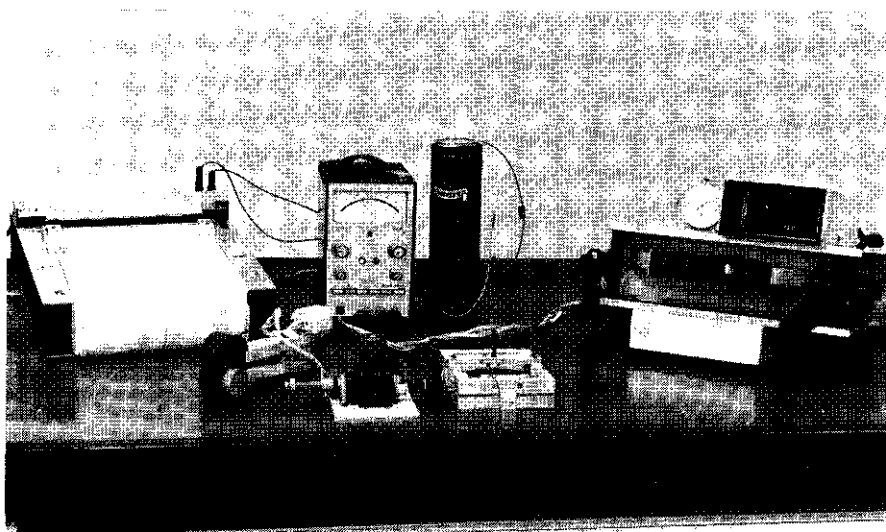

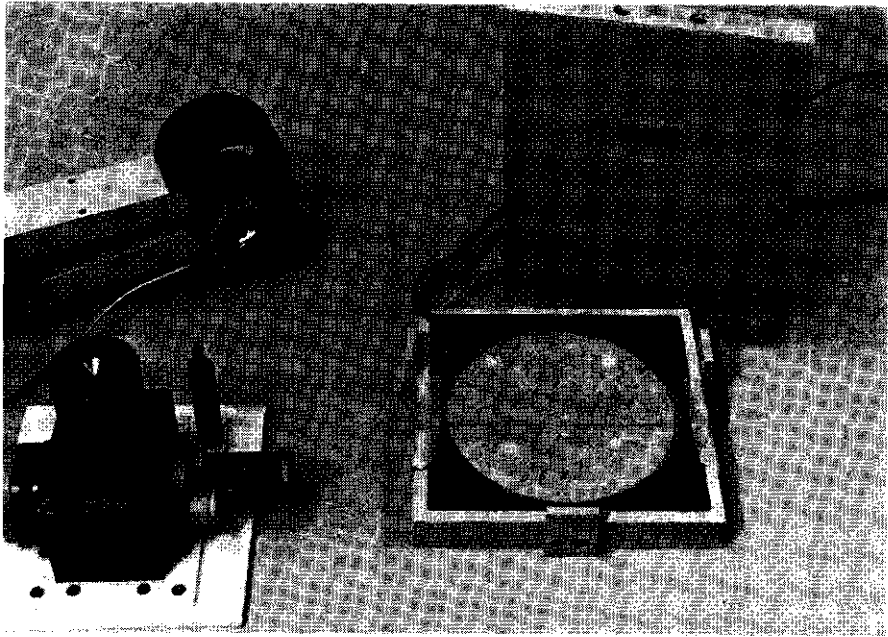FIG. 5. Calibration equipment, described in the text.

Fɪɢ. 6. The temperature controlled evaporating surface used in calibration measurements. One can see the thermojunction which measures the temperature in the middle of that part of the surface which evaporates into the cup during these measurements. The bottom of the P.P. container, placed over the wet filter paper during measurements, is shown more behind in a back-view, with its opening covered by a perforated calibration membrane.

a polypropylene container with a bottom of 2 mm thickness is placed over the wet paper. In the bottom an opening is made of the same dimensions as the porometer opening. Details of the container may be seen in Fig. 6 (back-view in the background) and Fig. 7 (top-view with calibration plate). Calibration plates are placed in a fixed position over the opening. The 2 cm² of the membrane measured in this way have been compared with the average of a series of measuring places to detect eventual inhomogeneity (III). Thin plates can be fixed by a screw clamp in the middle of the P. P.-container. In the measuring procedure to obtain reproducible results (Appendix 3), before each measurement the sensor resistance is held constant for two minutes at a fixed value. The sensor value is indicated by the digital volt meter on top of the portable registration equipment (Fig. 5, right hand side). After the two minutes indicated by the stop watch shown, the porometer grip is placed in a fixed position on the calibration plate over the opening in the P.P. container bottom (Fig. 8). Moving the porometer imitates the clamping movements made in the field. As soon as the electrical resistance passes its first fixed value, two counters (lower side of the portable equipment, Fig. 5) start running (for details see § 7).
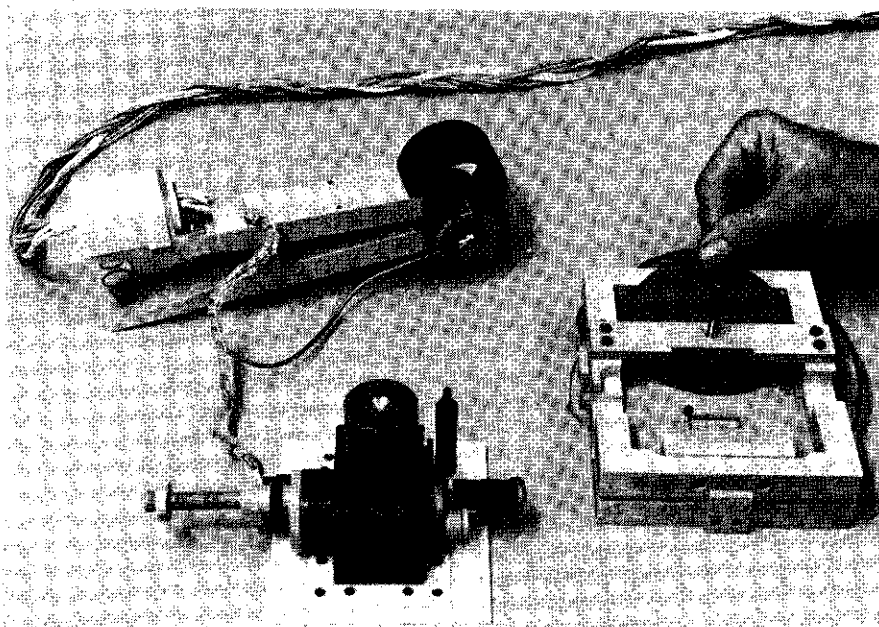
18

FIG. 7. The high resistance perforated calibration membrane is placed in its fixed position over the opening in the P. P. container bottom (top view). Left in the foreground the porometer in its grip for calibration measurements.
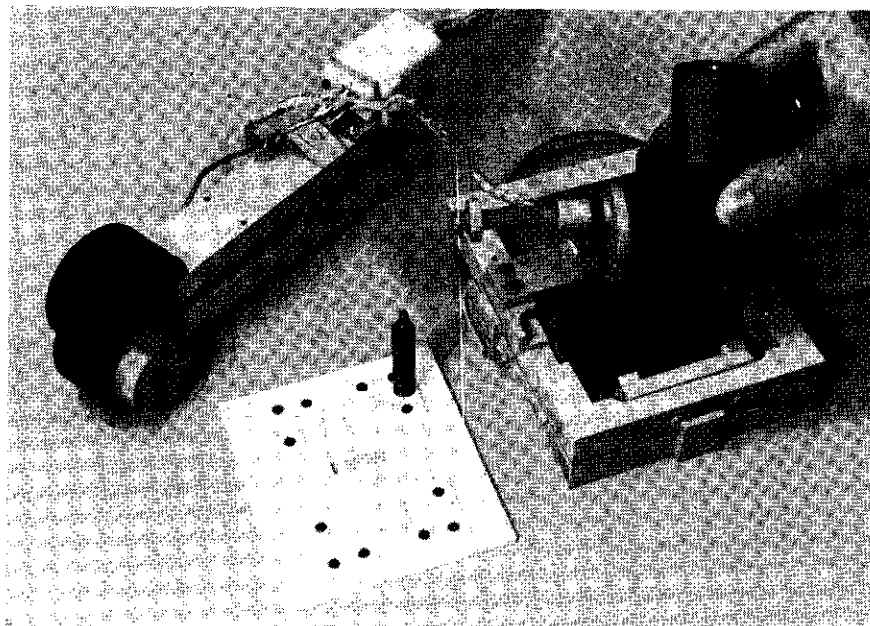

FIG. 8. A measurement of a calibration series is performed. The grip with the porometer is placed in its fixed position over the membrane. In the foreground the teflon base plate, also used for the 'time constant measurements' (Appendix 1).

The extra diffusion resistance added under the calibration plates could be calculated from the geometry of the opening in the bottom of the container: 0.83 ± 0.03 s/cm ($25\,°C$). By one observation with the porometer directly on the filter paper, after each series of calibration measurements, this resistance could also be determined experimentally: 0.79 ± 0.03 s/cm. These results indicate that the opening of the porometer was indeed completely over the opening in the P. P. container bottom.

Because of the fact that calibrations had to be done in an environment without temperature control, porometer temperature was influenced by the presence of the observer. The temperature rise over one hour was normally less than one degree. This, nevertheless, influences transient times because of the high temperature sensitivity of the sensor. Therefore each calibration contained 14 measurements, arranged symmetrically: 3 without calibration plate, directly on the P.P. base plate; 2 times 5 measurements with five different calibration membranes; 1 directly on the filter paper. A representative example, corresponding to line nr. 2 in Fig. 9, is given in table 1. In the way described an accuracy of porometer and surface temperatures of $\pm 0.1\,°C$ was always obtained by taking the means of corresponding measurements in the symmetrical arrangement.

TABLE 1. Calibration (Nr. 42), symmetrical with regard to measurement nr. 8, with five calibration membranes (Nr. 1, 2, 6, 7, 12, see (III)) and without a membrane. Measurement Nr. 15 is used to calculate R_p when V_f is determined from the slope of the line through the other observations.

Nr. meas.	Short time (s)	Long time (s)	Porometer Temperature (°C)	Surface Temperature (°C)	Nr. membrane	Nr. Membrane	Averages Short time	Long time	Por. temp.	Surf. Temp.
1			Dummy							
2	5.53	22.44	24.5	24.6	without					
3	17.94	74.36	24.6	24.8	1	1	17.85	73.70	24.95	24.90
4	18.01	74.23	24.7	24.8	2	2	17.85	73.65	24.95	24.90
5	11.78	48.38	24.8	24.9	6	6	11.80	48.35	25.00	24.90
6	8.54	34.88	24.9	24.8	7	7	8.55	34.85	25.00	24.85
7	6.85	27.97	25.0	24.9	12	12	6.95	28.15	25.05	24.85
8	5.65	22.85	25.05	24.8	without	with-	5.60	22.60	24.95	24.75
9	7.01	28.28	25.1	24.8	12	out				
10	8.54	34.78	25.1	24.9	7					
11	11.82	48.29	25.2	24.9	6	Mean surface temp.: $24.85° \pm 0.1$				
12	17.71	73.08	25.2	25.0	2	Mean porometer temp.: $25.00° \pm 0.1$				
13	17.76	73.04	25.3	25.0	1					
14	5.60	22.51	25.3	24.9	without					
15	3.95	15.70	25.4	24.9	Filter paper					

Using the heat source permits control of the temperature of the evaporating surface by control of the heating current (Fig. 5, at the background). This

temperature was registrated during the calibration measurement and held as constant as possible. The thermojunction between two wet filter papers on the heat source surface was of a rolled type as used earlier (STIGTER, 1968), measured against melting ice. The porometer thermistor resistance could be read at the digital volt meter by switching to the other circuit after passage of the second and/or third fixed sensor resistance value (§ 7).

6.4.a. *Absence of wall influence.*

As is seen from table 1, the calibrations are started without the usually prescribed series of dummy measurements to bring wall or sensor in a ready state. A proof that neither the wall nor the sensor need such a treatment in our case (Comp. Appendix 1 and 2) and that the wall does not influence the results is given in table 2. For long transient times and high resistances the proof is given in Appendix 1. The same calibration series as in table App. 1.1. are used in table 2, where the short transient times are given for calibration measurements without membrane. It is clear from the averages given that a possible dryer state of the wall at earlier measurements in a calibration series does on the average not lengthen the measuring times. So the calibration method may be used as such.

TABLE 2. Comparison of short transient times (between first two fixed electrical resistances) for the same kind of measurement, at low overall resistance (2.7 s/cm). The transient times are observed early and later in a calibration series such as given in table 1. The number in the left hand column is the order number in the series, as in the left hand column of table 1. Every series was preceded by a period of dry storage. The transient times given have been corrected for the course of temperature, which influences calibration values of the sensor as well as the value of V_s. The ten calibration series used were the first ones made in this way. Omitting the observation series with the question mark, the averages become 4.11, 4.13 and 4.13 respectively. The values of the averages as such have of course no physical meaning.

Nr. meas.	Reading (s)	Nr. meas.	Reading (s)	Nr. meas.	Reading (s)	Nr. meas.	Reading (s)	Nr. meas.	Reading (s)
2	3.53	2	2.91	2	2.69	2	3.11	2	4.73(?)
10	3.51	8	3.02	8	2.71	9	3.16	8	4.92
16	3.53	14	2.97	14	2.73	15	3.11	14	4.98
2	3.75	2	5.58	2	6.12	2	5.00	2	4.32
8	3.78	8	5.48	9	6.08	9	5.12	9	4.36
14	3.81	14	5.57	15	6.13	15	4.95	15	4.37

Averages (10 series)	
Nr. meas.	Reading (s)
2	4.17
8 (4 × 9, 1 × 10)	4.21
14 (4 × 15, 1 × 16)	4.21

6.4.b. *The relation between resistance and transient time.*

In the way described in 6.3 an appreciable amount of calibrations have been done. Each series resulted via (8) and (9) (or (14)) in a value for $V_s = V_t - V_p$. The first calibration series yielded for example the straight lines numbered 1 of Fig. 9 and Fig. 10. The value of $V_s = 94$ calculated from this straight line in Fig. 9 is included in Fig. 11 as the very lowest measured V_s-value. The other points of Fig. 11 have been obtained in the same way in the course of time. The observations given as examples in Fig. 9 and 10 show some important results.

Firstly it is confirmed that the time/resistance diagram produces straight lines at constant surface and sensor temperatures. This was also found by other investigators. Secondly the same remains true for the long transient times
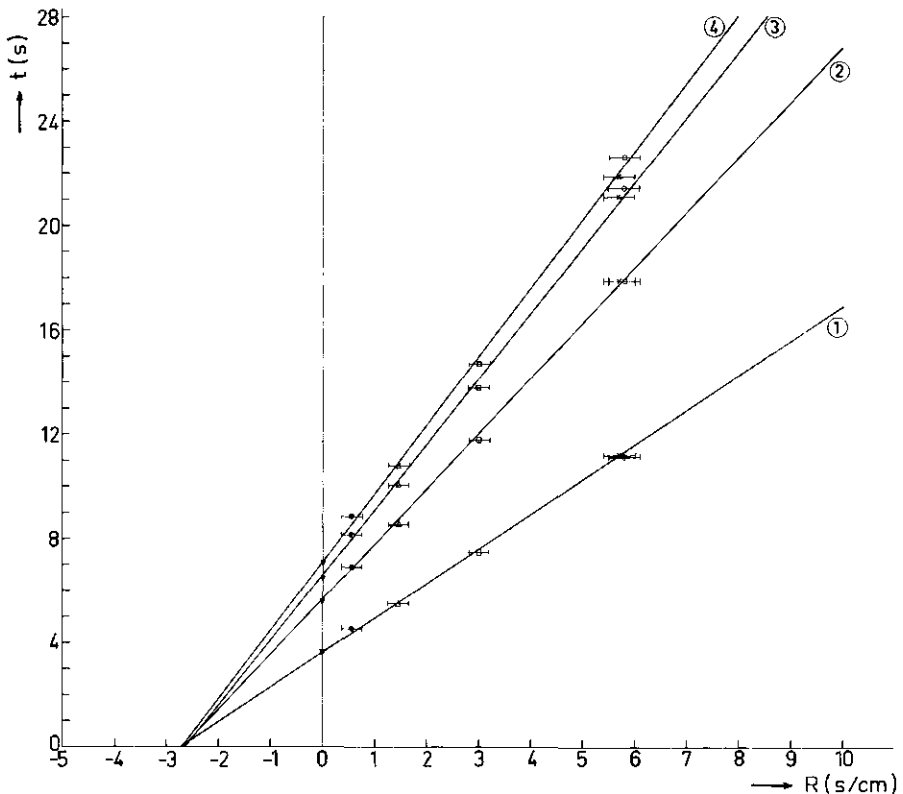

FIG. 9. Changing slopes in time/resistance diagrams in the course of time for calibration series with temperatures of evaporating surface and porometer both near 25 °C. The reversed filled triangles are measurements directly on the bottom of the P. P. container, without resistance membrane. Measuring points are short transient time measurements. Indication of the period passed between observation of the successive lines marked 1 to 4 is given in the text.
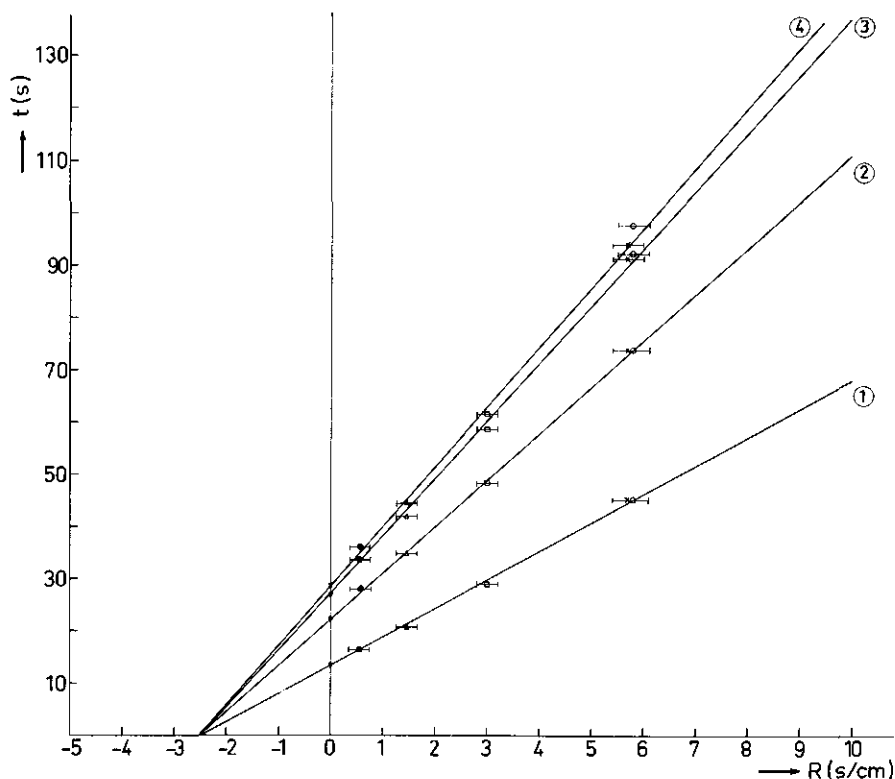
FIG. 10. Calibration lines as in Fig. 9 for the long transient times of the same calibration series.

(between passages of first and *third* fixed sensor resistances). Calculating V_s from corresponding lines such as in Fig. 9 and 10 results in only slight deviations. From the long transient times diagrams V_s is as a mean 3% higher than the value calculated from the short times. These results extend for higher diffusion resistance (I, p. 34) the results of TURNER and PARLANGE (1970). They also found *for low diffusion resistance* that V_s was almost independent of the part of the log-linear sensor calibration plot used (under the same measuring strategy).

From the observed straightness of the lines in Fig. 9 and 10 it can also be concluded that, under the measuring procedure applied (Appendix 3), V_s is also independent of the different rates of going through the same course of vapour concentration (for different diffusion resistances). But in that case there is no difference in dynamical response for different evaporation rates. Now the results of investigations of KOBAYASHI (1960) show that response time is only dependent on the amount absorbed water per unit of relative humidity change. This means that there is, *at least effectively as indicated by the sensor*, no difference in mass absorption per unit of relative humidity rise $(dM/d(rh))$ is apparently

constant). In other words: the dynamical response is apparently independent of the speed of water absorption by the sensor (dM/dt) as long as the starting point for a measurement is the same. The compound time constant, as discussed in Appendix 3 from KOBAYASHI's (1960) investigations on the LiCl-sensor, makes plausible that $dM/d(rh)$ is a constant. For the sulfonated polystyrene sensors the same empirical conclusion on the dynamical response was drawn by MONTEITH and BULL (1970).

Using the mathematical expression, we can say that dynamical response is independent from:

$$\frac{dM}{dt} = \frac{dM}{d\,(rh)}\frac{d\,(rh)}{dt} = c\,\frac{d\,(rh)}{dt}. \tag{15}$$

This once more formulates the result that V_s is not influenced by evaporation speed at constant sensor temperature. But in that case, and this is an important conclusion, V_s *would also be not influenced by evaporating surface temperature.*

Our first task now in the calibration performances was to follow the behaviour of V_s, in dependence of
1. the temperature of the sensor (cup);
2. the temperature difference between sensor cup and evaporating surface;
3. the time.

6.4.c. *The behaviour of V_s.*

The dependence on temperature and the trend of V_s in time have been collected for a first period in Fig. 11. As mentioned, each point is based on a calibration as given in table 1. The lowest two points, measured on the first day, form the lower limit. The highest four points, measured three months later, form the upper limit for this period of continuous use in the laboratory (ca. sixty calibration series) and in the field (six measuring days) and before a long period of dry storage.

From Fig. 11 one may conclude that a straight line gives a good approximation of the temperature dependence of V_s in this period of time and over the given temperature range. This is in agreement with TURNER and PARLANGE's preliminary results. The mean slope of curves H1 up to H6 amounts 6.5 ± 0.2 cm^3/°C. These curves are based on four or five points.

In the same period, on eleven different days, also lines have been obtained based on two or three points only. The mean slope of the lines through these observations was 6.6 cm^3/°C, but the variation was obviously much higher. The total number of calibration series perhaps may be too small to draw a definite conclusion about a trend in the slope measured. There was an indication, however, that within the three months period the mean slope for the same temperature range was increasing from about 6.2 to 6.9 cm^3/°C.

The maximum percentual error in each V_s-determination was almost constant over the temperature and time ranges involved. It was found to be about $\pm 3\%$. The main source of error is the uncertainty of $\pm 0.1°$ C in cup and surface temperatures.
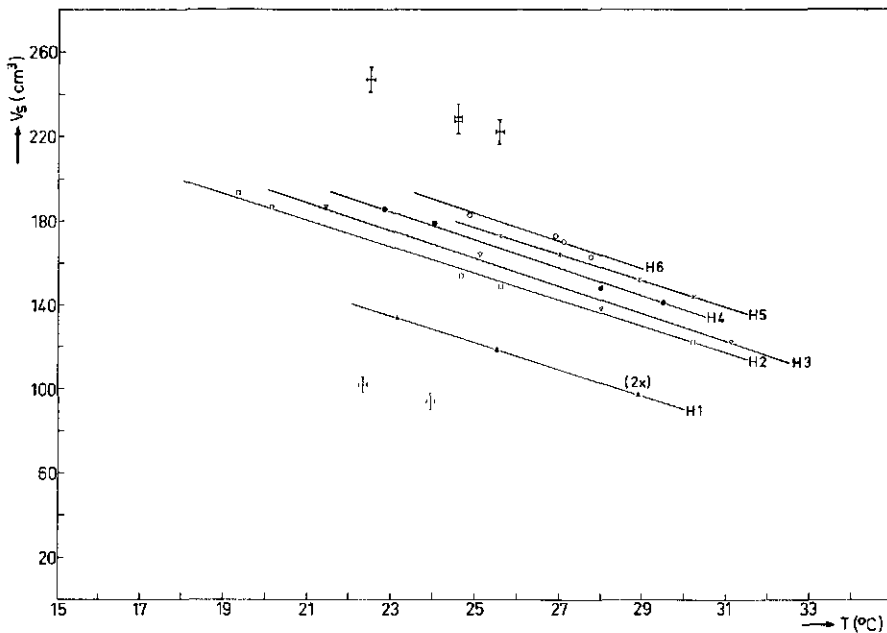
24

FIG. 11. The dependence of V_s on temperature in the course of time. The two lowest points were observed on the 9th of June. The four highest points were observed on the 28th and the 30th of August. Between the observations of the lines marked **H 1** and **H 6** a period of six weeks had passed. To make appreciation of the straight lines more feasible, accuracy limits have only been given for the points making up the limits for this period. The same accuracy does apply to the other observations.

As said before, most workers used (8) for calibration purposes, using the resulting lines obtained in different situations for comparable field conditions. As mentioned earlier MORROW and SLATYER (1971a) showed a time dependence of the calibration lines under equal conditions (if their sensors were not used inbetween). The lines in Fig. 9 and 10 are given for sake of comparison. We did use the sensor of course inbetween. The line nr. 1 was, as mentioned above, measured on the first day. Line nr. 2 is the highest point of H6 from Fig. 11. The third line is the one but highest point of Fig. 11, at 24.7°C, so measured at the end of the three months period. The final line, 4, is the point at 24.85°C of the lowest curve numbered 1 of Fig. 13. All lines were obtained with porometer and surface at the same temperature.

The intercept on the absciss in Fig. 9 lies between 2.65 and 2.75 s/cm. Indeed 2.7 s/cm was also the mean of all calibration curves. With a value for the opening in the bottom of the P.P. container (on the heat source) of 0.8 s/cm we indeed find the value of 1.9 s/cm, mentioned earlier, for the porometer resistance. For the long times diagrams this is found to be 1.8 s/cm. The difference arises from the 3 % increase in slope found for the longer times. It falls however far within the accuracy limits of the theoretically estimated porometer resistance.

Influences of temperature on this R_p value fall within the normal variation measured.

It is important to note that R_p being known with the accuracy obtained, the calibration can be simplified. It may be seen from for example Fig. 9 that the measuring points at the same resistance value have the same position in relation to the different lines. This is due to the error in the value of the resistance concerned, as determined by our evaporation experiments (III). It has been possible, by this consideration and from a series of measurements done for this purpose with the porometer equipment (III), to increase the accuracy with which the individual membrane resistances are known.

In that case a few measurements with only *one* calibration plate permit the determination of V_s at the moment and under the temperature conditions concerned. Doing the same without a calibration plate under identical conditions even permits control by a determination of both V_s and R_p. It is clear that this appreciably simplified procedure is permitted only because we *now* know that V_s is constant for different diffusion resistances (I, p. 34).
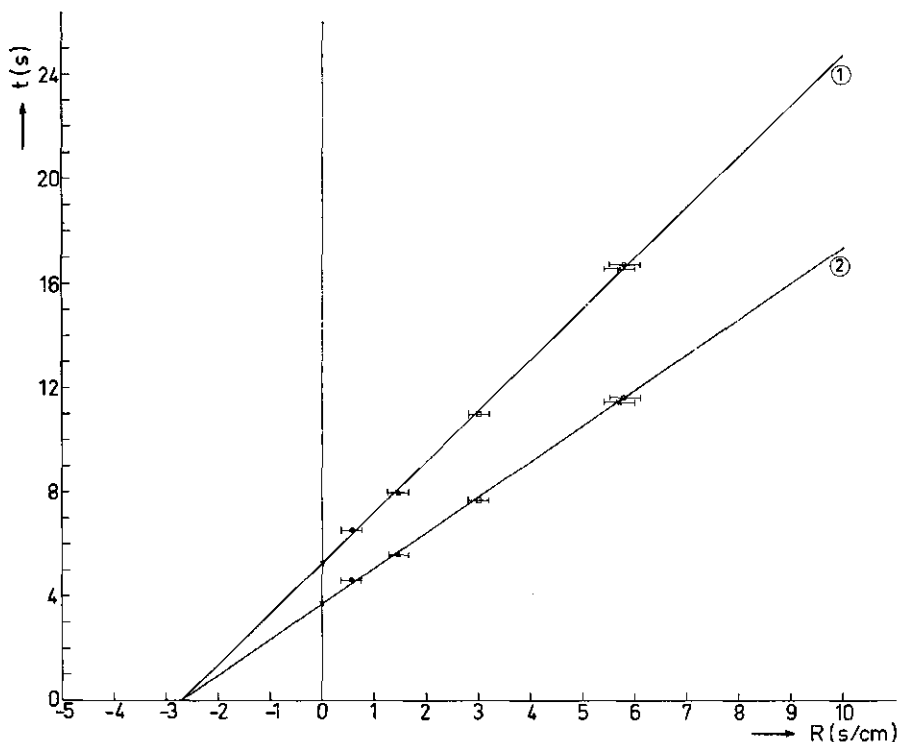

FIG. 12. Two calibration lines for the same cup (and sensor) temperatures. For the line marked 1 temperature of sensor and evaporating surface are equal. For the line marked 2 evaporating surface has a temperature 4°C higher than sensor temperature. Both lines yield the same V_s-value (see example IX of table 3). The intercept on the negative absciss is indeed again –2.7 $(1.9 + 0.8)$ s/cm.

TABLE 3. Porometer temperature T_p, evaporating surface temperature T_s, temperature difference $\Delta T = T_s - T_p$, measured V_s, to the lowest temperature corrected $V_{s,cor}$ and the difference in the $V_{s,cor}$ values ($\Delta V_{s,cor}$) for nine series of two to four calibration measurements. (Each V_s being obtained from a calibration series as in table 1). $\Delta V_{s,cor}$ is given for the observations with highest $|T_s - T_p|$ with regard to the observations with lowest $|T_s - T_p|$. The measurements marked * have a $\Delta V_{s,cor}$ from which the sign would be expected to be different from the other observations because of the fact that a possible temperature effect on V_s would have an other sign in these cases.

	I			II		III		IV		V			
T_p	20.4	20.1	20.1	20.5	21.1	28.9	28.9	22.05	22.95	19.3	20.1	24.75	25.6
T_s	19.7	20.3	21.5	20.6	24.8	29.05	32.1	22.1	26.65	19.2	22.3	25.75	24.7
ΔT	−0.7	+0.2	+1.4	+0.1	+3.7	+0.15	+3.2	+0.05	+3.7	−0.1	+2.2	+1.0	−0.9
V_s	122	126	126	135	128	108	107	159	154	194	187	154	149
$V_{s,cor}$	124	126	126	135	132	108	107	159	160	194	192	191	191
$\Delta V_{s,cor}$	−2*	.	0	.	−3	.	−1	.	+1	.	−2	−3	−3*

	VI		VII		VIII		IX	
T_p	31.1	25.1	20.9	21.3	31.1	31.4	26.9	27.15
T_s	33.6	25.6	20.9	23.3	31.4	33.4	26.7	31.25
ΔT	+2.5	+0.5	0.0	+2.0	+0.3	+2.0	−0.2	+4.1
V_s	122	164	192	191	128	128	173	170
$V_{s,cor}$	162	164	192	194	128	130	173	172
$\Delta V_{s,cor}$	−2	.	.	+2	.	+2	.	−1

6.4.d. *Independence of V_s on surface temperature.*

A series of measurements by the original procedure has been used to check the important hypothesis, derived from the considerations given earlier in this chapter: V_s should be independent from the difference between evaporation source (leaf) temperature and cup temperature (when the latter is constant). In that case using our calibration procedure would have solved the main draw back of this field method viz. the need for shadowing the leaf to bring it closer to air (that is cup) temperature, running the risk of influencing stomatal opening.

Shadowing is applied by others because of the fact that via (8) different lines are obtained for all temperature combinations, even under constant cup temperature (VAN BAVEL et al., 1965; KANEMASU et al., 1969; TURNER and PARLANGE, 1970; MEIDNER, 1970; MORROW and SLATYER, 1971a; Comp. also table 2 in (I, p. 35)). The number of calibration lines necessary in fact is prohibitive in this case, when shadowing is not applied.

An example to illustrate the influence of surface temperature is given in Fig. 12. The same example is also given as series IX in table 3. The line marked 1 in Fig. 12 was measured under almost equal temperatures of cup and source. For the line numbered 2 the source was more than 4°C higher in temperature. The difference in V_s for both lines is however as small as 0.5%, which is far within the accuracy limits mentioned earlier.

For further verification eight other series of successive calibration measurements have been made in the course of the period in which Fig. 11 was obtained. They are collected in table 3. For different porometer temperatures in one series V_s has, for the sake of comparison, been corrected (to the lowest temperature) by the slope 6.6 cm^3/°C ($V_{s,cor}$). The value $\Delta V_{s,cor}$ is given with regard to the measurement with the lowest absolute temperature difference between cup and filter paper on the adjustable heat source. The mean percentual difference in $V_{s,cor}$, taking the reverse sign for the series marked with an asterisk, is even less than 1% for the nine series together. So the slope of the calibration lines changes, but this is compensated for by the change in e_l, the saturated vapour concentration at the surface. This confirms the hypothesis concerned. Measuring the temperature of the leaf in a correct way (III)allows to use the instrument directly on sunlit leaves.

6.4.e. *V_s after a long dry storage period.*

The last remarks in this paragraph concern a series of observations made several months after the measuring season. The sensor used during that season had been stored for fifty days at silica gel relative humidity and was used afterwards in a series of laboratory and greenhouse measurements described in (III). For these measurements an accurate determination of the temperature dependence of V_s over a certain range was not of importance. Indoors calibration and measurements could be made at almost the same temperature. From the values of V_s it appeared that the sensor did not change very much any longer

28   *Meded. Landbouwhogeschool Wageningen 73-15 (1973)*

when compared with the highest points of Fig. 11. The two calibration lines marked 3 and 4 in Fig. 9 and 10 point into the same direction.

We wanted to check more thoroughly the existence of a slow trend preliminary supposed to exist, as mentioned earlier in 6.4.c., in the slope of the $V_s/$ temperature diagram. For that reason a series of four consecutive calibration measurements was done again at one and the same day. The result is represented by the lowest curve marked 1 in Fig. 13. This clearly was no longer a straight line. Therefore we repeated the measurements after five days. A small parallel shift was found in relation to the first curve, as given in the highest series marked 1 in Fig. 13. But no change in the non-linear shape.
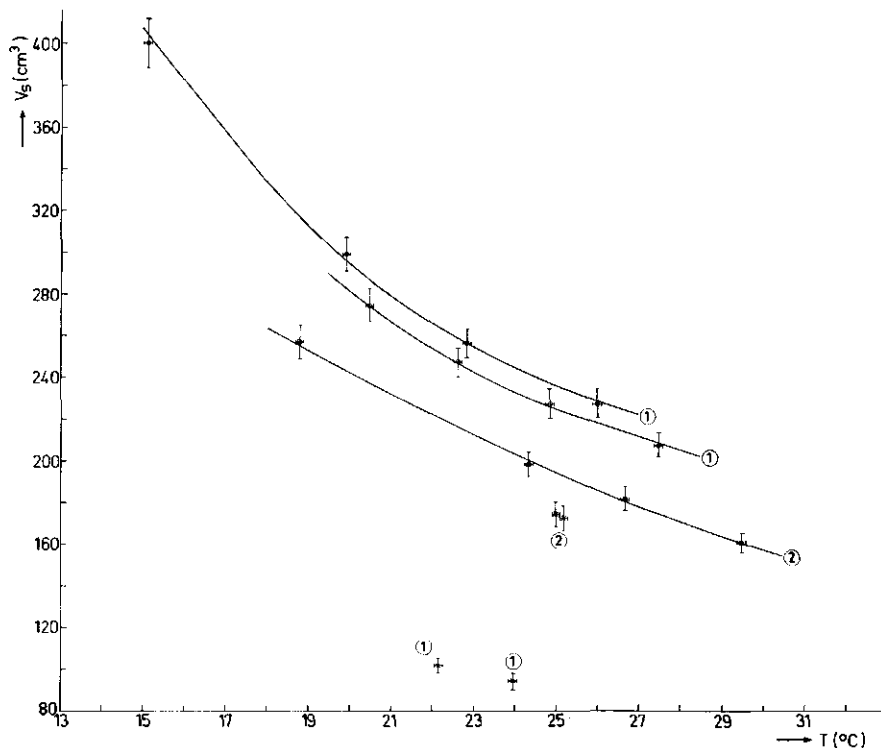

FIG. 13. The dependence of V_s on temperature in the course of time for the same sensor as in Fig. 11 in an other period (curves marked 1) and for an other sensor (points and curve marked 2). The lowest two points marked 1 are the same as the lowest two points of Fig. 11. Explanation on the diagram is given in the text.

One must draw the conclusion from these results that now only for small ranges ($\leqslant 5\,°C$) linear interpolation remains valid. For wider ranges, with this sensor used so intensively, now more than two calibration points have to be obtained on the day before or after a series of field measurements planned. It

remains of course possible to use a mean of two calibration curves measured before and after a day of field measurements.

Because of the final result obtained above it was of interest to measure, again for the sake of comparison, the temperature dependence of V_s for the sensor used in the unsuccessfull calibrations by the TURNER and PARLANGE method. Before its last storage period of six months only two measurements with the new calibration method were done for this sensor (Comp. Appendix 4). The two points marked 2 in Fig. 13 were obtained in this way. In a new series of measurements now the curve marked 2 was found. So the difference between the former points and the latter curve arised only from storage (Comp. Appendix 4). For this sensor V_s is still smaller, the temperature relation still more linear. This is more or less confirming what has been indicated in a graph by MORROW and SLATYER (1971a) showing slopes of the time/resistance diagrams against temperature.

It may be concluded from the above that at large time intervals a control of the temperature dependence of V_s has to be made. This does not violate the advantages of our empirical method. Calculating V_s from calibrations and taking changes in V_s in the course of time into account, by calibrating before and after a series of measurements on real leaves, have solved the troubles experienced before and met the objections made earlier.

7. THE ELECTRONICAL EQUIPMENT IN USE

The accuracy of the results obtained was, not last of all, due to the facts that the sensor signal could be read in digital form and that the transient times were measured electronically. The special circuits performing these functions are not essential for the measuring procedure but they are a necessary base for a high accuracy. To realize this accuracy at our very high sensor resistances and under field conditions we were forced to design specially adapted circuits.
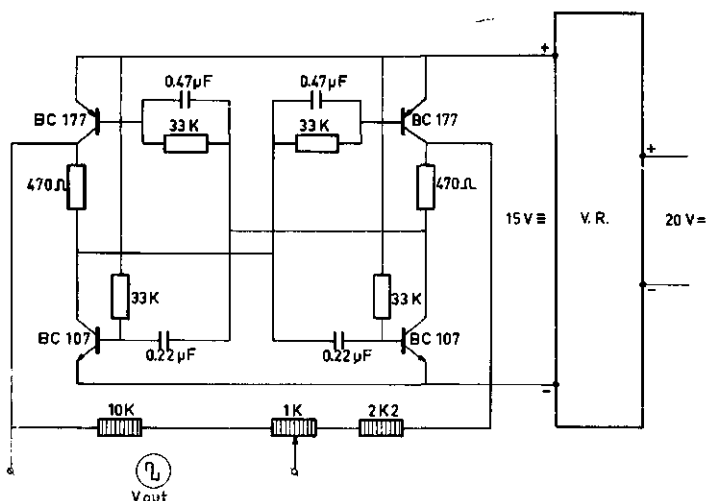

FIG. 14. Square wave oscillator with variable output voltage. The output impedance has no influence on the measurement accuracy. V. R. is the voltage regulator with temperature compensation.

The circuit used for calibration and field measurements is based on a square wave oscillator (Fig. 14). This oscillator, also used by KANEMASU et al. (1969), has an oscillating frequency of about 90 Hz. The totempole output configuration gives the circuit a very low output impedance, both for the low and the high state of the output.

It is essential that the amplitude of the square wave is independent of mains voltage fluctuations or changes in the ambient temperature. Therefore a stabilized power supply was applied, metallic film resistors were built in at critical places and carbon resistors, with a negative temperature coefficient to compensate for semiconductor temperature drift, were used. In this way the remaining temperature effect on the output voltage was less than one percent (between 20 and 50 °C). Interference of the 100 Hz counting pulses and the 90 Hz square wave could be reduced by careful decoupling of the power supply.
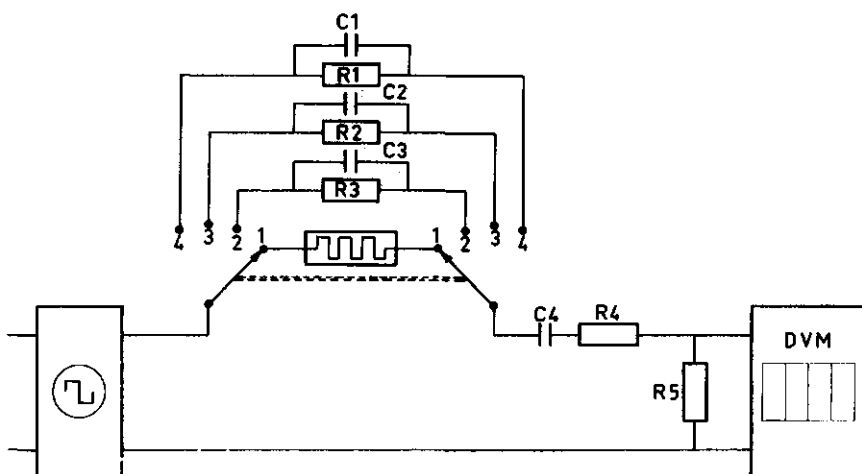
Fig. 15. Basic circuit to determine the humidity sensor resistance with the use of a D.VM..
Switch position 1 is for the humidity sensor, positions 2,3 and 4 are for calibration resistances
giving D.V.M. readings of 300, 600 and 1900. R1 = 0.485 MΩ; R2 = 2.964 MΩ; R3 = 6.681
MΩ; R4 = 0.475 MΩ; R5 = 0.182 MΩ; C1 = C2 = C3 = 3.5 pF; C4 = 0.68 μF.

The place of the capacitor C4 (Fig. 15) is essential for a good hum immunity.
The sensor and the measuring resistance are now connected to earth through
the low impedance of the oscillator. Sensor resistances up to 250 MΩ could be
measured in this way. The condenser C4 itself is necessary to block a direct
current flow through the sensor, if the square wave is not completely symmetri-
cal. The maximum dissipation in the sensor in this circuit is 0.33 mW at an
effective current of 11.5 μA. When the resistance of the sensor is high, the square
wave form of the current shows an overshoot (Fig. 16). This is due to the fact
that the sensor has a variable resistance and a constant stray capacitance of
3.5 pF.

The materials on which the circuits are built must be of high quality with
respect to insulation properties and resistance against surface leakage currents.
Also they must be moisture repellent. Actually P.V.C. and P. P. proved to have
poor insulating properties which resulted very easily in a hum signal. Therefore
steatite and teflon have been applied between the terminals of sensor and ther-
mistor leads and between the measuring resistances. These materials have been
used for switch and connectors as well.

As indicating instrument a digital voltmeter (D.V.M.) was used instead of a
needle instrument. An important advantage is its higher resolution. The temper-
ature dependence of the D.V.M. is reduced by using two power transistors,
type 2 N 3055, as heaters, mounted on the metal case of the D.V.M. Heat dissi-
pation in these transistors is controlled by a thermistor, resulting in a constant
temperature of the D.V.M. of 40 °C. The square wave signal from the sensor is
rectified by a Schneider circuit, type CO 20. The temperature stability of this
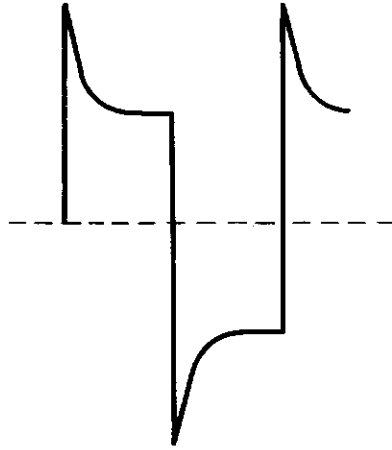
FIG. 16. Current wave form at a sensor resistance of 8 MΩ.

circuit is better than 0.1 % between 20 °C and 50 °C. The input circuit had to be rebuilt on steatite since the original insulating material showed a high moisture absorbing capacity.
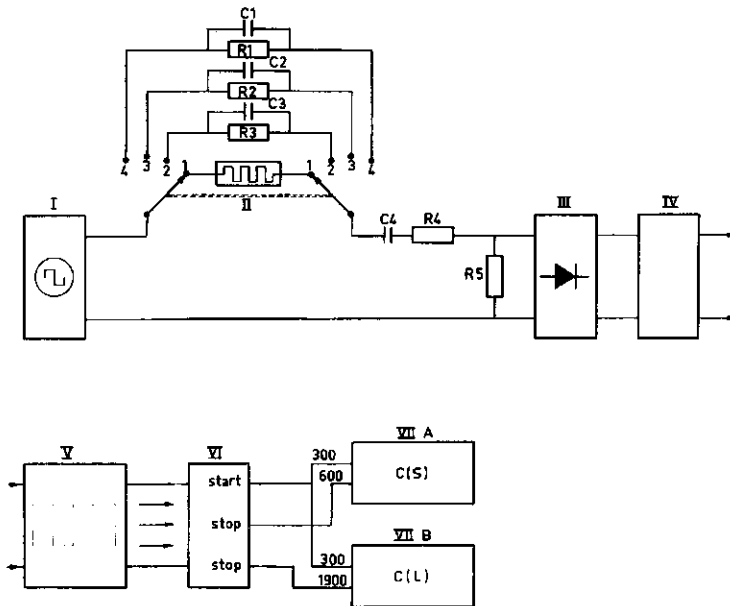

FIG. 17. Basic circuit with impedance transformer and digital switch. Comp. Fig. 15 for values of R's and C's.
I. square wave oscillator; II. humidity sensor; III. rectifier for the sensor signal; IV. impedance transformer; V. D.V.M.; VI. digital switch; VIIA. timer (short time); VIIB. timer (long time).

The digital output from the D.V.M. is used to start and stop two digital clocks. Both start by switch commands when the D.V.M. indicates 300 (Fig. 17). One clock stops at 600, the other at 1900. The corresponding sensor resistances are 6.70 MΩ, 2.95 MΩ and 0.485 MΩ. The electronic switches start and stop the clocks within 1/80th of a second after the passage of these limits by the D.V.M., as 80 Hz is the sample frequency of the latter. With a clock rate of 100 Hz the resulting error in the measured time is 0.023 s at maximum. The clocks can registrate up to 99.99 s. At an earlier stage of development the time was measured in a way (Fig. 18) more or less similar to the one used by KENNY and MC. GRUDDY (1972). We did not succeed to obtain the accuracy wanted for our research objectives.
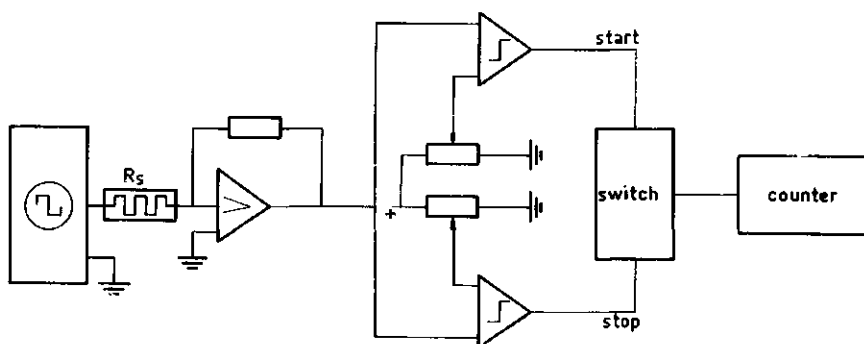

FIG. 18. Time measurement with two differential amplifiers. The indication is not stable because the bias currents change at the moment of transition.
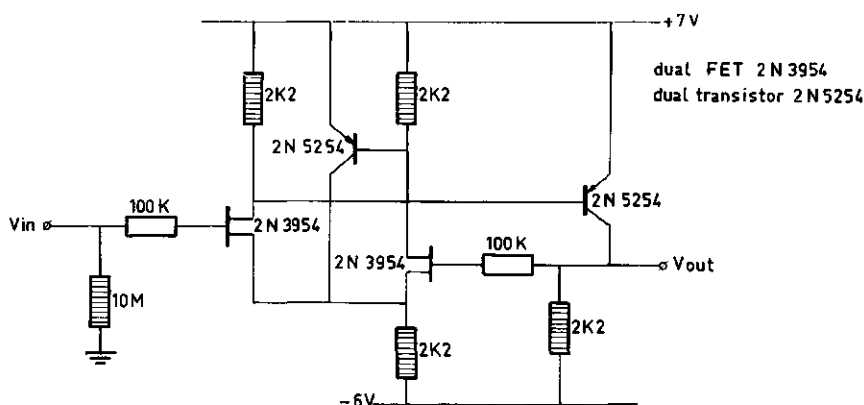

FIG. 19. Impedance transformer. The F. E. T.'s are matched with the drain resistors.

It was found that an asymmetrical source impedance of 10 KΩ gave a misreading of 2 mV on the D.V.M. Therefore an impedance transformer is used between the sensor and the D.V.M. (Fig. 19). A circuit with a dual F.E.T. and a dual transistor proved to be very stable and symmetrical. The difference between input and output signal was now not more than 0.1 mV, with the input voltage varying between 0 and 2 V and the environmental temperature varying between 20°C and 50°C. The impedance transformer made it also possible to use in parallel other recording instruments, such as a flat bed recorder. In this way it was possible to perform experiments regarding the lag time of the sensor (Appendix 3), the influence of leakage of the porometer or adsorption and absorption of the porometer wall material (Appendix 2) and the response time of the leaf thermistor (III).
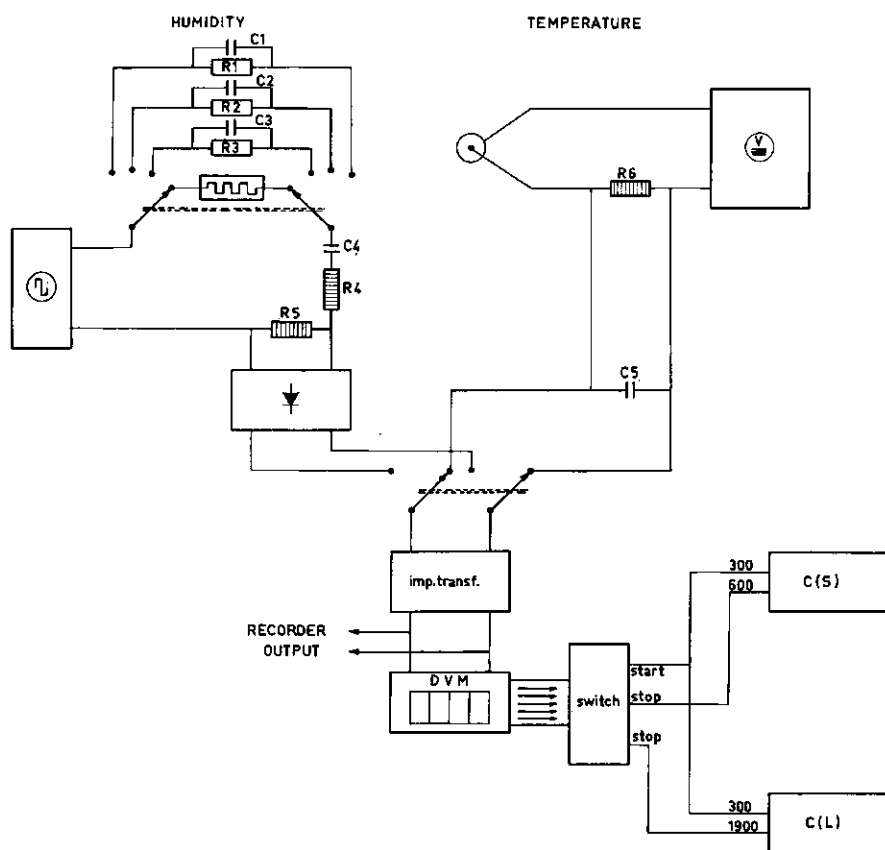

FIG. 20. The total system for humidity and temperature measurements. Comp. Fig. 15 for other values of R's and C's. R6 = 0.221 MΩ; C5 = 2.2 μF.

The Y.S.I.-thermistors are used in a direct current circuit (Fig. 20) because the calibration curves from the manufacturer are only valid under this condition. The condenser C5 of 2.2 μF is used to reduce hum. The temperatures that have to be measured generally vary between 20°C and 30°C (corresponding resistances of the thermistor are 1.30 MΩ and 0.775 MΩ, so within the range of occurring sensor resistances). According to the specifications, 1 mW dissipation in the thermistor gives an error of 1°C in still air. In our case the dissipation in the thermistor varies generally between 0.027 mW and 0.038 mW. The error in the temperature reading can thus be neglected.

The motor that drives the fan for agitating the air proved to be very stable without any regulation. The load from the fan didn't influence the motor speed.

8. SUMMARY

In this article we report on experiences gained in design and calibration of an improved leaf diffusion resistance meter of the type originally proposed by WALLIHAN and VAN BAVEL. We have also tried to explain a number of the observed phenomena from knowledge acquired by others on the electrical humidity sensor applied. This made it possible, among other things, to describe the theory of the instrument in more details.

We were able to demonstrate that the use of perspex as porometer cup material must be a serious source of errors. The choice of polypropylene removed wall influence by water vapour absorption on the measured transient times, as could be shown experimentally. By separate experiments the difference in adsorption and absorption capacity between perspex and materials such as polypropylene was shown quantitatively. It was found that perspex has a short term absorption capacity for water vapour and that materials such as polypropylene have only a low short term adsorption capacity worth mentioning, depending on the state of the surface.

We were also able to derive theoretically, from geometrical considerations and transport phenomena in turbulent flow, a value for the porometer resistance. This value was in excellent agreement with the resistance obtained from measurements. The theoretical determination was possible mainly because of the simple agitation air mixing system we have used, the simple form of the sensor cup, the small dimensions of the sensor and a built in low resistance anti-convection membrane.

Dealing with several calibration methods reported in the literature we have shown that the only reliable method is the use of perforated plates as calibration resistances. By combination of this method with the equation for the real course of cup concentration as a function of time, we were able to determine an apparent volume V_t, depending on cup temperature. These V_t-values represented the sum of cup internal volume and apparent water absorption capacity of the sensor. When these V_t-values, as calibration volumes, are known, the same equation as mentioned is used in the field for leaf diffusion resistance determination.

We have shown that the influence of the sensors lag time (dynamical response) as well as changes of this lag time and of calibration values of the sensor in the course of time do not violate the calibration method used. Recalibration by determining V_t in the course of time is sufficient for extended field use.

From our confirmation of earlier results by others that V_t is effectively constant for different evaporation rates we concluded that also evaporating surface temperature must have no influence on V_t. This was corroborated by some special observations. It could also be understood from what was found in literature on the processes determining the behaviour of the compound lag

time of the electrical humidity sensor. The most important consequence of the observed independence of V_t on evaporating surface temperature is that direct measurements on sunlit leaves are possible.

By using accurate digital indication of changes in sensor resistance it was possible to design an accurate measuring procedure. The rate of reproducibility of this strategy was of high influence on the accuracy of transient times. This again could be understood from LiCl-sensor knowledge.

Finally we used three fixed electrical resistance values and obtained in this way a short and a long transient time, automatically registrated by a self-timing circuit. Using the ratios of these transient times permits to collect information on the possible influence of the measuring device on the state of opening of the stomata.

We believe that under the conditions given, this method, which was highly unreliable up till now, has been improved considerably.

9. ACKNOWLEDGEMENTS

10. REFERENCES

BAVEL, C. H. M. VAN, NAKAYAMA, F. S. and EHRLER, W. L., 1965. Measuring transpiration resistances of leaves. *Plant Physiol.* **40**: 535–540.

BEARDSELL, M. F., JARVIS, P. G. and DAVIDSON, B., 1972. A null-balance diffusion porometer suitable for use with leaves of many shapes. *J. appl. Ecol.* **9** (3): 677–690.

BRAVDO, B. A., 1972. Photosynthesis, transpiration, leaf stomatal and mesophyll resistance measurements by the use of a ventilated diffusion porometer. *Physiol. Plant.* **27** (2): 209–215.

BRUNAUER, S., EMMETT, P. H. and TELLER, E., 1938. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **60**: 309–319.

BYRNE, G. F., ROSE, C. W. and SLATYER, R. O., 1970. An aspirated diffusion porometer. *Agric. Meteorol.* **7**: 39–44.

CHLECK, D., 1967. Reply to Morrissey and Brousaides. *J. appl. Meteor.* **6**: 967–969.

DAVIDSON, A., 1966. Handboek van de fijnmechanische techniek. Deel 2: Materialen. N.V. Uitg. Mij. CENTREX, Eindhoven, 419 pp.

DJAVANCHIR, A., 1970. Mise au point d'une chambre de transpiration pour mesurer la résistance stomatique. *Oecol. Plant.* **5**: 301–318.

EISENBERG, D. and KAUZMANN, W., 1969. The structure and properties of water. Oxford Univ. Press, London, 296 pp.

ELFVING, D. C., KAUFMANN, M. R. and HALL, A. E., 1972. Interpreting leaf water potential measurements with a model of the soil-plant-atmosphere continuum. *Physiol. Plant.* **27** (2): 161–168.

GEE, G. W. and FEDERER, C. A., 1972. Stomatal resistance during senescense of hardwood leaves. *Water Res. Res.* **8** (6): 1456–1460.

GOUDRIAAN, JAN and WAGGONER, Paul E., 1972. Simulating both aerial microclimate and soil temperature from observations above the foliar canopy. *Neth. J. agric. Sci.* **20**: 104–124.

GRIEVE, B. J. and WENT, F. W., 1965. An electric hygrometer apparatus for measuring water vapour loss from plants in the field. *UNESCO Arid Zone Research Series, vol.* **25**: 247–257.

GRIGULL, U., 1963. Die Grundgesetze der Wärmeübertragung. (3e Auflage des Buches H. Gröber/S. Erk) Springer Verlag, Berlin usw., 436 pp.

HANDEGORD, G. O., HEDLIN, C. P. and TROFIMENKOFF, F. N., 1965. A study of the accuracy of Dunmore type humidity sensors. In: A. Wexler (Ed.). Humidity and Moisture **I**: 265–272.

HEGGE ZIJNEN, B. G. VAN DER, 1957. Modified correlation formulae for the heat transfer by natural and by forced convection from horizontal cylinders. *J. appl. sci. Res.* A6: 129–140.

HEGGE ZIJNEN, B. G. VAN DER, 1958. Heat transfer from horizontal cylinders to a turbulent air flow. *J. appl. sci. Res.* A7: 205–223.

JARVIS, P. G., ČATSKÝ, J. et al., 1971. General principle of gasometric methods and the main aspects of installation design. In: Šesták, Z., Čatský, J. and Jarvis, P. G. Plant photosynthetic production, manual of methods. Dr. W. Junk N.V. Publ., Den Haag, 818 pp.

KANEMASU, E. T., THURTELL, G. W. and TANNER, C. B., 1969. Design, calibration and fileld use of a stomatal diffusion porometer. *Plant Physiol.* **44**: 881–885.

KAWASAKI, K. and KANOU, K., 1965. Control of atmospheric humidity by aqueous sulfuric acid solution. In: A. Wexler (Ed.). Humidity and Moisture IV: 531–534.

KENNY, P. and McGRUDDY, P. J., 1972. A circuit for a self-timing stomatal diffusion porometer. *Agric Meteorol.* **10**: 393–399.

KESTIN, J., 1966. The effect of free stream turbulence on heat transfer rates. *Advances in Heat Transfer* **3**: 1–31.

KLEIN, R. M. and KLEIN, P. T., 1970. Research methods in plant science. The Natural History Press, New York, p. 715.

KOBAYASHI, J., 1960. Investigations on Hygrometry. *Papers Meteorol. Geophys., Tokyo*, 11: 213–338.

KOBAYASHI, J. and TOYAMA, Y., 1965. The aging effect of an electric hygrometer. In: A. Wexler (Ed.). Humidity and Moisture I: 248–264.

LAI, J. R. and HIDY, G. M., 1968. Microsensor for measuring humidity. *Rev. Sci. Instr.* 39: 1197–1203.

LEE, R., 1967. The hydrologic importance of transpiration control by stomata. *Wat. Res.* 3: 737–752.

LEMON, E. R., 1970. Summary of section 2: Mass and energy exchange between plant stands and environment. In: Prediction and measurement of photosynthetic productivity. Proceed. IBP/PP Techn. Meet. Trebon: 199–205.

LEMON, EDGAR, Stewart, D. W. and SHAWCROFT, R. W., 1971. The sun's work in a cornfield. *Science* 174: 371–378.

MARCHGRABER, R. M. and GROTE, H. H., 1965. The dynamic behavior of the carbon humidity element – ML-476. In: A. Wexler (Ed.). Humidity and Moisture I: 331–345.

MARTIN, S., 1965. A laboratory standard manually operated dewpoint hygrometer using thermoelectric cooling. In: A. Wexler (Ed.). Humidity and Moisture I: 149–154.

MATHEWS, D. A., 1965. Some research on the Lithium Chloride radiosonde hygrometer and a guide for making it. In: A. Wexler (Ed.). Humidity and Moisture I: 228–247.

MEIDNER, H., 1970. A critical study of sensor element diffusion porometers. *J. exp. Bot.* 21: 1060–1066.

MONTEITH, J. L., 1972. Survey of instruments for micrometeorology. I. B. P. Handbook No. 22. Blackwell S.P., Oxford etc., 263 pp.

MONTEITH, J. L. and BULL, T. A., 1970. A diffusive resistance porometer for field use. II: Theory, calibration and performance. *J. appl. Ecol.* 7: 623–638.

MORESHET, S. and YOCUM, C. S., 1972. A condensation type porometer for field use. *Plant Physiol.* 49: 944–949.

MORRISSEY, J. F. and BROUSAIDES, F. J., 1967. Comments on 'Aluminium oxide hygrometer: laboratory performance and flight results'. *J. appl. Meteor.* 6: 965–967.

MORROW, P. A. and SLATYER, R. O., 1971a. Leaf resistance measurements with diffusion porometers: precautions in calibration and use. *Agric. Meteorol.* 8: 223–233.

MORROW, P. A. and SLATYER, R. O., 1971b. Leaf temperature effects on measurements of diffusive resistance to water vapor transfer. *Plant Physiol.* 47: 559–561.

MUSA, R. C. and SCHNABLE, G. L., 1965. Polyelectrolyte electrical resistance humidity elements. In: A. Wexler (Ed.). Humidity and Moisture I: 346–357.

PANDE, A., 1970. Modern hygrometry. Somaiya Publ., Bombay, 273 pp.

PARKINSON, K. J. and LEGG, B. J., 1972. A continuous flow porometer. *J. appl. Ecol.* 9 (3): 669–676.

PARLANGE, J.-Y., WAGGONER, P. E. and HEICHEL, G. H., 1971. Boundary layer resistance and temperature distribution on still and flapping leaves. I. Theory and laboratory experiments. *Plant Physiol.* 48: 439–442.

PARLANGE, J.-Y. and WAGGONER, P. E., 1972. Boundary layer resistance and temperature distribution on still and flapping leaves. II. Field experiments. *Plant Physiol.* 50: 60–63.

PEARMAN, G. I., WEAVER, H. L. and TANNER, C. B., 1972. Boundary layers heat transfer coefficients under field conditions. *Agric. Meteorol.* 10: 83–92.

ROGERS, M. N., 1965. A small electrical hygrometer for microclimate measurements. In: A. Wexler (Ed.). Humidity and Moisture I: 302–309.

STIGTER, C. J., 1968. On the possibility of determining thermal properties from contact-surface temperatures. *Physica* 39: 229–236.

STIGTER, C. J., 1972. Leaf diffusion resistance to water vapour and its direct measurement. I: Introduction and review concerning relevant factors and methods. *Meded. Landb. Hogesch. Wageningen* 72-3: 1–47.

STILES, W., 1970. A diffusive resistance porometer for field use. I. Construction. *J. appl. Ecol.* 17: 617–622.

STINE, S. L., 1965. Carbon humidity elements-manufacture, performance and theory. In: A. Wexler (Ed.). Humidity and Moisture I: 316–330.

STRUNK, M. R., MITROVIC, M. V. and BUNCH, D. W. A sensitive probe for measuring concentration profiles in water vapour – gaseous mixtures. *A. I. Ch. E. J.* **10** (3): 423–426.

SZULMEYER, W., 1968. Selenium dioxide hygrometric probes. *J. scient. Instr. Series 2*, **1**: 864–866.

TING, I. P. and LOOMIS, W. E., 1963. Diffusion through stomates. *Am. J. Botany* **50**: 866–872.

TING, I. P. and LOOMIS, W. E., 1965. Further studies concerning stomatal diffusion. *Plant physiol.* **40**: 220–228.

TURNER, N. C. and PARLANGE, J.-Y., 1970. Analysis of operation and calibration of a ventilated diffusion porometer. *Plant physiol.* **46**: 175–177.

VISSCHER, G. J. W. and SCHURER, K., 1972. Ontwikkeling van vochtgevoelige elementen. *T.F.D.L. Med.* **12**: 54–55.

WEXLER, A. (Ed)., 1965. Humidity and Moisture; Measurement and control in science and industry. I: Principles and methods of measuring humidity in gases. Reinhold P. C., New York, 678 pp.

WIT, C. T. de, BROUWER, R. and PENNING DE VRIES, F. W. T., 1970. The simulation of photosynthetic systems. In: Prediction and measurement of photosynthetic productivity. Proceed. IBP/PP Techn. Meet. Trebon: 47–70.

YOUNG, D. M. and CROWELL, A. P., 1962. Physical adsorption of gases. Butterworths, London, 426 pp.

APPENDIX 1

As mentioned earlier in this publication, many workers were troubled by a noticeable sensor drift, an increase (sometimes a decrease) in electrical sensor resistance without water vapour supply from outside the porometer. To find out the definite origin, also for our very small drift, it must be possible to separate the following eventual effects:
1. The sensor has not yet reached the steady state because of a lagging behind in relation to the porometer concentration (dynamical response).
2. Redistribution takes place of moisture within and among the LiCl-crystals of the hygroscopic surface layer (internal drift).
3. Transfer of water molecules between cup wall and sensor takes place.

To demonstrate the existence or absence of these effects and to separate them we have chosen the following method.

Over a surface of wet filter paper, the temperature of which could be adjusted, a teflon base plate was placed (Fig. 8). In the plate an opening was made of the same dimensions as those of the opening of the sensor cup. The porometer was placed in a special grip to minimize temperature influence of the observers hands and to facilitate moving the cup cylinder horizontally over the teflon base. The changes in sensor electrical resistance were shown on a digital volt meter and recorded (§ 7). To show accurately the moment of moving the cup an interruption switch was attached on top of the grip.

In the first experiment the porometer, having been wetted once, was dried onto a fixed value as indicated by the left arrow in Fig. App. 1.1. During this drying process the porometer and its grip were placed on the same base plate, but with the opening of the porometer not over the opening in the base plate. So the porometer was sealed over teflon. On the moment of reaching the fixed value the silica gel was pulled out of the cup and the cup opening brought over the opening in the teflon plate (by pushing it along two bar guides on the plate, Comp. Fig. 8). The sensor resistance now rapidly decreased (above the filter paper). At a second fixed value (right arrow in Fig. App. 1.1.) the grip was pulled back along the guides to its original position. The sensor now got the opportunity to come to equilibrium with its surrounding concentration.

The curve made from the right hand arrow in Fig. App. 1.1 onwards firstly gives an indication about the time needed for reaching a steady state. The result pointed out that the lag time of the sensor at the moment of measuring was appreciably higher than was to be expected from the manufacturers data (see main text and Appendix 4). The effect could be slightly underestimated because of consumption of the cup vapour content by sensor absorption, but the adjustment of the sensor is largely a matter of redistribution of water within
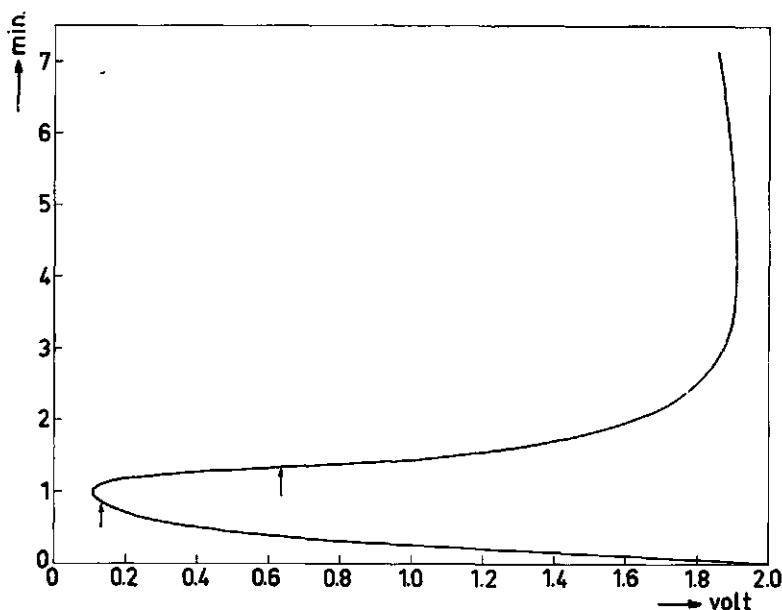
FIG. APP. 1.1. Course of a partial voltage drop indicating a change in sensor electrical resistance as a function of time. The curve is an example of the first 'time constant' – experiment described in the text, obtained with a relatively dry wall (early experiment).

the sensor (KOBAYASHI, 1960; comp. Appendix 3). Once at equilibrium an other phenomenon did occur: the sensor resistance slowly increased.

Doing a series of such measurements in rapid succession the speed of the increase of resistance after equilibrium decreased rapidly at first, more slowly afterwards. If the porometer was for about twenty minutes stored in a 'wet' condition (more humid than the highest point of the log-linear part of the calibration diagram of the sensor) before a measurement as described above, this phenomenon was weakest.

In a second kind of experiment the originally dry cup was wetted above the filter paper but immediately dried above teflon after reaching the wettest point of the log-linear scale (by pulling it over teflon and bringing the silica gel into the cup). Part of this drying stage is indicated as the most right hand part of the curve in Fig. App. 1.2. At a fixed value, indicated by the arrow, the silica gel was pulled out of the porometer cup. The curve made after such experiments showed a normal logarithmic adaptation to the dryest value. When the porometer was stored for 20 minutes in a 'wet' condition before starting the drying stage, a curve as shown in Fig. App. 1.2. was obtained. The resistance now decreased slowly after initial adaptational increase.

From these experiments we feel that the following four conclusions may be drawn:
1. the differences between the effects after dry and wet storage in the two ex-

44   *Meded. Landbouwhogeschool Wageningen 73-15 (1973)*
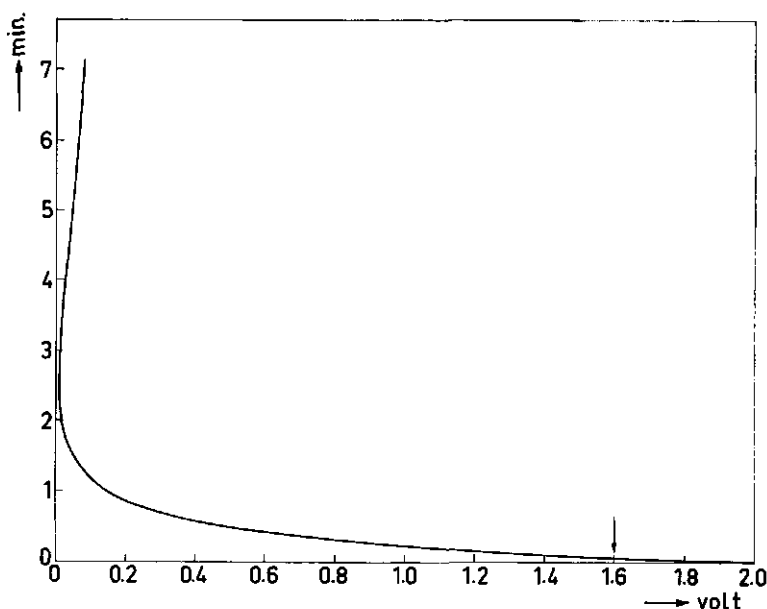
FIG. APP. 1.2. Course of a partial voltage drop indicating a change in sensor electrical resistance as a function of time. The curve is an example of the second 'time constant'-experiment described in the text, obtained after a period of wet storage.

periments point into the direction of *a wall effect* in stead of internal drift *as the driving force for sensor drift*.

2. *we have separated* in the above experiments *a slow wall effect* from influence of the (apparent) time constant.

3. it has been *the wall* which *has troubled other investigators*, who used wall materials with a high absorption capacity, *by causing heavy sensor drift* in the same type of sensor.

4. *the 'storage effect'* (different transient times measured after different storage methods when the apparatus is out of use) *and the influence of the number of preceding measurements* (especially at low diffusion resistance) on the drift time, as both observed by MORROW and SLATYER (1971a), *also have been wall effects*.

The experimental procedure described above is *not* suitable to obtain an idea on the eventual remaining quantitative wall influence on transient times under measuring conditions. The course of the water vapour concentration was completely different from that under use for resistance measurements. For example a rapid adsorption (Appendix 2) may in the above experiments not be distinguished from lag time influence. Such a phenomenon would in principle also influence transient times differently in the case of a relatively dry wall situation compared with a more wet condition. This would also lengthen the transient times under dryer conditions.

We have shown in the main text (§ 6.4) that for short transient times and low diffusional resistance such an effect was absent. We there compared a second measurement in a series with later ones in the same calibration series (table 2). Long transient times at high diffusional resistance could be an even better indication for remained influence. Only two of such measurements were done in each of the standard calibration series (table 1 in the bulk text). One may draw a fifth conclusion of this appendix from the figures given in table App. 1.1, which are obtained from the same calibration series as used in table 2:

TABLE APP. 1.1. Comparison of long transient times (between first and third fixed electrical resistance) at high overall resistance (8.5 s/cm). The transient times are observed early and later in calibration series such as in table 1. The number in the left hand column is the order number as in the left hand column of table 1. Every series was preceded by a period of dry storage. The measuring times given have been corrected for the course of temperature, which influences calibration values for the sensor as well as the value of V_s. The ten calibration series used were the first ones made in this way. In an other group of ten calibration series preceding the ones shown here, a measurement without membrane was *not* preceding the first high resistance measurement. This indeed yielded a mean difference of 1 %, presumably indicating a small wall influence. Such measurements therefore have not been repeated. The values of the averages as such have of course no physical meaning.

Nr. meas.	Reading (s)	Nr. meas.	Reading (s)	Nr. meas.	Reading (s)	Nr. meas.	Reading (s)	Nr. meas.	Reading (s)
3	42.86	3	34.02	3	31.57	4	37.34	3	64.15
15	42.81	13	34.35	13	31.84	14	37.82	13	64.43
3	45.11	3	71.49	3	79.73	3	62.29	3	54.56
13	44.56	13	70.55	13	79.21	13	61.68	13	54.80

Averages (10 series)

Nr. meas.	Reading (s)
3 (1 × 4)	52.31
13 (1 × 14, 1 × 15)	52.21

5. *the wall influence from water vapour adsorption* of the material used in our porometer *is negligible* after one dummy and one low resistance measurement. The former measurement is always necessary to be able to perform calibration measurements in an identical way.

The results above do not indicate whether the remaining wall effect which in itself is too small to be of influence on the transient times, is equal for different concentrations occurring over the measuring period. The results obtained in Appendix 2 as well as measurements made by us under successive different cup concentrations show clearly a concentration influence on the remaining long term drift. This means that for a more heavily absorbing material as perspex the determination of an average drift correction seems to be rather complicated.

APPENDIX 2

Adsorption and absorption

To learn more about the absorption and adsorption of porometer materials and to base a choice more quantitatively we carried out some simple experiments. Small sheets of perspex, teflon, P. P. and P.V.C. were put one by one on a Mettler B5-mg-balance, with a reproducibility of 0.03 mg for comparative measurements. The total surface of each sheet was about 60 cm², which is not much different from the internal surface of the sensor cup. After closing the balance with its glass windows, the weighing space was dried out to about 25% rh using dishes with silica gel, which were placed next to the balance pan. The relative humidity was checked by a small calibrated wall hair hygrometer, brought into the weighing space.

After a period of at least five hours at this low humidity a weighing was done. After that weighing the glas windows were opened, the silica gel was quickly removed and good ventilation over the sheets warranted. On the measuring days the relative humidity of the room air was between 40 and 45%. After one minute of ventilation the balance was closed again and a new weighing was done as soon as the air in the weighing space was at rest. After that the windows were opened again and the measurement was repeated after 10 minutes (counted from the first opening onwards) with sometimes a weighing after 5 minutes inbetween. To cancel zero point influences the same type of measurement was regularly repeated without a sheet on the balance pan. The net results are collected in table App. 2.1.

TABLE App. 2.1. Total increase in weight after 1, 5 and 10 minutes of sheets of $5 \times 5 \times 0.4$ cm, in our experiments, is given in the first three columns. The given values are averages of 10 to 20 measurements with the same sheet. Accuracy is ± 0.025 mg. In the fourth column long term increases in weight, from oven dry state, are given as a mean over several days in a saturated atmosphere (Δ long term).

	Δ 1 min	Δ 5 min	Δ 10 min	Δ long term	KLEIN and KLEIN
Perspex	0.25 mg	0.47⁵ mg	0.62⁵ mg	0.60 mg/hr	0.3–0.4%
Teflon	0.05		0.05	0.02	0.005
P.P (scoured)	0.05		0.05	0.01	< 0.010
P.V.C. (scoured)	0.10	0.15	0.17⁵	0.10	0.07–0.4

From these results the difference between short term sorption of perspex and materials such as teflon and P. P. is perfectly clear. It is also shown from this table that the values obtained by us for long term *absorption* of *water vapour* are in proportion to each other in general agreement with the ratios of percentual values for *absorption* of *liquid water* given by KLEIN and KLEIN (1970)

(columns four and five). The trend in these proportions is the same as found between the short term values.

There is obviously a difference between the conditions of the experiments described here and those existing in the porometer cup during resistance measurements. In both cases, however, intensive contact is made between a relatively dry wall (sheet) and an air stream with higher humidity conditions than correspond with the original equilibrium situation of the dry wall. The resistance to *ab*sorption will be found *within* the materials. Water vapour concentration level will only be of secondary importance as soon as it becomes higher than in the dry equilibrium situation. Table App. 2.1. therefore shows a sorption capacity.

TABLE APP. 2.2. Vapour fluxes through a 2 cm² surface to a space of constant relative humidity of 20% at 25°C. Fluxes are given for different resistance values between evaporating surface and half infinite space. The fluxes have simply been calculated from formula (1) of the main text.

R_{tot} (s/cm)	E' (mg/min)
1	2.2
2	1.1
5	0.45
10	0.2
15	0.15
25	0.07

Table App. 2.2. may be used to get an idea about the amount of water vapour entering through the cup opening, be it under simplified conditions.

From table App. 2.1. one would be inclined to draw the conclusion that we have a rapid adsorption, followed by a slow but sizable absorption. This inward diffusion of water molecules is evident for perspex and less so for P.V.C. It is hardly worth mentioning for teflon and P.P. We have measured for perspex also the reverse process, desorption. This yielded exactly the same mean speed as absorption when averaged over several hours.

If the short term increase by weight for P.P. and teflon is really an *ad*sorption phenomenon, the amount measured is too high for mere multi-layer adsorption at 60 cm². This may be seen from the following considerations.

We take the surface which is 'occupied' by one adsorbed water molecule as about 10 Å² (KAWASAKI and KANOU, 1965; EISENBERG and KAUZMANN, 1969). This would mean that only the increase in thickness, corresponding with the increase in weight as measured (table App. 2.1., first column), would amount ca. 25 water molecule diameters over the whole geometrical surface. So far from dew point concentrations such a multi-layer adsorption is physically unlikely (BRUNAUER et al., 1938; YOUNG and CROWELL, 1962). This would mean that either the effectively adsorbing surface is much higher than 60 cm² or surface pollution is involved. We found that thorough cleaning of the sheets, however,

did not influence the effect anyway, but we did show influence of the state of the surface after mechanical treatments (Table App. 2.3).

TABLE APP. 2.3. Weight increases after 1 minute of 60 cm² P.P. sheets under several surface and humidity conditions. Values given are averages of 10 measurements. Zero point corrections have been accounted for.

Series		r.h.	Increase in weight	Bal.
I	Scoured sheet as used in table App. 2.1	$25 \rightarrow 40\%$ $25 \rightarrow 40\%$	60 ± 5 μg 50 ± 25 μg	M5 B 5
II	Scoured sheet as used in table App. 2.1	$30 \rightarrow 50\%$	100 ± 5 μg	M5
III	Smooth sheet	$30 \rightarrow 50\%$ $25 \rightarrow 40\%$	45 ± 5 μg 25 ± 25 μg	M5 B 5
IV	Milled cylinder surface (same surface as sheet)	$25 \rightarrow 40\%$	200 ± 25 μg	B 5

For that purpose we could make use for a short period, in parallel measurements, of a more accurate Mettler M5-balance with a reproducibility for comparative measurements of ± 2 μg. Results have been collected in table App. 2.3. Measuring series I for the two balances appear to be in perfect agreement. Series II shows an influence of the moisture range covered on the surface *ad*sorption effect, when compared with series I. Comparison of series III with the measurements of I and IV reveals the influence of mechanical treatment (scouring and milling). These results have at least brought in an argument in favour of the idea that mainly the effective surface determines the adsorption effect.

Nevertheless also for a more smooth surface the increase in weight remains observable by our means. Therefore one must state that the use of surfaces which are as smooth as possible and of materials with a very low long term absorption is to be preferred for application in leaf diffusion resistance meters. Hygroscopic dust has to be kept out. Materials such as perspex have to be disregarded as their influence on V_t (and so on V_s in (14)) is troublesome.

APPENDIX 3

SENSOR PROPERTIES AND THEIR CONSEQUENCES FOR THE MEASURING
PROCEDURE

Apart from the two types of humidity sensors hitherto applied in porometers (§ 6.1) the main alternatives to be considered are the carbon element and the AL_2O_3-sensor. The former has certain advantages for use at relatively low temperatures ($+10° \rightarrow -30°C$) and where condensation can take place (STINE, 1965; PANDE, 1970). However, the element is less attractive in dynamic use (MARCHGRABER and GROTE, 1965). Advantages and disadvantages of the AL_2O_3-sensor were most recently discussed by LAI and HIDY (1968) and PANDE (1970). No common opinion seems to exist on its properties (MORRISSEY and BROUSAIDES, 1967; CHLECK, 1967). This combined with the fact that its sensitivity is an order of magnitude lower (if used as resistance) compared with the LiCl-sensor, makes the AL_2O_3-sensor less suitable.

We have seen that mainly the properties of our sensor determined use and results of the porometer. Our knowledge of interaction processes between water vapour molecules and all kinds of surfaces is however poor. Secondly the construction of a useful humidity element is complicated by the necessity of adding several chemical compounds to neutralize unfavourable properties of a pure LiCl-solution. Therefore no complete physical theory of the LiCl-sensor does exist (KOBAYASHI, 1960). We have met in § 3.2, § 6.1 and § 6.4.c. several sensor properties and their influences on *calibration* results. Here we will give additional information on those properties influencing especially the choice of the *measuring procedure*.

a. *Ageing* (e.g. KOBAYASHI, 1960; STRUNK et al., 1964; HANDEGORD et al., 1965; KOBAYASHI and TOYAMA, 1965).
    Little information appears to exist on events that promote or retard ageing. The most important observation relating this problem is that use under constantly varying humidity conditions (as in our cyclic use) does enhance ageing (KOBAYASHI). The origins of these changes in calibration in the course of time seem to be of (electro)chemical nature: changes in the composition of the hygroscopic film, changes in properties of the electrodes and their contact with the film and effects of polarisation. Pollution of course also influences calibration characteristics.
    Ageing is undoubtedly of influence on V_t (Appendix 4) but within one day of measurements the direct effect on Δe_p and e_p (t_i), hence on V_t, will be constant. So for the measuring procedure for each measurement direct ageing effects are not of importance.

b. *Hysteresis* (e.g. KOBAYSHI, 1960).

In our dynamical method we always bring the sensor from a dry onto a more wet condition. Hysteresis therefore is not of influence on the transient times as such. We checked reproducibility of the results, if the sensor was held for two minutes at the accurately reproduced starting point of each individual measurement (see also below). This indicated that the starting point used was in the equilibrium situation on the base of the hysteresis loop.

c. *Temperature sensitivity* (e.g. KOBAYASHI, 1960; MATHEWS, 1965; ROGERS, 1965). The temperature sensitivity of the sensor originates from two effects. The first one is the usual decrease in resistance for increase in temperature of an electrolyte. An opposing effect on the resistance is the loss of water at increasing temperature, to meet the changing equilibrium vapour pressure of the solution. The temperature effect on V_s, as given in Fig. 11 and 13, is presumably not a *direct* temperature effect. It may be explained at least qualitatively by the temperature dependence *of the response time*, as measured by KOBAYASHI and others.

A completely different effect, in relation to temperature, is the high sensor lag time for temperature variations. Influence on transient times can only be prevented by taking care that no sudden temperature variations do occur within the cup. In field work the cup is therefore shielded by an 'Aluminized Mylar on tempex' – shade attached to the field clamp. As in our construction the agitated air is nowhere touching the leaf surface, the temperature within the cup indeed hardly changes during a measurement.

d. Time constant (response time, time lag; e.g. KOBAYASHI, 1960; MATHEWS, 1965).

As dealt with in § 3.2 and § 6.4.c., the time constant and its behaviour are of particular importance to the results obtained. Again an important observation by KOBAYASHI was starting point of our considerations: the time constant at constant temperature and air movement is merely dependent on *the amount* of absorbed water per unit of relative humidity increase $(dM/d(rh))$. The speed of uptake seems to have no influence on the time lag, which indeed explains the constant V_s under different measuring conditions.

The cause for this independence on rate of uptake is indicated by the characteristics of the time constant as found by KOBAYASHI. When drawn in a semilogarithmic graph of humidity difference against time, a simple first order sensor would yield a straight line after a step in humidity. The LiCl-sensor, however, was found to have a compound time constant, if brought suddenly from lower into higher humidity. One may represent its observed response as a sudden discontinuity (break) in a line originally sharply sloping down after the humidity step. After the break the situation may be represented by a line which slopes down much more slowly. The latter part contributes most to the final value of the compound time constant.

A physical explanation may be found in the assumption that very rapidly

a high amount of water can be stored in a surface layer of the sensor. But a much slower process of inward diffusion takes place. This latter process determines the final adaptation to a new environmental condition. Differences in speed of water uptake may influence only the first process, if any. One can however imagine that the absorption process of water *in the surface layer* is a self regulating process keeping $dM/d(rh)$ constant, even under different $d(rh)/dt$, as long as the (air) boundary layer resistance remains constant.

The given description explains that V_s is constant over a day.

The gradual increase of the time constant appears not to be of particular influence on its compoundness. The lines from which V_s is determined remain straight throughout the period in which the sensors were used.

TABLE APP. 3.1. Influence of the 'starting point' on short transient times. The starting point used in calibrations and field work is 0.137 Volt, 0.022 Volt is the dryest point to be reached in the drying process within an acceptable amount of time. The difference between the first two and the last two values is a temperature effect from the environment. The measurements were done without calibration membrane, directly on the bottom of the P.P. container.

Starting point (Volt)	Short transient time (s)
0.137	7.72
0.137	7.71
0.054	7.14
0.054	7.08
0.022	6.64
0.022	6.55
0.137	7.95
0.137	8.03

The characteristic behaviour of the lag time provides also an explanation for an other effect observed. Our observations confirm the experience of MORROW and SLATYER (1971a) that, without changing the fixed resistance values between which the transient times are measured, only the use of another initial sensor resistance value for the starting up period does change the transient times. An example is given in table App. 3.1. An explanation of the effect may be found from the observation of KOBAYASHI that the position of the break in the linear relation between the logarithm of humidity difference and time depends on the applied initial humidity difference. This means that *the same electrical resistance* may be inidicated for a *different water distribution* within the sensor. Consequently the distribution of water, and so the course of resistance, *as a function of time* will also be different. For our conditions this results in a different transient time.

One may observe an inconsistency, comparing results of MORROW and SLATYER (1971a) with ours, as to the effect mentioned above. The former authors measured longer transient times when starting at a dryer point. Our representative example in table App. 3.1. yields the reverse. Studying in detail a graph of KOBAYASHI showing the dependence of the second part of the com-

pound time constant on differences in initial and final humidity, reveals however the following. At relatively higher humidities the results are in correspondence with those of MORROW and SLATYER. At relatively lower humidities our effect may be supposed to exist. We therefore believe that only a difference in measuring procedure is the reason for the apparent inconsistency observed.

One of the main differences in our procedure compared with that of others is the application of a 'waiting time' at the fixed starting point. For example in the experiments dealt with in Appendix 1 we found that approaching with different speeds the return point between right and left arrow in Fig. App. 1.1. resulted in different adaptation curves of the sensor resistance. Cautioned by these results we determined the effect of starting a new measurement as soon as the fixed starting point was indicated and starting after waiting times of 1, 1.5, 2, 2.5 and 3 minutes. From these measurements we found that even with fresh silica gel, which resulted in the highest drying speed, 2 minutes waiting time were enough for getting consistent results. A representative example of the difference between measurements with and without waiting time is given in table App. 3.2.

TABLE APP. 3.2. Influence of waiting time of two minutes on short transient times. Measurements were done immediately after those of table App. 3.1. with starting point at 0.137 Volt. Differences in results without waiting time indicate differences in drying speed prior to the measurement, resulting from silica gel ageing.

Waiting time (min)	Reading (s)
2	7.95
2	8.03
0	9.18
0	9.17
0	9.11
0	9.00
2	7.96
2	8.04

The explanation of the effect may again be found in the water distribution in the sensor at the moment of indication of the starting point. Starting without and with a waiting time means starting at *different water distribution* at the same volt meter reading, resulting in different water diffusion processes afterwards. This again *influences the time constant, so the transient times* measured.

The different effects dealt with above do indicate that an accurately reproducible measuring procedure is necessary for obtaining realiable results with the porometer.

APPENDIX 4

POSSIBLE CAUSES OF A CHANGE OF V_s IN TIME

During preliminary use of the TURNER and PARLANGE calibration method we got indications for increasing transient times, under completely identical measuring conditions. The increase of V_s in time proved that such changes took place continuously. During progress of our research it became clear that the compound time constant was the main parameter involved in these phenomena. Therefore we wanted, as an ultimate check, to have occasionally an indication for the real time constant.

One can see in Fig. 1 that the right side-wall bearing the sensor can be removed from the cup (0-ring construction). To have an indication of the real time constant the sensor was brought in equilibrium at the standard starting point of a measurement (as in all calibrations). Then the wall bearing the sensor was suddenly pulled out of the porometer into the observation room where relative humidity amounted $45 \pm 5\%$ at a temperature of $22 \pm 1\,°C$. The short transient times were used as relative indications of the time constant value. In table App. 4.1. some results are shown. I is the result of the eldest sensor, immediately before a storage period of six months. A value for the same sensor immediately after that period is given in II.

TABLE APP. 4.1. Values (in seconds) of short transient times, taken after pulling the sensor from one constant humidity environment (cup) into an other (room) of constant humidity, for different cases as described in the text. For II and IV differences between ventilated and unventilated observations fall within the measuring accuracy.

	I	II	III	IV
Still air	6.6	16	1.7	67
Ventilation (4 m/s)	5.5	15	0.8	71

Directly before and after observation I we made a standard calibration, cleaning the wall inbetween. The results, shown as the two points in Fig. 13 marked 2, reveal that no silica gel dust was present on the walls. If hygroscopic dust had been present it would have shortened transient times of the first calibration irregularly, influencing V_s. From this we draw the conclusion that also no silica gel dust occurred on the sensor. Therefore this can not be responsible for the changes in time constant in our case.

We also made measurements, in the way described above, for the fresh sensor with which the results of figures 9 to 12 (and partially 13) were obtained. Observations in column III were done with this sensor immediately before its first use. Though this transient time is very short indeed, one can estimate

54

from the value given here that the real time constant is higher than stated by the manufacturer. This indicates a gradual increase in the time constant during one year of dry storage prior to its first use. Measurement IV was taken immediately after its last use in a point of the highest curve (marked 1) in Fig. 13.

It is clear from these simple observations that increase of lag time will indeed be at least the main reason for increasing V_s. One can see that influence of ventilation diminishes in the course of time and finally is absent. This stems from the growing importance of internal retarding effects. The increase in time constant takes place during storage *as well as* during use. From our many measurements we can proof that as long as the porometer is used successively, without long storage, the differences in V_s are negligible. If the sensor is stored for several hours, for example between a final afternoon observation and an early evening measurement, already some change can be observed. Intensive alternate use and storage do influence the increase of V_s presumably more at lower time constant values and surely more than storage alone. We also have the strong impression that the course of increase in V_s will be a rather 'individual' property of the sensor involved, even under identical use. It seems likely that the intrinsic properties suffering from change in the course of time will do so differently for different sensors. As far as the increase of V_s was followed for both sensors, it did not restrain their usefulness throughout.

During measurements II en IV we found also the calibration values for the sensors as specified by the manufacturer markedly changed. Via the values of $e_p(t_i)$ and $e_p(t_f)$ this has influence on V_s. As long as this calibration change is slow, the effect on V_s is again at least constant over a day or longer. Whether the same (electro)chemical phenomena or eventual external surface variations are responsible for ageing as well as for time constant change we can not determine.

The fact that the sensor from the examples III and IV in table App. 4.1. showed a higher time constant alteration *and* a more pronounced deviation from the linear relation between V_s and temperature (Fig. 13) may not tempt us to ascribe these two effects to the same cause. Such a statement needs more pertinent research and periodical recalibration of the sensors, as this may influence the relation. BRAVDO (1972) indeed recalibrated his sensor periodically but he did not account for the dynamical nature of the measurement. Moreover his determination of the porometer resistance is in error. Also his measurements don't yield a temperature dependence of V_s, which quantity moreover is taken too small. No ageing effect on V_s is reported by the mentioned author.

From our experience we would not recommend to do the painstaking and troublesome work of periodical sensor recalibration. It will only take away part of the increase of V_s in time and will not reduce the need for a calibration procedure as used by us and explained in the foregoing pages of this article.