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Simultaneous Determination of Mass and Dielectric Constant of Small Samples with the Microbalance

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SUMMARY

Permittivity and loss factor of dielectric materials can be determined by measuring forces and torques on small samples in especially shaped electrostatic fields. Owing to the high useful resolution of recently available electromagnetic microbalances, the dielectric properties are measurable simultaneously with mass by the following procedure. An electrode system generates vertical forces on the sample which is suspended from the balance beam. These forces depend on exciting voltage and dielectric properties and can be separated from weight by consecutive readings with the field switched on and off.

An automated apparatus for the ponderometric measurement of permittivity and loss factor as functions of frequency and temperature is presented and preliminary results are shown.

INTRODUCTION

Measurement of dielectric properties with the aid of an electro- magnetic microbalance has been published by Alpers and Gast "(ref.1)" as early as 1948. The method is advantagous with regard to the smallness of the sample and the broad frequency range which extends from zero to 100 MHz without change of apparatus. No electrodes are applied to the sample, whose total surface is therefore accessible to the surrounding atmosphere.

In order to study the influence of material changes on permittivity and loss factor of a substance it is desirable to record these properties simultaneously with mass . This can be effected with:

Sufficient available resolution of the balance,

vertical forces generated in special electrostatic fields and dependent on the dielectric properties of the sample ,

consecutive recording of the forces with and without the exciting voltage applied to the electrodes in chosen intervals of time.

METHODS,APPARATUS AND MEASUREMENTS

<u>The generation of forces on dielectric samples in a nonuniform electric field</u>

The forces, utilized for the measurement of permittivity, arise from the polarization of the sample by the internal electric field which is caused by the external field and generally reduced in comparison with it by depolarization .The force acting on a spheric sample is given by

$$F = 4\pi r^3 \varepsilon_0 \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \nabla (E^2) \qquad (1)$$

For a cylindric rod we get

$$F = 2\pi r^2 l \varepsilon_0 \frac{\varepsilon_r - 1}{\varepsilon_r + 1} \nabla (E^2) \qquad (2)$$

and for a plate , transverse to the field lines

$$F = l\, b\, h\, \varepsilon_0 \frac{\varepsilon_r - 1}{\varepsilon_r} \nabla (E^2) \qquad (3)$$

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where F signifies the force , r the radius , l the length, ε_r the relative permittivity of the sample , ε_0 the permittivity of vacuum, E the field strength (ref.2). To make the force on unit of volume independent of size and indifferent to deflection of the sample, the condition
$\nabla(E^2)$ = constant has to be fulfilled.

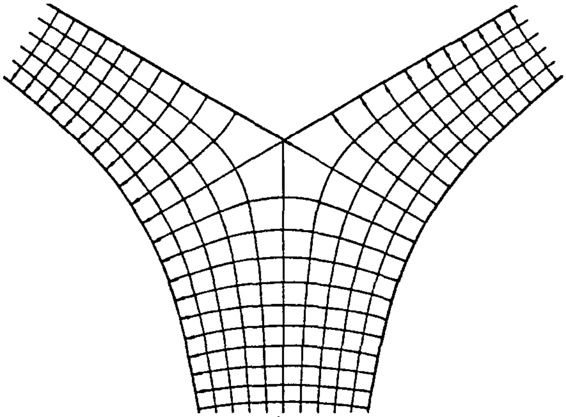

Fig.1. Electric field with $\nabla(E^2)$ independent of location.

Fig.1 shows the form of such a field , which is cylindric and generated by a prismatic electrode and two symmetrically arranged curved ones.
The first has the potential zero, the others lie on ± U.
The curved electrodes obey the equation (4)

$$r = r_0 \sin^{-2/3}(3\phi/2)$$

while the flat surfaces enclose an angle of 120°.

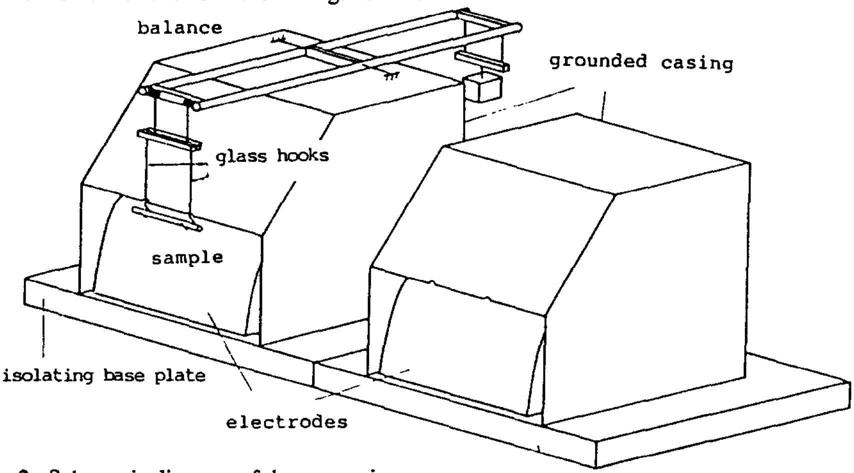

Fig.2. Schematic diagram of the measuring arrangement.

Fig.2 shows schematically the measuring arrangement for the dielectric constant. One curved electrode and one half of the prismatic electrode respectively are mounted on an insulating base plate. Above the lefthand section , the beam of an electromagnetic balance is sketched. A pair of glass hooks as supports for a cylindric sample hangs down from the left hand side of the beam by two thin metal bands, while a balance pan for counterweights is similarly connected to the other end. The operative electrode system results by putting together the base plates so that the front edges meet. A minimal radius r_0 =10 mm has been chosen for the electrodes.

It is an advantage of the arrangement , that suspension and center of sample lie in the plane with zero potential. There is no potential difference along the suspension or between suspension and through hole in the prismatic electrode which could give rise to charging of the sample.

The generation of forces on dielectrics in a travelling field.

The electrode system for measuring the dielectric loss factor is schematically depicted in fig. 3. Twelve metal rods are inserted in each of two insulating plates , opposite to each other so that the horizontal and vertical distances between rods are equal. The flat sample is suspended from the balance in the plane of symmetry by the already mentioned hooks. It can be also used for measurement of permittivity and has a relatively large surface which is favourable to mass transfer with the environment.

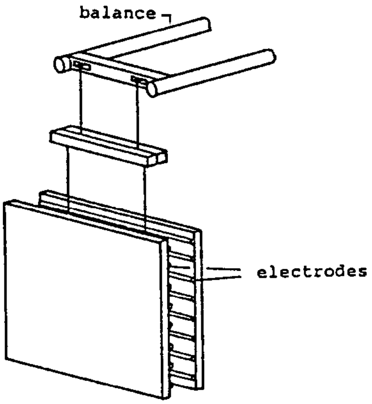

Fig.3. Schematic diagram of the measuring arrangement for the dielectric loss factor.

Four alternating voltages referred to ground with mutual phase shifts of 90° are fed to the rods in such a manner, that the generated electrostatic field travels in vertical direction. In a loss affected dielectric sample this field produces a force in its moving direction. The calculation of the force is very complicated and will not be carried out here. The strongly nonuniform field also generates forces which do not depend on the moving direction of the field . For suitable form and position of the sample, they disappear by averaging . The part of force exclusively based on loss factor is obtained by forming the difference of the forces with upward and downward moving field. The field systems for permittivity and loss can be exchanged beneath the balance by an electromotor drive. They are enclosed in a thermostated casing with the balance attached to the top surface in a separate thermally insulating box. The suspension threads for the sample pass through glass tubes with diaphragms inserted to suppress convection currents.

The balance

It works in a closed control loop according to the principle of automatic compensation. The taut band suspended balance beam consists of two silica tubes which are connected by horizontal tie bars of metal and enclose two symmetric force coils which act together with stationary permanent magnets and serve also for position indication.(ref.3) The current through these coils represents the measured value of force and is digitized by successive approximation. A digitally adjusted additional current is used for taring. The mechanical load capacity is 20g, the electromechnanical range is 2g and the resolution is1 µg = 10^{-8} N . A photograph of the balance is shown in fig. 4. (ref.4)

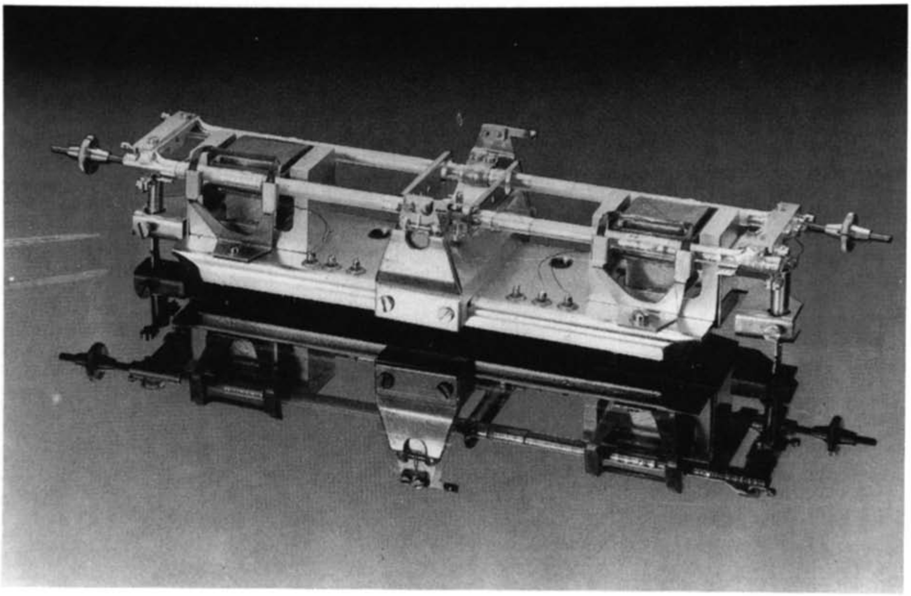

Fig.4. Self compensating microbalance.

After recording the current corresponding to weight, the sensitivity of the balance is increased, the chosen electrode system is excited and the force increment is measured (ref 4).

The generation of the field voltages

In order to generate the sinusoidal voltages with variable frequency and constant mutual phase difference which are necessary for the measurement of permittivity and loss factor, a multichannel digital signal generator was built. It contains four programmable read only memories which are programmed with the sine function in phases of 0°, 90°, 180° and 270°. A ring counter actuated by a timing pulse generator actuates the address lines of the proms. Coarse frequency adjustment is possible by variegating the number of stages of the ring counter, fine adjustment by changing the frequency of the timing pulse generator. (ref.5) The frequency range extends from 15 Hz to nearly 1 MHz and could be expanded by faster electronic components, using resonant ciruits in the final stages. The data lines of the proms are connected with digital to analog converters whose output voltages are amplified to the level of kV by special transistor stages. The amplitude is controlled via the reference voltage of the d.a-converters. Moreover, the d.c. component is suppressed by an auxiliary control loop .Excitation of the nonuniform field system with direct voltage is also possible.

The computer

Together with the analog interface, the computer adjusts and observes the measuring conditions. According to the desired frequency it determines the programming of the function generator. It positions the chosen electrode system, measures the voltages and controls the temperature. Further it calculates permittivity and loss factor from the measured forces with regard to the data of the samples. The introduced as well as measured and calculated data are printed or plotted. A scheme of the total measuring desk is presented in fig.5

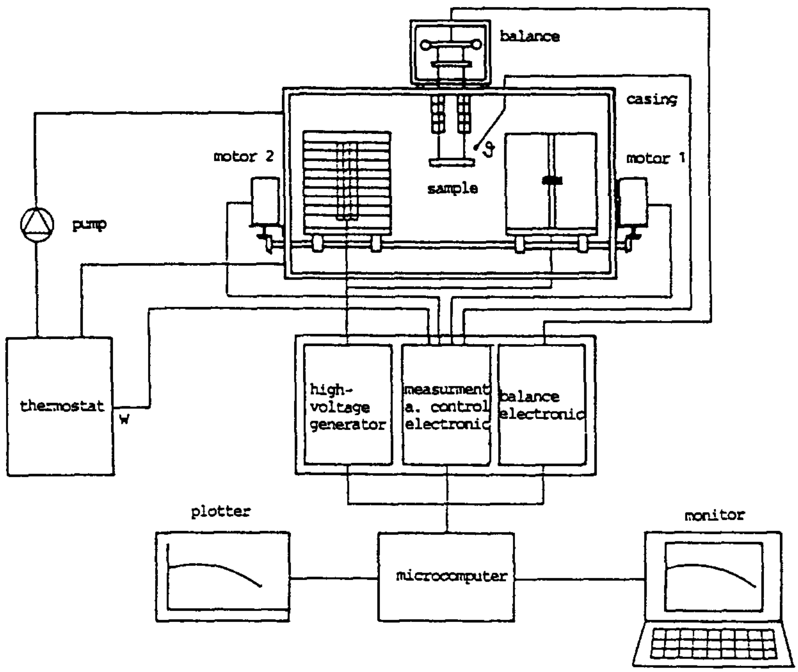

Fig. 5. Scheme of the complete measuring desk.

Measurements of permittivity and loss factor

Measurements have ben carried out with a good many samples of different shapes and volumes in order to find out suitable forms .Cylindric samples proved favourable for the measurement of permittivity in the nonuniform field. For loss measurement in the travelling field, plate shaped samples were found to be better adapted . Using empirical corrections , both shapes of samples can be applied in each system. (ref.6)

The graph of force in Fig. 6 was obtained with a constant voltage of 0,4 kV at 1 kHz in the nonuniform measuring field with the temperature rising slowly from 20°C to 50°C during 12 h. The cylindric sample consists of aluminum and has a volume of 0,5 cm^3. No larger fluctuations than 0,02μN,roughly 1 % of the measured value , are observed. Nevertheless, the error in force measurement limits the accuracy of the method, because voltage and volume can be determined with much better precision.

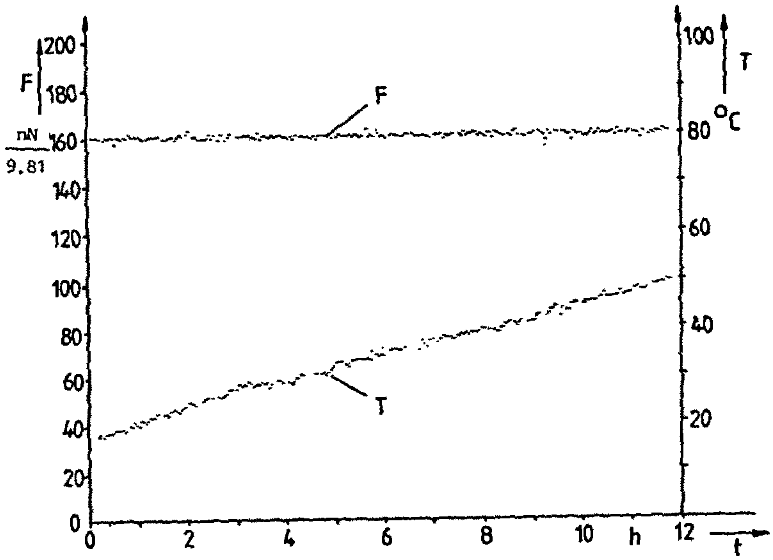

Fig.6. Electrostatic force on a cylindric aluminum sample with constant voltage and changing temperature.

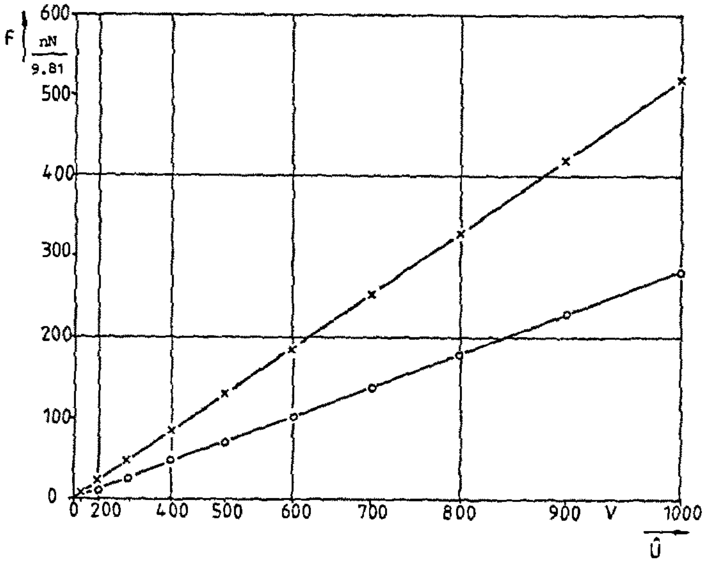

Fig. 7. Forces in the nonuniform field on an aluminum cylinder x and on an insulating plate o in the travelling field as function of voltage.

Fig. 7 shows the dependence on voltage of the field forces on a plate shaped sample of hard paper in the travelling field and on a cylindric aluminum sample in the nonuniform field. In compliance with theory , straight lines are obtained, if the square of voltage is plotted.

This relation holds in the total frequency range and with diverse materials. Samples of aluminium , to which an infinite permittivity can be ascribed , can serve for calibration in the measurement of permittivity with the nonuniform field. From the measured forces for the specific sample and a congruent sample of metal, the required permittivity is obtained according to the equations

$$\varepsilon = \frac{F_{max} + 2\,F}{F_{max} - F} \quad \text{for spheres,} \tag{5}$$

$$\varepsilon = \frac{F_{max} + F}{F_{max} - F} \quad \text{for cylinders,} \tag{6}$$

$$\varepsilon = \frac{F_{max}}{F_{max} - F} \quad \text{for plates .} \tag{7}$$

If the force on a cylindric sample of aluminum with a volume of 300 mm^3 in the nonuniform field at a voltage of 400 V is approximately 1μN, the uncertainty in permittivity for a sample of $\varepsilon \approx 1$ is roughly $\pm$ 0,03 , for $\varepsilon \approx$ 5,0 it is about $\pm$ 0,17 , while with $\varepsilon \approx 20$ the measurement is uncertain to $\pm$1,6 and for $\varepsilon \approx$ 100 the error can exceed $\pm$ 50. For the chosen form of electrodes with a minimum radius of r^o=10 mm,
$\nabla (E^2) = 2{,}25\, m^{-3} U^2$ is calculated . According to equation (6) a force per unit volume of $K_o = 39{,}4.10^{-6} N/V^2$ results. From measurements on a good many cylindric aluminum samples , a mean force referred to volume and $\nabla(E^2)$ of $K_{exp.} = (40{,}1 \pm 0{,}5) 10^{-6} N/V^2$ results. The deviation of 2 % from the theoretical value could be corrected by bending the electrodes if desired.

In fig. 8 the forces on clindric samples of diverse materials are plotted as functions of length. The graph is linear up to 60 mm, where the ends of the cylinders reach the edge disturbance of the field. The values of permittivity calculated from the forces agree very well with data in literature.

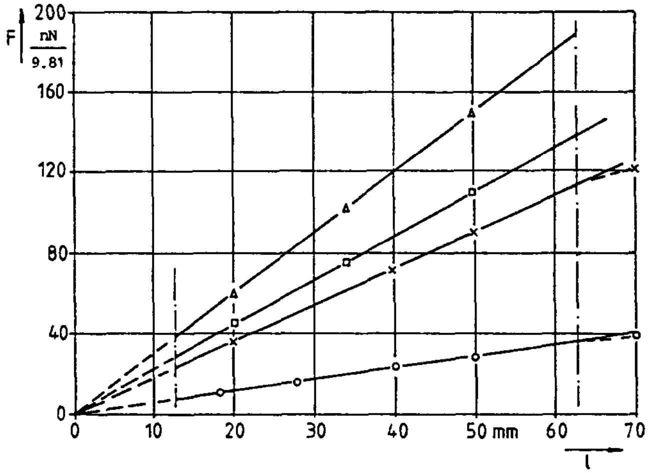

Fig. 8. Forces in the nonuniform field on samples of
o: PMMA ⌀ 2mm , x: PMMA ⌀ 3 mm,
Δ: SiO2 ⌀ 3,8 mm, ◻ CaSO4 2H2O ⌀ 4 mm at 400 V, 1 kHz.

Measurements with cylindric aluminum samples of different diameters proved that the forces in the nonuniform field are proportional to volume. If only length is varied , this relationship holds also for plates . But the forces increase superproportional with thickness and height because the polarization retroacts on the generating field. This effect can be seen in fig. 9, where the slope of the straight lines F = F(V) depends on the thickness of the sample. This can be taken into account by a correcting factor:

$$\frac{K}{K_o} = \frac{1}{1+(ah+bd)(\varepsilon-1)/\varepsilon} \qquad (8)$$

K_0 is the force referred to volume and the product V (E2), a und b are empiric constants , h is the height and d the thickness of the sample . This correction reduces the influence of sample dimensions in a sufficient range of d and h below the error in force measurement.

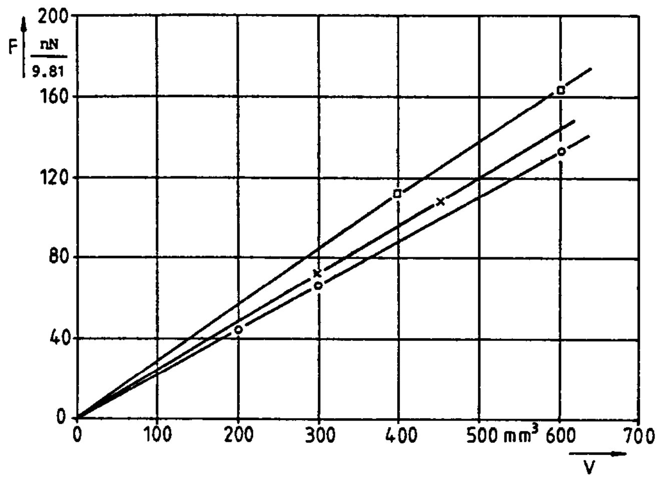

Fig. 9. The influence of thickness on the force-volume-relationship in the travelling field d =0,5 mm o, 1,0 mm x, 2 mm ◻ .

Fig. 10 shows the force on a plate shaped sample of hard paper in a travelling field as a function of height. The two lower parts correspond to upward and downward travelling field. The values of the first one are positively plotted . Forming the difference of the forces , we obtain the upper graph. The influence of the nonuniform field , perceptible in the first two graphs, is cancelled in the third. The linearly extrapolated third graph does not pass through the origin of ordinates. This may be attributed to the variation of the depolarization factor corresponding to the change in ratio of height to width. Fig 11 presents force measurements in the nonuniform field and in the travelling field with a sample of hard paper, humidified in a water bath and drying in the measuring chamber at 50°C. During 12 h the weight decreased by 630 µg, corresponding to 0,5‰ of the original mass. After further 20 h , the loss in weight was 1200 µg which is about 1 ‰ of sample mass.

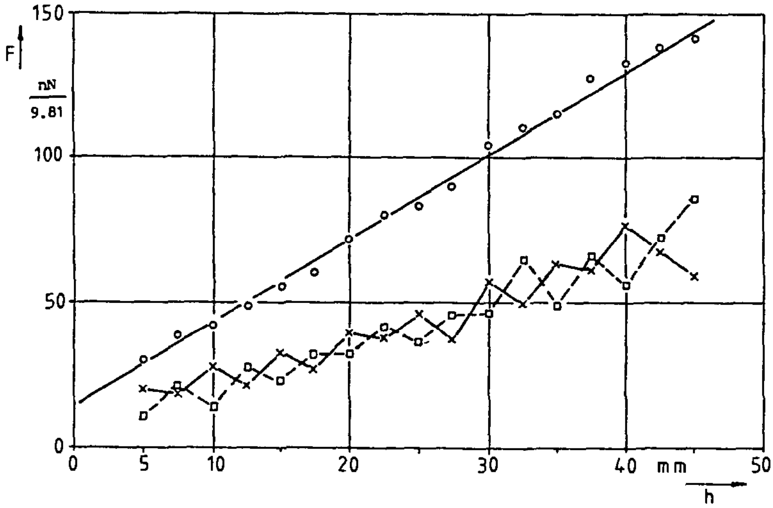

Fig.10. Forces on hard paper as a function of sample height □ : upward travelling field, x: downward travelling field, o : difference of forces.

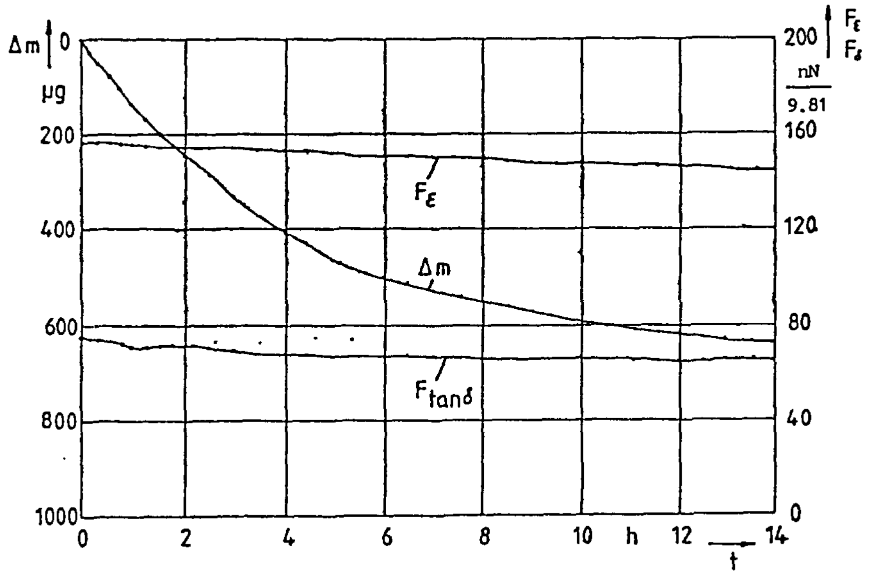

Fig.11. Graph of mass and dielectric forces with drying hard paper.

The force measured in the nonuniform field decreased within 12 h from 1520 to 1395 nN, corresponding to a decline by 8,3 % , while the force in the travelling field decreased from 736 to 608 nN , a decline by 17,3 %. After further 20 h final values of 1354 and 598 nN were attained.

The force measured with a congruent aluminum plate being F_{max}=1815 nN, it results from equation (7) that the permittivity of the sample decreases by the desiccation from 6,6 to 3,9.

The force on a plate shaped sample in the travelling field is less than proportional to dielectric loss by the factor $(1/1+tg2\partial)$. It depends linearly on length and, if measured as the difference of upward and downward forces , also on height of the sample. But the connection with the width of the sample and the dimensions of the field system is rather complicated. Calculation of the loss factor is therefore difficult. The system has to be calibrated with samples of the same thickness as the test object, their dielectric properties determined by an independent method. Using samples of perspex and hard paper for the calibration, it has been found , that the loss factor of the drying sample decreases from 0,085 to 0,07.

Fig. 12 is obtained with plaster of Paris , which was cast as a plate and put into the measuring cell shortly before complete binding . Because of the fast change in weight of the rather humid samples , the force in the electric field had to be assigned to the mean value of weight in the time interval of measurement. Compared with the drying of hard paper, greater variations of the loss induced forces are observed. They correspond to a decrease of loss factor from 0,14 to 0,085. The changes of the force by permittivity are comparatively small. A peculiar arrest point is observed in the mass curve , three hours after begin. The mass of the sample remains constant for about one hour , while the loss induced force continuously decreases.

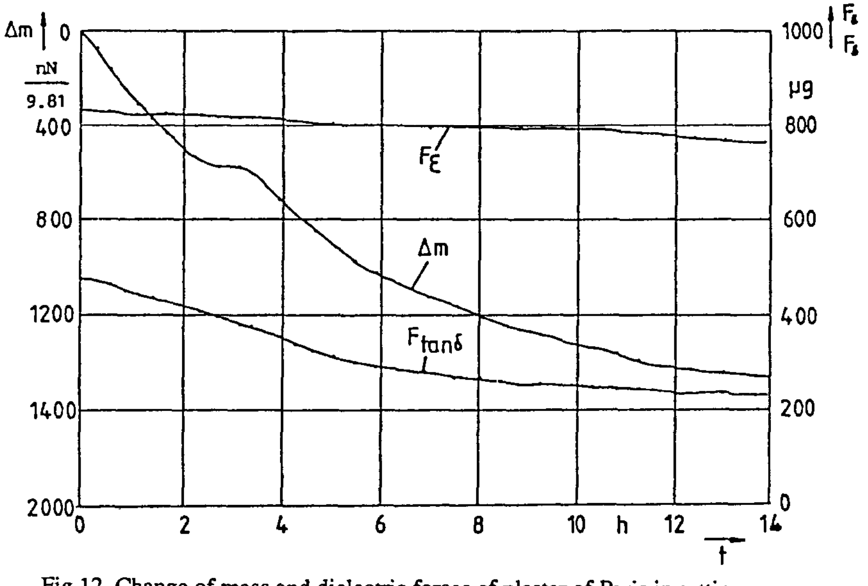

Fig.12. Change of mass and dielectric forces of plaster of Paris in setting.

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