

Calibration Techniques and Testing of Hygrometers for Horizontal Soundings of the Troposphere and Lower Stratosphere

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(Manuscript received 4 August 1971, in revised form 5 November 1971)

ABSTRACT

The measurement of the water vapor content of the atmosphere from a constant level balloon imposes new requirements, involving very long term stability for several months of flight, and light weight.

In the first plan, a precise relative humidity calibration chamber was developed to measure the long-period drift of state-of-the-art sensors, particularly aluminium oxide elements. All were found to have a significant drift over a one month period, including a specially built sensor made of a vibrating quartz microbalance with an adsorbing coating.

1. Introduction

The use of superpressure balloons in meteorological studies has created new sensor constraints. In fact, unlike conventional meteorological sondes (radiosondes), constant-level balloons practically follow the horizontal flow of air masses (Morel, 1969) and are designed to operate for several months. One such craft, launched in 1969, was still operating after more than 600 days.

Consequently, the response of the sensors used on the balloons must be very stable with the lowest possible drift (in the absence of updated calibrations). They must either not be sensitive to temperature or else have a controlled sensitivity in the absence of significant ventilation. In addition, they must be light weight to comply with air security standards.

There are a great number of physical and chemical phenomena sensitive to ambient humidity, but only very few give a real measure of water vapor concentration. Most "hygrometers" described in the literature or commercially available operate according to ill-defined physical processes, difficult to reproduce, and rarely stable on a long-term basis.

Discarding all devices based on the selective absorption of an IR or UV light beam, hygrometers generally use a more or less reversible "equilibrium" between water vapor and a hygroscopic substance. At first, it was necessary to develop an absolute calibration device, accurate and reliable enough to confirm or invalidate the existence and reversibility of such adsorption "equilibria" at low or very low temperatures and in the presence of very small quantities of water. This absolute calibration device allowed us to show a slow but unquestionable drift of almost all tested hydrometers; we have also been able to study very accurately (by

weight measurements) water vapor adsorption on layers of different substances, particularly on silica gel and aluminum oxide deposited on one face of a quartz crystal set up as an oscillator.

2. Calibration techniques

The first thing to do in any metrological work is to obtain a reliable and accurate calibration device or standard. As far as hygrometer measurements are concerned, the only physical phenomenon which can be easily reproduced is the equilibrium between solid or liquid water and water vapor, if we discard weighing methods which would allow accurate measurements of small amounts of water but which would also require very complex titrations.

However, one of the water vapor equilibrium methods is an open circuit process in which air is saturated at

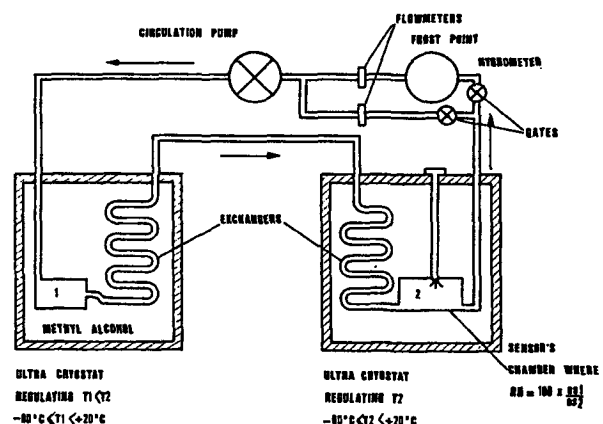


FIG. 1. Schematic diagram of calibration apparatus.

high pressure and expanded to the pressure of the experimental chamber; thus, temperature and pressure measurements must be made both before and after expansion.

Consequently, we selected a more reliable method using a flow of humid air in *closed circuit* on a saturator at temperature T_1 , followed by a test (sensor) chamber at temperature T_2 higher than T_1 (Fig. 1). When normal working conditions are reached, we are sure that water vapor is saturating at T_1 , and we can then adjust the relative humidity in the chamber by modifying T_1 . Hence, calibration requires only two temperature measurements, T_1 and T_2 , as relative humidity is given by the ratio of the saturation vapor pressures at T_1 and T_2 .

a. Laboratory system

1) TECHNOLOGY

Control and regulation of T_1 and T_2 are essential, and we selected "ultra-cryostats" which allow excellent temperature regulation and good homogeneity throughout a liquid bath. Temperature regulations obtained are $\pm 0.01^\circ\text{C}$ above -10°C and 0.0075°C below -30°C in the saturator, and $\pm 0.0075^\circ\text{C}$ above $+10^\circ\text{C}$ and $\pm 0.005^\circ\text{C}$ below 0°C in the sensor chamber.

The different parts of the circuit in direct contact with air of controlled humidity must be made of materials with low water adsorbing capacity. Therefore, we made use of polished stainless steel (Henry, 1969; Walker and Campion, 1965) teflon joints and electrical insulators. However, in order to obtain a perfectly homogeneous temperature, the saturator is made of nickel-plated copper.

The first saturator built consisted of a tank followed by an exchanger, the air going through the tank where the water vapor condensed on a set of baffles. This tank had a glass port which allowed us to see the phase of the condensed water. Thus, we have been able to note that ice deposits in fine crystals almost solely on the first baffle facing the air inlet. Hence, water vapor is sufficiently well collected by such a device. In its final version the saturator is completely closed, except for an aperture used for a platinum temperature sensor. The sensor chamber and saturator are about the same size and volume, with the volume (230 cm^3) being kept as low as possible in order to maintain a homogeneous temperature and to reduce the time response of the system.

Connecting pipes are made of polished stainless steel with a minimum of flexible connections. The air circulation is provided by a free diaphragm pump, its flow ranging from 400 to $3200\text{ cm}^3\text{ min}^{-1}$.

2) CONTROL HYGROMETER

A frost point hygrometer (AQMEL) is located, in parallel, in the air flow. Gates and flowmeters regulate

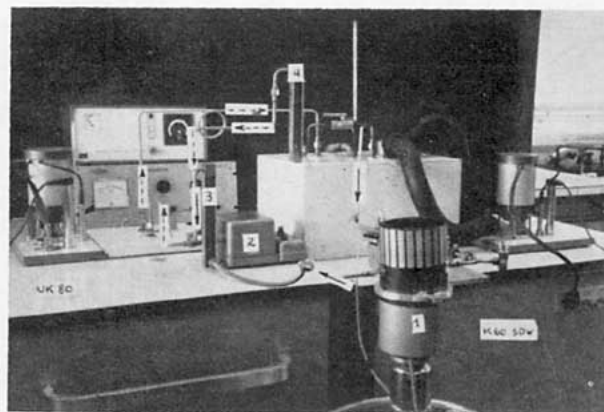


FIG. 2. Photograph of calibration equipment showing the frost point hygrometer (1), the circulation pump (2), the hygrometer circuit flowmeter (3), and the direct air circuit flowmeter (4). Solid arrows show the hygrometer circuit flow and the dashed arrows show the direct air circuit flow from the sensor chamber to the frost point chamber.

the circulation speeds in both the direct and diverted flows. The hygrometer permits permanent control of the frost point during an experiment and detection of any abnormal behavior. A plane observation port, located above the hygrometer condensation mirror, allows control of condensed water and replaces the port of our first saturator.

The difference between the frost points given by our system and the hygrometer never exceeds 1°C (the precision given by the hygrometer manufacturer being $\pm 1^\circ\text{C}$). Since relative humidity determinations were obtained from temperature measurements in the saturator, the frost point hygrometer was used only as a control.

3) PROCESS

Fig. 2 shows the system built in the laboratory. The whole system is periodically vacuumed with a Zeolite pump to outgas all surfaces in contact with the air.

To carry out a calibration, a mixture of 80% nitrogen and 20% oxygen, with traces of water vapor (frost point, -50°C), is first connected to the circulation pump and added to the calibration system. Then, by means of a microsyringe, a few cubic millimeters of distilled water are added to the saturator.

b. Performance

1) ACCURACY

Accuracy in relative humidity measurement depends upon temperature measurement and control. To calculate this accuracy we used an analytical expression, the so-called Goff and Gratch formula giving saturation vapor pressure as a function of temperature (*Smithsonian Meteorological Tables*, 1968). This formula is valid only for pure vapor in equilibrium with its solid or liquid phase, and in the presence of air it is

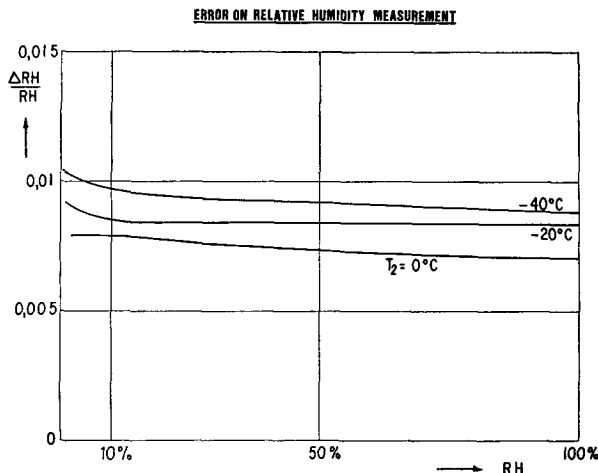


FIG. 3. Error in relative humidity measurement, as a function of relative humidity at various sensor chamber temperatures.

necessary to apply a correction factor to the saturation vapor pressure obtained (*Smithsonian Meteorological Tables*). However, calculations showed that the effect of this factor was negligible under normal flight and calibration conditions.

Temperature measurements are carried out by means of platinum sondes, the best devices presently available. Because of their small dimensions, we selected so-called "secondary" standards, 20 mm long and 3 mm in diameter, and reproducible to 0.01°C. Their calibrations are carried out with an accuracy of 0.01–0.02°C (Laboratoire National d'Essais, France).

In addition to the error due to the sonde itself, we have to take into account the error caused by heat transfer through the sonde environment (particularly, conduction through the wires and frame of the sonde). We found that this error was always smaller than 0.0035°C.

The resistance of the platinum sensors are measured with a Smith bridge (AOIP), which has an absolute error of $\pm 0.025^\circ\text{C}$ at 0°C and $\pm 0.017^\circ\text{C}$ at -80°C . On the other hand, variations of 0.0025°C can be detected. In short, for error calculations, errors due to sonde calibration, heat transfer through the sonde frame, the Smith bridge, and regulation of temperature in both chambers, will have to be taken into account. Fig. 3 shows the error in relative humidity measurement, using the temperature T_2 of the sensor chamber as a parameter.

2) TIME RESPONSE

The UK 80 cryostat used to measure the saturation temperature T_1 is limited to -80°C , and the time response is limited by outgassing. The influence of outgassing was studied in the following way. At a given frost point, the flow speed in the control hygrometer being constant, we measured the influence of the global

flow speed on the frost point value (as determined by the AQMEL hygrometer).

It has been noted at prevailing speeds that the influence of outgassing is negligible. However, below -70°C , it becomes necessary to increase the air flow in the hygrometer section to a value above the limit imposed by the manufacturer in order to obtain correct measurements. The branching devices coupled to the hygrometer include flexible pipes with a bellow, both of which are effective in increasing the outgassing rate.

The time response of the calibration system depends on the operating temperature; for example, from 0 to -10°C we need 6 min, between -60 and -70°C , 50 min and from -70°C to -80°C , approximately 2 hr, to obtain the real frost point.

3. Analyses of adsorption-type hygrometers

Long-duration flights of constant-level superpressure balloons impose new technological constraints on the moisture sensors carried by these craft. This led us to study sensors based on adsorption, a physical phenomenon linked to the surface state and porosity of a substance resulting from forces similar to those involved in condensation. Generally, an adsorbant is characterized by its adsorption isotherms, i.e., a graphical representation of the adsorbed gas volume in terms of the ratio of partial and saturation pressures, at a constant temperature. It is well known, for a given gas, that these adsorption isotherms are not always reproducible due to the possibility of porosity, aging or chemical reactions (Brunauer, 1945; Adamson, 1967). Since the ratio of partial and saturation water vapor pressures represents the relative humidity, all sensors using an adsorbing substance will be sensitive to both temperature and relative humidity.

There are essentially two ways of using the adsorption phenomenon for hygrometric measurements: 1) measuring the impedance variation of the hygroscopic substance, or 2) measuring the weight variation of the substance. In the case of impedance measurements, we should note that the phenomenon used is not well known as it involves a relationship between conductivity and adsorbed water vapor. On the other hand, weight variation measurements are directly related to the above-defined adsorption isotherms.

a. Hygristors

There are a great number of sensors for which relative humidity is a function of impedance. Our initial effort involved a bibliographic study in order to discard undesirable sensors of this type, particularly those having known drifts (Wexler *et al.*, 1965). In the case of ordinary meteorological soundings, for example, this type of sensor is calibrated just before the launch. After a series of tests and analyses, we found, to our knowledge, that commercially available sensors based on impedance variation presented unacceptable drifts

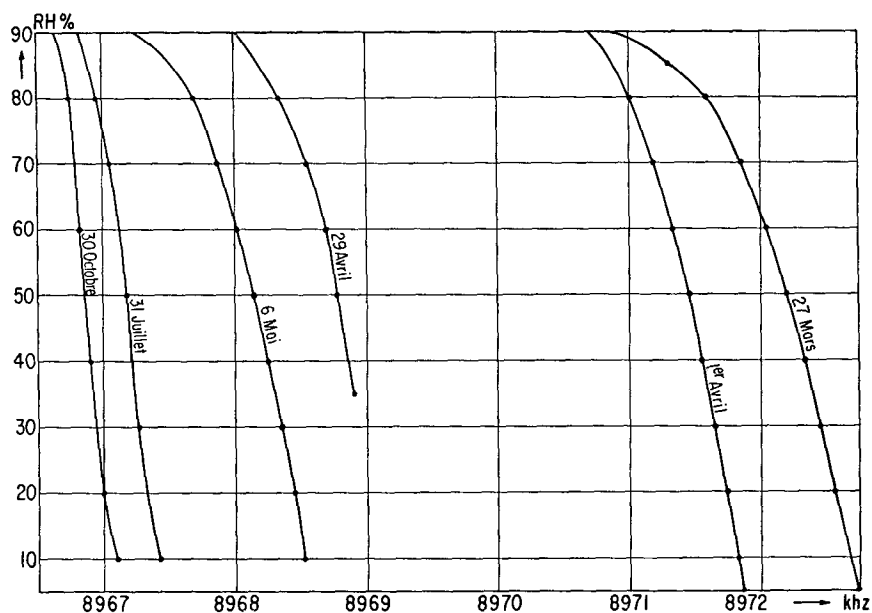


FIG. 4. Time variation of the sensitivity of a quartz crystal covered with silica gel, at a constant temperature of -20°C for a crystal prepared on 25 March.

over the several month period involved in the balloon flights.

However, a great number of users were and still are uncertain about aluminum oxide hygrometers (Jason and Wood, 1955; Booker and Wood, 1969; Stover, 1963; Chleck, 1966; Morrissey and Brousaides, 1967). We tested a number of such commercially available sensors and it appeared to us that the most reliable has a drift corresponding to about a 5% relative humidity error per month.

On these sensors, a first electrode is coated with the hygroscopic material which is itself then covered with a thin gold layer, forming the second electrode. We noted, however, that this layer would flake off in some cases.

b. Quartz sensors

In order to make a direct use of the adsorption phenomenon, Dr. King of the ESSO Research Laboratories (King, 1966) developed a method based on microweighing of adsorbed water vapor by quartz. This method was used by Dupont de Nemours in the design of a laboratory apparatus.

The frequency variation Δf of a quartz crystal vibrating at frequency f , resulting from a variation Δm related to an added mass m , is given by

$$\frac{\Delta f}{f} = -k \frac{\Delta m}{m},$$

k being a constant of the quartz crystal (Sauerbrey, 1959). Thus, the frequency of such a crystal coated with a hygroscopic substance will change with the quantity of water adsorbed in the substance.

The above formula implies a uniform distribution of the mass m . However, it is known that only the central part of the coating surface has an effect on the frequency. In practice, it is sufficient to cover the electrodes with the water vapor adsorbing substance (Sauerbrey, 1959; Mueller and White, 1968). This layer should be thin, and since the acceptable frequency depends on the total added mass f should be as high as possible. On the other hand, we selected an AT cut quartz because its temperature sensitivity is the lowest and can be made zero at a selected temperature (on account of the cutting angle). However, the problem is to select the adsorbing material. Following Dr. King's advice, we first chose silica gel.

1) SILICA GEL

Silica gel seemed to meet our requirements since the adsorption isotherms are reproducible, though they show a high hysteresis (Brunauer, 1945). In order to cover the electrodes, we used a gel in colloidal dispersion (Nalcoag). Fig. 4 shows the frequency variation as a function of relative humidity, at constant temperature. We noted that the total frequency variation is large enough to be easily used but that the time drift is considerable. In addition, after a certain period of time, the sensitivity and drift decrease simultaneously. We also noted that at -20°C the relative humidity hysteresis can reach 10%. Since some authors have shown that when silica gel is heated at high temperature and in vacuum the adsorption isotherms are linearized and the hysteresis cancelled (Asher *et al.*, 1965), we heated a certain number of quartz up to 200°C under a pressure of 10^{-4} mm Hg. As expected, we

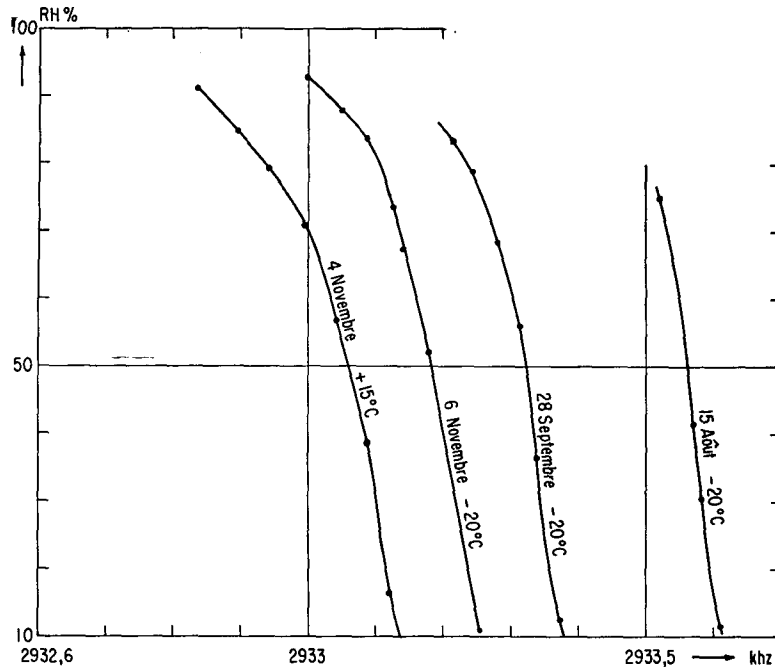


FIG. 5. Time variation of the sensitivity of a quartz crystal covered with aluminum oxide for a crystal prepared on 12 August.

obtained a linearized response but with a frequency variation too low to be easily used.

2) DUPONT MOISTURE ANALYZER

Similar tests were carried out with the Dupont 510 moisture analyzer crystal. This sensor is extremely sensitive because its frequency variation is about 10 kHz around 9 MHz. However, its use presents some drawbacks. When the quartz experiences a relative humidity of about 100%, its sensitivity seems to become infinite; i.e., in several hours the quartz frequency has decreased to such an extent that it has reached the critical damping point value of the quartz, causing the oscillation to stop. This phenomenon is probably due to the fact that the Dupont substance is soluble in water; at 100% relative humidity, a slow dissolving of the substance occurs which corresponds to a continuous water adsorption.

For relative humidity values lower than 100%, we noted a similar phenomenon, although considerably weaker. Thus, for an abrupt change of relative humidity, the quartz frequency shifts rapidly to the new equilibrium value, then a slow drift occurs which can last for several hours. The observed phenomenon has been studied by adsorption specialists and is attributed either to the superposition of chemical adsorption, to rapid physical adsorption, or to the slow penetration of molecules in the small pores (Brunauer, 1945; Adamson, 1967). These observations showed us why it is necessary to cycle the sensitive Dupont quartz crystals such that they are dried out every 30 sec and submitted to humid

air the following 30 sec. Thus, we could not easily use this sensor in airborne conditions.

3) ANODIZED ALUMINUM

If it exists, one should be able to determine the physical-chemical stability of anodized aluminum by the quartz micro-weighing method.

The production of such quartz crystals involves two different steps: 1) through vacuum evaporation, depositing aluminum on the quartz as an electrode, in a sufficiently thick layer to allow oxidation (which limits the frequency and hence the quartz sensitivity); and 2) anodically oxidizing the aluminum under optimum oxidizing conditions. These procedures raised a great number of technological problems too long to be listed here. As an example, we can emphasize that in order to make the thick aluminum layer adhere to the quartz, it is first of all necessary to evaporate a thin layer of titanium (or silicon), and then, once the aluminum is deposited, to find the oxidizing conditions giving the best humidity sensitivity and time stability. The anodically oxidized aluminum has a network of identical and evenly distributed pores. The distribution and dimensions of these pores depend upon the oxidizing conditions: that is, the electrolyte and its temperature, the density of the current going through the device, and the duration the oxidation.

Our research was guided by various publications on the development of Al_2O_3 sensors with variable conductance (Jason and Wood, 1955; Booker and Wood, 1969; Stover, 1963; Chleck, 1966; Morrissey and Brou-

saides, 1967). We oxidized a first set of quartz crystals under different temperatures and direct current densities. The results obtained with these crystals show an insufficient sensitivity for relative humidity between 0 and 70%, and a very high sensitivity beyond this point. In our view, this lack of sensitivity may stem from the fact that oxidation is carried out with direct current.

A second set of quartz crystals was oxidized at the Centre d'Études Nucléaires in Grenoble, where a team is currently studying the development of aluminum oxide sensors with variable impedance. Oxidations under different conditions were carried out. The frequency variation obtained under the best conditions (33 mA cm⁻² during 10 min at 26C), is too small, particularly between 0 and 50% relative humidity. However, this sensitivity problem can be solved by using higher central frequencies.

As it is shown in Fig. 5, for the most sensitive quartz available, we noted a very important sensitivity drift with time for all completed sensors. The curves in Fig. 5 also allow the assessment of the influence of sensor temperature on its sensitivity. On the other hand, we noted that the hysteresis effect decreases with a decrease in sensitivity, and is negligible for small humidity variations. The curves in Fig. 6 give evidence of the sensitivity of such aluminum oxide layers to relative humidity and temperature and not, as it is sometimes believed, to frost (or dew) point.

4) ALUMINUM OXIDE AND TITANIUM OXIDE LAYERS

Recent work (Ermolenko and Korunnaya, 1969) has shown that the autoclaving of aluminum oxide and titanium oxide layers in a water vapor atmosphere considerably increases the adsorption capacity of these

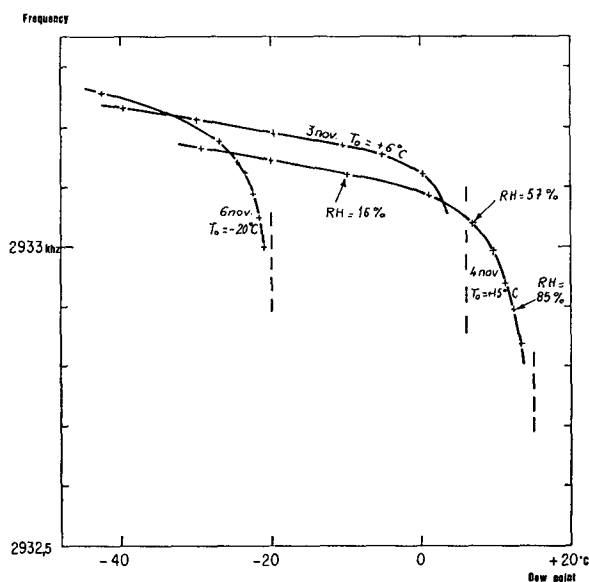


FIG. 6. Sensitivity of an Al₂O₃ quartz crystal to dew point.

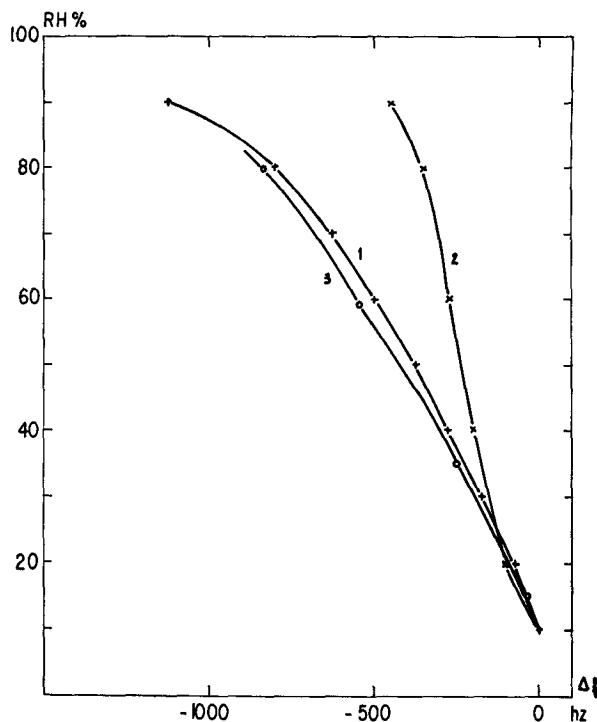


FIG. 7. Sensitivity of a quartz crystal covered with silica gel: 1, "fresh" quartz; 2, after 7 months aging; 3, aged quartz after autoclave treatment.

substances. They concluded from this that autoclaving, between 150 and 270C, for several hours, influences the porosity of Al₂O₃ and TiO₂ compounds.

Our own tests took place at 120C over a 5-hr period, as our autoclave could not reach higher temperatures. The resulting titanium oxide quartz oscillated around 7 MHz and had superficially oxidized titanium electrodes (Iwaki and Miura, 1967). Before autoclaving, these quartz crystals were practically insensitive to water vapor, the frequency variation between 10 and 90% being 55 Hz around 7 MHz. However, after autoclaving (120C at 5 hr), the sensitivity had considerably increased. The frequency range was approximately 800 Hz between 10 and 90%, but fell back to 300 Hz after one month and then, eventually, practically to its original value. However, we must emphasize that our autoclaving temperature was lower than that quoted by Ermolenko and Korunnaya (1969).

Similar tests were carried out with aluminum oxide quartz. In this case, the layer sensitivity increased with lower humidities, whereas it remained constant for values > 60%. This is most interesting as the drawback of a great number of Al₂O₃ layers is their excessive sensitivity around 100%, and a lack of sensitivity at lower humidities.

Incidentally, the silica gel quartz crystals which lost their original sensitivity with aging recover it after an autoclave treatment (Fig. 7). However, the autoclaved

crystals still showed a time drift of the same magnitude as that for similar but newly made crystals.

Thus, autoclave tests seem to be extremely interesting. Although we could not reproduce the conditions quoted by Ermolenko and Korunnaya (1969), we have shown that such treatment could have a major influence on the activity of the hygroscopic layers.

4. Conclusions

The systematic study of water vapor adsorption under different temperature and humidity conditions, on a variety of adsorbing layers, did not allow us to achieve a real equilibrium.

There seems to be some contradiction between the required sensitivity and stability of a good sensor; we can treat an adsorbing layer so as to improve its sensitivity but only at the expense of the "equilibrium" stability, and vice versa. However, it would be interesting to make further studies of high temperature autoclaving of aluminum oxide layers. Nevertheless, it seems that the only real equilibrium thus remaining is that of water vapor with either of the two condensed phases, liquid water or ice. This is the reason why we are now directing our efforts toward the simultaneous use of a conventional adsorption hygrometer and a frost-point hygrometer, the latter being used only at night, to systematically recalibrate the former (Sitbon and Tardieu, 1971).

REFERENCES

- Adamson, A., 1967: *Physical Chemistry of Surfaces*, 2nd ed. New York Interscience, 747 pp.
- Asher, R. C., J. F. Goodman and S. J. Greg, 1965: The adsorption of water vapor by some inorganic oxides. *Proc. Brit. Ceramic Soc.*, 125-132.
- Booker, C. J. L., and J. L. Wood, 1959: Further electrical effects of the adsorption of water by anodized aluminum. *Proc. Phys. Soc. London*, 76, 721-731.
- Brunauer, P., 1945: *Physical Adsorption of Gases and Vapors*, Vol. I. Oxford University Press, 504 pp.
- Chleck, D., 1966: Aluminium oxide hygrometer: Laboratory performance and flight results. *J. Appl. Meteor.*, 5, 878-886.
- Ermolenko, N. F., and G. G. Korunnaya, 1969: Structure and adsorption properties of coprecipitated titanium and aluminum hydroxides in relation to their composition and hydrothermal treatment. *Vestsi Akad. Navuk Belarusk. SSR, Ser. Khim. Navuk*, No. 4, 16-21.
- Henry, R. P., 1969: Mesure du taux de dégazage. *Vide*, No. 144, 316-351.
- Iwaki, Toru, and Masaji Miura, 1967: Studies of the surface of titanium dioxide. *J. Sci. Hiroshima Univ. Ser. AII*, 31, 209-215.
- Jason, A. C., and J. L. Wood, 1955: Some electrical effects of the adsorption of water vapor by anodized aluminium. *Proc. Phys. Soc. London*, B68, 1105.
- King, W. H., Jr., 1965: The piezoelectric sorption hydrometer. *Humidity and Moisture*, Vol. 1, New York, Reinhold, 578-583.
- Morel, P., 1969: Constant level balloon flights program in France. *Proc. W. M. O. Tech. Conf.*, Paris, 267-284.
- Morrissey, J. F., and F. J. Brousaides, 1967: Comments on aluminum oxide hygrometers: Laboratory performance and flight results. *J. Appl. Meteor.*, 6, 965-969.
- Muller, R. M., and W. White, 1968: Direct gravimetric calibration of a quartz crystal microbalance. *Rev. Sci. Inst.*, 3, 291-295.
- Ovarlez-Fourrier, J., 1971: Étalonnage absolu et dérive au cours du temps des capteurs hygrométriques. Thésis, Faculté des Sciences de Paris.
- Sauerbrey, G., 1959: Verwedung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung. *Z. Phys.*, 155, 206-222.
- Sitbon, P., and J. Tardieu 1971: Unpubl. Rept., Laboratoire de Météorologie Dynamique, Meudon-Bellevue, France.
- Smithsonian Meteorological Tables*, 1968: Washington, D. C., Smithsonian Institution Press.
- Stover, C. N., 1963: Aluminium oxide humidity element for radiosonde weather use. *Rev. Sci. Inst.*, 34, 632-635.
- Walker, J. A., and P. Campion, 1965: The use of electrolytic hygrometers for the determination of water and hydrogen. *Analyst*, 90, 199-209.
- Wexler, A., 1950: Recirculating apparatus for testing hygrometers. *J. Natl. Bur. Stds.*, 45, 357-362.
- , and W. G. Brombacher, 1951: Methods of measuring humidity and testing hygrometers. NBS Circular 512.
- , et al., 1965: *Humidity and Moisture*, Vol. 1. New York, Reinhold, 687 pp.