The Effect of Air Laden Soluble Salts on Dew Point Measurement Using Condensation Hygrometers

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Condensation hygrometers are used as humidity transfer standards for calibrating a wide variety of humidity sensors and instruments. Condensation hygrometers measure the partial pressure of water in gases by directly measuring the dew point temperature. Dew point temperature measurement is accomplished by controlling the temperature of a condensation target to equilibrium where the mass of condensate (dew or frost) is constant. The temperature of the condensation surface is, by definition, the dew point. A variety of feedback control methods to maintain mass constancy are utilized including optical, acoustic wave, capacitance, resistance or mass measurements.

When used to measure environments laden with soluble salts, deposits that accumulate on the condensation target will affect the localized water vapor pressure resulting in errors. Raoult's law provides a model to describe the rationale for errors due to salt deposits. Since there are differences between the vapor pressure over water versus ice, the colligative properties of a salt dissolved in solution will also affect the freezing point of water, thereby creating ambiguity in humidity measurements. An experiment was conducted where an optical chilled mirror condensation sensor was connected to a dew point generator that produced constant dew points at various levels. A dilute solution of saltwater was allowed to dry on the surface of an optical chilled mirror sensor to produce a salt residue. The results were compared against a clean chilled mirror. Methods of mitigating the effects of deposited salts such as manual cleaning with prepared solutions and distilled water as well as automated self-cleaning methods were compared to the baseline readings.

1. Overview of Condensation Hygrometers

Dew point temperature can be defined as the temperature where the partial pressure water vapor pressure in an environment is equal to saturation water vapor pressure. In a given environment where the water vapor pressure is below the saturation point, any plane surface that is below the dew point temperature will accumulate condensation layer. Condensation hygrometers measure dew point temperature by measuring the temperature of a condensation target while dew or frost that has condensed is in an equilibrium state such that the mass is constant. Heat is typically removed from the condensing surface by coolants, mechanical refrigeration and thermoelectric cooling. Feedback to control the regulation of the heat flux is accomplished by various means: optical, acoustic, mass change, or electrical properties such as resistance or capacitive changes.

One of the most widely used condensation hygrometers utilizes optical feedback control. Infrared light is reflected off a polished metal mirror (typically made of rhodium, platinum, stainless steel or gold). The reflected light is received by a solid-state photodetector. When the mirror is dry, virtually 100% of the reflected light signal is received. As the mirror is cooled to or below the dew point temperature, a condensation layer will form. As the condensation layer forms, the reflected light scatters, resulting in a decrease in the output of the photodetector. The signal from the photodector is used for "feedback" in "closed loop" control of the thermoelectric power and polarity or coolant flow to mirror. A four-wire PRTD (Platinum Resistance Temperature Detector) imbedded in the mirror block is used to measure the temperature. The temperature measured by PRTD is, by definition, equal to the dew or frost point temperature.

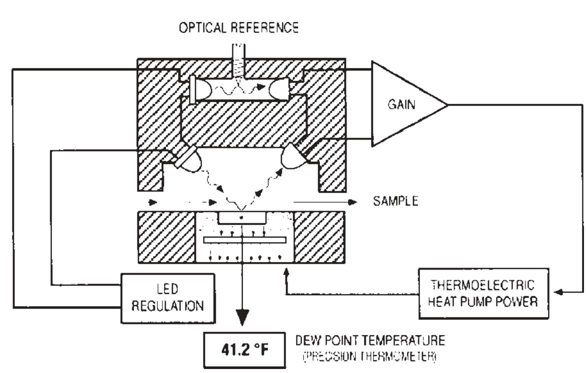

Figure 1. Schematic of an optically controlled chilled mirror dew point sensor.

2.0 The Relationships of Humidity Measurement Parameters to Water Vapor Pressure

$$e_w = (1.007 + 4.18 \times 10^{-6} P)6.115 \exp\left(\frac{22.452 t_d}{272.55 + t_d}\right) \quad (1)$$

$$e_i = (1.007 + 3.466 \times 10^{-6} P)6.1121 \exp\left(\frac{17.502 t_d}{240.97 + t_d}\right)$$

$$(2)\mathbf{(3)} \quad \%RH = \frac{100e}{e_s}$$

e_s = Partial pressure of water vapor (mbar) over water
e_i = Partial pressure of water vapor (mbar) over ice
P = Total pressure (mbar)
t_d = Dew Point temperature (°C)

The equations above yield the saturation vapor pressure from the dew point temperature and barometric pressure. The equations can also be used to compute the relative humidity (%RH) if the dew/frost point and dry bulb temperatures are known. The partial pressure of water vapor (e) is computed using equation (1) or (2) using the respective frost point or dew point temperature(t_d). The saturation water vapor (e_s) is computed by substituting the ambient temperature (t_a) in equation (1) if the ambient is greater than 0°C and equation (2) if the ambient temperature is less than 0°C. The relative humidity is computed as follows

$$\%RH = \frac{100e}{e_s} \quad (3)$$

The absolute humidity (AH) in g/m^3 is computed from the partial pressure of water and temperature by the following equation (4).

$$AH = \frac{216.7e}{t_a + 273.16} \quad (4)$$

The volumetric mixing ratio defined as the volume of water vapor over the volume of dry air is expressed in PPM_v (parts per million by volume) by equation (5)

$$PPM_v = \frac{e}{P - e} * 10^6 \quad (5)$$

The mass mixing ratio is defined as the mass of water vapor over the mass of dry air is expressed in PPMw (parts per million by weight) by equation (6). The gram-molecular weight of water is 18 and 28.96 is the gram-molecular weight of standard dry air. If the carrier gas were a different species, the value would correspond to the gram-molecular weight of the gas or gas mixture.

$$PPM_w = \frac{e18}{(P - e)28.96} * 10^6 \quad (6)$$

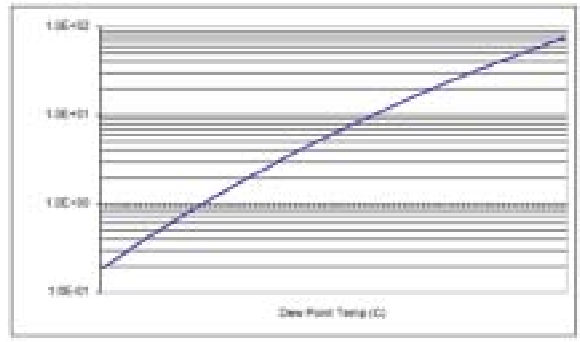

Figure 2. Plot of the water vapor pressure (mbar) vs. dew/frost point temperature (°C).

3. Dew vs. Frost Point

A condensation hygrometer provides a direct correlation to the partial pressure of water vapor based on the species (ice or water) that exist on the condensation surface. "Supercooled water" is defined as pure water, in the liquid state, below the freezing point (0°C). Supercooled water can exist on smooth plane surfaces down to approximately -20°C. If sufficient dwell time below 0°C is allowed, all of the condensate will convert to ice. Since the saturation water vapor pressure is different over water versus ice, measurements made by condensation hygrometers in the 0 to -20°C dew/frost point region can be ambiguous unless the condensate species is known.

One of the best methods of determining the condensate species is observation via a viewport, boroscope or microscope. Frost ice will appear crystalline while dew or water appears to be a haze on the condensation surface.

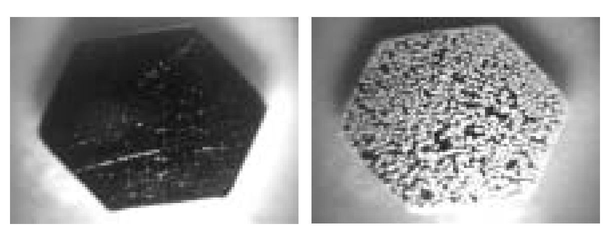

Figure 3. The image on the left is a dry mirror and the image on the right is mirror at -10ºC "frost point". Frost accumulation can clearly be seen.

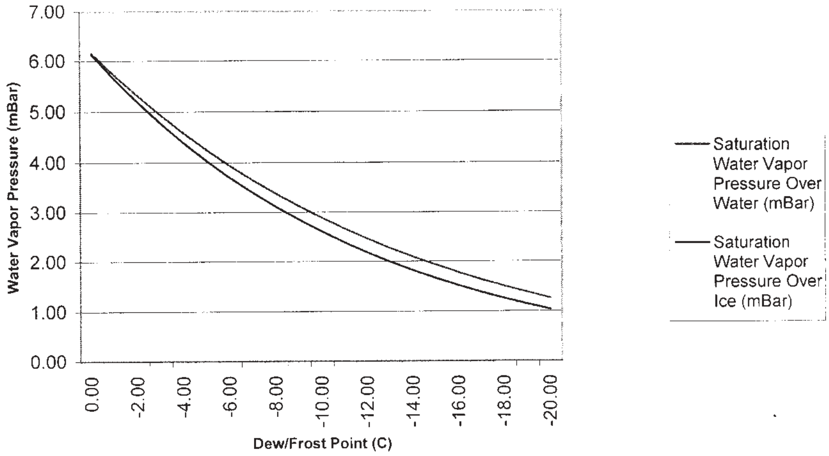

Figure 4. Plot of the saturation water vapor pressure over water vs ice.

4. Raoult's Law and the Effect on Condensation Hygrometer Measurements

Raoult's law, named for the French chemist Francois Marie Raoult (1830-1901), who first expressed it, states: "the vapor pressure of a solution is the sum of the vapor pressure of each component multiplied by the ratio of molecules (mole fraction) of each component." In a binary solution consisting of water and a salt, the vapor pressure (e) will be equal to the product of the mole fraction of the water/salt and vapor pressure of pure water.

$$e = xe_o \qquad (7)$$

e = water vapor pressure over water/salt solution

e_o = water vapor pressure of pure water

x = Mole fraction of the solvent = moles of solvent / total number of moles of solution

Equation (7) predicts that a salt-water solution will have a lower vapor pressure than that of pure water at the same temperature. The addition of salt to water will also lower the freezing point. When airborne salts are deposited on the condensing surface of condensation hygrometer, the local vapor pressure of the condensate/salt solution is lowered. When a condensation hygrometer is reading a stable dew/frost point, the mass of condensate is constant. The rate of water molecules condensing and the rate of water molecules evaporating is equal. Lowering the water vapor pressure of the condensate by the addition of salt will cause the control algorithm of the hygrometer to increase the surface temperature of the condensation target to achieve mass equilibrium with the surrounding environment. Figure 4. depicts a comparison of two condensation dew point sensors measuring the same environment: (Td_1) has pure water condensed while (Td_2) has deposits of salt dissolved in the condensate. Td_2 is expected to read a higher dew point because the salt is in effect impeding the water molecules from evaporating. The system adjusts by increasing the surface temperature to drive those molecules into the vapor phase.

5. Mitigating the Effects of Airborne Contaminants

5.1 Solid airborne contaminates can be classified into two basic categories:

- Insoluble contaminants: dust, fibers, oil mist, aerosols, sand, etc.
- Soluble contaminants: salts, water miscible aerosols, etc

In costal or marine environments the concentration of airborne salts can vary from 0.1 to 5ppm by weight. One cubic meter of air at one atmosphere and room temperature weighs about 1.28kg (1.28g/l). Salts can exist suspended in air as solids or as aerosols dissolved in water.

5.2 When condensation hygrometers are used to sample atmospheres where airborne salts are present certain techniques to mitigate the contaminants should be employed including:

- Use a filter with non-hygroscopic media and an optimal porosity of 5µm. The filter media should not retain or outgas water vapor. Suitable media includes spun-borosilicate glass and PTFE. The filter housing body should be stainless steel.
- Use only stainless steel tubing. Make sure the tubing is clean and oil free.
- When humidity sensors are being calibrated against or compared to a condensation hygrometer sensor, the EUT should be installed downstream. The EUT may be contaminated with salts, oils or other contaminants, particularly when used in industrial applications.

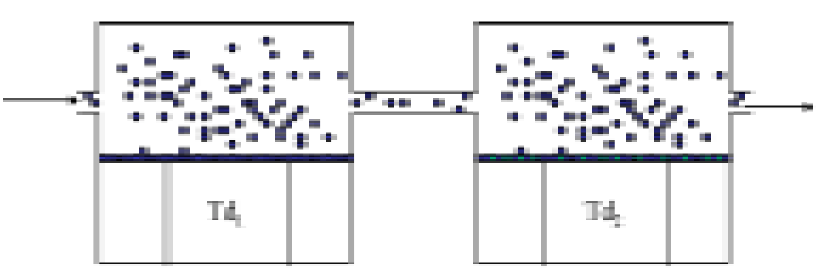

Figure 5.Ilustration of two identical condensation dew point sensors sensing the same environment. Due to salt dissolved in the condensate of Td2, it reads a higher dew point.

- Use low flow rates. The recommended flow rate through a chilled mirror hygrometer is 0.25-2.5 l/m (liters per minute). 0.25 to 0.5 l/min is optimal. The greater the flow rate, the greater the accumulated contaminants over time.
- The condensation hygrometer's condensation surface should be cleaned on a regular interval and prior to every use. During operation, the frequency of cleaning will depend on the severity of contaminates in the environment and the effectiveness of the filter. Only clean the mirror with the prepared solution or distilled water. After cleaning visually inspect the mirror to make sure it has a bright stainless shine. Buffing the mirror with a soft cotton swab might be appropriate. Use only clean cotton swabs to clean the mirror. Some cotton swabs, such as "Q-Tips", are impregnated with lanolin that leaves a residue. Never use abrasives to clean the mirror. This can cause scratches.
- A number of condensation hygrometers are equipped with auto-balancing or self-cleaning systems. These may be programmed to run automatically in the example of GE Infrastructure's patented PACER cycle. When using data acquisition systems, it is helpful to provide documentation as to when the self-cleaning cycles were engaged.

6.0 The PACER Cycle

GE Infrastructure Sensing developed an automatic patented contamination mitigation scheme called PACER (Program Automatic Error Reduction). The PACER cycle may be initiated manually from the instrument's front panel or by programming a timed cycle. The cycle starts by capturing the data (during the PACER cycle a constant reading is displayed and transmitted if this option is selected) and cooling the mirror well below the dew point such that a thick dew or frost layer forms on the mirror. The mirror is then rapidly heated. During heating a significant amount of soluble and some non-soluble contamination is "flash evaporated." The contamination left on the mirror tends to aggregate in dry "islands." The process empirically leaves approximately 85% of the mirror area clean. The light signal received by the photodetector is compared against a reference emitter/photodetector and the two signals are "balanced", effectively negating the effect of the residual contamination left on the mirror. The PACER cycle works very well, but eventually manual cleaning might be required as residual contaminants accumulate over time.

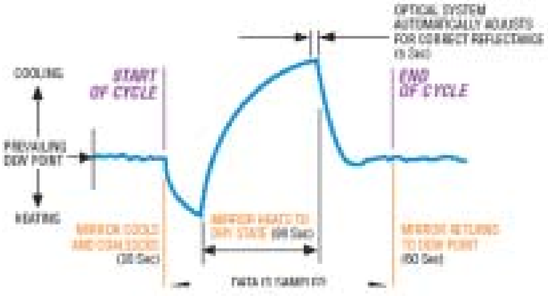

Figure 6. PACER Cycle

7.0 Test Procedure

7.1 Equipment

7.1.1 DPG-300 Dew/Frost Point Generator: The DPG-300 is a dew/frost point generator which utilizes precision needle valve/rotameters to volumetrically mix streams of dry air and saturated air in finite proportions. The DPG-300 provides a stability of ±0.5°C dew point (T_d) when used in a temperature-controlled environment of ±1°C. The ambient temperature of the environment was recorded throughout the test and was maintained to 25°C, ±0.5°C. A flow rate of 0.5 l/min (liters per minute) was used throughout the test procedure.

Figure 7. Test equipment setup. The DPG-300 provides a controlled dew/frost output measured with two-stage chilled mirror sensor and Optica analyzer.

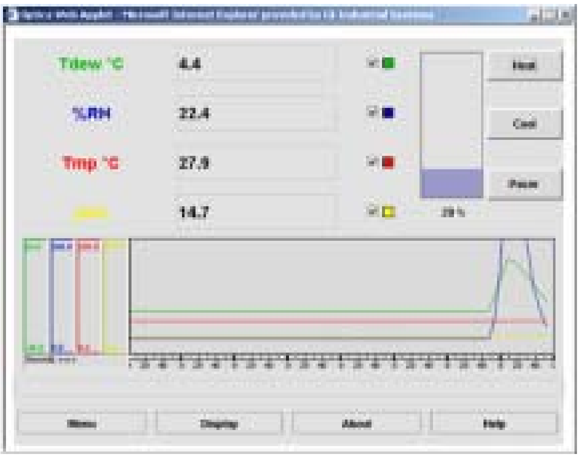

Figure 8. Remote "screen shot" from the Optica hygrometer. The unit is equipped with an Ethernet port and programmable IP address which enables the data and controls to be accessed from any internet browser.

7.1.2 Dry Compressed Air: Dry compressed air was delivered via stainless steel piping from the facility's air supply. The air is dried by a series of refrigeration dryers, pressure swing desiccant dryers and "zero air" generators. The compressed air was delivered at 6.2 bar (90 psia) and -80°C frost point. The feed air to the DPG-300 was regulated to 3.1 bar (45 psia).

7.2.3 Optica Two Stage Chilled Mirror Hygrometer: The model D2-SR chilled mirror sensor is a flow-through cell with 65°C depression capability at 25°C ambient and 1 atmosphere. The chilled condensation surface is made of rhodium. The Optica analyzer is equipped a configurable VGA display, data logger and ethernet interface which enabled the data to be accessed remotely. The sensor is equipped with a viewport and internal illumination for observing the condensation surface. The internal illumination is of a wavelength (color) which does not interfere with the IR emitter. The accuracy of the system is ±0.15°C T_d. When a stable dew/frost layer is attained the display provides an annunciator displays the word "control."

7.2.4 Salt Solution: A solution of reagent grade sodium chloride (common table salt) and distilled water was prepared. 0.28g of NaCl was weighed on a laboratory balance and placed in a 50ml volumetric flask. On an initial test, it was found that this solution was too concentrated. The residue left on the mirror by placing one drop of solution on a heated mirror produced a white residue that appeared to the optical system as a thick dew layer. This resulted is no cooling (in fact the system tried to heat to reduce the "dew layer.") 10ml of the solution was diluted with distilled water to 50ml. The resultant solution was still too concentrated; therefore a second aliquot of 5ml diluted to 50 ml was used. The volume per drop was calibrated by using a graduated cylinder. 82 drops = 5ml. It is estimated that one drop of solution contained approximately 0.68mg of NaCl.

$$\frac{0.28g}{50ml} \times \frac{10ml}{50ml} \times \frac{5ml}{50ml} \times \frac{5ml}{82drops} = \frac{0.000683g}{drop} = \frac{0.68mg}{drop} \quad (8)$$

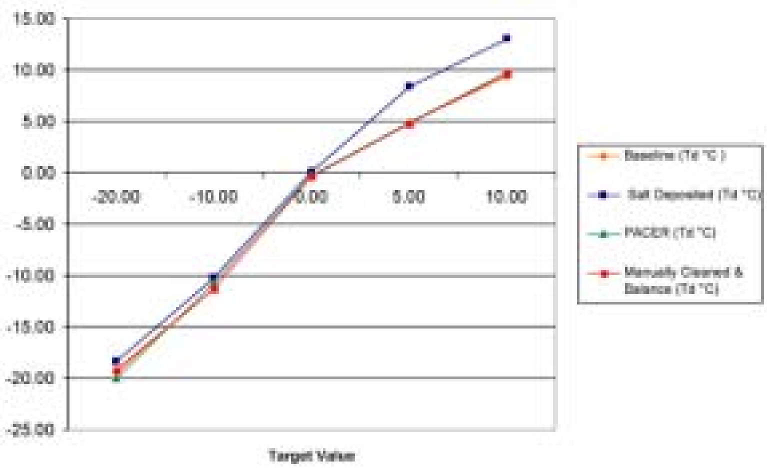

Figure 9. Test results.

Target Dew/Frost Point (T_d°C)	-20.00	-10.00	0.00	5.00	10.00
Baseline (T_d°C)	-19.37	-11.32	-0.36	4.87	9.45
Salt Deposited (T_d°C)	-18.41	-10.27	0.16	8.32	13.07
PACER (T_d°C)	-19.96	-10.68	-0.19	4.83	9.82
Manually Cleaned & Balance (T_d°C)	-19.19	-11.28	-0.32	4.79	9.64

All condensate species below 0°C were observed as ice.

Table1. Test Results.

7.3 Test Procedure

7.3.1 The DPG-300 Dew/Frost Point Generator is equipped with a booklet that provides the rotameter settings to achieve a desired dew/frost point. The generator was set to target values of -20, -10, 0, +5 & +10°C respectively. The chilled mirror sensor was connected via stainless steel tubing to the sensor and the flow rate was regulated to 0.5 l/min.

7.3.2 The chilled mirror sensor was cleaned by using the standard procedure of heating the mirror, wiping the mirror with a cotton swab saturated with a prepared cleaning solution, followed by wiping the mirror with a cotton swab saturated with distilled water. The water was allowed to dry. The optical bridge was balanced per the unit's instructions and the PACER cycle initated. Once the PACER cycle was completed, 90 minutes elapsed prior to recording the readings. A base-line reading for each set point was established.

7.3.3 The mirror was then heated to the maximum level (106°C) by using the Optica's "heat switch". One drop of the prepared salt solution was placed on the mirror and allowed to dry. The unit was taken out of the heat mode and allowed to establish a reading. 90 minutes elapsed and the reading was recorded.

7.3.4 The Pacer cycle was engaged and a reading recorded 90 minutes later.

7.3.5 The mirror was then heated, clean by the identical procedure as described in section (7.3.2) and a reading was taken after 90 minutes.

7.3.6 At each reading, the mirror was observed via the viewport to determine if the condensate species was either dew or frost.

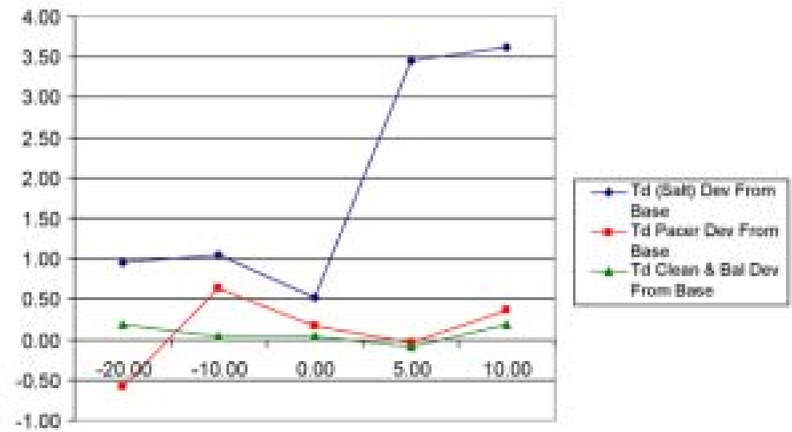

Figure 10. Deviations from baseline readings.

9. Conclusions

9.1 The effect of depositing approximately 0.68mg of NaCl on an optical chilled mirror hygrometer caused the dew point measurement to increase. The increase was approximately 1°C at -20 & -10°C Td. 0.5°C at 0°C and 3.5°C at 5 &10°C.

9.2 The condensate species below 0ºC was observed on all readings to be frost (the crystalline structure of ice observed). This was observed through the chilled mirror's viewport. Sufficient dell time at the readings elapsed for the condensate to convert completely to ice.

9.3 The PACER cycle was effective for automatically cleaning the condensation surface (mirror) and rebalancing the optics. At all data points, the reading returned to the base line readings to within approximately ±0.5°C.

9.4 Manual cleaning proved to be very effective. After manual cleaning all of the readings returned to within ±0.2ºC T_d of the baseline readings. Since manual cleaning is effective, perhaps an automated mechanical means of cleaning might be employed. (A miniature windshield washer/wiper system comes to mind).

9.5 The remote connectivity of the analyzer via the internet and data logging proved to be very useful. One could check the operation of the unit from a remote office or even from the comfort of one's home.

9.6 It was not possible to test high concentrations of salt residue on the mirror. NaCl residue appears to the optics as a thick dew or frost layer.

9.7 Additional studies with a more advanced optical detector systems should be conducted. GE Infrastructure Sensing has patented a condensation hygrometer using a high resolution CCD camera. The camera based system might be able the discriminate between dew, frost and contaminants such as salt residue.

9.8 Additional studies should be conducted to develop a mathematical function relating the mass of salt deposited on the mirror to the dew point error. The mass of salt deposited might also be correlated to the mass concentration of salt air and "run-time" between cleanings.

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