Effect of polytetrafluoroethylene (PTFE) phase transition at 19°C on the use of Spectralon as a reference standard for reflectance

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Sintered polytetrafluoroethylene (PTFE) is highly reflective and is widely used as a reference standard in remote sensing, radiometry, and spectroscopy. The relative change in output flux from a PTFE integrating sphere over the room temperature phase transition at 19°C has been measured at a monochromatic wavelength of 633 nm as $1.82 \pm 0.21\%$. The change in output flux was attributed to a small change of $0.09 \pm 0.02\%$ in the total hemispherical reflectance of PTFE, caused by a change in its material density as a result of the phase transition. For the majority of users, this small change measured in total hemispherical reflectance is unlikely to impact significantly the accuracy of PTFE flat panel reflectors used as reference standards. However, owing to the multiple reflections that occur inside an integrating sphere cavity, the effect is multiplied and remedial action should be applied, either via a mathematical correction or through temperature stabilization of the integrating sphere when high accuracy (<5%) measurements of flux, irradiance, or radiance are required from PTFE-based integrating spheres at temperatures close to the phase transition at 19°C.

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1. Introduction

Sintered polytetrafluoroethylene (PTFE), which is also known under the trade names Spectralon from Labsphere and OP.DI.MA from Gigahertz-Optik, is widely used in terrestrial remote sensing, spectroscopy, and radiometry as a primary reference standard for reflectance [1–6]. PTFE is also used in integrating spheres for the spatial integration of irradiance [7,8] and as a uniform radiance source for the calibration of remote sensing systems [9]. PTFE has wide application in the remote sensing community because it exhibits approximately Lambertian reflectance over the UV–VIS–NIR region of the spectrum and is chemically inert, washable, and extremely hydrophobic [10,11], making it ideal for field use.

As an optical diffuser, the optical transmittance of PTFE has been shown to change by up to 3% between the temperatures of 13°C and 22°C [12]. The authors ascribe these changes in transmittance to a phase transition that results in a change in the crystalline structure of PTFE at 19°C [12]. The phase transition may represent a particular problem because of its proximity to common field operating conditions in temperate climates. For example, McKenzie *et al.* (2005) reported a significant impact on the accuracy of measured UV irradiances (~2%) when using PTFE diffusers in the field at ambient temperatures that straddle the phase transition temperature at 19°C.

PTFE is known to undergo phase transitions at both 19°C and 30°C [13–15]. Studies involving

x-ray diffraction have shown that these phase transitions result from an uncoiling of the helical structure of fluorine atoms around a central carbon backbone [16]. In combination, the transitions at 19°C and 30°C result in a reversible change of ~1% in the volume of PTFE [13,14]. The transition at 19°C accounts for the majority (~85%) of the total volumetric change [13].

The reflectance of pressed PTFE is known to depend on its density [11], and given the widespread use of PTFE as a reference standard for reflectance, the observed changes in transmittance of visible light [12,17] and the known structural changes at 19°C [13–16], it is pertinent to assess whether the phase transition affects the reflectance of PTFE.

The investigation described here used a temperature-controlled sintered PTFE (Spectralon) integrating sphere, making use of the amplifying nature of the multiple internal reflections in the sphere cavity to study the signal produced by a change in reflectance of the PTFE coating with temperature. A Spectralon integrating sphere was used because sintered PTFE is more widely used in integrating spheres and as flat panel reflectors. Pressed PTFE and sintered PTFE exhibit slightly different properties in reflectance [18], although they are based on the same raw material.

2. Materials and Methods

A. Experimental Setup

The change in total hemispherical reflectance (hereafter referred to as reflectance) of PTFE, over the temperature range 14°C–28°C was measured relative to the reflectance at a reference temperature of 14°C. The output flux from the exit port of a temperature-controlled PTFE integrating sphere was measured during the experiment with a stabilized and monitored input flux of monochromatic light. The use of an integrating sphere for this application is apt because the calculated flux from the sphere's exit port is very sensitive to changes in the reflectance of the PTFE sphere due to the multiple reflections that occur inside the sphere's cavity. The use of an integrating sphere rather than a flat panel reflector also allowed the PTFE to be heated and cooled uniformly because the integrating sphere's aluminum casing provided good thermal conductance around the PTFE material, which was relatively thick (~10 mm), and a poor thermal conductor.

The experiment was carried out in a temperature-controlled laboratory at the National Physical Laboratory (NPL). The integrating sphere was placed in contact with a copper plate inside the thermally insulated chamber, and the copper plate was temperature controlled by circulating water from a water bath as shown in Fig. 1.

A 5 mW intensity-stabilized He–Ne laser with a wavelength of 633 nm was directed via a beam splitter into the integrating sphere input port. The flux

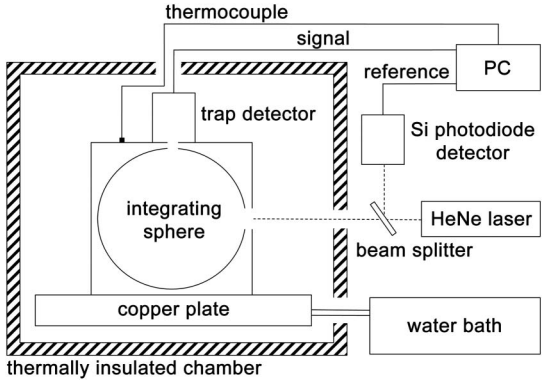

Fig. 1. Schematic of the experiment setup.

from the exit port of the PTFE integrating sphere was measured using a reflectance trap detector over a period of 18 h as the temperature of the sphere was incrementally increased. The light in the trap detector undergoes a total of 5 internal reflections between 3 Hamamatsu S1337 PN photodiode detectors and the photocurrent from all 3 detectors are summed to produce the measured output current. The multiple reflections in the trap detector result in almost no net reflectance (<0.25%) and an external quantum efficiency near 1, leading to a response that is relatively insensitive to external factors, such as ambient humidity [19]. The second beam from the beam splitter was a reference beam, and a silicon photodiode detector was used to monitor its intensity. The signal from each detector was logged to a PC with an integration time of 5 s.

Quinn *et al.* [13] found that a minimum of 2 h was required for PTFE to reach a steady state volume after heating through part of the transition temperature. For this reason, the temperature of the water bath was incremented at 3 h intervals, allowing stabilization at temperatures of 14°C, 17°C, 21°C, 24°C, and 28°C. The temperature of the integrating sphere was monitored with a type-T thermocouple attached to the aluminum casing of the sphere and the data was logged to the PC.

The flux from the integrating sphere's exit port was corrected for drifts in the laser radiant power during the experiment by taking the quotient of the signal from the trap detector and the signal from the reference beam. A correction for the temperature response of the trap detector was not applied because the effect was considered negligible (the temperature coefficient at a wavelength of 633 nm over the temperature range studied for the Hamamatsu silicon photodiode detectors is $< -0.01\%\,°C^{-1}$). No dark current correction was applied to the measurement of exit port flux because the ratio of signal to dark current was found to be in excess of 3×10^4 and therefore the temperature sensitivity of the dark current has a negligible uncertainty contribution.

To test that the observed change in output flux was not due to the temperature response of the detector, or other factors related to the experiment setup, the experiment was repeated by substituting the

PTFE integrating sphere with a barium sulfate coated integrating sphere (that has no known temperature sensitivities over the temperature range studied), which showed no detectable change in signal over the temperature range of interest.

B. Relationship Between Sphere Radiance, Output Flux, Thermal Expansion, and Reflectance

The integrating sphere radiance is the photon flux density per unit solid angle of light emitted from the surface of the sphere and is a function of input flux, sphere diameter, reflectance, and port fraction and is given by [20]

$$L = \frac{\Phi_i}{\pi A_s} \times \frac{\rho}{1-\rho(1-f)}, \tag{1}$$

where L is the integrating sphere radiance, Φ_i is the input flux, A_s is the surface area of the integrating sphere, ρ is the reflectance of the PTFE sphere, and f is the sphere port fraction. The port fraction is the ratio of the surface area of the sphere's ports to the surface area of the sphere [20].

The input flux and port fraction remain constant with temperature but the surface area of the sphere will change with temperature owing to thermal expansion of the sphere. The total change in radiance may be written as

$$\delta L = \left(\frac{\partial L}{\partial r_s}\right)\delta r_s + \left(\frac{\partial L}{\partial \rho}\right)\delta\rho, \tag{2}$$

where r_s is the radius of the integrating sphere at the reference temperature of 14°C, ρ is the reflectance of the PTFE sphere at the reference temperature, and L is the integrating sphere radiance.

Partial differentiation of Eq. (1) with respect to r_s and ρ and substitution into Eq. (2) gives

$$\frac{\delta L}{L} = \frac{-2\delta r_s}{r_s} + \frac{\delta\rho}{\rho} \times \frac{\rho}{1-\rho(1-f)}. \tag{3}$$

The first term in Eq. (3) is the effect of thermal expansion and the second term is the effect of a change in reflectivity.

The measurement system (Fig. 1) has a detector mounted externally to the integrating sphere at a short distance from the sphere exit port. There are no additional apertures and therefore the PTFE integrating sphere exit port and the detector size define the radiometric measurement configuration.

The radiometric flux onto the detector is given by [20]

$$\Phi = A_p \Omega_{\mathrm{det}-p} L, \tag{4}$$

where A_p is the port area and $\Omega_{\mathrm{det}-p}$ is the solid angle subtended by the detector from the port.

The signal on the detector is proportional to the incident flux. Therefore the change in detector signal can be given by

$$\frac{\delta\Phi}{\Phi} = \frac{\delta A_p}{A_p} + \frac{\delta\Omega_{\mathrm{det}-p}}{\Omega_{\mathrm{det}-p}} + \frac{\delta L}{L}. \tag{5}$$

The final term in Eq. (5) is given by Eq. (3). The solid angle subtended by the detector from the exit port does not change with temperature, and therefore the second term in Eq. (5) is zero. The relative change in exit port size is calculated by a derivative of the circular port area, πr_p^2, with respect to port radius, r_p, thus

$$\frac{\delta A_p}{A_p} = \frac{2\delta r_p}{r_p}. \tag{6}$$

The port aperture is formed from the PTFE sphere and the relative change in radius of the port owing to thermal expansion is equivalent to the relative change in radius of the sphere under the assumption of isotropic linear expansion $\delta r_p/r_p = \delta r_s/r_s$. Therefore the first term in Eq. (5) cancels out with the first term in Eq. (3), and combining Eqs. (3), (5), and (6) gives

$$\frac{\delta\Phi}{\Phi} = \frac{\delta\rho}{\rho} \times \frac{\rho}{1-\rho(1-f)}. \tag{7}$$

Therefore, for the experiment described, where the sphere exit port is one of the radiance-defining apertures, the change in flux with temperature depends solely on the change in the reflectivity of the PTFE sphere. Thus, the relative change in reflectance, $\delta\rho/\rho$, can be determined without accurate knowledge of the PTFE expansion coefficient or other geometrical information.

The multiplicative term, $\rho/(1-\rho(1-f))$ in Eq. (7), termed the sphere multiplier, represents the gain in sensitivity to reflectance due to the multiple reflections within an integrating sphere relative to a flat panel. Given the high reflectivity of PTFE ($\rho \sim 0.99$) and the small port fraction used here, this sphere multiplier, and the magnitude of the enhanced sensitivity, is of the order of 20.

Equation (4) is an approximation, where the constant solid angle assumption is only true for "small" solid angles. The approximation has been compared to the fuller configuration factor treatment [21] and found to hold for the specific measurement configuration. The fractional change in configuration factor with port area expansion over the full temperature range considered in this study has been calculated to be ~0.001%, so allows for the simplified treatment presented here.

C. System Stability

Prior to undertaking the experiment, the stability of the illumination source was measured by monitoring the flux from the PTFE sphere for a 12 h period at a constant temperature of 14°C. The results are shown in Fig. 2. No change in flux was observed and the

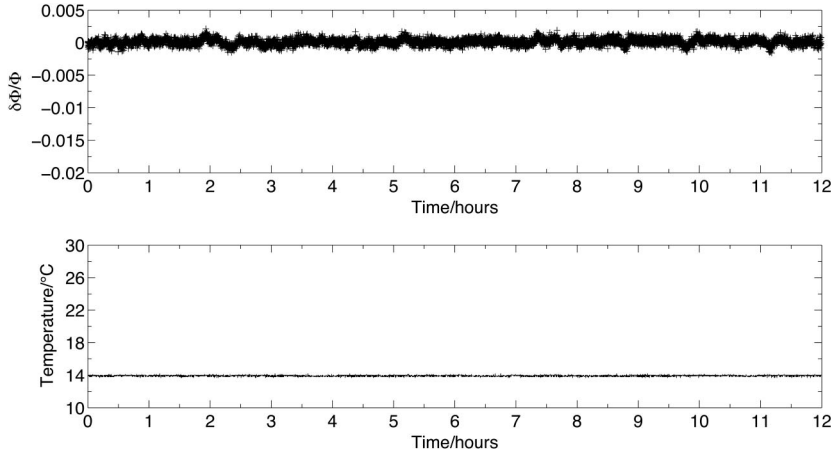

Fig. 2. Relative change in flux (top) and temperature (bottom) over a 12 h period for the PTFE integrating sphere, demonstrating the stability of the measurement setup.

relative standard deviation of the signal, $\sigma(\Phi)/\Phi$, was $\sim 5 \times 10^{-4}$.

3. Results

The relative change in integrating sphere output flux with temperature and time is presented in Fig. 3 for the PTFE sphere, and in Fig. 4 for the barium sulfate sphere. The output flux from each integrating sphere was averaged over the final 30 min period of each temperature step and the data are presented in Fig. 5. The uncertainty bars in Fig. 5 represent two standard deviations (2σ) of the averaged measurements of output flux.

Inspection of Fig. 3 demonstrates that the output flux from the PTFE integrating sphere decreases with each increment in the temperature, leading to a total decrease of $1.82 \pm 0.21\%$ in output flux between 14°C and 28°C. Within the measurement uncertainty, there is no detectable effect on the output flux from the barium sulfate sphere over the same temperature range, demonstrating that the change in output flux with temperature in Fig. 3 is due to the phase transition in PTFE, and not an artifact of the measurement system.

The magnitude of the decrease in output flux with temperature from the PTFE sphere is largest in the temperature steps from 17°C to 21°C (~0.75% of magnitude); compared to a decrease in output flux between 14°C and 17°C of approximately 0.17% and between 24°C and 28°C of approximately 0.20% of the total observed magnitude change. The position of greatest change in output flux correlates with the position of the 19°C phase transition, where PTFE undergoes a first-order phase change from phase II to phase IV [15]. The relative change in reflectance of the PTFE coating over the temperature range 14°C–28°C from the reference temperature at 14°C has been calculated using Eq. (7) and is presented in Fig. 6. The total decrease in reflectance over temperature range 14°C–28°C is $0.09 \pm 0.02\%$.

The uncertainty associated with the calculated reflectance is dominated by the limited knowledge of the sphere multiplier. The relative change in reflectivity is calculated from the sphere reflectance and the port fraction, itself a function of the sphere and

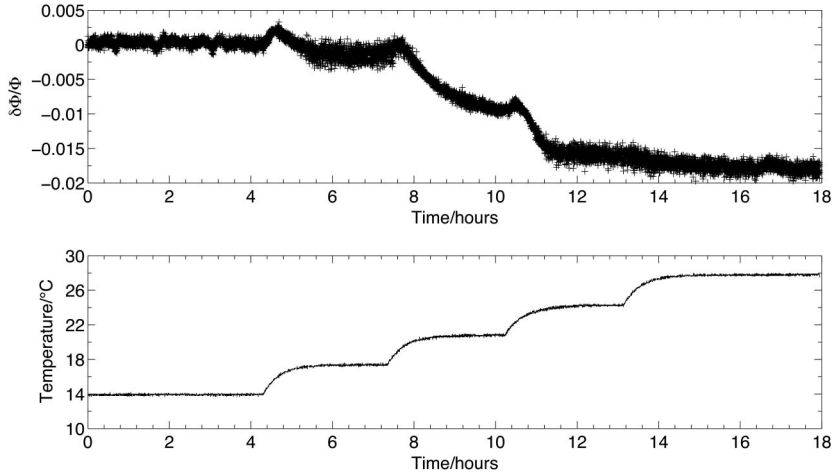

Fig. 3. Relative change in flux (top) and the measured temperature (bottom) of the PTFE integrating sphere, when the temperature is increased in a stepwise fashion.

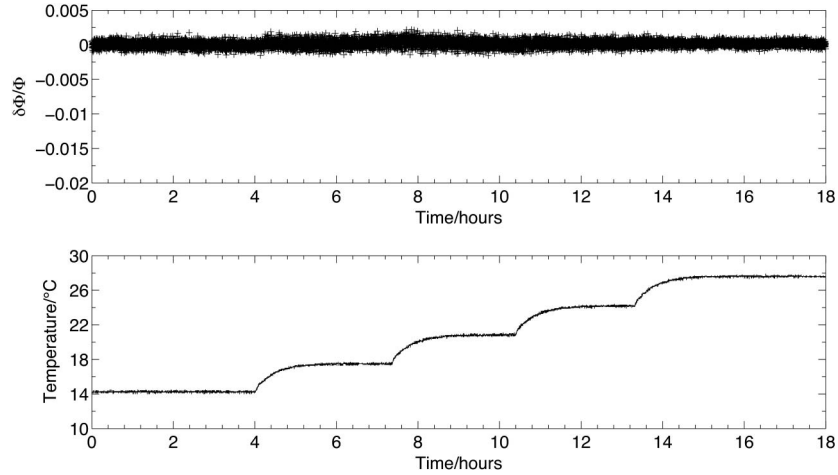

Fig. 4. Relative change in flux (top) and the measured temperature (bottom) of the barium sulfate integrating sphere, when the temperature is increased in a stepwise fashion.

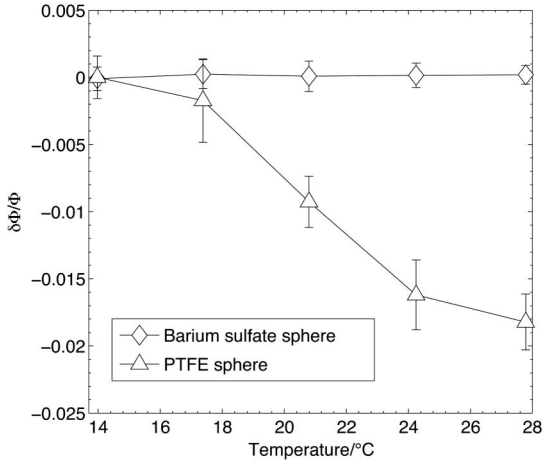

Fig. 5. Relative change in output flux with temperature for the PTFE sphere and the barium sulfate sphere. Uncertainty bars are given at 2σ.

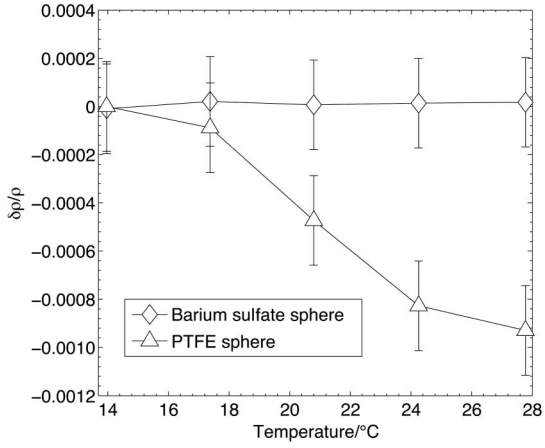

Fig. 6. Relative change in reflectance with temperature from 14°C to 28°C for the PTFE sphere and the barium sulfate sphere. Uncertainty bars are calculated using the standard error of the averaged measurements with an additional uncertainty term of 20% owing to uncertainty associated with the sphere multiplier.

port areas. Since these terms are only known approximately, a conservative estimate of 20% is given to the uncertainty associated with the sphere multiplier. The uncertainty in the port multiplier dominates the uncertainty budget, relegating the RMS noise contribution to a negligible component and meaning that the uncertainty associated with the measured signal ratio is insignificant.

4. Discussion

The discussion leading to the derivation of Eq. (7) associates all the observed change in output flux to the PTFE reflectance, for this particular experimental setup. It should be noted that this is not automatically the case, so should be evaluated for any alternative configuration. The temperature at which the greatest change in output flux from the PTFE sphere is observed correlates with the position of the phase change identified in the literature at 19°C. A control experiment with a barium sulfate sphere has confirmed that the output flux changes observed are not a consequence of the experimental setup.

Equation (7) assumes isotropic linear expansion, whereby the relative change in the sphere and exit port radii as a function of thermal expansion are equivalent. The integrating sphere is contained within an aluminum box, which could potentially restrict the free expansion of the sphere. However, the cancellation of terms in Eq. (7) does not require a detailed knowledge of the internal strain, only that the forces acting on the sphere are to first-order isotropic. Through analysis of the construction of the apparatus, the authors do not find a realistic mechanism that could produce significant anisotropic behavior.

There is, however, some temporal smearing of the effect across the temperature range. This suggests that the full phase transition is not contained solely in the 17°C–21°C temperature range, but extends above 21°C. The rapid flattening of the curve beyond 11 h in Fig. 3 suggests that there is little effect above

24°C. The observed width of the transition is likely to be widened by temperature gradients across the sphere exacerbated by the low thermal conductivity of the PTFE material. Further studies could be performed to better understand this behavior with measurements over narrower temperature steps and longer stabilization periods between these steps. However, the observations presented here suggest that researchers using PTFE as a reflectance medium anywhere in the 17°C–24°C temperature range should consider the effect of the material phase transition, and also consider the likely magnitude of any temperature gradients that may exist in the experimental setup.

An approximate 1% change in the density of PTFE across the 19°C phase transition temperature is predicted for pressed PTFE [13–15], with the reflectance of pressed PTFE known to be dependent on its density [11]. Given this prior knowledge, a change in reflectance of PTFE owing to a change in the density of the PTFE caused by the phase transition at 19°C is a likely explanation for the observed change in output flux from the PTFE sphere. Owing to the amplifying effect of the sphere multiplier, a change of $1.82 \pm 0.21\%$ in output flux represents only a small change ($0.09 \pm 0.02\%$) in the reflectance of the PTFE sphere. For the majority of applications using a PTFE flat panel reflector as a reference standard, and particularly in field studies, this small change is unlikely to be a significant contribution to the uncertainty budget.

The effect on output flux from a PTFE integrating sphere is significantly larger. Therefore, neglecting to correct for, or adequately stabilize, the temperature when operating in this temperature regime would introduce a significant source of error for measurements of flux, irradiance, or radiance made from PTFE integrating spheres. From Eq. (1), the magnitude of the effect observed is dependent on the specific dimensions of the integrating sphere. For example, the effect will be magnified with decreasing port fraction.

The phase transition of PTFE may also have a small effect on the bidirectional reflectance (BRDF) of the PTFE material. The use of an integrating sphere prevents the investigation of this effect. However, investigation of the BRDF over the PTFE phase transition may be important for flat panel reflectors, and is worthy of investigation.

The experiment required a very stable collimated beam, hence a He–Ne laser was used, and thus the study presented here investigated the change in reflectance at a single wavelength of 633 nm. The reflectance of PTFE across the UV–VIS wavelengths is effectively constant and the temperature-dependent phase change is a bulk material mechanism, so a wavelength dependence in the temperature induced reflectance change is considered very unlikely.

The phase transition of PTFE at a temperature of 19°C (with smeared effect to a few degrees each side of this temperature) is of particular importance as it is a typical operating temperature for both field studies in many temperate zones of the planet and laboratory studies. Depending on the configuration, environmental challenges, and uncertainty requirements of the measurement, the optimal strategy will be one of temperature monitoring and application of a correction algorithm and/or active temperature stabilization.

5. Conclusion

The relative change in output flux at 633 nm from a sintered PTFE (Spectralon) integrating sphere over the room temperature phase transition of PTFE at 19°C was measured as $1.82 \pm 0.21\%$ for a change in temperature from 14°C to 28°C. The change in flux from the integrating sphere is related to the PTFE phase transition at 19°C as a result of a change in density of the PTFE, and has been explained by a small change of $0.09 \pm 0.02\%$ in total hemispherical reflectance of the PTFE material. These results have implications for both field and laboratory studies that make use of PTFE as a flat panel reflector or within an integrating sphere in room temperature conditions. The magnitude of effect observed is strongly dependent on the measurement configuration, and may vary for pressed PTFE. The maximum effect is observed when PTFE is employed in a multiple reflection scenario, such as in an integrating sphere.

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