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Characterization of the Temperature Dependence of Brewer Spectrophotometer

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Introduction

Ozone calculation in Brewer can be summarized as:

$$TOC = \frac{R_6 - ETC - B}{A\mu}$$

Where:

$$R_6 = \sum_{i=1}^{n} w_i F(\lambda_i)$$

$$F(\lambda_i) = 10^4 log(I(\lambda_i))$$

$$ETC = \sum_{i=1}^{n} w_i F_0(\lambda_i)$$

$$B = \nu \frac{p}{p_0} \sum_{i=1}^{n} w_i \beta(\lambda_i)$$

$$A = \sum_{i=1}^{n} w_i \alpha(\lambda_i)$$

Classic definition of linear temperature coefficient τ

$$I = I_c - \tau_0 (T - T_0) \qquad I_c = \frac{I}{1 - \tau(T - T_0)}$$

$$\tau = \tau_0 / I_c$$

Brewer definition of Temperature coefficient τ_b

$$ln(I_c) \simeq ln(I) + \tau (T - T_0)$$

$$10^4 log(I_c) \simeq 10^4 log(I) + \tau_b T$$

$$F_c = F + \tau_b T \qquad \tau_b = 10^4 log(e) \tau$$

Brewer definition of Relative Temperature coefficient τ'_b

$$\tau'_b(\lambda_i) = \tau_b(\lambda_i) - \tau_b(\lambda_0)$$

By definition the weights verify:

$$\sum_{i=1}^{n} w_i = 0$$

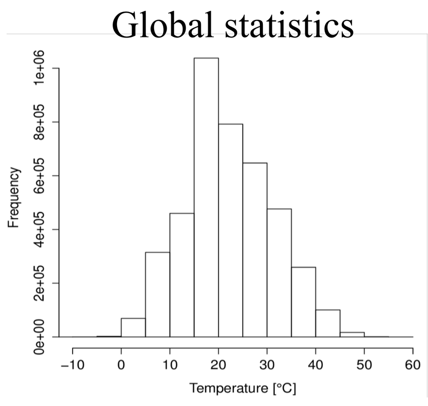
so R6 can be calculated either using the standard or relative coefficients:

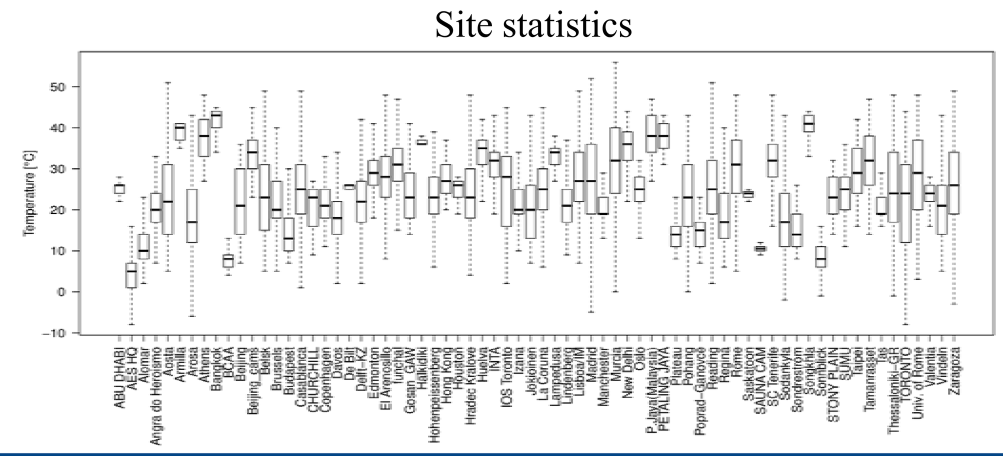
The relative coefficients are preferably used as they can be calculated even if the light source is not stable during the temperature coefficients determination. It is only required that the change of the light source is proportional in all wavelengths.

$$R_6 = \sum_{i=1}^{n} w_i F_c(\lambda_i) = \sum_{i=1}^{n} w_i F(\lambda_i) + \sum_{i=1}^{n} w_i \tau_b(\lambda_i) T = $$
$$= \sum_{i=1}^{n} w_i F(\lambda_i) + \sum_{i=1}^{n} w_i \tau'_b(\lambda_i) T$$

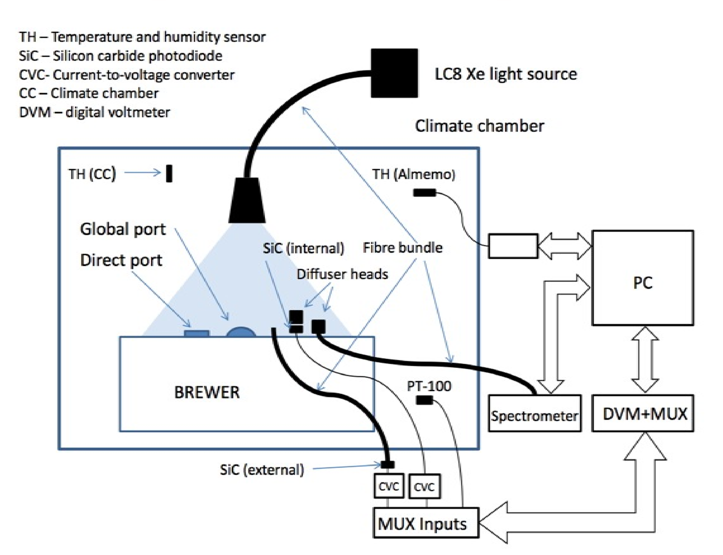
$$F(\lambda_i) - F(\lambda_0) = F(\lambda_i) - F(\lambda_0) - \tau'_b(\lambda_i) T$$

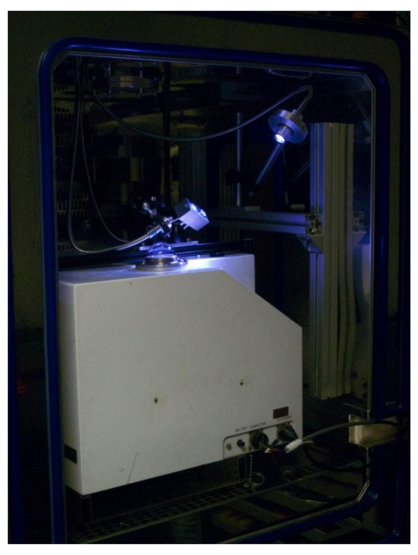
Statistics of operative instrument temperature from The EUBREWNET database





Description of the experiment





Set of measurements repeated during the experiment:

Mode	Input Port	Duration (min)	Cycles	Filter1	Filter2
ozone	Internal Lamp	10	20	256	0
aod	Internal Lamp	20	10	256	0/64
uv	Internal Lamp	15	4	256	0
ozone	Global Port	5	50	128	0
aod	Global Port	15	10	128	0
uv	Global Port	10	1	128	0
ozone	Direct Port	5	20	256	0/64
aod	Direct Port	15	10	256	0/64
uv	Direct Port	10	1	256	64

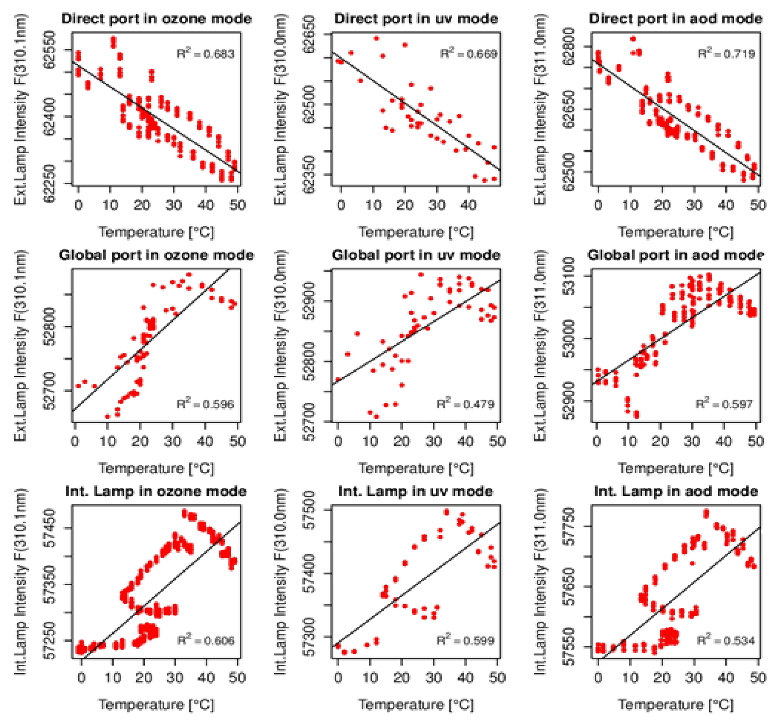
The reference RBCC-E Brewer spectrometer #185 was characterized for the temperature dependencies in a temperature controlled climate chamber at PTB facilities. The temperature of the climate chamber was varied between -5 °C to +40 °C over a ~ 90 h period.

A Hamamatsu LC8 UV source with a built-in Xe lamp equipped with a quartz fiber bundle as a light guide was used to illuminate simultaneously both global direct input ports of the Brewer. To monitor the output stability of the UV source, a set of monitor detectors were placed close to the Brewer input ports.

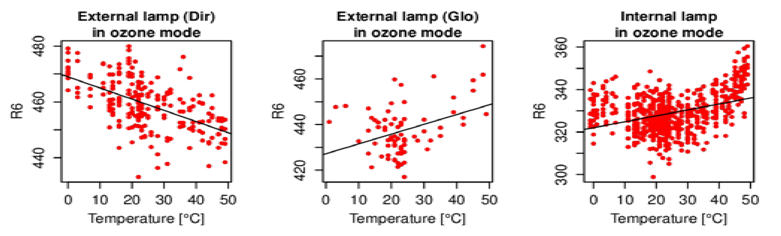
The internal halogen lamp was also used for the temperature characterization.

A first analysis of the measurements

F(λ) (before temperature correction) vs. Temperature parameter for 3 different modes and 3 different light sources.



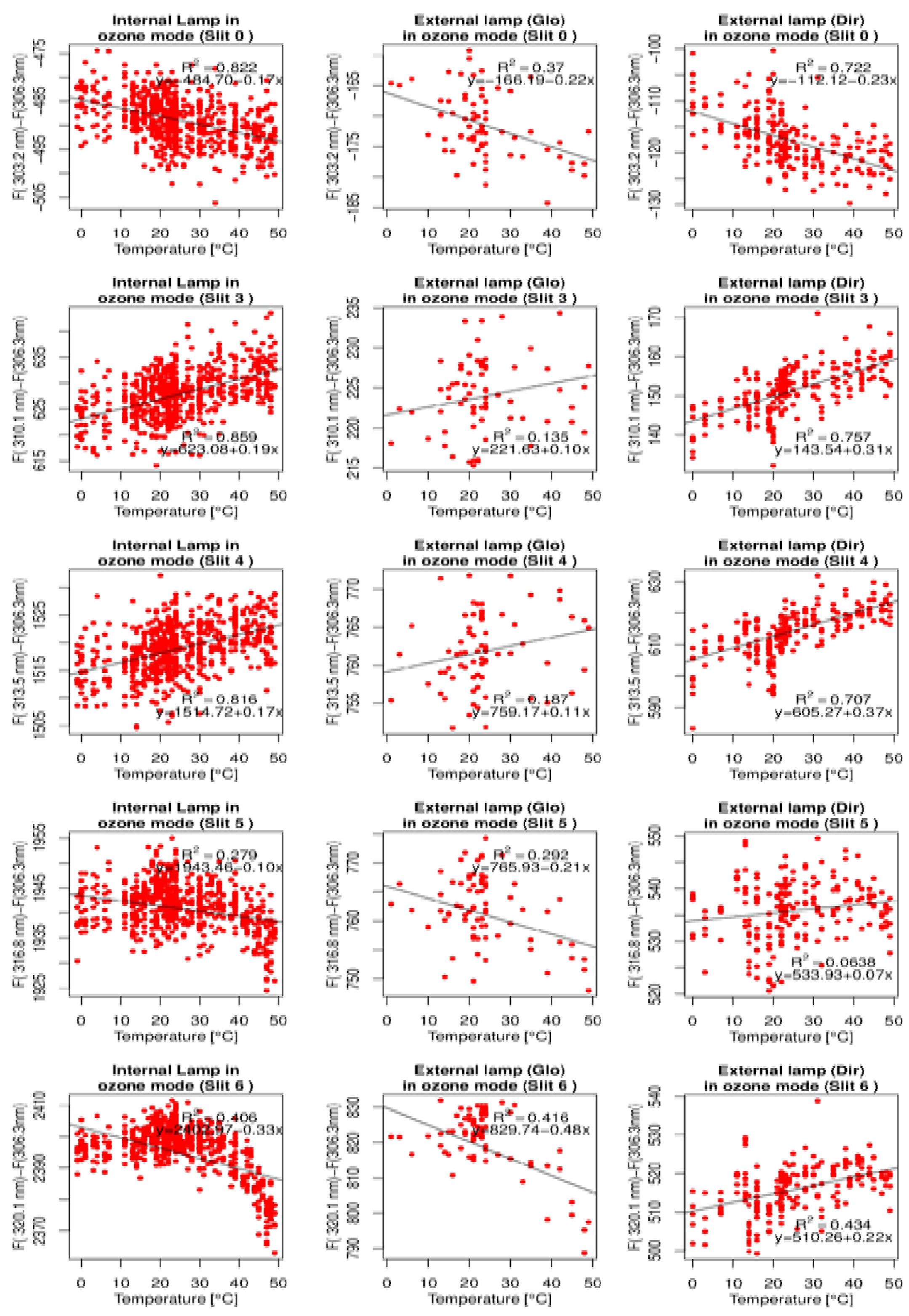
R6 parameter for measurements in ozone mode before temperature correction for 3 different light sources

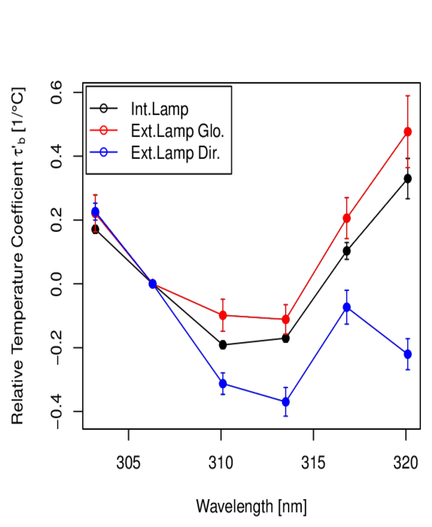


The measurements made using the internal lamp show some discontinuities, suggesting an unstable behavior of the lamp. Therefore we can only make an analysis of relative temperature coefficient with these measurements.

R6 parameter obtained from the measurements to the external lamp (Dir) shows a significant different behavior than the other two cases. This may reveal faults in direct measures, probably an alignment failure.

Relative Temperature coefficients in ozone mode



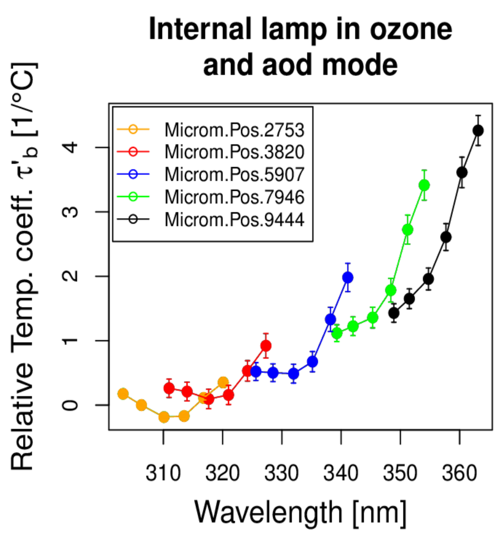


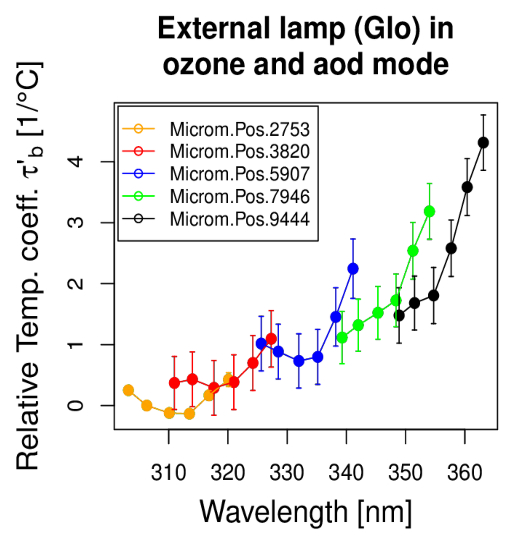
Relative temperature coefficients are similar in the case of internal and external lamp using global port, while being noticeably different from those obtained using the external lamp through the direct port. Again this may suggests that direct port measurements were affected by some kind of problem.

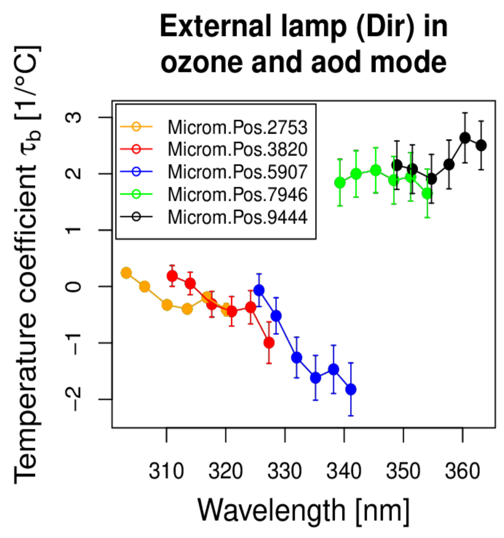
It is worth noting that the temperature dependence for the slit 5 and 6 show a nonlinear behavior above 30°C, which is more evident for internal lamp measurements.

Relative Temperature coefficients in AOD mode

We can see here the relative temperature coefficients for ozone and AOD modes retrieved using measurements to the internal lamp and to the external lamp through the global and direct Brewer ports. Relative temperature coefficients are calculated with respect to the coefficient at wavelength 306.3 nm in ozone mode.







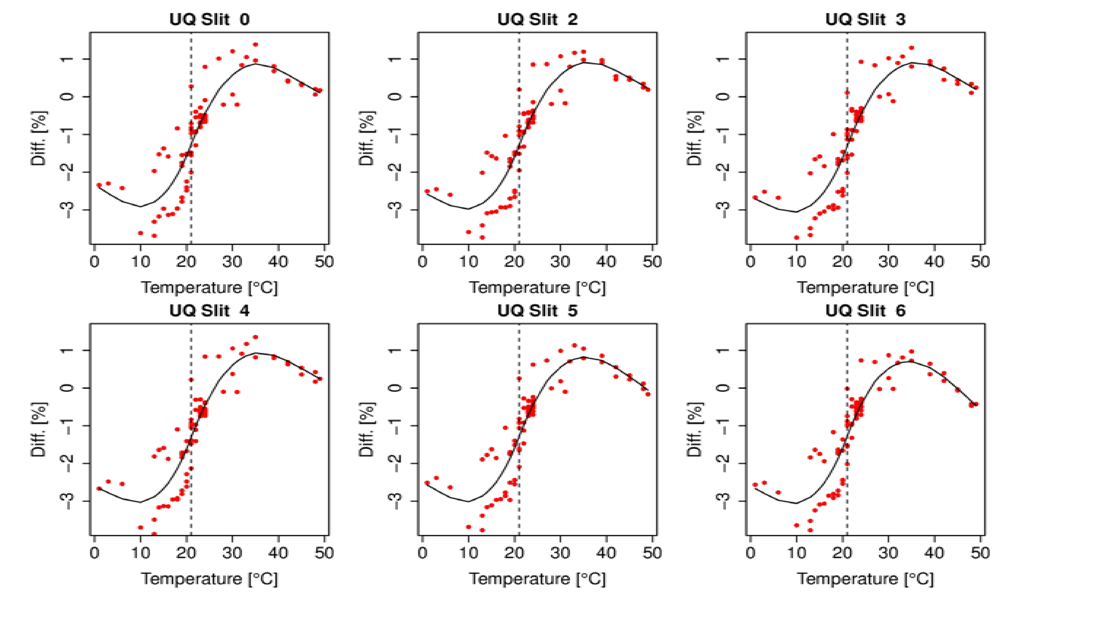
Results obtained from the measurements to the internal lamp and the external lamp through the global port are very similar despite using different light sources. However difference with the coefficients obtained from measurements to the external lamp through the direct port in AOD mode are even more important than in the case of ozone mode.

The coefficients obtained from the measurements of the internal lamp and through the global port show that the temperature coefficients will be different for each combination of micrometer position and slit.

We can see also that the temperature coefficients for nearly coincident wavelengths may be notably different if they are retrieved using different micrometer positions. This may indicates that the temperature effect is not due to optical elements such as the detector or filters, but it is mainly due to the monochromator. This happens even if we have made an alignment of the monochromator using HPHG routines in each cycle. New measures will be needed to clarify this point.

Effect of PTFE diffuser on the instrument temperature dependence

The following graphs show the change in % of the measurement to the external lamp through the global port.

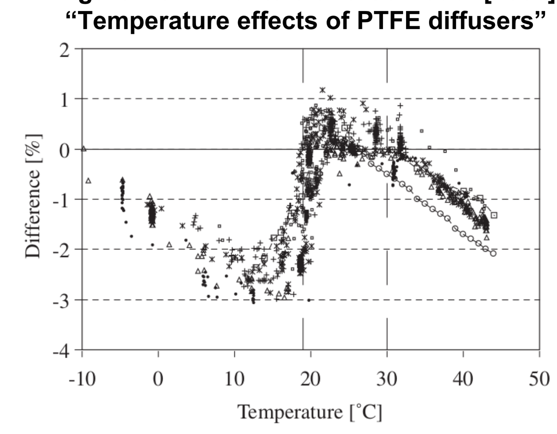


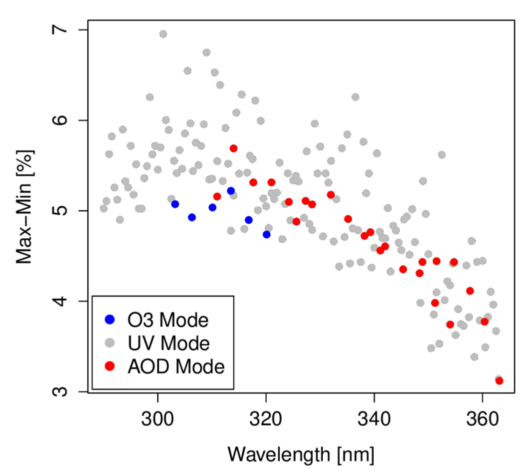
These measures are very similar compared to results obtained by other authors studying temperature dependence of PTFE diffusers. Ylianttila and Schreder [2005] describe an increase of about 4% in PTFE transmittance at about 19°C.

In our measurements we can observe that the increase in transmittance varies with wavelength from 5% at 300nm to about 3% at 360nm.

This non-linear temperature dependence can hinder the treatment of UV Brewer measurements.

Figure from Ylianttila and Schreder [2005] "Temperature effects of PTFE diffusers"





Acknowledgments

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