

A NEWLY DEVELOPED KRISS OZONE STANDARD REFERENCE PHOTOMETER

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Abstract: A new standard reference photometer (SRP) for ambient ozone measurement was developed and its performance was characterized. The *Guide to the Expression of Uncertainty in Measurement (GUM)* approach was followed to estimate uncertainty budget for the KRISS O₃ SRP.

Keywords: ozone, standard reference photometer, uncertainty.

1. INTRODUCTION

Elevated ambient ozone concentrations have adverse impacts on human health and ecosystem. Korea Ministry of Environment has promulgated enhanced ambient air quality standards (60 nmol/mol for 8-hour average, 100 nmol/mol for 1-hour average) for ozone since 1993. It is essential to establish national reference method not only for accurate measurement, but also for effective implementation of air quality management policy. The reference method for ambient ozone measurement is based on ultraviolet (UV) photometry [1]. This study describes a new ozone standard reference photometer (SRP) developed by KRISS and its uncertainty budget.

2. A NEWLY DEVELOPED KRISS OZONE STANDARD REFERENCE PHOTOMETER

The basic principle of the KRISS O₃ SRP is to determine the absorption of ultraviolet radiation at a specific wavelength, 253.7 nm, by ozone in air. The concentration of ozone is calculated by converting the transmittance of UV radiation through the Beer-Lambert Law.

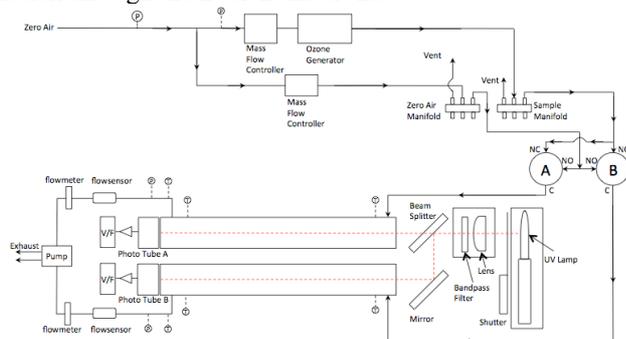


Figure 1. Schematic Diagram of KRISS O₃ SRP-3

The description of the KRISS O₃ SRP is shown in Figure 1. The SRP consists of two parts; one is an optical bed with electronic board, and the other is a flow controller with ozone generator. The SRP measures the absorption of ozone and reference air flowing through the two cells of the optic bed. The SRP has two optical cells to overcome the instability of UV light source (i.e., a low pressure mercury lamp). The number concentration (C) and mole fraction (x) of ozone is calculated from

$$C = \frac{-1}{\sigma L_{opt}} \frac{T_{mes}}{P_{mes}} \frac{P_{std}}{T_{std}} \ln(F), \quad (1)$$

$$x = \frac{-1}{\sigma L_{opt}} \frac{R}{N_A} \frac{T_{mes}}{P_{mes}} \ln(F), \quad (2)$$

where σ is the absorption cross-section of ozone ($1.1476 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$) at 253.7 nm in standard conditions of temperature and pressure [2]. L_{opt} is the optical path length of two cells, T_{mes} is the temperature measured in the cells, T_{std} is the standard temperature (273.15 K), P_{mes} is the measured pressure, P_{std} is the standard pressure (101.325 kPa), R is the gas constant, $8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$, N_A is the Avogadro constant, $6.022142 \times 10^{23} \text{ mol}^{-1}$ and F is the product of transmittances of two cells, defined as

$$F = \tau_A \tau_B = \left(\frac{f_{ozone}}{f_{ref}} \right)_A \times \left(\frac{f_{ozone}}{f_{ref}} \right)_B, \quad (3)$$

where f_{ozone} is the UV radiation intensity (as frequency) measured in the cell when ozone/air mixtures flow and f_{ref} is the UV radiation intensity measured in the cell when only reference air flows, τ_A is the transmittance of the cell A and τ_B is the transmittance of cell B.

3. UNCERTAINTY ESTIMATION

The model equation for uncertainty estimation is the same in the equation 2. The combined standard uncertainty for the measurement of ozone mole fractions can be expressed as in equation (4) according to the GUM.

$$\frac{u^2(x)}{x^2} = \frac{u^2(F)}{(F \ln F)^2} + \frac{u^2(\sigma)}{L_{opt}^2} + \frac{u^2(T_{mes})}{T_{mes}^2} + \frac{u^2(P_{mes})}{P_{mes}^2}, \quad (4)$$

The equation (4) can be rearranged as

$$u(x) = \sqrt{(u(F)B)^2 + \left[\left(\frac{u(L_{opt})}{L_{opt}} \right)^2 + \left(\frac{u(\sigma)}{\sigma} \right)^2 + \left(\frac{u(T_{mes})}{T_{mes}} \right)^2 + \left(\frac{u(P_{mes})}{P_{mes}} \right)^2 \right] x^2} \quad (5)$$

where F is assumed as approximately 1 for the measurement range and B is a constant term defined by

$$B = \frac{-RT_{mes}}{\sigma L_{opt} N_A P_{mes}}, \quad (6)$$

The uncertainty budget for the measurement of ozone mole fractions with the KRISS O₃ SRP is summarized in Table 1.

4. CONCLUSIONS

The KRISS O₃ SRP has been developed to measure ozone mole fractions in air and the uncertainty of its measurements have evaluated. The characteristics of the KRISS O₃ SRP will be confirmed through the BIPM.QM-K1. Since then, the SRP will be used as the reference for the measurement of ambient ozone in Korea.

5. REFERENCES

- [1] R.J. Paur, A.M. Bass, and J.E. Noris, T.J. Buckley, "Standard Reference Photometer for the Assay of Ozone in Calibration Atmospheres", NISTIR 6369, 2003.
- [2] J. Viallon, P. Moussay, J.E. Norris, F.R. Guenther, and R.I. Wielgosz, "A Study of Systematic Biases and Measurement Uncertainties in Ozone Mole Fraction Measurements with the NIST Standard Reference Photometer", Metrologia, vol. 43, pp. 441-450, 2006.

Table 1. Uncertainty Budget for the measurement of ozone mole fractions with KRISS O₃ SRP

Component (y)	Source	Distribution	Standard Uncertainty	Combined Standard Uncertainty $u(y)$	Sensitivity Coefficient, $c_i = \partial x / \partial y$	Contribution to $u(x)$, $ c_i \times u(y)$, nmol/mol
Optical path L_{opt} , cm	Measurement scale	Rectangular	0.003	0.52	$-x / L_{opt}$	$2.89 \times 10^{-3} x$
	Variability	Rectangular	0.03			
	Divergence	Rectangular	0.52			
Pressure P , kPa	Pressure gauge	Rectangular	0.029	0.032	$-x / P$	$3.23 \times 10^{-4} x$
	Difference between cells	Rectangular	0.014			
Temperature T , K	Temperature probe	Rectangular	0.029	0.09	$-x / P$	$2.15 \times 10^{-4} x$
	Temperature bias	Rectangular	0.058			
Ratio of intensities F	Resolution	Rectangular	1.38×10^{-6}	1.21×10^{-5}	$-x / F \ln(F)$	0.24
	Repeatability	Triangular	1.20×10^{-5}			
Absorption cross-section σ , cm ² /molecule	Hearn value		1.22×10^{-19}	1.22×10^{-19}	$-x / \sigma$	$1.06 \times 10^{-2} x$