

Laboratory Air Pollution / Environmental Technology

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Certificate-No. 5214028540-O3-2

Date: 2022-03-15

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Order-No. 5214028540
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Calibration Certificate

| | | |
|---------------------------------|--|--|
| Test object: | Ozone calibrator Calibration settings | Type: Thermo Scientific 49i-PS S/N 1404860524 COEF 1.000, BKG -0.3 |
| Primary standard: | Ozone primary standard NIST, Gaithersburg | type SRP S/N 15 |
| Measurement Conditions: | Date of the calibration: Location: | 2022-03-09/10 Empa Dübendorf Air-conditioned laboratory (LA 028) |
| | Environmental conditions: | Temperature: 23.0 ± 1.0 °C Pressure: 970.8 – 974.2 hPa |
| | Absorption coefficient (α): | 308.32 cm ⁻¹ (Base e, 1013hPa, 273.15K, 253.7nm) |
| | Warm-up time: | >24 hours |
| | Conditioning: | >2 hours at 500 nmol mol ⁻¹ ozone |
| | Zero air / ozone generator: | The zero air unit and the ozone generator of the SRP were used. |
| Measurement program: | A measurement cycle consisted of ozone measurements at 11 mole fractions, ranging between 0 – 250 nmol mol ⁻¹ . Nine measurement cycles were made. | |
| Measurement uncertainty: | The reported expanded uncertainty of measurement is stated as the standard uncertainty of measurement multiplied by the coverage factor k = 2, which for a normal distribution corresponds to a coverage probability of approx. 95%. | |

This calibration certificate documents the traceability to internationally recognised standards in accordance with the International System of Units (SI).

The measurements, the uncertainty with confidence probability and calibration methods are given on the following pages and are part of the certificate.

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The test results are valid solely for the object tested. The use of the test reports for the purpose of publicity, the mere reference to them or publication of excerpts require approval by Empa.

Results: The result of the comparison between the Thermo Scientific 49i-PS #1404860524 ozone calibrator (OC) and the Empa ozone reference (SRP) is shown in the following table.

Table 1: Mean values computed over at least five minutes for the comparison between the Thermo Scientific 49i-PS #1404860524 ozone calibrator (OC) and the NIST Standard Reference Photometer (SRP).

| Run | SRP | sd SRP | OC | sdOC | OC-SRP | OC-SRP (%) |
|-------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|------------|
| Index | (nmol mol ⁻¹) | |
| 1 | -0.06 | 0.29 | 0.19 | 0.06 | 0.25 | NA |
| 2 | 100.34 | 0.26 | 100.79 | 0.07 | 0.45 | 0.45 |
| 3 | 228.14 | 0.28 | 228.64 | 0.20 | 0.50 | 0.22 |
| 4 | 88.87 | 0.21 | 89.15 | 0.20 | 0.27 | 0.31 |
| 5 | 200.73 | 0.29 | 201.12 | 0.15 | 0.39 | 0.19 |
| 6 | 252.37 | 0.30 | 252.80 | 0.14 | 0.43 | 0.17 |
| 7 | 60.79 | 0.30 | 60.98 | 0.17 | 0.19 | 0.31 |
| 8 | 32.65 | 0.23 | 32.83 | 0.09 | 0.18 | 0.56 |
| 9 | 173.85 | 0.31 | 174.52 | 0.15 | 0.67 | 0.39 |
| 10 | 128.13 | 0.38 | 128.42 | 0.12 | 0.29 | 0.23 |
| 11 | 152.09 | 0.39 | 152.35 | 0.16 | 0.26 | 0.17 |
| 12 | -0.10 | 0.17 | 0.22 | 0.11 | 0.33 | NA |
| 13 | 89.55 | 0.23 | 89.85 | 0.33 | 0.30 | 0.34 |
| 14 | 252.44 | 0.57 | 253.00 | 0.23 | 0.56 | 0.22 |
| 15 | 201.37 | 0.39 | 201.84 | 0.16 | 0.47 | 0.23 |
| 16 | 60.58 | 0.25 | 60.93 | 0.15 | 0.35 | 0.58 |
| 17 | 229.05 | 0.19 | 229.48 | 0.15 | 0.43 | 0.19 |
| 18 | 176.88 | 0.27 | 177.21 | 0.18 | 0.33 | 0.19 |
| 19 | 101.26 | 0.19 | 101.68 | 0.13 | 0.42 | 0.41 |
| 20 | 151.86 | 0.19 | 152.31 | 0.11 | 0.45 | 0.30 |
| 21 | 125.60 | 0.28 | 125.68 | 0.21 | 0.08 | 0.07 |
| 22 | 32.36 | 0.28 | 32.72 | 0.18 | 0.35 | 1.09 |
| 23 | 253.33 | 0.27 | 253.88 | 0.18 | 0.55 | 0.22 |
| 24 | 176.86 | 0.22 | 177.30 | 0.21 | 0.44 | 0.25 |
| 25 | -0.13 | 0.16 | 0.28 | 0.12 | 0.41 | NA |
| 26 | 100.19 | 0.26 | 100.66 | 0.17 | 0.47 | 0.46 |
| 27 | 225.16 | 0.20 | 225.52 | 0.18 | 0.36 | 0.16 |
| 28 | 60.59 | 0.38 | 60.97 | 0.23 | 0.38 | 0.63 |
| 29 | 151.55 | 0.24 | 152.04 | 0.18 | 0.49 | 0.32 |
| 30 | 88.96 | 0.25 | 89.35 | 0.18 | 0.39 | 0.44 |
| 31 | 32.32 | 0.19 | 32.71 | 0.15 | 0.39 | 1.22 |
| 32 | 200.05 | 0.26 | 200.67 | 0.15 | 0.62 | 0.31 |
| 33 | 125.11 | 0.23 | 125.48 | 0.14 | 0.37 | 0.30 |
| 34 | 201.43 | 0.26 | 201.73 | 0.13 | 0.30 | 0.15 |
| 35 | 254.30 | 0.28 | 254.80 | 0.21 | 0.50 | 0.20 |
| 36 | 176.90 | 0.31 | 177.32 | 0.18 | 0.42 | 0.24 |
| 37 | 125.48 | 0.23 | 125.83 | 0.14 | 0.35 | 0.28 |
| 38 | 101.57 | 0.21 | 101.84 | 0.10 | 0.27 | 0.26 |
| 39 | 89.15 | 0.31 | 89.37 | 0.11 | 0.22 | 0.25 |
| 40 | 151.83 | 0.24 | 152.26 | 0.14 | 0.43 | 0.28 |
| 41 | 32.49 | 0.34 | 32.70 | 0.16 | 0.21 | 0.65 |
| 42 | 61.22 | 0.25 | 61.55 | 0.09 | 0.33 | 0.53 |

| Run | SRP | sd SRP | OC | sdOC | OC-SRP | OC-SRP (%) |
|-------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|------------|
| Index | (nmol mol ⁻¹) | |
| 43 | -0.03 | 0.37 | 0.34 | 0.11 | 0.37 | NA |
| 44 | 225.35 | 0.23 | 225.83 | 0.09 | 0.48 | 0.21 |
| 45 | 101.44 | 0.16 | 101.81 | 0.16 | 0.37 | 0.36 |
| 46 | 125.49 | 0.32 | 126.07 | 0.12 | 0.58 | 0.47 |
| 47 | 0.12 | 0.28 | 0.13 | 0.13 | 0.01 | NA |
| 48 | 198.28 | 0.23 | 198.79 | 0.14 | 0.51 | 0.26 |
| 49 | 225.36 | 0.35 | 225.80 | 0.18 | 0.44 | 0.20 |
| 50 | 89.17 | 0.16 | 89.74 | 0.16 | 0.57 | 0.64 |
| 51 | 61.38 | 0.33 | 61.51 | 0.09 | 0.14 | 0.22 |
| 52 | 175.96 | 0.26 | 176.36 | 0.12 | 0.40 | 0.23 |
| 53 | 32.67 | 0.35 | 32.76 | 0.09 | 0.09 | 0.28 |
| 54 | 151.54 | 0.30 | 151.82 | 0.18 | 0.28 | 0.18 |
| 55 | 249.86 | 0.20 | 250.34 | 0.28 | 0.48 | 0.19 |
| 56 | 125.54 | 0.21 | 125.90 | 0.14 | 0.36 | 0.29 |
| 57 | 176.59 | 0.37 | 176.95 | 0.20 | 0.36 | 0.20 |
| 58 | 200.99 | 0.37 | 201.55 | 0.10 | 0.56 | 0.28 |
| 59 | 150.34 | 0.52 | 150.65 | 0.16 | 0.31 | 0.21 |
| 60 | 61.29 | 0.36 | 61.60 | 0.12 | 0.31 | 0.50 |
| 61 | 225.10 | 0.18 | 225.72 | 0.15 | 0.62 | 0.27 |
| 62 | 101.87 | 0.28 | 101.98 | 0.13 | 0.11 | 0.11 |
| 63 | 250.14 | 0.36 | 250.36 | 0.18 | 0.22 | 0.09 |
| 64 | 32.55 | 0.44 | 32.84 | 0.11 | 0.29 | 0.89 |
| 65 | 0.12 | 0.32 | 0.28 | 0.11 | 0.15 | NA |
| 66 | 90.44 | 0.24 | 90.76 | 0.30 | 0.31 | 0.35 |
| 67 | 100.92 | 0.32 | 101.19 | 0.11 | 0.27 | 0.27 |
| 68 | 89.88 | 0.18 | 90.29 | 0.09 | 0.41 | 0.46 |
| 69 | 152.23 | 0.34 | 152.67 | 0.15 | 0.44 | 0.29 |
| 70 | 249.49 | 0.33 | 249.96 | 0.16 | 0.47 | 0.19 |
| 71 | 200.92 | 0.16 | 201.45 | 0.24 | 0.53 | 0.26 |
| 72 | -0.06 | 0.23 | 0.29 | 0.13 | 0.35 | NA |
| 73 | 225.42 | 0.29 | 226.07 | 0.19 | 0.65 | 0.29 |
| 74 | 61.49 | 0.57 | 61.42 | 0.26 | -0.07 | -0.11 |
| 75 | 176.70 | 0.29 | 176.90 | 0.17 | 0.20 | 0.12 |
| 76 | 32.73 | 0.25 | 32.97 | 0.12 | 0.24 | 0.74 |
| 77 | 126.70 | 0.34 | 127.08 | 0.13 | 0.38 | 0.30 |
| 78 | 249.80 | 0.20 | 250.44 | 0.12 | 0.64 | 0.26 |
| 79 | 125.58 | 0.43 | 126.05 | 0.14 | 0.47 | 0.37 |
| 80 | 176.79 | 0.20 | 177.18 | 0.15 | 0.39 | 0.22 |
| 81 | 89.78 | 0.35 | 90.20 | 0.10 | 0.43 | 0.48 |
| 82 | 200.52 | 0.33 | 201.02 | 0.16 | 0.50 | 0.25 |
| 83 | 32.59 | 0.39 | 32.93 | 0.11 | 0.35 | 1.06 |
| 84 | 0.09 | 0.14 | 0.21 | 0.06 | 0.12 | NA |
| 85 | 150.94 | 0.32 | 151.32 | 0.15 | 0.38 | 0.25 |
| 86 | 61.45 | 0.25 | 61.65 | 0.21 | 0.20 | 0.33 |
| 87 | 225.46 | 0.31 | 226.12 | 0.13 | 0.66 | 0.29 |
| 88 | 101.37 | 0.27 | 101.81 | 0.12 | 0.44 | 0.44 |
| 89 | 201.22 | 0.30 | 201.83 | 0.08 | 0.61 | 0.30 |
| 90 | 101.51 | 0.14 | 102.04 | 0.13 | 0.53 | 0.52 |
| 91 | 250.03 | 0.29 | 250.49 | 0.19 | 0.46 | 0.18 |

| Run | SRP | sd SRP | OC | sdOC | OC-SRP | OC-SRP (%) |
|-------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|------------|
| Index | (nmol mol ⁻¹) | |
| 92 | 177.31 | 0.48 | 177.77 | 0.09 | 0.46 | 0.26 |
| 93 | -0.10 | 0.17 | 0.35 | 0.22 | 0.45 | NA |
| 94 | 225.23 | 0.28 | 225.76 | 0.20 | 0.53 | 0.24 |
| 95 | 32.50 | 0.30 | 32.93 | 0.13 | 0.43 | 1.33 |
| 96 | 61.42 | 0.19 | 62.02 | 0.09 | 0.59 | 0.97 |
| 97 | 126.68 | 0.30 | 127.22 | 0.13 | 0.54 | 0.42 |
| 98 | 89.90 | 0.30 | 90.23 | 0.10 | 0.33 | 0.37 |
| 99 | 152.35 | 0.28 | 152.75 | 0.11 | 0.40 | 0.27 |

Pressure sensor: The pressure sensor reading of the Thermo Scientific 49i-PS #1404860524 (973.1 hPa) was compared to the reference barometer (GB-1, meteolabor AG) (973.5 hPa). The pressure sensor was adjusted to the reference pressure of 973.5 hPa before the comparison with the SRP.

Calibration settings: The calibration settings of the Thermo Scientific 49i-PS #1404860524 (BKG -0.3, COEF 1.000) were not changed before, during or after the comparison.

Calibration function: The following calibration function for the range between 0-250 nmolmol⁻¹ was determined from the comparison on 2022-03-09/10 at a temperature of 23.0±1°C and a pressure of 970.8 – 974.2 hPa. The corresponding expanded measurement uncertainties for selected amount fractions are shown in Table 2.

Reference value (SRP#15) = (0.9990 x 49i-PS#1404860524 - 0.25) nmol mol⁻¹

Table 2: Measurement uncertainties of the calibration for selected amount fractions

| Reference value (SRP#15) (nmol/mol) | Value (OC, Thermo Scientific 49i-PS) (nmol mol ⁻¹) | Expanded measurement uncertainty (U) (nmol mol ⁻¹) |
|---|---|--|
| 0 | 0.3 | 1.0 |
| 25 | 25.3 | 1.1 |
| 50 | 50.3 | 1.5 |
| 75 | 75.3 | 2.0 |
| 100 | 100.4 | 2.5 |
| 125 | 125.4 | 3.0 |
| 150 | 150.4 | 3.6 |
| 175 | 175.4 | 4.1 |
| 200 | 200.5 | 4.7 |
| 225 | 225.5 | 5.2 |
| 250 | 251.5 | 5.8 |

The measurement uncertainties given in the above table reflects the minimal uncertainty that can be guaranteed for the current state of the tested instrument. To estimate the complete uncertainty budget of a specific instrument, additional parameters such as long-term drift, temperature and pressure variability, maintenance and competence of the staff have to be considered. Thus, a careful evaluation of the uncertainty budget considering customer specific circumstances is recommended.

Figure 1 shows the linear regression of the difference between the Thermo Scientific 49i-PS #1404860524 ozone calibrator (OC) and the reference value versus the reference value, including the prediction interval (95%), and the regression residuals versus the time and the mole fraction. The measurement values of the inter-comparison are within the range of the prediction interval with a probability of 95%. The prediction interval is a measure of the uncertainty of the calibration function.

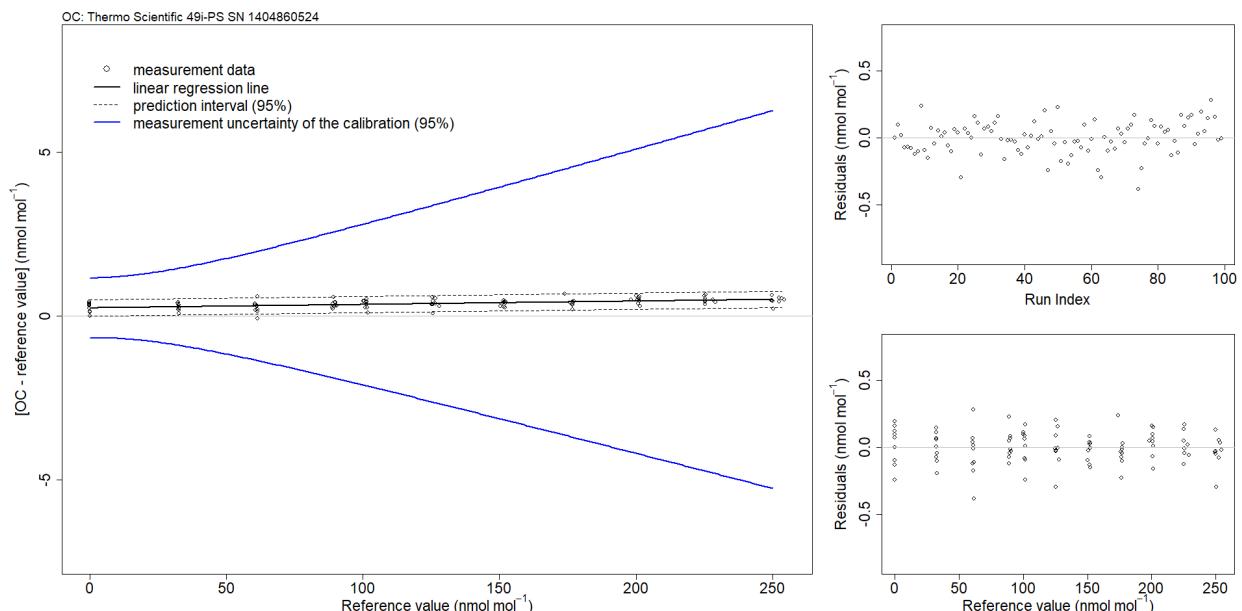


Figure 1. Left: Bias of the Thermo Scientific 49i-PS #1404860524 ozone calibrator with respect to the reference value as a function of mole fraction. Each point represents the average over at least five minutes at a given level. The dashed lines about the regression lines are 95% prediction intervals. Right: Regression residuals of the comparison as a function of time (top) and mole fraction (bottom).

Dübendorf, 15 March 2022

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