

## Laboratory Air Pollution / Environmental Technology

**Certificate-No. 5214028540-03-1**

Calibration Laboratory accredited by the Swiss Accreditation Service

**Date: 2022-03-15**

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**Multilateral Agreement for the recognition of calibration certificates**

**Pages: 5**

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# Calibration Certificate

<b>Test object:</b>	Ozone calibrator Calibration settings	Type: Thermo Scientific 49i-PS S/N 1118511036 COEF 1.013, BKG -0.3
<b>Primary standard:</b>	Ozone primary standard NIST, Gaithersburg	type SRP S/N 15
<b>Measurement Conditions:</b>	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 ( $\alpha$ ):	308.32 cm <sup>-1</sup> (Base e, 1013hPa, 273.15K, 253.7nm)
	Warm-up time:	>24 hours
	Conditioning:	>2 hours at 500 nmol mol <sup>-1</sup> ozone
	Zero air / ozone generator:	The zero air unit and the ozone generator of the SRP were used.
<b>Measurement program:</b>	A measurement cycle consisted of ozone measurements at 11 mole fractions, ranging between 0 – 250 nmol mol <sup>-1</sup> . Nine measurement cycles were made.	
<b>Measurement uncertainty:</b>	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 #1118511036 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 #1118511036 ozone calibrator (OC) and the NIST Standard Reference Photometer (SRP).

Run	SRP	sd SRP	OC	sdOC	OC-SRP	OC-SRP (%)
Index	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	
1	-0.06	0.29	0.16	0.08	0.22	NA
2	100.34	0.26	100.97	0.16	0.63	0.63
3	228.14	0.28	229.35	0.20	1.21	0.53
4	88.87	0.21	89.26	0.24	0.39	0.43
5	200.73	0.29	201.74	0.17	1.01	0.50
6	252.37	0.30	253.65	0.16	1.28	0.51
7	60.79	0.30	61.08	0.20	0.29	0.48
8	32.65	0.23	32.81	0.11	0.16	0.49
9	173.85	0.31	175.05	0.12	1.20	0.69
10	128.13	0.38	128.69	0.19	0.56	0.44
11	152.09	0.39	152.83	0.08	0.74	0.48
12	-0.10	0.17	0.23	0.08	0.34	NA
13	89.55	0.23	89.94	0.29	0.39	0.43
14	252.44	0.57	253.71	0.20	1.27	0.50
15	201.37	0.39	202.50	0.17	1.13	0.56
16	60.58	0.25	60.99	0.17	0.41	0.68
17	229.05	0.19	230.05	0.17	1.00	0.44
18	176.88	0.27	177.65	0.16	0.77	0.44
19	101.26	0.19	101.87	0.15	0.61	0.60
20	151.86	0.19	152.83	0.18	0.97	0.64
21	125.60	0.28	125.97	0.12	0.37	0.30
22	32.36	0.28	32.66	0.08	0.30	0.92
23	253.33	0.27	254.54	0.26	1.21	0.48
24	176.86	0.22	177.74	0.13	0.88	0.50
25	-0.13	0.16	0.19	0.08	0.32	NA
26	100.19	0.26	100.84	0.10	0.65	0.64
27	225.16	0.20	226.12	0.12	0.96	0.43
28	60.59	0.38	61.18	0.13	0.59	0.97
29	151.55	0.24	152.35	0.14	0.80	0.53
30	88.96	0.25	89.50	0.13	0.54	0.61
31	32.32	0.19	32.73	0.13	0.41	1.26
32	200.05	0.26	201.18	0.15	1.13	0.56
33	125.11	0.23	125.96	0.22	0.85	0.68
34	201.43	0.26	202.36	0.20	0.93	0.46
35	254.30	0.28	255.61	0.07	1.31	0.51
36	176.90	0.31	177.80	0.12	0.90	0.51
37	125.48	0.23	126.17	0.13	0.69	0.55
38	101.57	0.21	102.06	0.08	0.49	0.48
39	89.15	0.31	89.64	0.15	0.49	0.55
40	151.83	0.24	152.73	0.13	0.90	0.59
41	32.49	0.34	32.74	0.12	0.25	0.77
42	61.22	0.25	61.64	0.12	0.42	0.69

Run	SRP	sd SRP	OC	sdOC	OC-SRP	OC-SRP (%)
Index	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	
43	-0.03	0.37	0.21	0.07	0.24	NA
44	225.35	0.23	226.45	0.14	1.10	0.49
45	101.44	0.16	102.00	0.11	0.56	0.55
46	125.49	0.32	126.31	0.15	0.82	0.66
47	0.12	0.28	0.20	0.12	0.08	NA
48	198.28	0.23	199.41	0.14	1.13	0.57
49	225.36	0.35	226.42	0.15	1.06	0.47
50	89.17	0.16	89.91	0.13	0.73	0.82
51	61.38	0.33	61.62	0.12	0.24	0.39
52	175.96	0.26	176.87	0.12	0.91	0.52
53	32.67	0.35	32.76	0.15	0.09	0.28
54	151.54	0.30	152.30	0.14	0.76	0.50
55	249.86	0.20	251.17	0.21	1.31	0.52
56	125.54	0.21	126.13	0.12	0.59	0.47
57	176.59	0.37	177.40	0.13	0.81	0.46
58	200.99	0.37	201.98	0.23	0.99	0.49
59	150.34	0.52	151.01	0.15	0.67	0.45
60	61.29	0.36	61.75	0.12	0.46	0.74
61	225.10	0.18	226.44	0.17	1.34	0.59
62	101.87	0.28	102.37	0.08	0.50	0.49
63	250.14	0.36	251.22	0.16	1.08	0.43
64	32.55	0.44	32.87	0.16	0.32	0.98
65	0.12	0.32	0.20	0.09	0.08	NA
66	90.44	0.24	90.97	0.27	0.52	0.58
67	100.92	0.32	101.43	0.11	0.51	0.51
68	89.88	0.18	90.40	0.11	0.53	0.58
69	152.23	0.34	153.07	0.12	0.84	0.55
70	249.49	0.33	250.67	0.18	1.18	0.47
71	200.92	0.16	201.93	0.11	1.01	0.50
72	-0.06	0.23	0.19	0.08	0.25	NA
73	225.42	0.29	226.60	0.19	1.18	0.52
74	61.49	0.57	61.66	0.24	0.18	0.29
75	176.70	0.29	177.44	0.14	0.74	0.42
76	32.73	0.25	32.98	0.15	0.24	0.75
77	126.70	0.34	127.38	0.11	0.68	0.53
78	249.80	0.20	251.14	0.13	1.34	0.54
79	125.58	0.43	126.39	0.11	0.81	0.64
80	176.79	0.20	177.64	0.18	0.85	0.48
81	89.78	0.35	90.34	0.25	0.56	0.63
82	200.52	0.33	201.61	0.10	1.09	0.54
83	32.59	0.39	32.86	0.12	0.27	0.84
84	0.09	0.14	0.25	0.14	0.16	NA
85	150.94	0.32	151.73	0.14	0.79	0.53
86	61.45	0.25	61.84	0.12	0.39	0.64
87	225.46	0.31	226.66	0.18	1.20	0.53
88	101.37	0.27	102.02	0.15	0.65	0.65
89	201.22	0.30	202.40	0.16	1.18	0.59
90	101.51	0.14	102.22	0.08	0.71	0.70
91	250.03	0.29	251.30	0.13	1.27	0.51

Run	SRP	sd SRP	OC	sdOC	OC-SRP	OC-SRP (%)
Index	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	
92	177.31	0.48	178.34	0.11	1.03	0.58
93	-0.10	0.17	0.25	0.14	0.34	NA
94	225.23	0.28	226.40	0.22	1.17	0.52
95	32.50	0.30	32.83	0.20	0.33	1.02
96	61.42	0.19	62.08	0.13	0.66	1.08
97	126.68	0.30	127.50	0.09	0.82	0.65
98	89.90	0.30	90.52	0.16	0.62	0.69
99	152.35	0.28	153.06	0.11	0.71	0.47

**Pressure sensor:** The pressure sensor reading of the Thermo Scientific 49i-PS #1118511036 (970.5 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 #1118511036 (BKG -0.3, COEF 1.013) were not changed before, during or after the comparison.

**Calibration function:** The following calibration function for the range between 0-250 nmolmol<sup>-1</sup> 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.

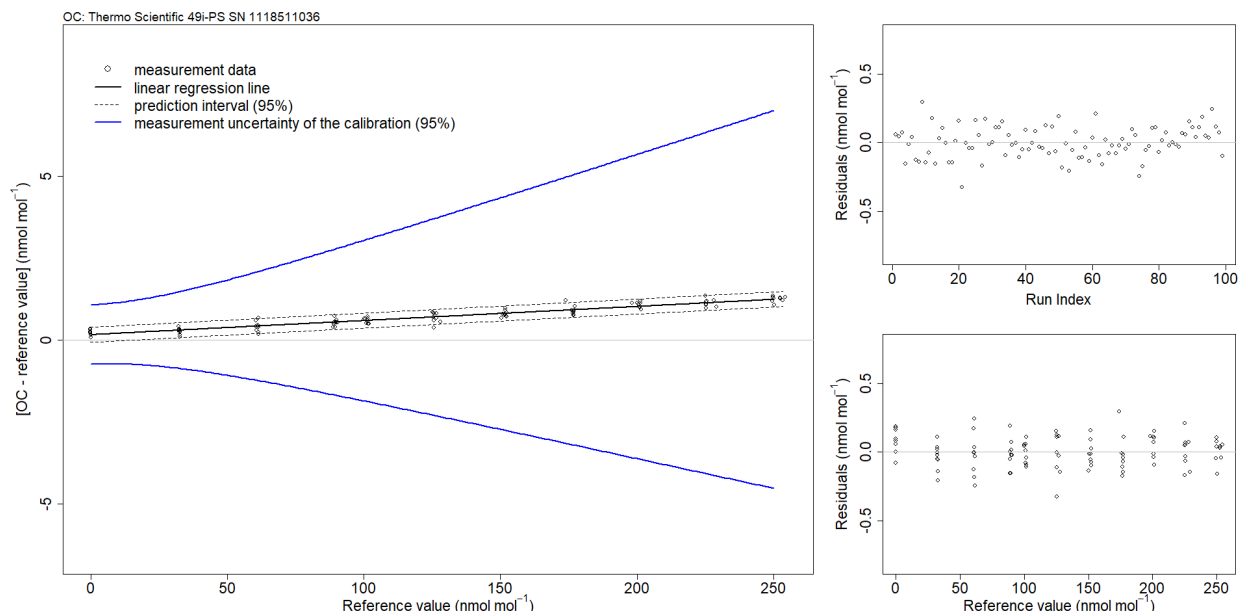
**Reference value (SRP#15) = (0.9957 x 49i-PS#1118511036 - 0.16) nmol mol<sup>-1</sup>**

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

Reference value (SRP#15)	Value (OC, Thermo Scientific 49i-PS)	Expanded measurement uncertainty (U)
(nmol/mol)	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )
0	0.2	1.0
25	25.3	1.1
50	50.4	1.5
75	75.5	2.0
100	100.6	2.5
125	125.7	3.0
150	150.8	3.6
175	175.9	4.1
200	201.0	4.7
225	226.1	5.2
250	251.2	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 #1118511036 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 #1118511036 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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