Eidgenössische Materialprüfungs- und Forschungsanstalt
Laboratoire fédéral d'essai des matériaux et de recherche
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Empa
Materials Science and Technology

Laboratory Air Pollution / Environmental Technology

Calibration Laboratory accredited by the Swiss Accreditation Service

The Swiss Accreditation Service is one of the signatories to the EA Multilateral Agreement for the recognition of calibration certificates

Certificate-No. 5214032595-O3

Date: 2023-11-13

Pages: 7

Client: CNR-ISAC
Via Gobetti 101
40129 Bologna
Italy

Order-No. 5214032595
Contact person: Paolo Cristofanelli

Calibration Certificate

Test object:	Ozone calibrator Calibration settings	Type: Thermo Scientific 49i-PS #1118511036 COEF 1.013, BKG -0.3
Primary standard:	Ozone primary standard NIST, Gaithersburg	Type Standard Reference Photometer (SRP) S/N 15
Transfer standard:	Ozone calibrator Calibration settings	Type Thermo Scientific 49i-PS #1171430027 COEF 0.991, BKG +0.0
Measurement Conditions:	Date of the calibration: Location:	2023-09-20/21 Mt. Cimone
	Environmental conditions:	Temperature: Between 15.8 and 22.3°C Pressure: Between 783.0 and 790.9 hPa
	Absorption coefficient (α):	308.32 $cm^{-1}atm^{-1}$ (Base e, 1013hPa, 273.15K, 253.7nm)
	Warm-up time: Conditioning:	>3 hours ~1 hour at 500 nmol mol^{-1} ozone
	Zero air / ozone generator:	The Empa zero air and the ozone generator of the transfer standard were used.
Measurement program:	A measurement cycle consisted of ozone measurements at eleven amount fractions, ranging between 0 – 250 nmol mol^{-1}. Each level was measured for 10 minutes, and the last 5 minutes of each level were used for the data analysis. Nine cycles were used for the certificate.	
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.

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 results of the comparison between the Thermo Scientific 49i-PS #1118511036 ozone calibrator (OC) and the Empa transfer standard (TS) are shown in the following table. The bias of the TS was corrected based on comparisons against the primary standard in the Empa calibration laboratory (see Appendix).

Table 1: *Five-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the Thermo Scientific 49i-PS #1118511036 ozone calibrator (OC) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OC (nmol mol^{-1})	sdOC (nmol mol^{-1})	OC-TS (nmol mol^{-1})	OC-TS (%)
2023-09-20 15:56	0.24	0.05	0.53	0.13	0.29	NA
2023-09-20 16:06	75.05	0.10	75.68	0.14	0.63	0.84
2023-09-20 16:16	149.99	0.05	150.68	0.29	0.69	0.46
2023-09-20 16:26	50.04	0.05	50.55	0.12	0.51	1.02
2023-09-20 16:36	249.91	0.14	251.73	0.16	1.82	0.73
2023-09-20 16:46	199.94	0.09	201.68	0.22	1.74	0.87
2023-09-20 16:56	100.01	0.08	101.15	0.15	1.14	1.14
2023-09-20 17:06	25.10	0.08	25.50	0.28	0.40	1.59
2023-09-20 17:16	175.00	0.08	176.52	0.23	1.52	0.87
2023-09-20 17:26	224.91	0.09	226.75	0.39	1.84	0.82
2023-09-20 17:36	125.06	0.03	126.12	0.16	1.06	0.85
2023-09-20 17:46	0.11	0.09	0.36	0.24	0.25	NA
2023-09-20 17:56	149.99	0.09	151.15	0.32	1.16	0.77
2023-09-20 18:08	25.13	0.12	25.38	0.15	0.25	0.99
2023-09-20 18:16	175.01	0.07	176.25	0.33	1.24	0.71
2023-09-20 18:26	199.97	0.03	201.28	0.11	1.31	0.66
2023-09-20 18:36	50.03	0.04	50.63	0.11	0.60	1.20
2023-09-20 18:46	75.08	0.09	75.94	0.21	0.86	1.15
2023-09-20 18:56	224.96	0.12	226.48	0.29	1.52	0.68
2023-09-20 19:06	100.10	0.08	101.06	0.24	0.96	0.96
2023-09-20 19:16	125.03	0.09	125.96	0.10	0.93	0.74
2023-09-20 19:26	249.98	0.06	251.79	0.15	1.81	0.72
2023-09-20 19:36	0.24	0.08	0.41	0.15	0.17	NA
2023-09-20 19:46	50.07	0.12	50.81	0.14	0.74	1.48
2023-09-20 19:56	200.02	0.06	201.59	0.08	1.57	0.78
2023-09-20 20:06	149.97	0.17	151.52	0.26	1.55	1.03
2023-09-20 20:16	100.04	0.03	100.96	0.24	0.92	0.92
2023-09-20 20:26	250.00	0.03	251.87	0.17	1.87	0.75
2023-09-20 20:36	75.03	0.05	75.87	0.15	0.84	1.12
2023-09-20 20:47	15.31	0.12	15.68	0.30	0.37	2.42
2023-09-20 20:56	175.01	0.08	176.40	0.22	1.39	0.79
2023-09-20 21:06	125.02	0.05	125.99	0.13	0.97	0.78
2023-09-20 21:16	224.96	0.11	226.78	0.20	1.82	0.81
2023-09-20 21:26	0.19	0.19	0.43	0.12	0.24	NA
2023-09-20 21:36	75.04	0.09	75.61	0.21	0.57	0.76
2023-09-20 21:46	150.02	0.06	151.07	0.19	1.05	0.70
2023-09-20 21:56	50.09	0.08	50.49	0.18	0.40	0.80
2023-09-20 22:06	249.92	0.14	251.39	0.19	1.47	0.59
2023-09-20 22:16	199.97	0.11	201.22	0.27	1.25	0.63
2023-09-20 22:26	100.07	0.09	100.95	0.30	0.88	0.88

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OC (nmol mol^{-1})	sdOC (nmol mol^{-1})	OC-TS (nmol mol^{-1})	OC-TS (%)
2023-09-20 22:36	25.11	0.12	25.48	0.14	0.37	1.47
2023-09-20 22:46	175.01	0.05	176.45	0.10	1.44	0.82
2023-09-20 22:56	225.01	0.09	226.80	0.15	1.79	0.80
2023-09-20 23:06	125.03	0.07	126.02	0.27	0.99	0.79
2023-09-20 23:16	0.26	0.08	0.19	0.08	-0.07	NA
2023-09-20 23:26	149.96	0.13	151.16	0.21	1.20	0.80
2023-09-20 23:36	25.13	0.12	25.66	0.17	0.53	2.11
2023-09-20 23:46	175.00	0.13	176.21	0.19	1.21	0.69
2023-09-20 23:56	200.06	0.07	201.48	0.30	1.42	0.71
2023-09-21 00:06	50.10	0.06	50.58	0.02	0.48	0.96
2023-09-21 00:16	75.07	0.06	75.99	0.22	0.92	1.23
2023-09-21 00:26	224.95	0.08	226.53	0.19	1.58	0.70
2023-09-21 00:36	100.01	0.08	100.95	0.08	0.94	0.94
2023-09-21 00:46	125.05	0.09	126.09	0.24	1.04	0.83
2023-09-21 00:56	249.97	0.10	251.56	0.15	1.59	0.64
2023-09-21 01:06	0.17	0.11	0.52	0.13	0.35	NA
2023-09-21 01:16	50.12	0.00	50.76	0.15	0.64	1.28
2023-09-21 01:26	200.02	0.02	201.31	0.16	1.29	0.64
2023-09-21 01:36	150.04	0.10	151.11	0.16	1.07	0.71
2023-09-21 01:46	100.09	0.09	100.75	0.29	0.66	0.66
2023-09-21 01:56	249.92	0.14	251.44	0.27	1.52	0.61
2023-09-21 02:06	75.07	0.07	75.80	0.07	0.73	0.97
2023-09-21 02:16	15.17	0.08	15.45	0.09	0.28	1.85
2023-09-21 02:26	175.04	0.07	176.25	0.09	1.21	0.69
2023-09-21 02:36	125.05	0.03	125.93	0.18	0.88	0.70
2023-09-21 02:46	224.93	0.02	226.58	0.24	1.65	0.73
2023-09-21 02:56	0.18	0.10	0.28	0.04	0.10	NA
2023-09-21 03:06	75.03	0.07	75.74	0.09	0.71	0.95
2023-09-21 03:16	150.00	0.06	151.11	0.17	1.11	0.74
2023-09-21 03:26	50.06	0.07	50.84	0.21	0.78	1.56
2023-09-21 03:36	249.94	0.04	251.58	0.15	1.64	0.66
2023-09-21 03:46	200.00	0.08	201.37	0.38	1.37	0.69
2023-09-21 03:56	100.05	0.07	100.94	0.15	0.89	0.89
2023-09-21 04:06	25.11	0.12	25.55	0.19	0.44	1.75
2023-09-21 04:16	174.95	0.08	176.40	0.16	1.45	0.83
2023-09-21 04:26	224.92	0.06	226.47	0.09	1.55	0.69
2023-09-21 04:36	125.03	0.05	126.06	0.23	1.03	0.82
2023-09-21 04:46	0.31	0.14	0.41	0.12	0.10	NA
2023-09-21 04:56	149.97	0.07	151.23	0.14	1.26	0.84
2023-09-21 05:06	25.15	0.08	25.48	0.12	0.33	1.31
2023-09-21 05:16	174.97	0.07	176.36	0.21	1.39	0.79
2023-09-21 05:26	199.96	0.10	201.22	0.26	1.26	0.63
2023-09-21 05:36	50.09	0.08	50.66	0.16	0.57	1.14
2023-09-21 05:46	75.09	0.15	75.91	0.24	0.82	1.09
2023-09-21 05:56	224.90	0.06	226.32	0.13	1.42	0.63
2023-09-21 06:06	100.08	0.11	101.13	0.20	1.05	1.05
2023-09-21 06:16	125.03	0.07	126.15	0.19	1.12	0.90

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OC (nmol mol^{-1})	sdOC (nmol mol^{-1})	OC-TS (nmol mol^{-1})	OC-TS (%)
2023-09-21 06:26	249.94	0.12	251.56	0.21	1.62	0.65
2023-09-21 06:36	0.18	0.05	0.45	0.27	0.27	NA
2023-09-21 06:46	50.16	0.08	50.75	0.11	0.59	1.18
2023-09-21 06:56	199.95	0.07	201.32	0.24	1.37	0.69
2023-09-21 07:06	150.00	0.08	150.94	0.29	0.94	0.63
2023-09-21 07:16	100.04	0.06	100.88	0.19	0.84	0.84
2023-09-21 07:26	249.89	0.03	251.84	0.31	1.95	0.78
2023-09-21 07:36	75.09	0.03	75.89	0.28	0.80	1.07
2023-09-21 07:46	15.13	0.13	15.40	0.08	0.27	1.78
2023-09-21 07:56	174.96	0.07	176.37	0.20	1.41	0.81
2023-09-21 08:06	125.03	0.05	126.26	0.16	1.23	0.98
2023-09-21 08:16	224.98	0.04	226.84	0.20	1.86	0.83

Pressure sensor: The pressure sensor of the Thermo Scientific 49i-PS #1118511036 (789.7 hPa) was compared to the reference pressure sensor of the Mt. Cimone Observatory (790.6 hPa) at ambient pressure. No adjustments were made. The pressure sensor of the transfer instrument Thermo Scientific 49i-PS #1171430027 (789.8 hPa) was also compared to the Mt. Cimone pressure reference (789.6 hPa). No adjustments were made.

Calibration settings: The calibration settings of the Mt. Cimone Thermo Scientific 49i-PS #1118511036 (BKG -0.3, COEF 1.013) ozone calibrator and the Empa Thermo Scientific 49i-PS #1171430027 (BKG 0.0, COEF 0.991) transfer standard were not changed before, during or after the comparison.

Calibration function: The following calibration function for the range between 0-250 nmol mol^{-1} was determined from the comparison on 2023-09-20/21 at a temperature of 15.8 - 22.3°C and a pressure between 783.0 and 790.9 hPa. The corresponding expanded measurement uncertainties for selected amount fractions are shown in Table 2.

Unbiased O_3 amont fraction = 0.9938 x TEI 49i-PS#1118511036 - 0.22 nmol mol^{-1}

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

Reference value (bias corrected TS) (nmol mol^{-1})	Value (OC, Thermo Scientific 49i-PS) (nmol mol^{-1})	Expanded measurement uncertainty (U) (nmol mol^{-1})
0	0.2	1.6
25	25.4	1.7
50	50.5	2.0
75	75.7	2.4
100	100.8	3.0
125	126.0	3.5
150	151.2	4.1
175	176.3	4.6
200	201.5	5.2
225	226.6	5.8
250	251.8	6.4

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 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.

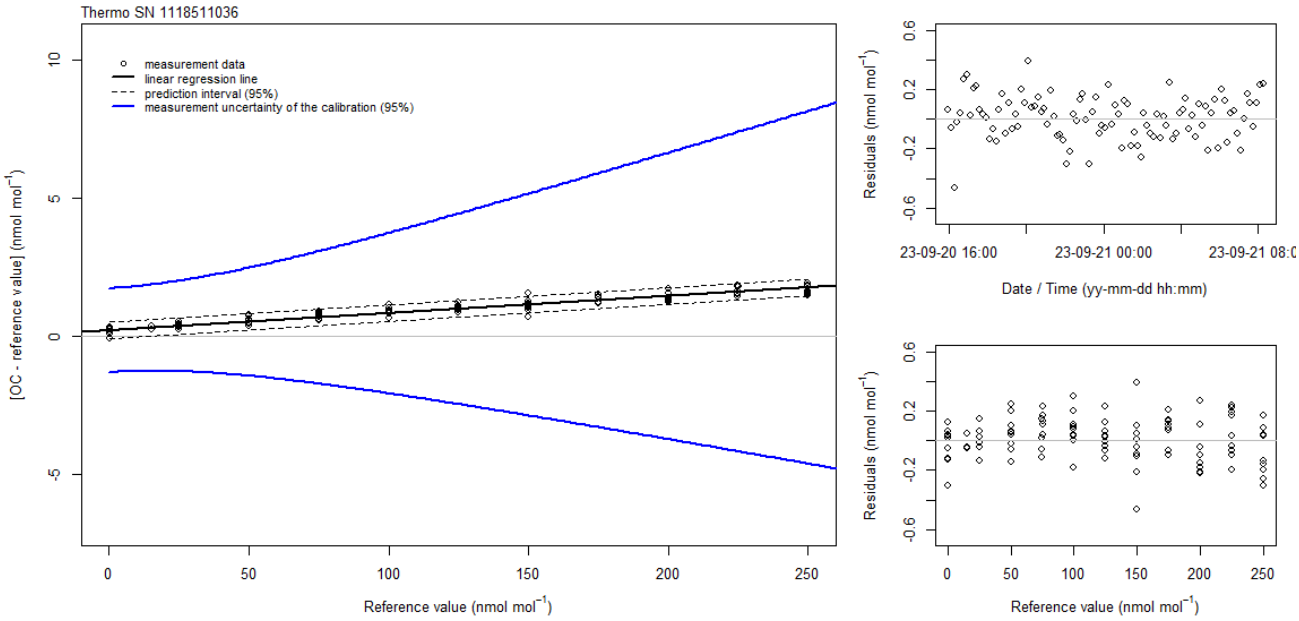

Figure 1. *Left: Bias of the Thermo Scientific 49i-PS #1118511036 ozone calibrator with respect to the reference value as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The dashed lines about the regression lines are 95% prediction intervals. Right: Regression residuals of the comparison as a function of time (top) and mole fraction (bottom).*

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Dübendorf, 13 November 2023

Empa Dübendorf,
Laboratory Air Pollution/Environmental Technology

Head of the calibration service

Digitally signed by
Christoph Zellweger
Date: 2023.11.13
17:08:06 +01'00'

Dr. C. Zellweger

Head of the Laboratory

Digital unterschrieben von
Lukas Emmenegger
Datum: 2023.11.13
17:36:14 +01'00'

Dr. L. Emmenegger

Appendix: Traceability and stability of the Empa ozone transfer standard

The Empa transfer standard (TS) was compared with the Standard Reference Photometer before and after the field use. The following instruments were used:

WCC-Empa ozone reference: NIST Standard Reference Photometer SRP #15 (Master)

WCC-Empa TS: Thermo Scientific 49i-PS #1171430027, BKG +0.0, COEF 0.991

Zero air source: Pressurized air - Dryer – Breitfuss zero air generator – Purafil – charcoal – outlet filter

The results of the TS calibration before and after the field are shown in Figure 2. The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mole fraction X_{TS} produced (and measured) by the TS can be computed with the following equation.

X_{TS} (nmol mol^{-1}) = ([TS] + 0.13 nmol mol^{-1}) / 1.0008

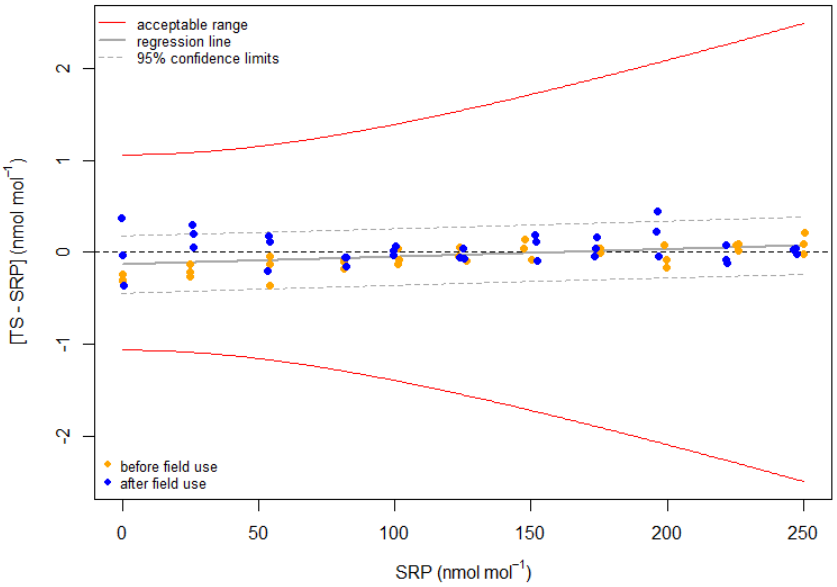

Figure 2. *Deviations between the transfer standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*