OZONE ANALYSER INTERCOMPARISON 24/06/2021
(Thermo Tei49i – SN CM08460046)

Intercomparison conditions

The intercomparison has been conducted at the ISAC "Open Lab" in Bologna. The performance of the laboratory ozone analyser (OA), Thermo TEI49i, was evaluated against the Laboratory Standard (TS), TEI49i-PS (SN 1404860524), located at the same laboratory. The TS was evaluated by EMPA on year 2018 against the Standard Reference Photometer (SRP#15). For this intercomparison, the ozone source was the TS internal ozone generator (UV lamp). The zero source was scrubbed ambient air scrubbed with purafilll© and active charcoal. <u>The intercomparison was operated after the cell cleansing, pump replacement and elimination of a broken flow sensor (Flow A).</u>

Intercomparison procedure

The TS was warmed-up for > 12 hours and conditioned by cleansing at 200 ppb for more 1 hours. Data from the OA and TS were acquired by Modbus TCP/IP with a 1-minute frequency. For the intercomparison, the 10-minute average values from OA were compared against 10-minute average values from TS.

The OA was evaluated at 9 different concentration levels ranging from 0 to 150 ppb. Zero level (0 ppb) was evaluated by flowing in the instrument ambient air scrubbed with activated charcoal. Ozone reading was corrected for T/P.
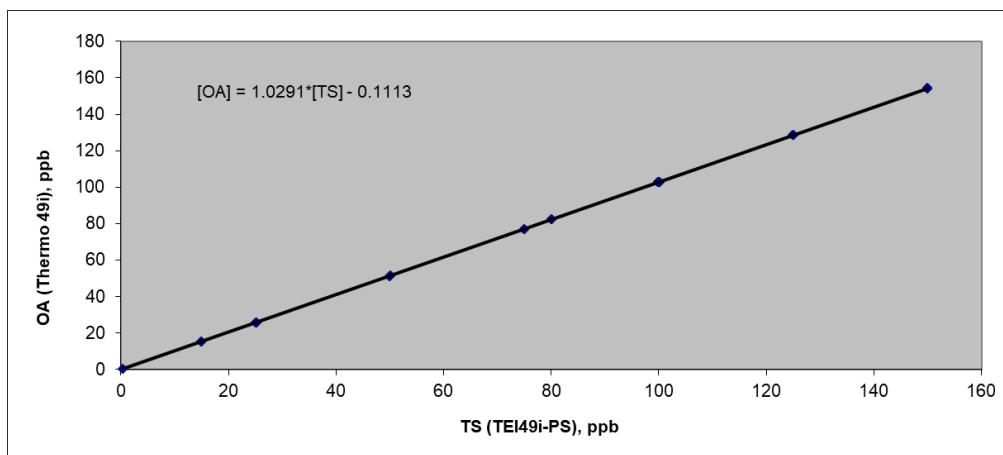
OA and TS conditions

OA (1425162557): BKG = -0.5; COEFF = 1.049
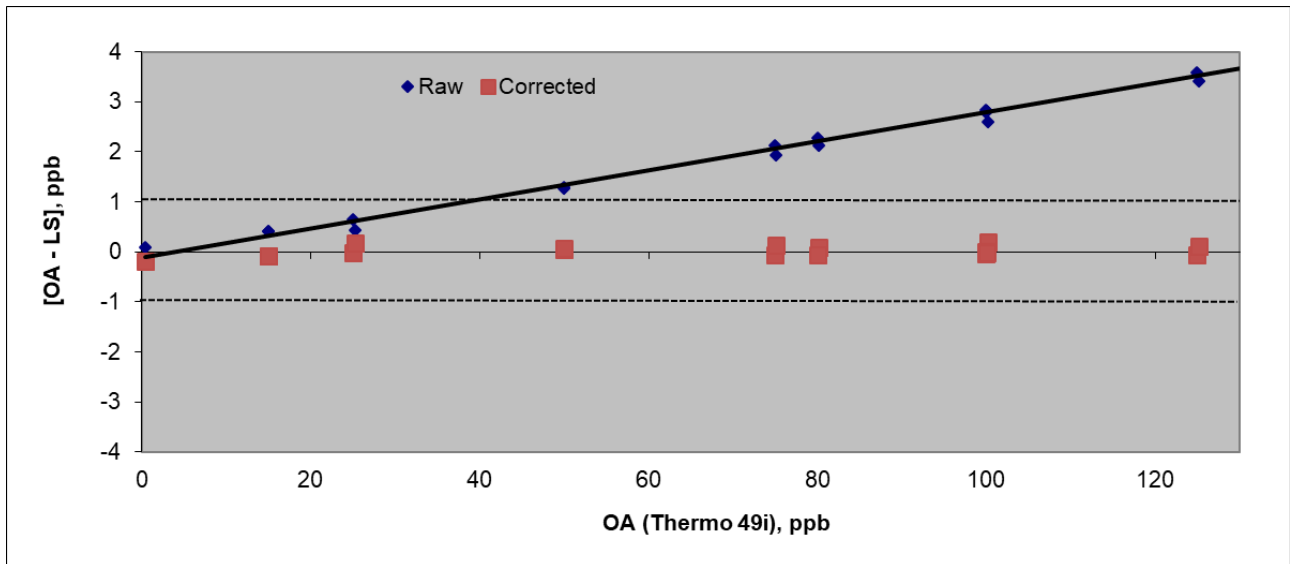TS (1404860524): BKG= -0.3 ppb, SPAN 1.000

Intercomparison results:

The TS was considered to be the independent instrument, the OA to be the dependent one. The resulting regression parameters were

$$[OA] = 1.0291 * [TS] -0.113$$

$$[OA] = 1.0291*[TS] - 0.1113$$

Scatterplot between OA and TS reading (averaged over each concentration step)

Deviation between OA and TS (blue, raw data) and OA residuals after linear correction (red). The horizontal dashed lines represent the GAW data quality objective for inter-laboratory comparability of +/- 1 ppb

Standard Reference Photometer
Calibration Report

Calibrating Institute:	ISAC-CNR				Date:	23-Jun-21	
Operator:	Francescopiero Calzolari				Start Time:	6-23-2021 0:00	
Instrument:	Thermo 49c				End Time:	6-24-2021 0:58	
Comment:	Corr T/P on				Filename:	TEI49I_20210617WCC	

Calibrated Instrument:	TEI49i			Calibration			Standard
Owner:	ISAC-CNR			Results	Value		Uncertainty
Contact:	Paolo Cristofanelli			Slope	0.97173		0.00056
Make:	Thermo Electron			Intercept	0.10859		0.05055
Model:	49i			Covariance			5.5131E-21
Serial Number:	CM08460046			Res Std Dev	0.108643326		

Calibration Parameters:	Zero Start;Randomized;Raw Saved;T/P on; BKG = -0.5; COEFF = 1.049						
Air Flow Rate:	3.5 l/min						
Lamp Intensity Range:	to						
Number Conc. Points	9		Points/Concentration:				
Conditioning:	200 ppb for 1 hours						

Calibration Data Points	TEI49iPS		TEI49i		TEI49i		Deviation (Raw - Ref)	
	Result	Std. Dev	Result	Std. Dev	Predicted	Residual		
1	74.9	0.1	77.1	0.2	75.01	-0.06	2.1	
2	149.9	0.1	154.3	0.1	150.07	-0.18	4.4	
3	124.9	0.1	128.5	0.2	124.95	-0.07	3.6	
4	25.0	0.1	25.6	0.2	25.03	-0.02	0.6	
5	100.1	0.1	102.7	0.1	99.92	0.20	2.6	
6	80.1	0.1	82.2	0.2	80.02	0.10	2.1	
7	50.0	0.1	51.3	0.2	49.98	0.05	1.3	
8	15.0	0.1	15.4	0.2	15.09	-0.09	0.4	
9	99.9	0.1	102.8	0.1	99.96	-0.03	2.8	
10	149.9	0.0	154.3	0.2	150.00	-0.07	4.3	
11	0.4	0.1	0.5	0.1	0.55	-0.18	0.1	
12	50.0	0.1	51.2	0.2	49.89	0.08	1.3	
13	25.2	0.7	25.7	0.1	25.04	0.18	0.4	
14	99.9	0.1	102.7	0.2	99.93	0.00	2.8	
15	125.1	0.1	128.5	0.2	124.99	0.11	3.4	
16	15.0	0.1	15.4	0.1	15.07	-0.07	0.4	
17	75.0	0.1	77.0	0.2	74.92	0.13	1.9	
18	100.1	0.1	102.9	0.2	100.10	-0.02	2.8	
19	80.1	0.1	82.3	0.1	80.12	-0.05	2.3	

Following Klausen et al (2003), we derived the following parameters for OA (Thermo Tei 49C) at 100 ppb levels (after correction is applied):

U_{noise}: 0.2 ppb (as the average of OA standard deviations for each calibration point)
$U_{linearity}$:0.105 ppb (as the standard deviation of the TS-OA residuals)
$U_{repeatibility}$: 0.188 ppb (SQRT($U_{noise}^2 + U_{linearity}^2$))
U_{drift}: 0.631 ppb (as derived by Klausen et al., 2003)
U_{OA}: 0.659ppb (SQRT($U_{repeatibility}^2 + U_{drift}^2$))
$U_{combined\ at\ 100\ ppb}$: 0.683 ppb (as calculated following Klausen et al (2003))

Based on these data the ozone analyser show statistically significant bias (at the 95% confidence level) in respect to TS. And the following compensation equation should be applied to obtain unbiased data:

$$[O_3^{unbiased}]= ([OA]-0.079)/1.029$$