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WMO

GAW

Empa
Materials Science and Technology

Measurements of Tropospheric Ozone

Christoph Zellweger

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Rationale for trace gas measurements

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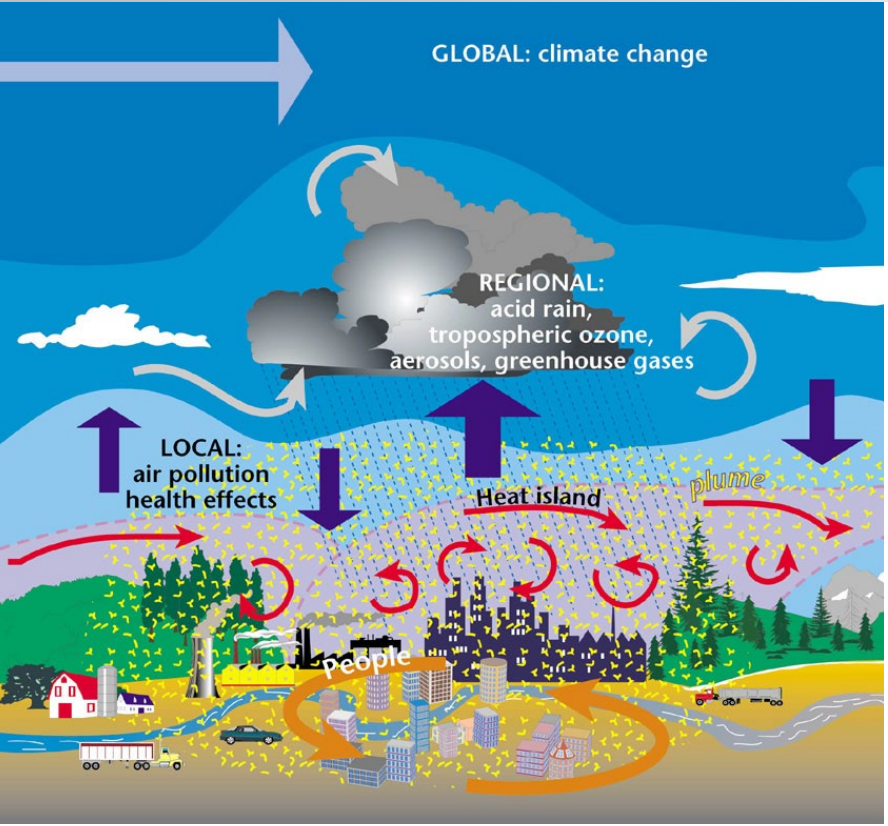


Source: Hidalgo et al.: Advances in Urban Climate Modeling, Trends and Directions in Climate Research: Ann. N.Y. Acad. Sci. 1146: 354–374 (2008).

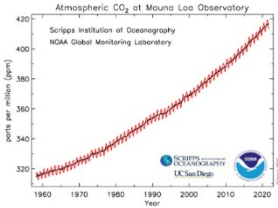
- Air Pollution and Climate – different scales.

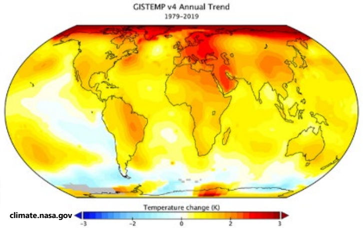
summer smog
O_3 (VOCs/NO_x)

winter smog
Particles (SO_2/NO_x/VOCs), CO

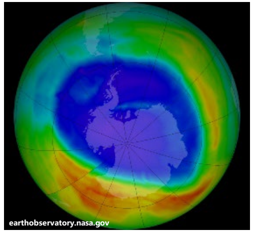
acid rain
SO_2, NO_x

global warming
CO_2/CH_4/N_2O/**O_3**/halocarbons





ozone depletion
halocarbons



- In the troposphere, near ground-level, ozone is mainly an air pollutant, threatening health and eco systems.
- Elevated ozone can lead to leaf injury, resulting in crop loss (food security).
- Ozone plays an important role in the stratosphere, absorbing UV radiation from the Sun.

Global Atmosphere Watch and other Networks

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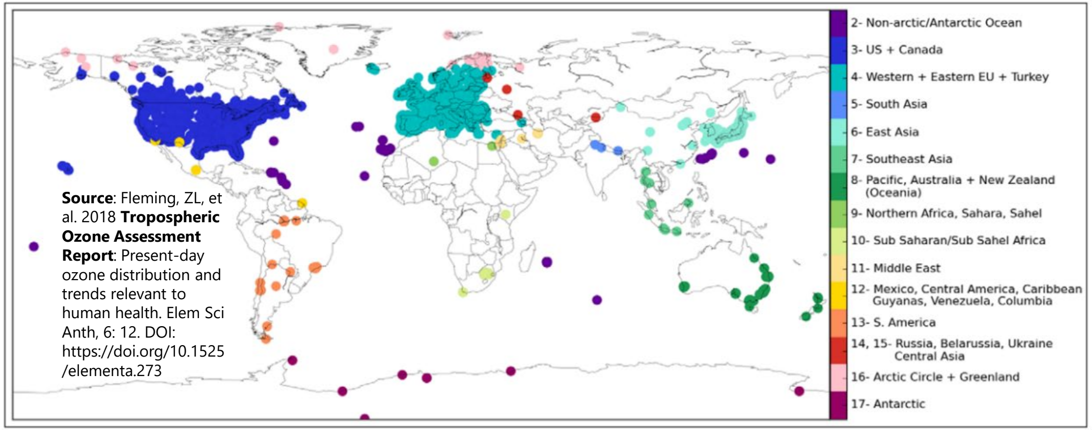
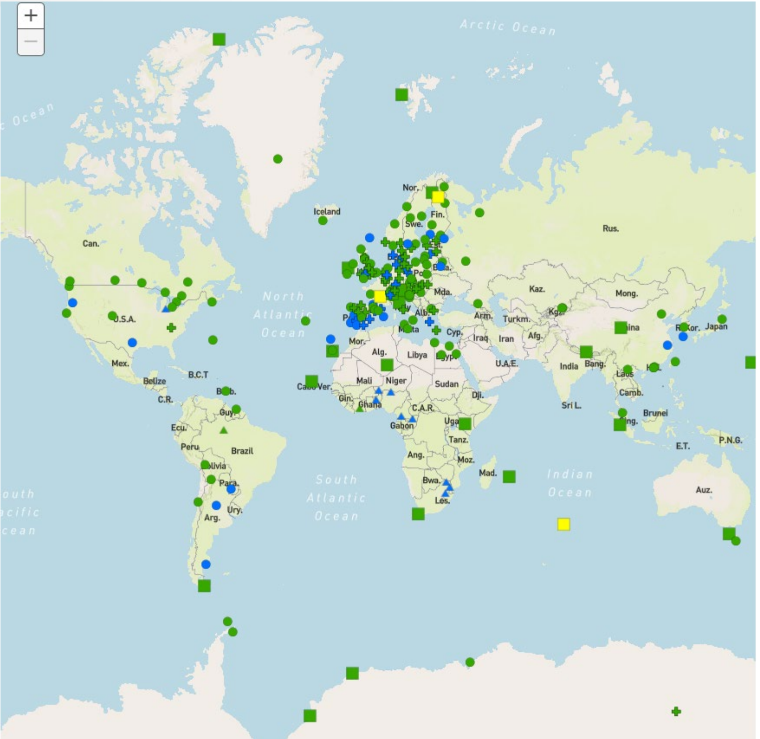
(Global) Stations of the Global Atmosphere Watch Programme



(TOAR) Ozone stations grouped into 15 world regions

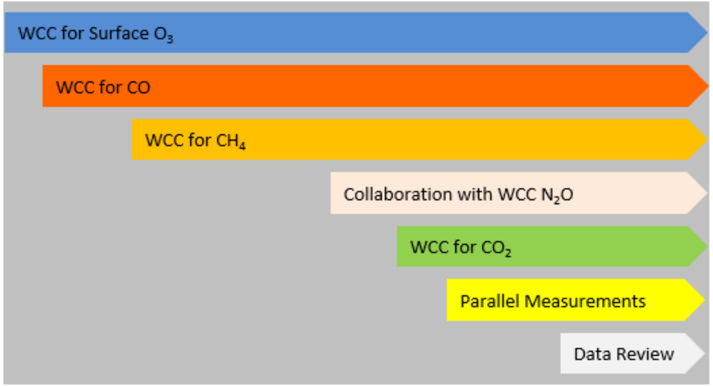


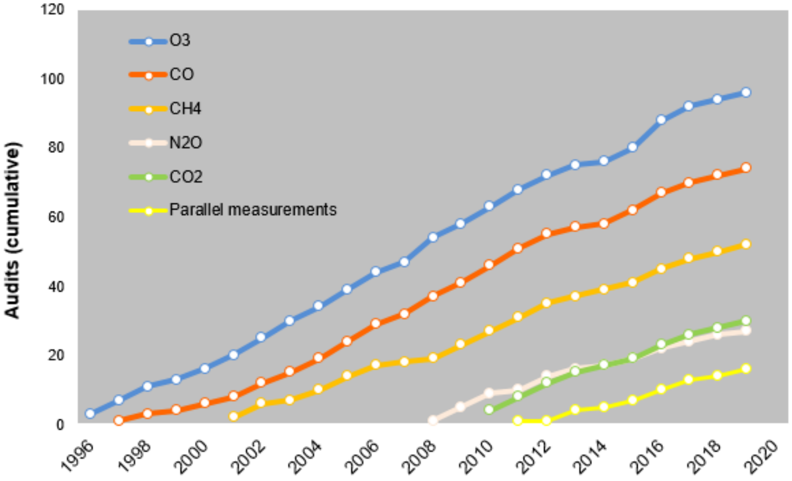
Ozone measuring stations according to GAWSIS
https://gawsis.meteoswiss.ch

World Calibration Centre WCC-Empa

- Supports global research and policies since 1996
- More than 100 station audits at mainly global GAW stations
- Covers four important greenhouse and reactive gases
- Collaborates with other calibration centres to improve traceability
- Assesses the performance of stations also with parallel measurements
- Audit procedure includes data and metadata review

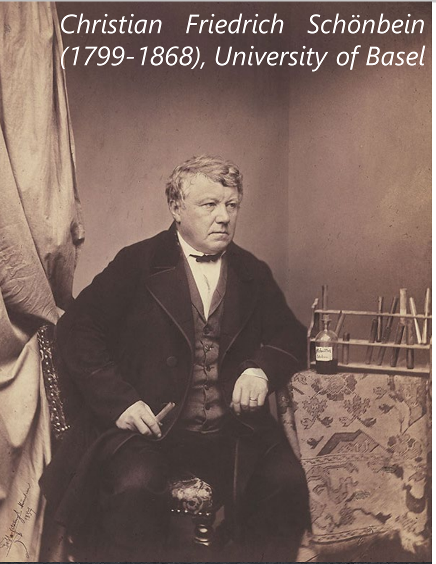
Audited stations by WCC-Empa since 1996 (red triangles)





Scope (top) and cumulative number (bottom) of WCC-Empa audits

History of Ozone



Christian Friedrich Schönbein (1799-1868), University of Basel

Swiss postage stamp (1999)

- 1839: O_3 is detected by Christian Friedrich Schönbein
- 1845: Schönbein detects O_3 in the atmosphere
- until 1950: O_3 in troposphere is from stratosphere
- From 1950: Linkage of O_3 with photochemical smog (Los Angeles)

- Potassium Iodide measurement techniques

$$O_3 + 2KI + H_2O \rightarrow O_2 + I_2 + 2KOH$$

Later, measurements with KI-impregnated papers which – when exposed to ozone – develop a blue color.

Interest in ozone was very high, in part because of its role as an "air purifier" and its suggested role in eliminating disease organisms, particularly cholera.

Arie Haagen-Smit & Los Angeles Smog

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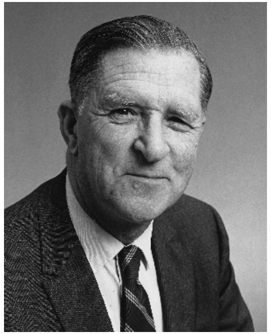
- Investigation of photochemical smog – origins and effects



Arie Haagen-Smit
(1900-1977)

Industrial and Engineering Chemistry, 1952

Chemistry and Physiology of Los Angeles Smog

A. J. HAAGEN-SMIT
California Institute of Technology, Pasadena, Calif., and Los Angeles County Air Pollution Control District, Los Angeles, Calif.

Air pollution in the Los Angeles area is characterized by a decrease in visibility, crop damage, eye irritation, objectionable odor, and rubber deterioration. These effects are attributed to the release of large quantities of hydrocarbons and nitrogen oxides to the atmosphere. The photochemical action of nitrogen oxides oxidizes the hydrocarbons and thereby forms ozone, responsible for rubber cracking. Under experimental conditions, organic peroxides formed in the vapor phase oxidation of hydrocarbons have been shown to give eye irritation and crop damage resembling closely that observed on smog days. The aerosols formed in these oxidations are contributors to the decrease in visibility. The odors observed in oxidation of gasoline fractions are similar to those associated with smog. Hydrocarbons present in cracked petroleum products, harmless in themselves, are transformed in the atmosphere into compounds highly irritating to both plants and animals, and should therefore be considered as potentially toxic materials. A proper evaluation of the contribution of air pollutants to the smog nuisance must include not only the time and place of their emission, but also their fate in the air.

AIR pollution in the Los Angeles area is characterized by a ... damage in this area. It has long been known that ozone has a ...

Plant Physiology, 1952

INVESTIGATION ON INJURY TO PLANTS FROM AIR POLLUTION IN THE LOS ANGELES AREA

A. J. HAAGEN-SMIT, ELLIS F. DARLEY, MILTON ZAITLIN, HERBERT HULL AND WILFRED NOBLE

(WITH THREE FIGURES)

Received July 24, 1951

Introduction

The remarkable increase in population and number of industries in the Los Angeles area since 1940 has given rise to a serious problem of air pollution known as smog. Leaf injury to plants, particularly leafy vegetable crops, was first noted in 1944 and has increased in severity since then. The injury was not incited by any pathogen but was associated with periods of heavy smog (7, 10). Endive, spinach, Romaine lettuce, garden and sugar beets, Swiss chard, and, at times, oats, were badly damaged. Alfalfa, barley, egg plant, tomatoes and head lettuce were injured to a less extent, and cabbage, cauliflower, cantaloupe, and cucumbers were very resistant.

Industrial and Engineering Chemistry, 1953

F. E. LITTMAN, H. W. FORD, and N. ENDOW
Stanford Research Institute, Pasadena, Calif.

Formation of Ozone in the Los Angeles Atmosphere

Oxidant formation in Los Angeles atmosphere is explained by assumption that ozone is formed by nitrogen dioxide photolysis aided by rapid conversion of nitric oxide to nitrogen dioxide in presence of certain hydrocarbons. The quantitative aspects of such systems are under investigation

sunlight, suggested that the oxidant was produced by the action of light. This assumption was further borne out when it was demonstrated that an oxidant could be formed by irradiation of night air with artificial light.

Other possible sources of oxidant had been examined previously, but neither electrical discharges nor transportation from the upper atmosphere could be substantiated experimentally. Photochemical formation seemed unlikely at first, because the wave lengths necessary for the dissociation of oxygen are not available at sea level. The indirect formation of ozone, with a substance other than oxygen acting as light absorber, was then considered. Recent experimental evidence lends this hypothesis much credence.

The daily fluctuations of oxidant con- ... disappeared, and oxidant concentrations of the same order of magnitude as those existing in daytime resulted from irradiation of night air.

Continued monitoring of outside air showed that the oxidant formed by irradiation of night air followed a daily and an annual cycle. The daily cycle frequently showed two maxima, one around 7:00 P.M., the other about 8:00 A.M. High concentrations of oxidant could be formed regularly by irradiation of night air during fall and winter, from September through March. During the summer months little, if any, oxidant was formed at night, despite the fact that, during that period high concentrations occurred in the daytime.

Isolation of Oxidant Precursors

Air Repair, 1954

Photochemical Ozone Formation with Hydrocarbons and Automobile Exhaust

A. J. HAAGEN-SMIT
California Institute of Technology
AND
M. M. FOX
Los Angeles County Air Pollution Control District

The most typical characteristic of the Los Angeles smog is its strong oxidizing effect.[1] This effect can be demonstrated by bubbling smog air through buffered potassium iodide solution, which is readily oxidized with liberation of iodine. Dyes such as indigo sulfonic acid and crystal violet are decolorized. On the other hand, leuco compounds such as phenolphthalin, the reduced form of the acid-base indicator, phenolphthalein, are oxidized to colored derivatives.[2] ... the Los Angeles air during smog attacks.[6][7] Ozone formation during photochemical oxidation is not limited to hydrocarbons but is also shown by their oxidation products—acids, aldehydes, ketones and alcohols. From a practical point of view, it is important that the irradiation of gasoline in the presence of NO_2 also leads to the formation of ozone and causes severe rubber cracking, and the Los Angeles County Air Pollution Control District has demonstrated the ozone forming property of the air near

Industrial and Engineering Chemistry, 1956

Ozone Formation in Photochemical Oxidation of Organic Substances

A. J. HAAGEN-SMIT AND C. E. BRADLEY
California Institute of Technology, Pasadena 4, Calif.
M. M. FOX
Los Angeles County Air Pollution Control District, Los Angeles 58, Calif.

SMOG periods in the Los Angeles area are chemically characterized by a pronounced oxidizing effect, in the order of 0.6 p.p.m. (volume per volume), calculated as hydrogen peroxide, and usually measured by the liberation of iodine from neutral buffered potassium iodide solution.

The oxidizing action of smog can also be measured by the decolorization of dyes such as indigo sulfonic acid or crystal violet. On the other hand, leuco dyes are readily oxidized to the corresponding colored compounds. A convenient smog indicator is colorless phenolphthalin which is oxidized to phenolphthalein, giving a red color in alkaline solution. The intensity of the red color is a direct measure of the smog concentration. The rapid oxidation of cysteine and glutathione during smog periods is of ... period can be as short as 4 minutes, whereas on normal days this takes from 45 to 60 minutes. These cracking times correspond, respectively, to 0.3 and 0.02 p.p.m. of ozone.

The natural ozone concentration on the earth's surface is reported to be of the order 0.02 to 0.03 p.p.m. These values have been confirmed by the authors of this paper using the rubber cracking test in unpolluted desert and beach areas. It is unlikely that additional ozone could be drawn from the higher atmosphere when the presence of inversion conditions characteristic for smog conditions prevents this free exchange. Further evidence against such a possibility is presented by the nearly complete absence of rubber cracking at night. This observation points to photochemical processes in the formation of the rubber cracking material.

Rationale for measurements of O_3 in the atmosphere

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Effects on human health

- O_3 harms lung function and irritates the respiratory system.
- O_3 can lead to premature death, respiratory illnesses like asthma and bronchitis, heart attack, and other cardiopulmonary problems up to permanent pulmonary damage.

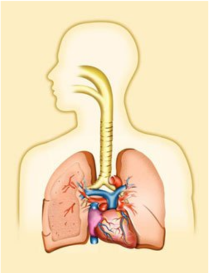
Effects on the environment

- O_3 affects sensitive vegetation and ecosystems, including forests, parks, wildlife refuges and wilderness areas, in particular, during the growing season.
- In addition to reduced tree growth and visible injury to leaves, continued ozone exposure over time can lead to increased susceptibility of sensitive plant species to disease, damage from insects, effects of other pollutants, competition, and harm from severe weather.

Source: US EPA (https://www.epa.gov/ground-level-ozone-pollution)

Health Effects of Ozone Pollution

Ozone in the air we breathe can harm our health, especially on hot sunny days when ozone can reach unhealthy levels. Even relatively low levels of ozone can cause health effects.



Ozone is a powerful oxidant that can irritate the airways.

For Healthcare Providers

Ozone and Your Patients' Health: Training for Healthcare Providers

Who is at risk?

People most at risk from breathing air containing ozone include people with asthma, children, older adults, and people who are active outdoors, especially outdoor workers. In addition, people with certain genetic characteristics, and people with reduced intake of certain nutrients, such as vitamins C and E, are at greater risk from ozone exposure.

Children are at greatest risk from exposure to ozone because their lungs are still developing and they are more likely to be active outdoors when ozone levels are high, which increases their exposure. Children are also more likely than adults to have asthma.

What does ozone exposure do to sensitive plants?

When sufficient ozone enters the leaves of a sensitive plant, it can:

- Reduce photosynthesis, which is the process that plants use to convert sunlight to energy to live and grow.
- Slow the plant's growth.
- Increase sensitive plants' risk of:
  - disease
  - damage from insects
  - effects of other pollutants
  - harm from severe weather.

Also, some plants can show visible marks on their leaves when ozone is present under certain conditions.

tulip poplar

Ground level ozone regulations

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- Surface ozone is a regulated air pollutant, and threshold levels are set by many countries

Table 4: Threshold levels set by the Council Directive on air pollution by ozone

Threshold value set by	Description	Criteria based on	Value µg.m^{-3}
European Council Directive 92/72/EEC	Population information threshold	1 hour average concentration	180
	Population warning threshold	1 hour average concentration	360
	Health protection threshold	Fixed 8 hour mean concentrations (period hours 0:00-8:00, 8:00-16:00, 16:00-24:00, 12:00-20:00)	110
	Vegetation protection threshold	1 hour average concentration	200
	Vegetation protection threshold	24 hour average concentration	65

Source: www.eea.europa.eu/publications/TOP08-98/page006.html

Ozone (O_3)	100 µg/m^3	98% of half-hour means for one month ≤ 100 µg/m^3
	120 µg/m^3	1-hour mean; must not be exceeded more than once per year

Source: www.fedlex.admin.ch/eli/cc/1986/208_208_208/en

EPA United States Environmental Protection Agency

Search EPA.gov

Environmental Topics | Laws & Regulations | Report a Violation | About EPA

Related Topics: Criteria Air Pollutants

CONTACT US

NAAQS Table

An official website of the United States government

The Clean Air Act, which was last amended in 1990, requires EPA to set National Ambient Air Quality Standards (40 CFR part 50) for six principal pollutants ("criteria" air pollutants) which can be harmful to public health and the environment. The Clean Air Act identifies two types of national ambient air quality standards. ***Primary standards*** provide public health protection, including protecting the health of "sensitive" populations such as asthmatics, children, and the elderly. ***Secondary standards*** provide public welfare protection, including protection against decreased visibility and damage to animals, crops, vegetation, and buildings.

Periodically, the standards are reviewed and sometimes may be revised, establishing new standards. The most recently established standards are listed below. In some areas of the U.S., certain regulatory requirements may also remain for implementation of previously established standards.

Units of measure for the standards are parts per million (ppm) by volume, parts per billion (ppb) by volume, and micrograms per cubic meter of air (µg/m^3).

Pollutant [links to historical tables of NAAQS reviews]	Primary/ Secondary	Averaging Time	Level	Form
Carbon Monoxide (CO)	primary	8 hours	9 ppm	Not to be exceeded more than once per year
		1 hour	35 ppm	
Lead (Pb)	primary and secondary	Rolling 3 month average	0.15 µg/m^3 [(1)]	Not to be exceeded
Nitrogen Dioxide (NO_2)	primary	1 hour	100 ppb	98th percentile of 1-hour daily maximum concentrations, averaged over 3 years
	primary and secondary	1 year	53 ppb [(2)]	Annual Mean
Ozone (O_3)	primary and secondary	8 hours	0.070 ppm [(3)]	Annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years

Source: www.epa.gov/criteria-air-pollutants/naaqs-table

Surface Ozone Measurement Techniques

- “Historic” measurement techniques (e.g. Schönbein method) are no longer relevant.
- Chemiluminescence method, reaction of ozone with ethene to ethylen oxide

  $O_3 + C_2H_4 \text{--->} C_2H_4O + O_2 + h\nu$

  Detection with photo multiplier

- Chemiluminescence is not widely used. This technique can be an advantage in the presence of interfering species, such as volatile organic compounds (VOCs). A few instruments are on the market.

- Spectroscopic techniques (mostly UV absorption) are most widely used.

- Many different instruments (brands) are commercially available.

Absorption spectrum and measurement principle

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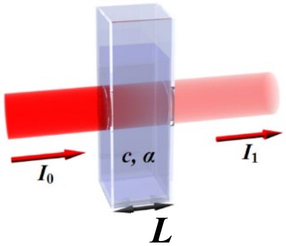
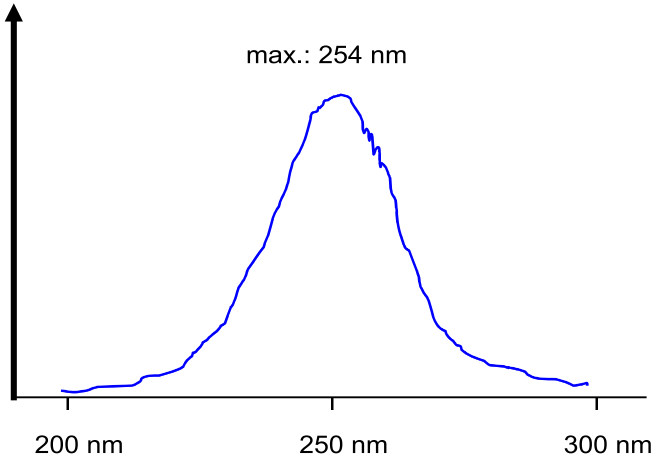


The Law of Lambert-Beer

$$C = \frac{1}{k \bullet L} \bullet \frac{T}{T_0} \bullet \frac{p_0}{p} \bullet 10^9 \bullet \log \frac{I_0}{I_1}$$

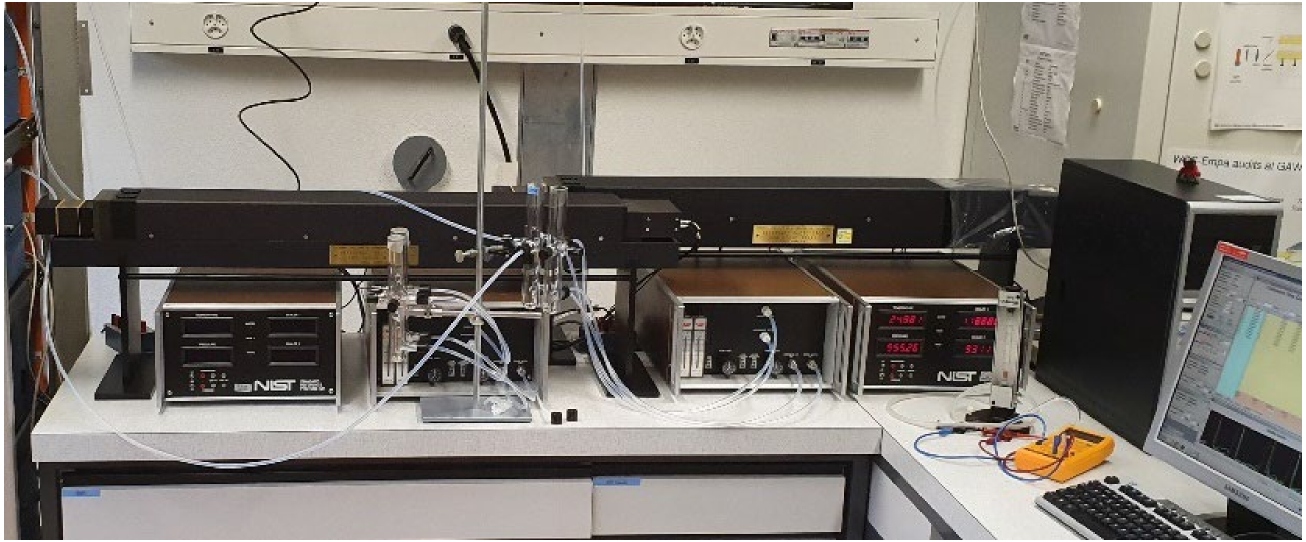
C	=	ozone mole fraction
T	=	gas temperature in Kelvin
T_0	=	standard temperature: 273 K
P	=	pressure [mbar]
P_0	=	standard pressure: 1013 mbar
I_0	=	light intensity with zero air
I_1	=	light intensity with ozone
k	=	absorption coefficient 134 atm^{-1} cm^{-1}
L	=	optical lenght [cm]

Absorption spectra of ozone



Ozone reference - NIST Standard Reference Photometer

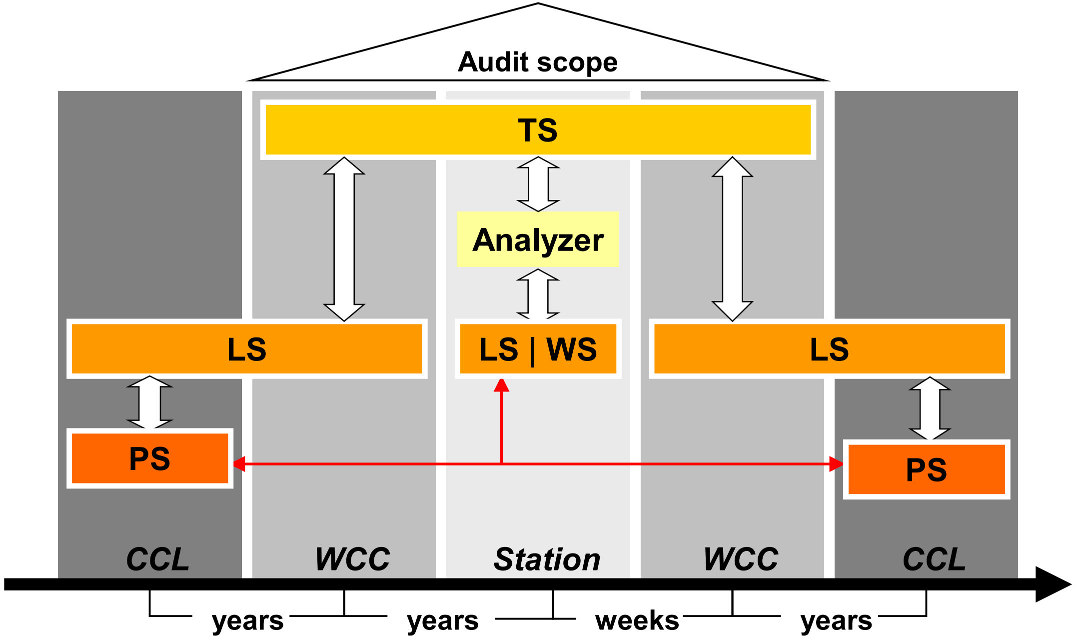
- NIST Standard Reference Photometer (SRP)
- About 60 instruments worldwide
- Traceable to SI



SRPs (#15 and #23) operated by Empa

Arnauld Bass and Jim Norris with the first SRP (#0) in 1982

Traceability Chain within GAW



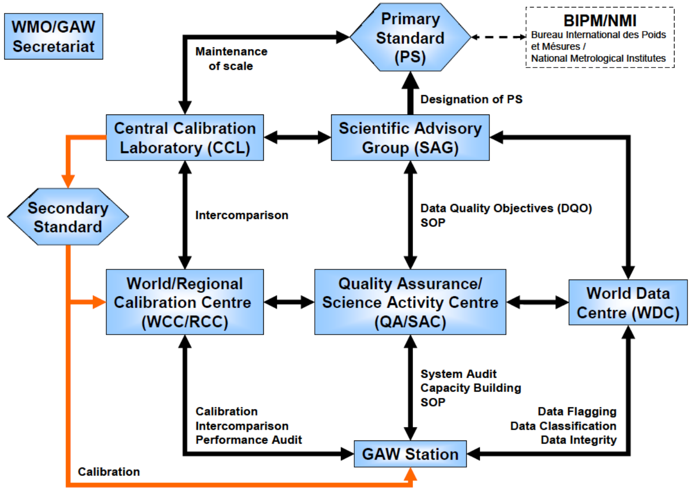
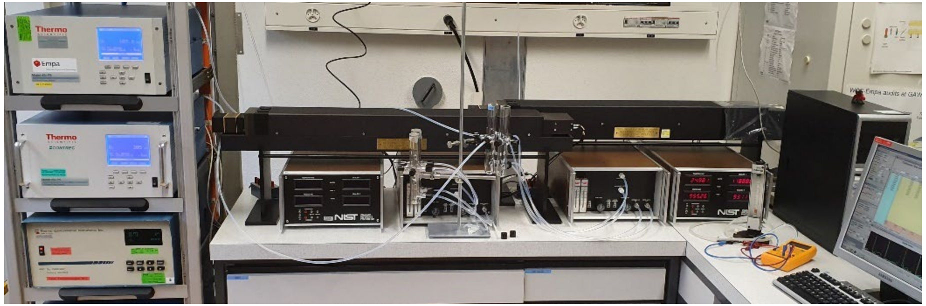


Figure 15 - Elements of the Quality Assurance system, QA activities and workflow in GAW

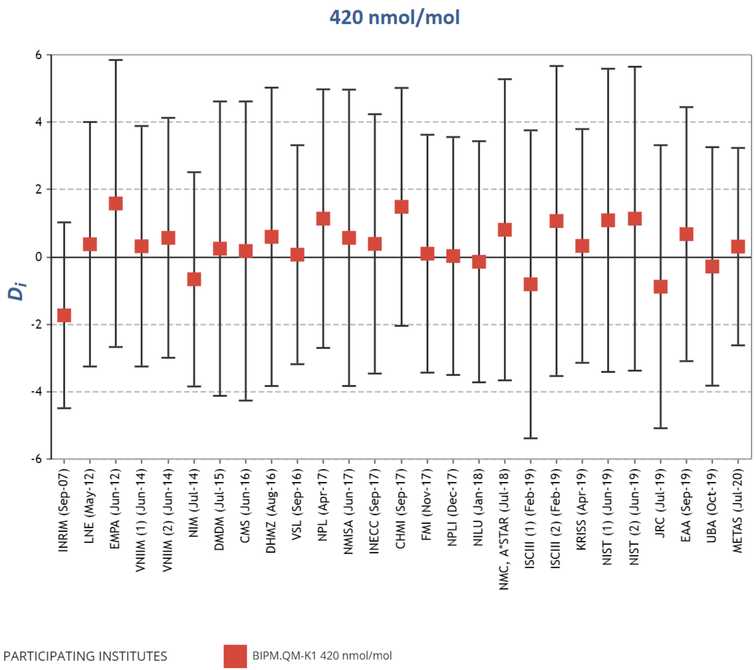
- Central Calibration Lab (CCL) maintains Primary Standard (PS) (NIST)
- WCC / RCC has a Laboratory Standard (LS) (WCC-Empa, RCC O3)
- GAW station also must have a LS traceable to CCL

Traceability of Ozone is different!

- Each NIST Standard Reference Photometer (SRP) is a realisation of a Primary Standard
- CCL is NIST, which maintains SRP#2 (=reference for GAW), but SRP#X is also a primary standard
- The ‘SRP family’, which defines the O_3 reference, is compared in an ongoing Key Comparison organized by BIPM (www.bipm.org)



Degrees of equivalence D_i and expanded uncertainty U_i (k = 2) expressed in nmol/mol.



https://www.bipm.org/kcdb/comparison?id=1428#tabsPage

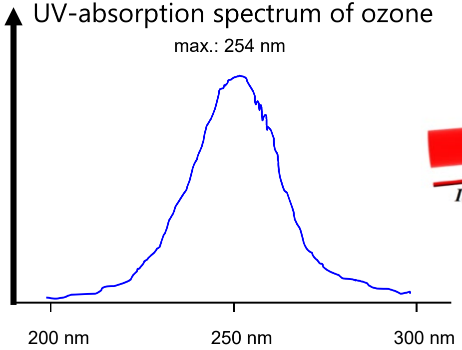
Why is every SRP a primary standard?

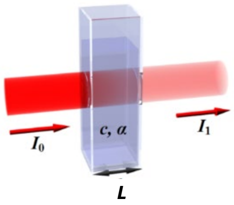
- Measurements are traceable to the SI.
- This is realized in every SRP independently.
- They are not identical due to uncertainties in the determination of e.g. the cell length.
- Absorption cross section is by far the most dominant source of uncertainty for ozone measurements.
- However, as it is a conventional value, it can be neglected for traceability within this convention.

Table 1: Uncertainty budget for the SRPs maintained by the BIPM

Component (y)	Uncertainty $u(y)$: Source	Distribution	Standard Uncertainty	Combined standard uncertainty $u(y)$	Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to $u(x)$ $\lvert c_i \rvert \cdot u(y)$ nmol/mol
Optical Path L_{opt}	Measurement scale	Rectangular	0.0006 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89 \times 10^{-3} x$
	Repeatability	Normal	0.01 cm			
	Correction factor	Rectangular	0.52 cm			
Pressure P	Pressure gauge	Rectangular	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	$3.37 \times 10^{-4} x$
	Difference between cells	Rectangular	0.017 kPa			
Temperature T	Temperature probe	Rectangular	0.03 K	0.07 K	$\frac{x}{T}$	$2.29 \times 10^{-4} x$
	Temperature gradient	Rectangular	0.058 K			
Ratio of intensities D	Scaler resolution	Rectangular	8×10^{-6}	1.4×10^{-5}	$\frac{x}{D \ln(D)}$	0.28
	Repeatability	Triangular	1.1×10^{-5}			
Absorption Cross section σ	Hearn value		1.22×10^{-19} cm²/molecule	1.22×10^{-19} cm²/molecule	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2} x$

From: Viallon et al., Final report, ongoing key comparison BIPM.QM-K1: Ozone at ambient level, comparison with EMPA (June 2012), Metrologia, 49, 2012.



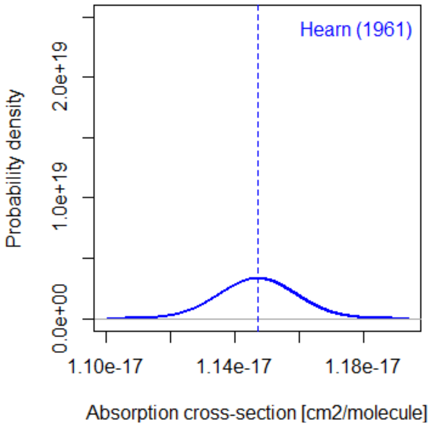


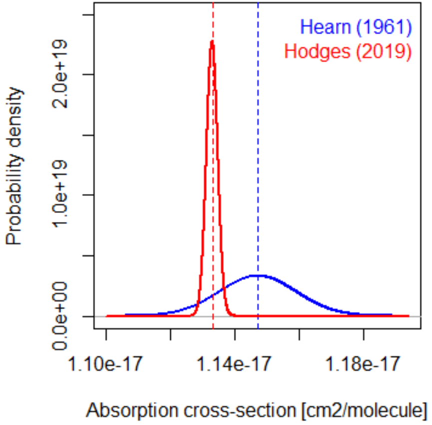
The Lambert-Beer Law

$$c = \frac{1}{\alpha \cdot L} \cdot \frac{T}{T_0} \cdot \frac{p_0}{p} \cdot 10^9 \cdot \log \frac{I_0}{I_1}$$

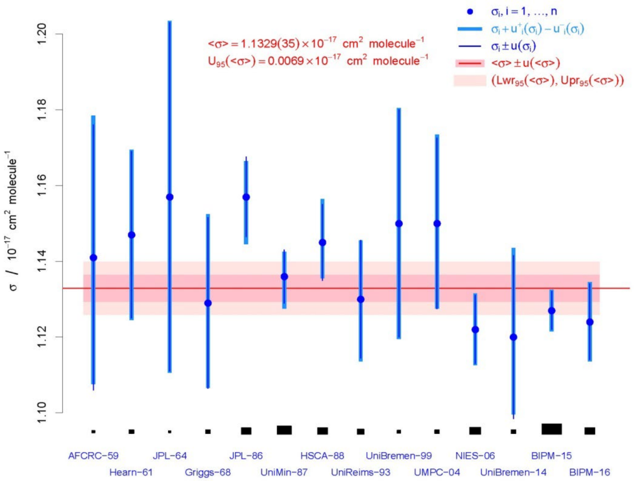
c	=	ozone amount fraction
T	=	gas temperature in Kelvin
T_0	=	standard temperature: 273.25 K
P	=	pressure [mbar]
P_0	=	standard pressure: 1013.15 mbar
I_0	=	light intensity with zero air
I_1	=	light intensity with ozone
α	=	absorption coefficient 134 $atm^{-1}cm^{-1}$
L	=	optical lenght [cm]

Largest uncertainty: Absorption cross-section





- Absorption cross section is largest source (Hearn-61 et al. 2.1%, 95% confidence)
- New value is proposed by Hodges et al. (2019).
- The recommended value is ~1.29% lower than the current value (Hearn-61) implemented in reference instruments for tropospheric ozone measurements.
- The uncertainty of the proposed value is 3 times smaller than Hearn-61.
- Implementation of the new value is proposed by Working Group on Gas Analysis (BIPM).
- Ozone amount fraction will shift by about +1.29% with the new value.

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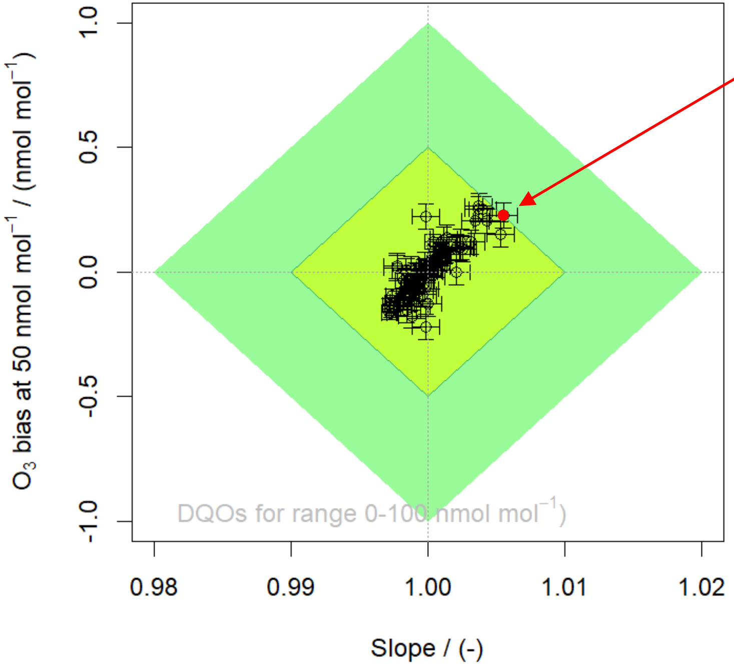
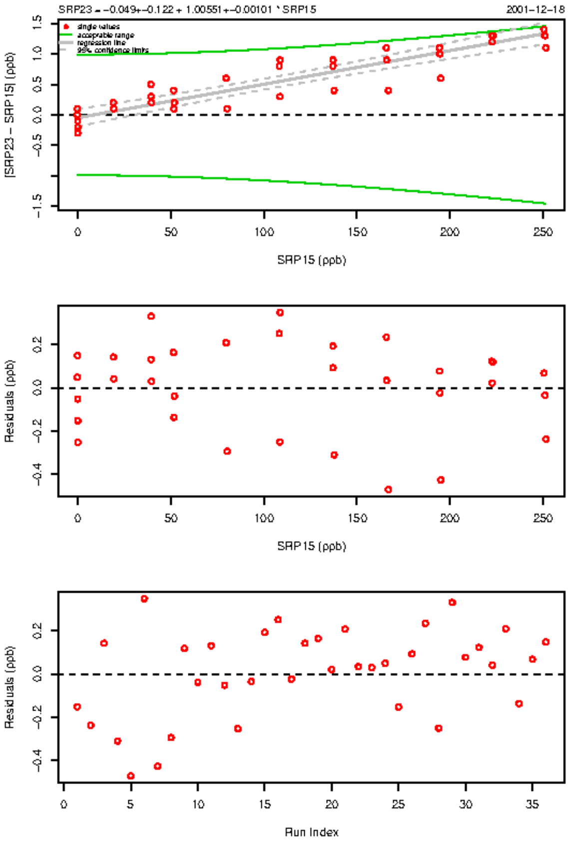
Recommendation of a consensus value of the ozone absorption cross-section at 253.65 nm based on a literature review

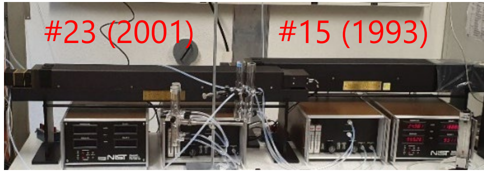
J T Hodges[1], J Viallon[2,10], P J Brewer[3], B J Drouin[4], V Gorshelev[5], C Janssen[6], S Lee[7], A Possolo[1], M A H Smith[8], J Walden[9] and R I Wielgosz[2]

[1] National Institute of Standards and Technology (NIST), Gaithersburg, MD, United States of America

Stability of the SRPs @ Empa

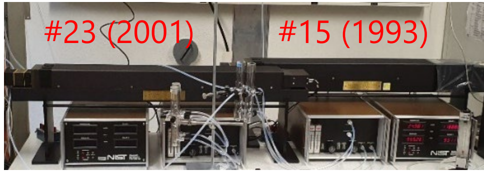


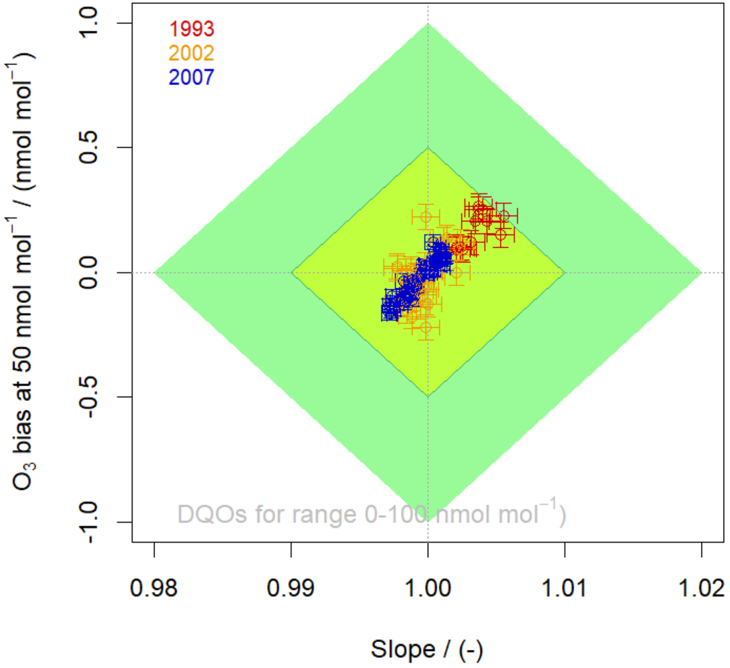




- Regular comparisons were made between SRPs #23 and #15 since 2001.

Stability of the SRPs @ Empa





- Initial version of SRP#15 (from 1993 until the electronics upgrade in 2002) was biased by -0.3% due to a wrong capacitor in the detector circuit.

  >>> "James E. Norris" <jnorris@email.nist.gov> 01/08 9:56 pm >>>
  Hello Christoph,...

  ...in some cases there was an increase in concentration measurement relating in a 0.3% shift in the slope. This is due to the fact that these SRPs had 0.022 uF capacitors on the detector circuits. This came about from a mistake on the drawing and the value should have been 0.0022 uF. This changes the time constant of the detector circuit which changes the concentration measurement.

Stability of the SRPs @ Empa

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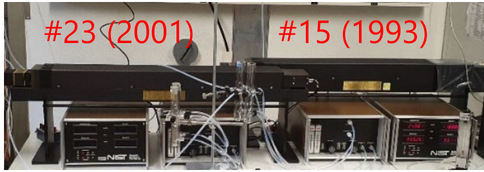
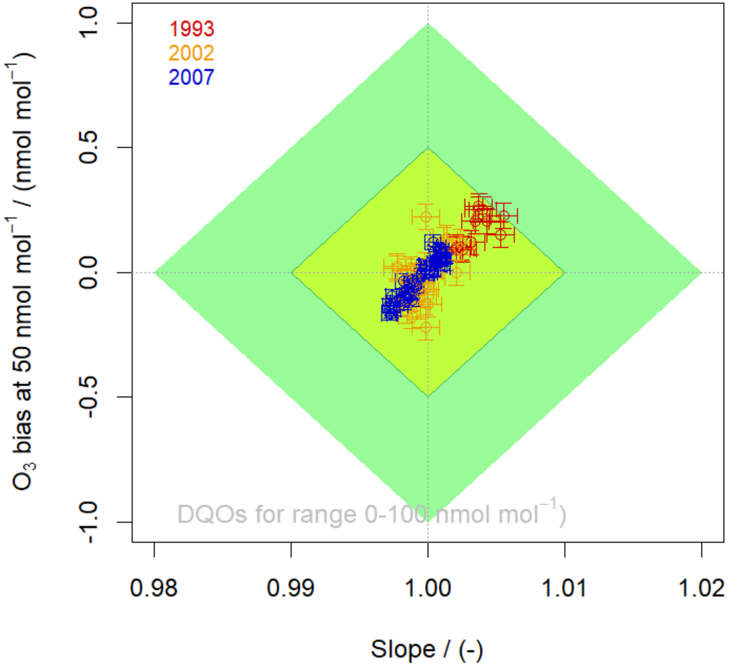




- The difference between #15 and #23 disappeared with the electronics upgrade in 2002.
- Another upgrade (tilted windows, better thermal insulation of light source) in 2007 improved reproducibility of SRP-SRP comparisons. There is still variation in the slope, but zero offsets improved significantly.

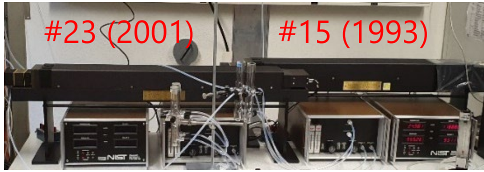
Institute of Physics Publishing Metrologia
Metrologia 43 (2006) 441–450 doi:10.1088/0026-1394/43/5/016

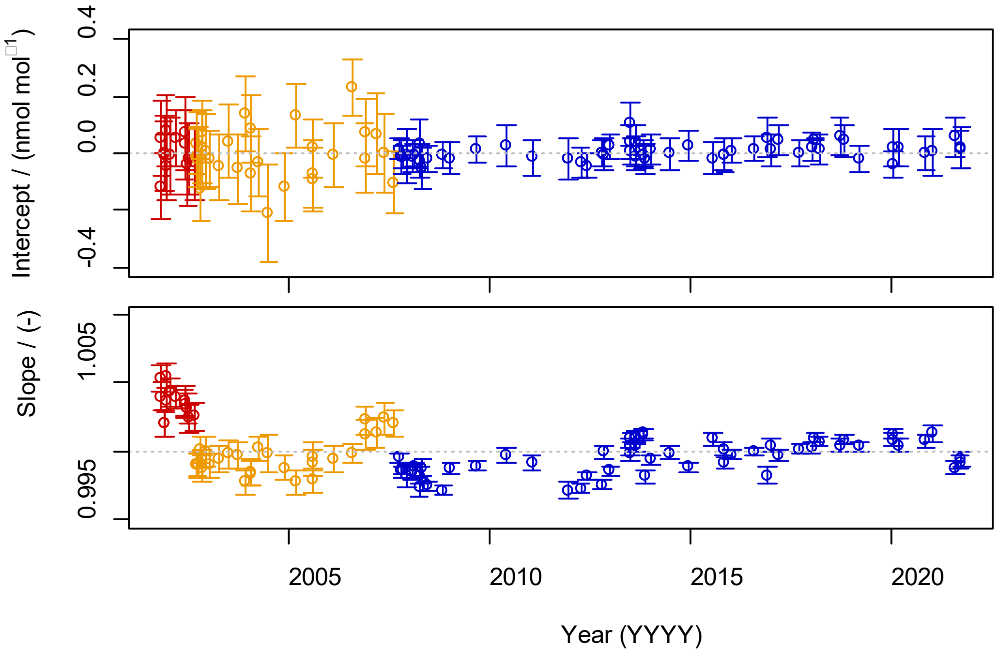
A study of systematic biases and measurement uncertainties in ozone mole fraction measurements with the NIST Standard Reference Photometer

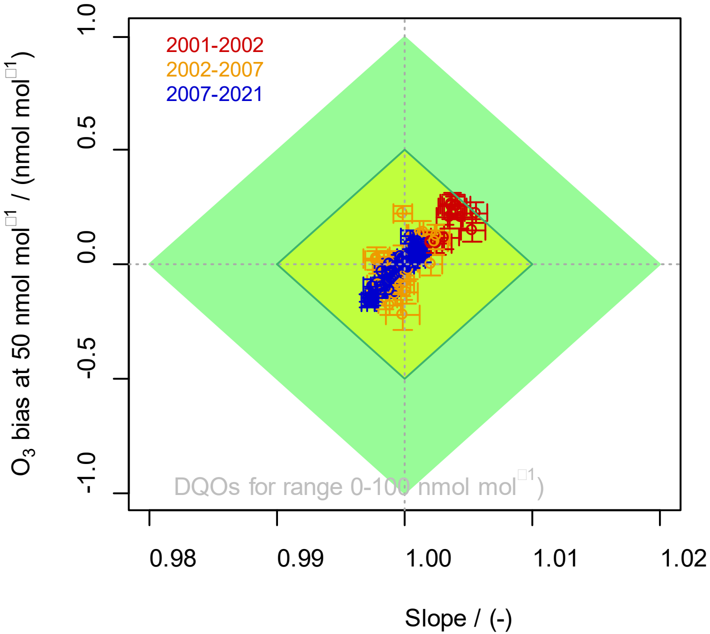
J Viallon[1], P Moussay[1], J E Norris[2], F R Guenther[2] and R I Wielgosz[1]

[1] Bureau International des Poids et Mesures, Pavillon de Breteuil, F-92310 Sèvres, France
[2] National Institute of Standards and Technology, Gaithersburg, MD, USA

20 years of SRP-SRP comparisons @Empa







SRP-SRP comparisons between Empa and other Institutes

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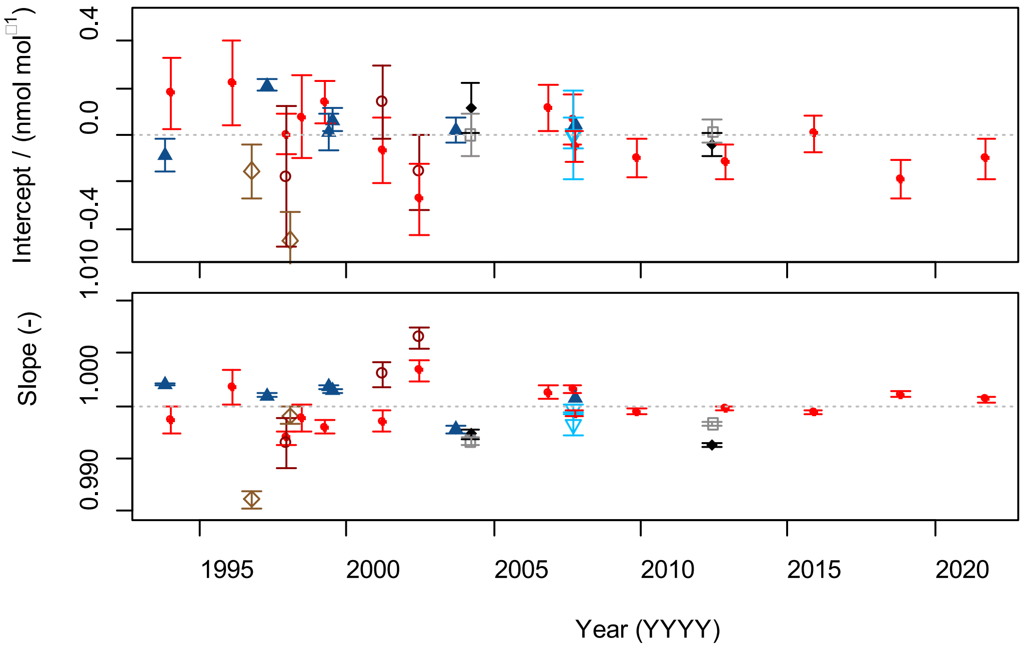
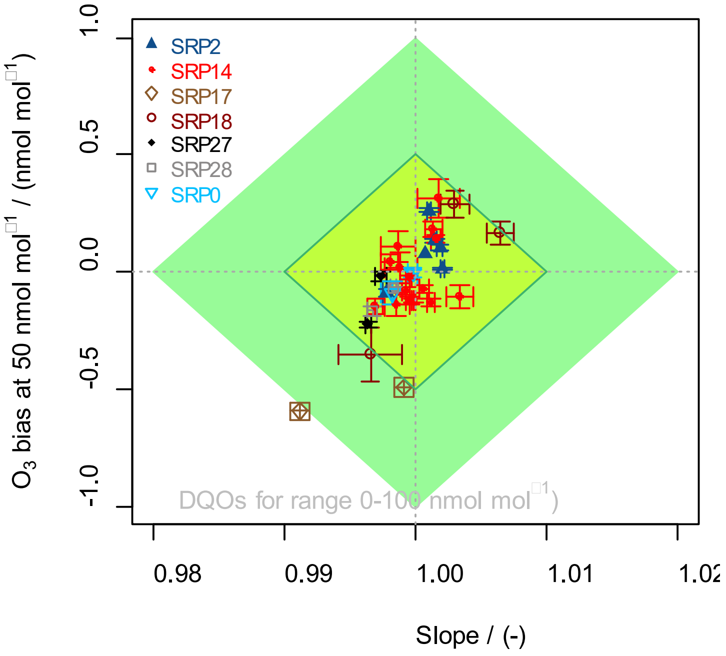
NIST: SRP #0 and #2 / BIPM: SRP #27 and #28 / METAS: SRP #14 and #18 / CHMI: SRP #17

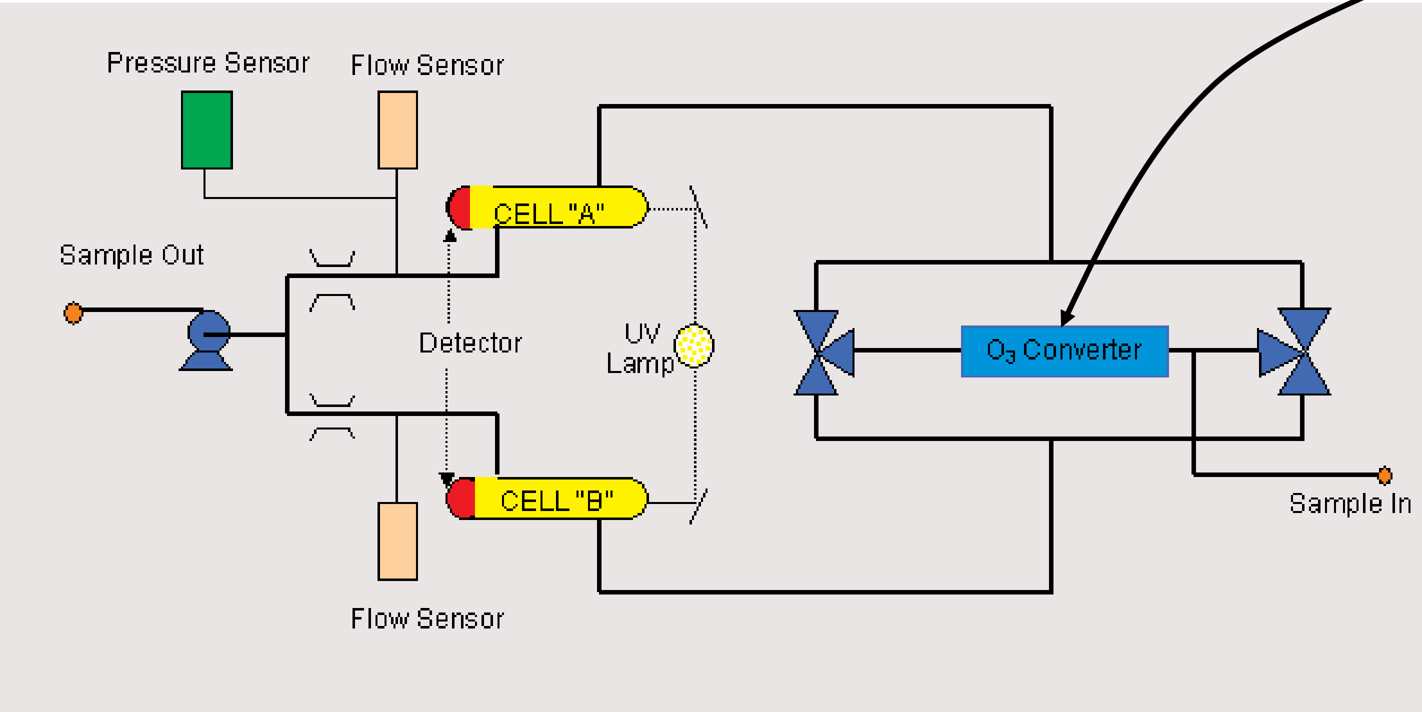




Ozone analyzers

- Same operating principle as the reference instruments (SRPs)

removes ozone



Example: Thermo, Model 49C O_3 Analyzer

Instrument development: High-end (example for CO)

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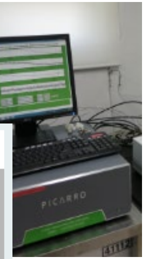
GC/HgO @ MLO

N



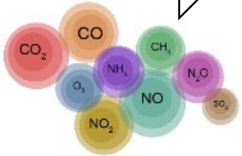
S @ AMY

4, CO_2

Mid-infrared (MIR) direct laser absorption spectroscopy

1990 → 2020

CO



- Measurement of c
- Often slow, quasi
- Frequent calibrati
- Partly non-linear r
- Noise and reprodu compared to curre

- n of multiple species
- ntinuous
- d calibration frequency varies
- ear over a large range
- d noise and reproducibility

Webinar with Martin Steinbacher

Carbon monoxide in the atmosphere – measurement techniques

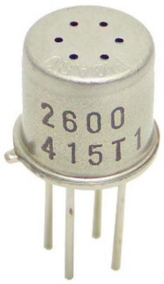
November 4th, 2 pm UTC

Carbon monoxide (CO) is a central molecule in atmospheric composition monitoring and research. Mole fractions in the troposphere range from less than 100 ppb in remote areas to a few ppm in urban environments. Major sources are fossil fuel combustion, biomass burning and oxidation of methane and nonmethane hydrocarbons. Despite being a reactive gas with an atmospheric lifetime of a few days to months, CO is also considered as an indirect greenhouse gas as it interacts in the oxidative chain reactions and, consequently, also influences the lifetime of long-lived greenhouse gases such as methane. Thus, carbon monoxide plays an important role in atmospheric chemistry, the carbon cycle, and the Earth's radiative budget.

The Global Atmosphere Watch Programme (GAW) of the World Meteorological Organization lists CO as one of its recommended measurement variables. Several fundamentally different measurement techniques exist for CO observations. The lecture will give a comprehensive overview of the most common techniques and related quality assurance / quality control recommendations.

Register for 4th Webinar

Instrument development: Low-end



Metal oxide
~ CHF 5
~ 1960

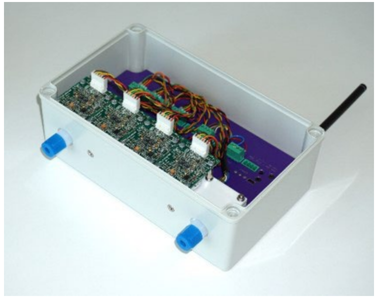
Electrochemical
/ voltammetric
~ CHF 50
~ 1980

Photochemical
~ CHF 200
~ 1990

Model 106-L-OEM Ozone Monitor

Micro-optical
> CHF 100
~ 2000

decentlab



Trend:

- Miniaturization
- Design improvements
- Integration into units
- Ancillary parameters (e.g. p, T)
- Multiple sensors
- Communication (LoRa / GSM)
- Cloud processing
- …

Sensor → Micro-electro-mechanical (MEMS) type device

- Sensors: Challenging component diversity. Mainly 'old' technologies.
- Technical information provided by manufacturers often not sufficient.

Low cost sensor recommendations

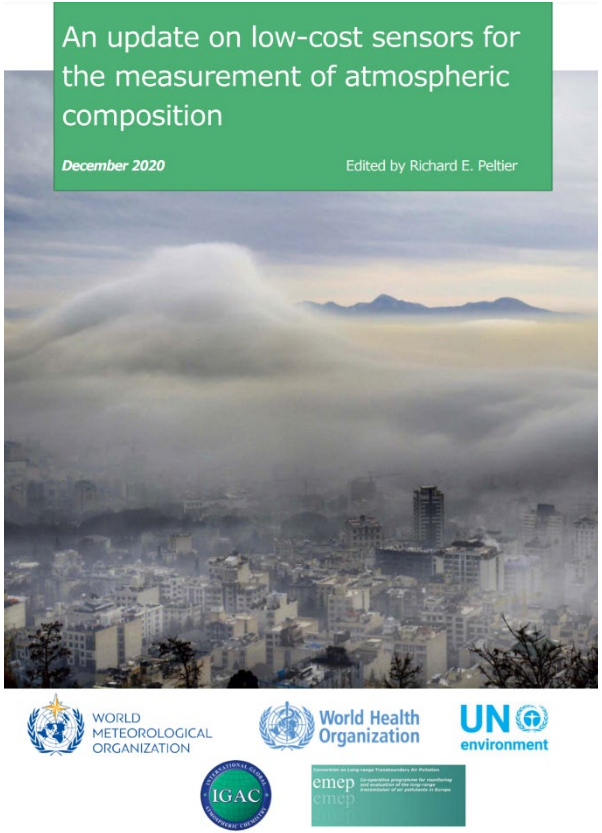
Empa
Materials Science and Technology

Low-cost sensors for the measurement of atmospheric composition: overview of topic and future applications

valid as of May 2018

Editors: Alastair C. Lewis, Erika von Schneidemesser and Richard E. Peltier

WORLD METEOROLOGICAL ORGANIZATION
World Health Organization
UN environment
IGAC
emep



WMO Report No. 1215, https://library.wmo.int/doc_num.php?explnum_id=10620

Instrument development - Ozone

- No large changes in the measurement techniques in contrast to other parameters over the past decades.
- Mainly UV absorption.
- At global GAW stations, instruments from Thermo are most widely used.

? – 1995: 49/49PS Series

- Resolution 1 ppb
- Only analog output
- No remote control
- Significantly poorer performance compared to newer models

1996 – 2007: 49C/49C-PS Series

- Resolution 0.1 ppb
- RS-232 and analog output
- Remote control
- Better performance compared to 49-series

2008 – 2022(?): 49i/49i-PS Series

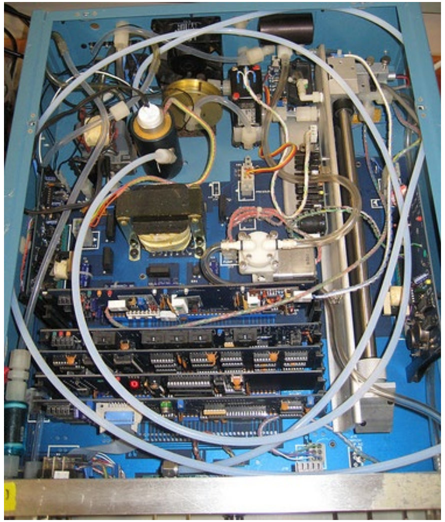
- Resolution 0.1 ppb
- Ethernet, RS-232 and analog output
- Remote access and control
- No further improvement regarding performance to 49C-series

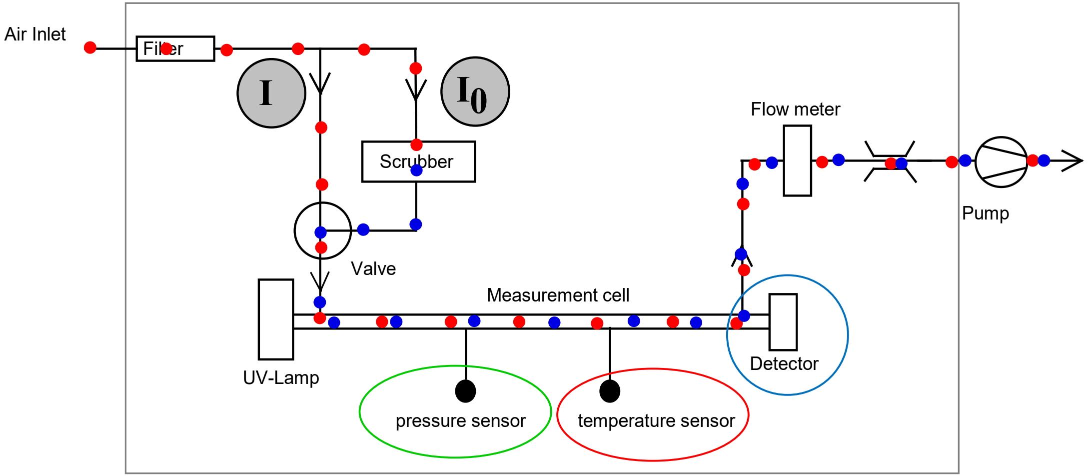
2019 – ?: 49iQ/49iQ-PS Series

- Resolution 0.1 ppb
- Ethernet, RS-232 and analog output
- Remote access and control
- Cheaper components, no further improvement regarding performance to 49i-series

Operating principle: one measurement cell

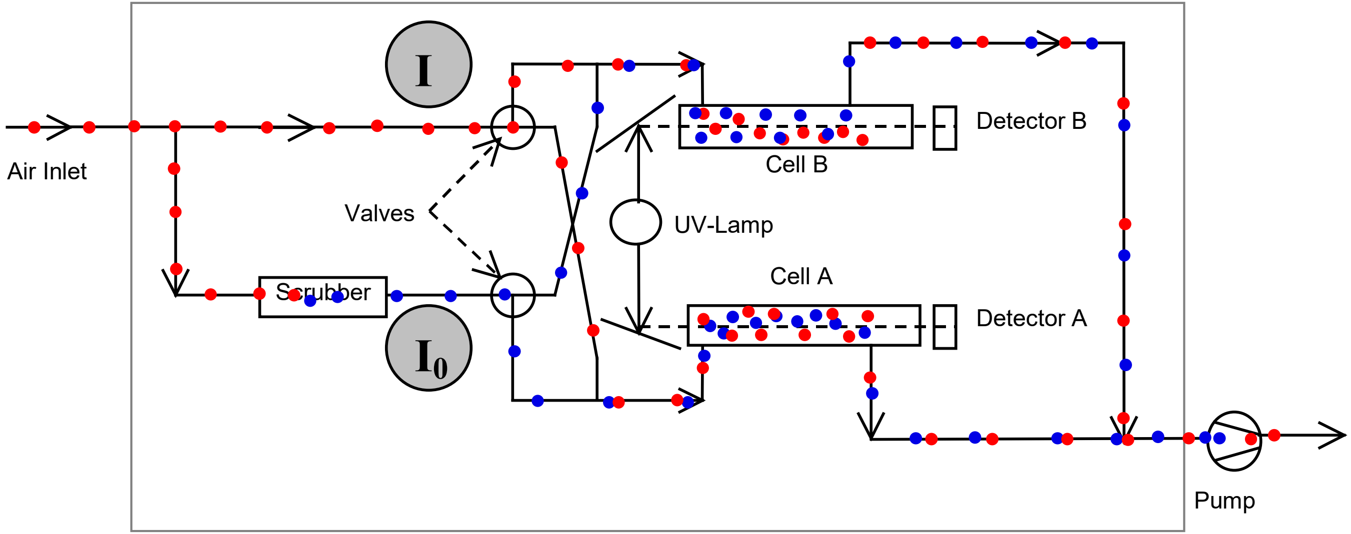
Most instruments except Thermo analyzers





$$C = \frac{1}{k \cdot L} \cdot \frac{T}{T_0} \cdot \frac{p_0}{p} \cdot 10^9 \cdot \log \frac{I_0}{I_1}$$

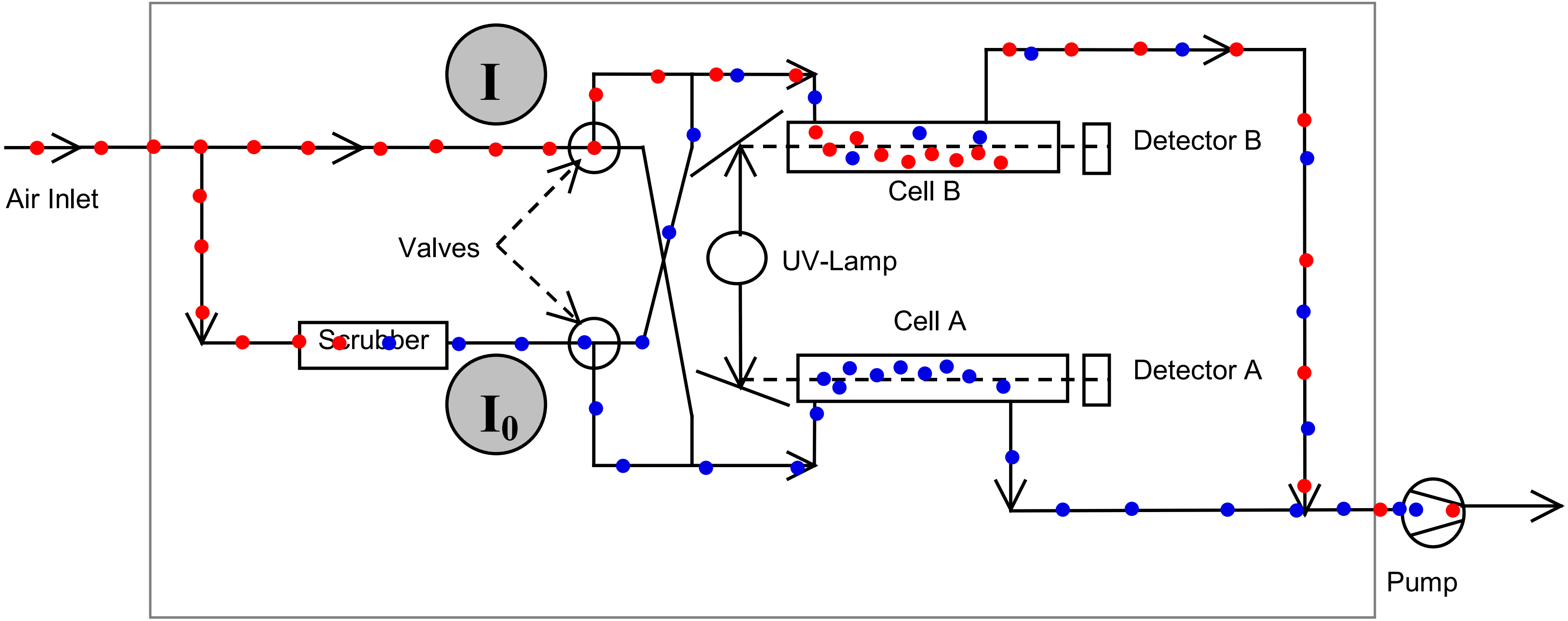
Operating principle: two measurement cell



Measurement principle of two cell analyzers (e.g. Thermo analysers, 2B Model 205 Ozone Monitor)

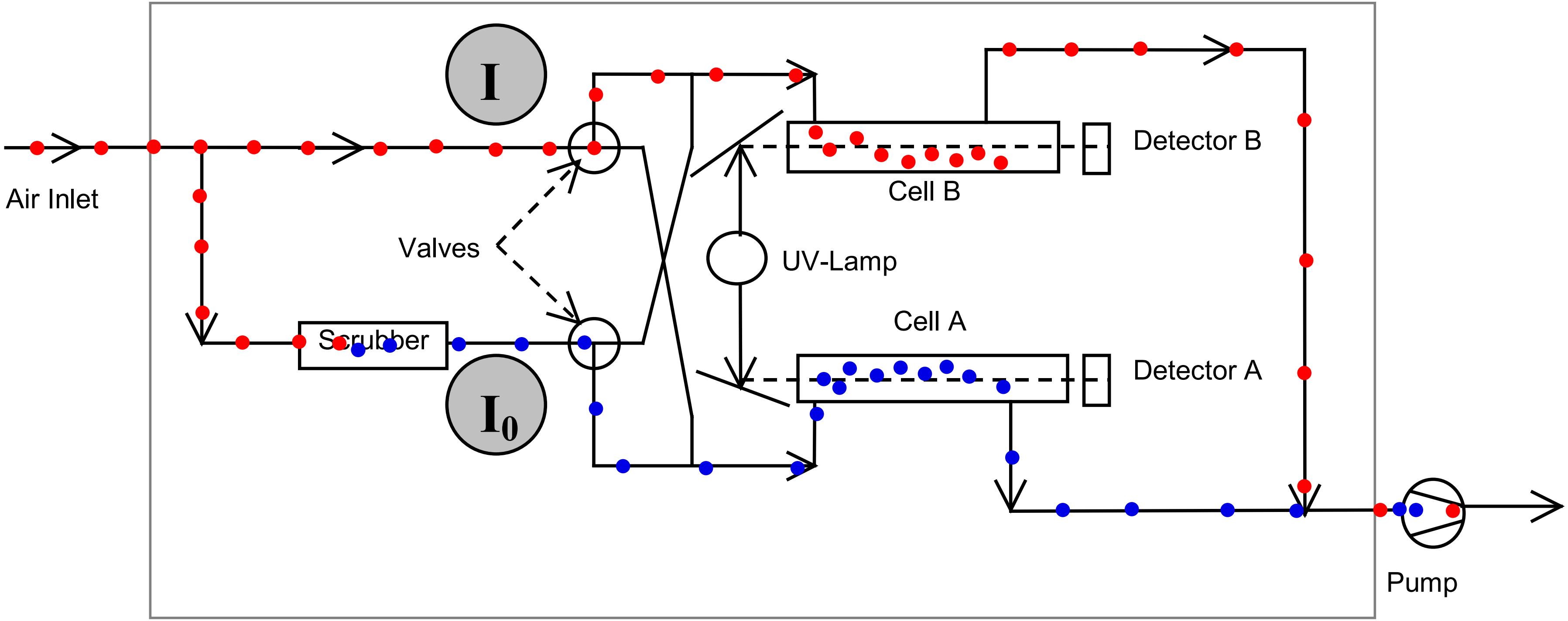
$$C = \frac{1}{k \bullet L} \bullet \frac{T}{T_0} \bullet \frac{p_0}{p} \bullet 10^{9} \bullet \log \frac{I_0}{I_1}$$

What can go wrong? Leaking solenoid valves



- Internal leaks (solenoid valves) result in mixing of reference and sample air
- Consequently, ozone values will be low

What can go wrong? Scrubber efficiency



- A scrubber with 100% efficiency destroys all ozone (a good scrubber removes ONLY ozone!)
- This is needed for well defined reference air with the SAME matrix as the sample air
- The scrubber MUST NOT remove other UV absorbing species (H_2O, VOCs etc.)

What can go wrong? Scrubber efficiency

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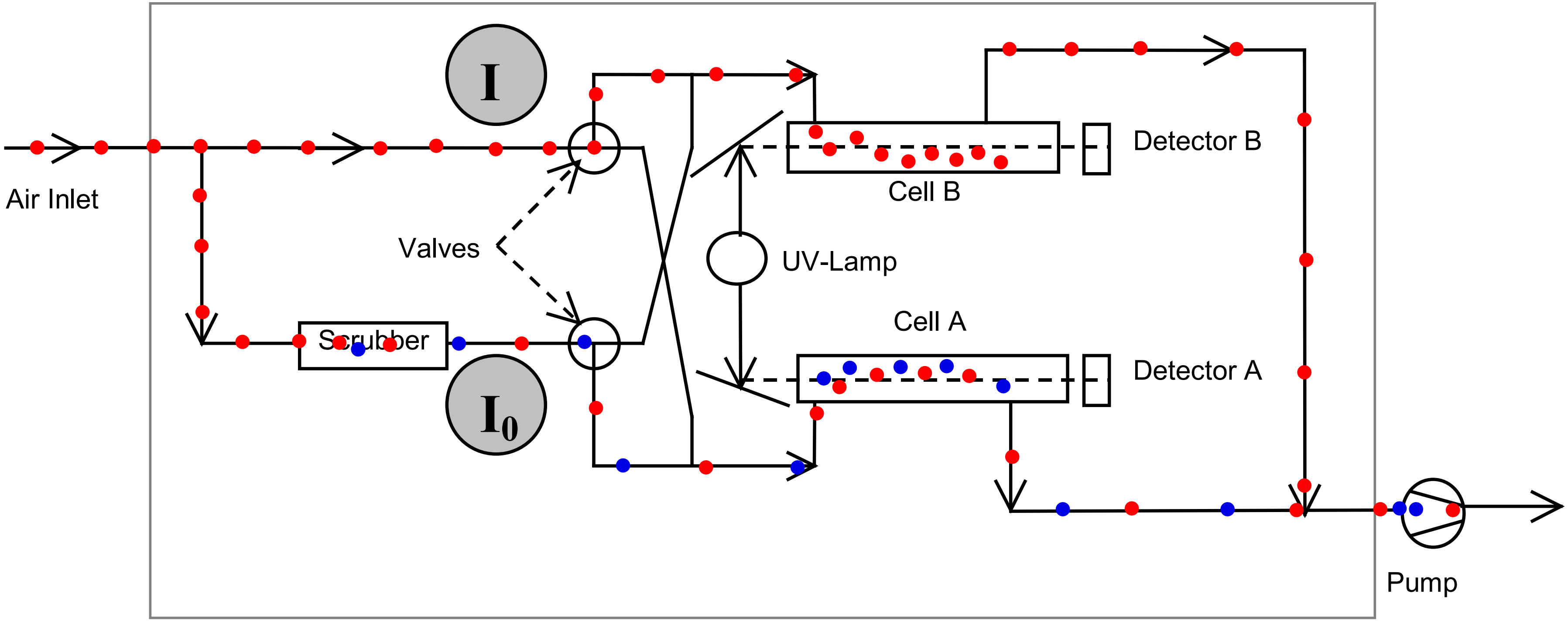
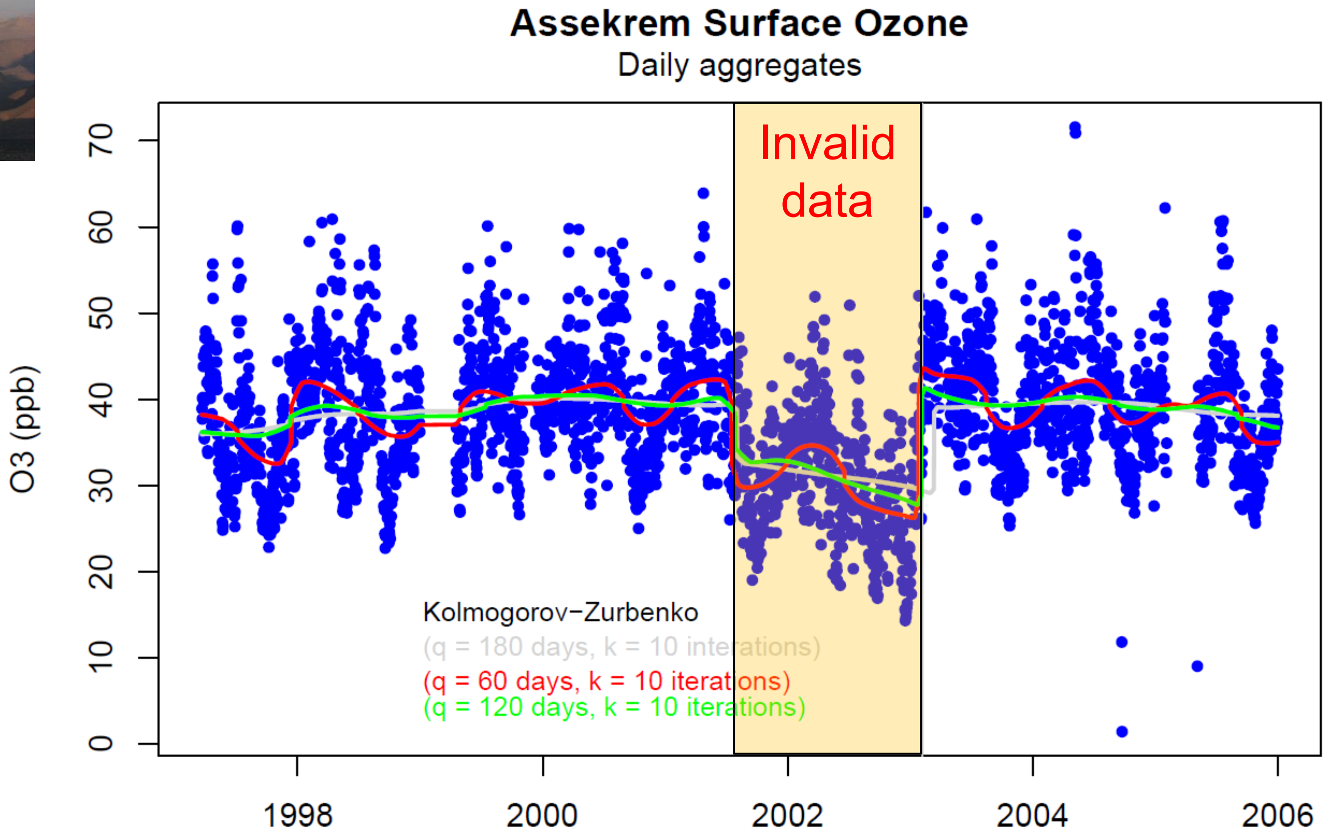


- A scrubber with an efficiency of <100% removes only part of the ozone
- The reference air will not be free of ozone
- Consequently, ozone values will be low

Example of a bad scrubber

- Scrubber degradation started in 2001 and was not realized until a WCC-Empa audit in 2003.
- It is not possible to quantify the loss due to the degraded scrubber; however, the period of the degradation could be identified using statistical filters.
- Consequently, 1.5 years of ozone data had to be flagged as invalid.



Detection of internal leaks (Thermo analyzers)

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- If a calibrator or ozone generator is available, leaks through solenoids can be detected using the cell A/B O_3 test.
- At 500 ppb ozone, 10 consecutive averages of A and B should not differ by more than 3%.
- If a leak is indicated, it can be confirmed by using the internal pressure sensor and pump (see manual for details).
- Internal leaks are difficult to find if no ozone generator (or calibrator) is available, but it can be tested (see manual, confirmation of leak trough solenoid).

	#	A	B
	1	488	510
	2	500	499
	3	490	509
	4	500	500
	5	489	511
	6	511	489
	7	496	504
	8	501	498
	9	480	518
	10	510	491
AVG		496.5	502.9
Difference		1.3 %	

	#	A	B
	1	464	510
	2	475	499
	3	466	509
	4	475	500
	5	465	511
	6	485	489
	7	471	504
	8	476	498
	9	456	518
	10	485	491
AVG		471.7	502.9
Difference		6.6 %	

Regular checks

- It is recommended to acquire as many instrument parameters as possible (e.g. flows, pressure, temperatures, intensities, calibration settings,…)
- Other maintenance:
- Change of inlet filters (Teflon filters!)
- Cleaning of measurements cells (as required)
- Cleaning of air inlet system (as required)

Checklist Thermo Ozone Instruments

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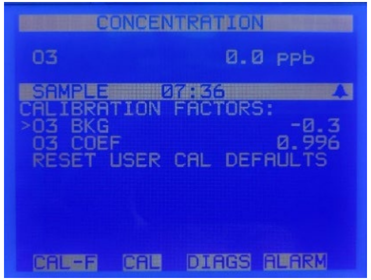
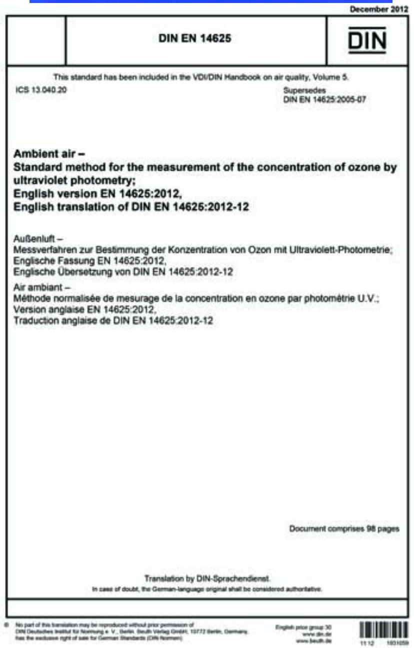
4	Operator	zc				
5	Date	2021-10-04				
6	Location	Empa LA028				
7	Instrument OA	49i-PS	Serial #	1171430027		
8						
9	P/T compensation ON	Yes				
10	Leak Check OK	Yes				
11						
12	Pressure		mmHg	hPa	Type	
13	**Standard**		727.6	970.1		
14	OA unadjusted		733.0	977.3		
15	OA adjusted		727.6	970.1		
16	Temperature		°C			
17	Laboratory		23.0			
18	Bench		27.1			
19	Bench lamp		53.3			
20	O3 lamp		67.3			
21	Flows		ml/min			
22	Cell A		639			
23	Cell B		643			
24	Frequencies		Counts	Noise		
25	Cell A		80776	1.0		
26	Cell B		80026	0.8		
27	Calibration Factors		Initial	Final		
28	BKG		-0.3			
29	COEF		0.991			
30	Cell A/B Check	A	B		AVG A	AVG B
31		1	378	351	367.9	360
32		2	369	358	Deviation %	
33		3	367	361	-2.1%	
34		4	365	362		
35		5	370	360		
36		6	370	356		
37		7	364	365		
38		8	362	366		
39		9	371	358		
40		10	363	363		
41	Remarks					

Example of a checklist for an ozone instrument

Calibration of ozone analyzers

- Ozone analyzers and calibrators have adjustable calibration settings (span, offset).
- The reference (SRP) has no adjustable calibration settings. It is a direct realization of SI traceability.
- Ozone instrument (calibrators and analyzers) must be calibrated against an SRP, or a transfer standard with traceability to an SRP.
- Zero air is required (<150 ppm H_2O, <1 ppb O_3, toluene, and xylene).
- Check:
  - flows (enough flow of zero air and air with O_3)
  - pressure sensor (should also be calibrated)




December 2012

DIN EN 14625 | DIN

This standard has been included in the VDI/DIN Handbook on air quality, Volume 5.

ICS 13.040.20

Supersedes DIN EN 14625:2005-07

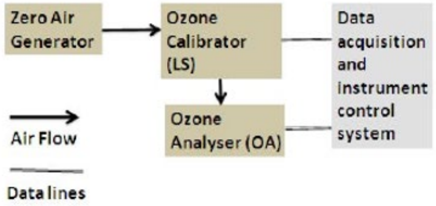
Ambient air – Standard method for the measurement of the concentration of ozone by ultraviolet photometry; English version EN 14625:2012, English translation of DIN EN 14625:2012-12

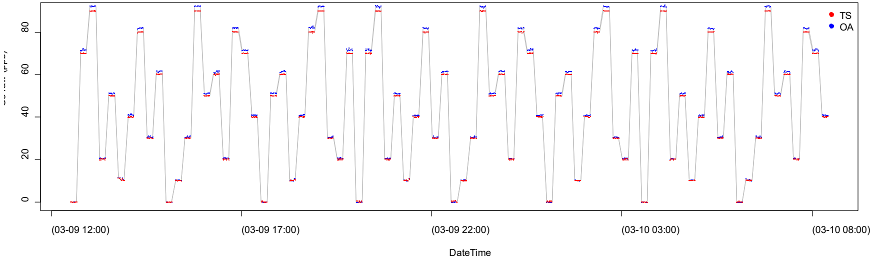
Außenluft – Messverfahren zur Bestimmung der Konzentration von Ozon mit Ultraviolett-Photometrie; Englische Fassung EN 14625:2012, Englische Übersetzung von DIN EN 14625:2012-12

Air ambiant – Méthode normalisée de mesurage de la concentration en ozone par photométrie U.V.; Version anglaise EN 14625:2012, Traduction anglaise de DIN EN 14625:2012-12

Document comprises 98 pages

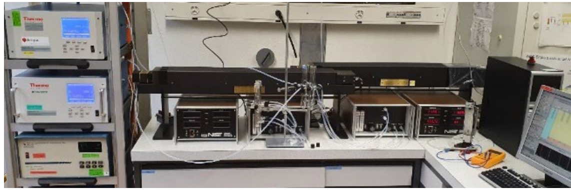
Translation by DIN-Sprachendienst.
In case of doubt, the German-language original shall be considered authoritative.

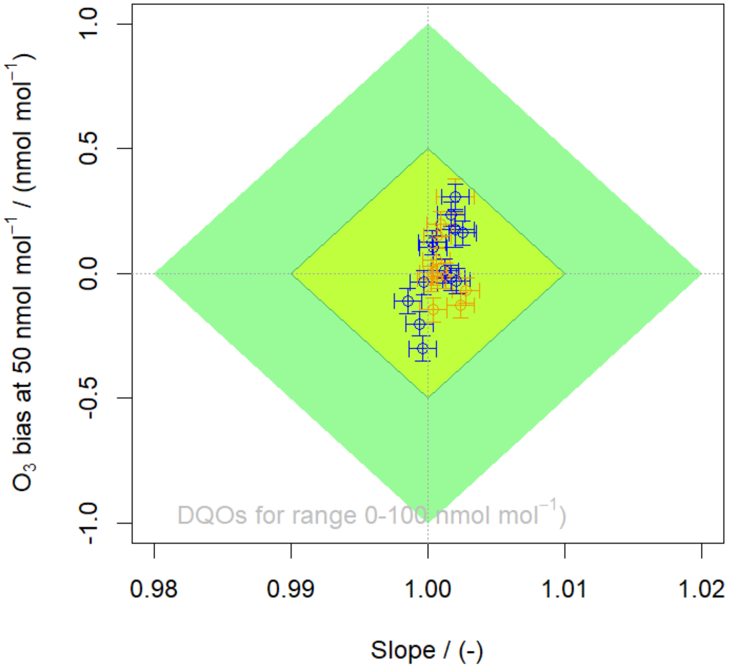


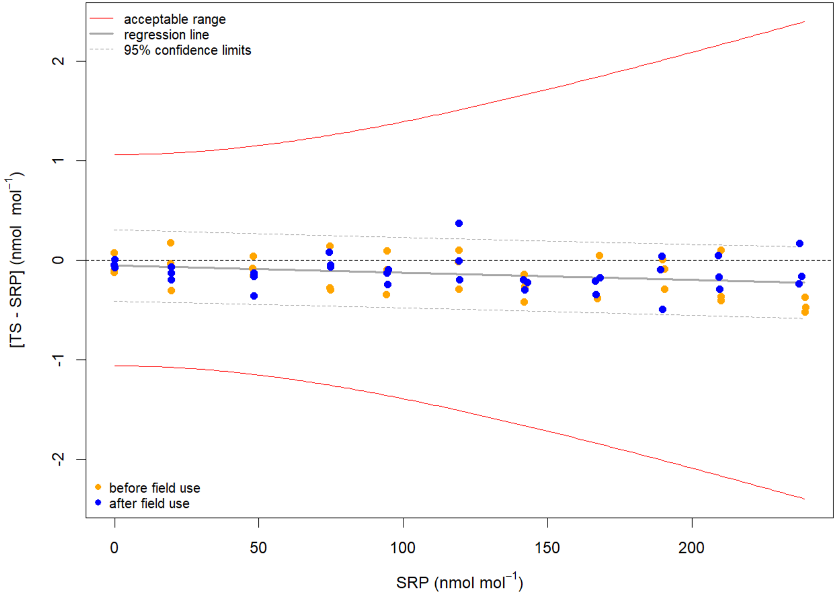


TS-SRP comparisons

Example below shows a number of TS-SRP comparisons before and after the field use of the calibrator

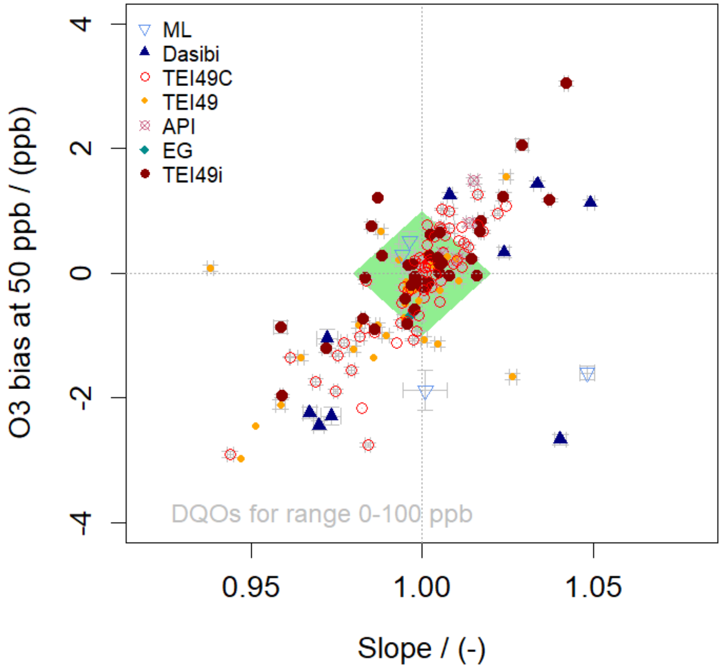


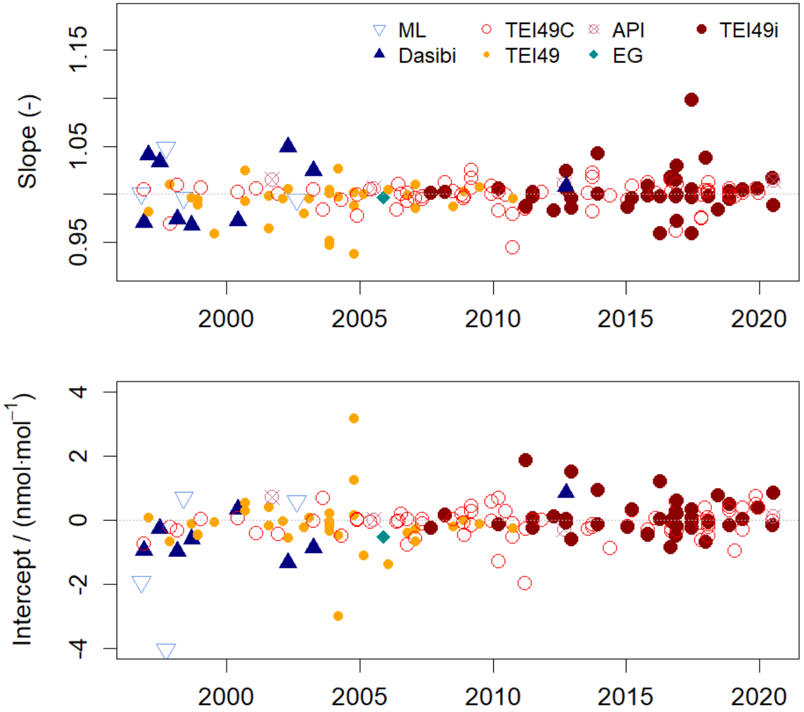




Ozone comparisons at GAW stations

~100 ozone audits at GAW stations during the past 25 years





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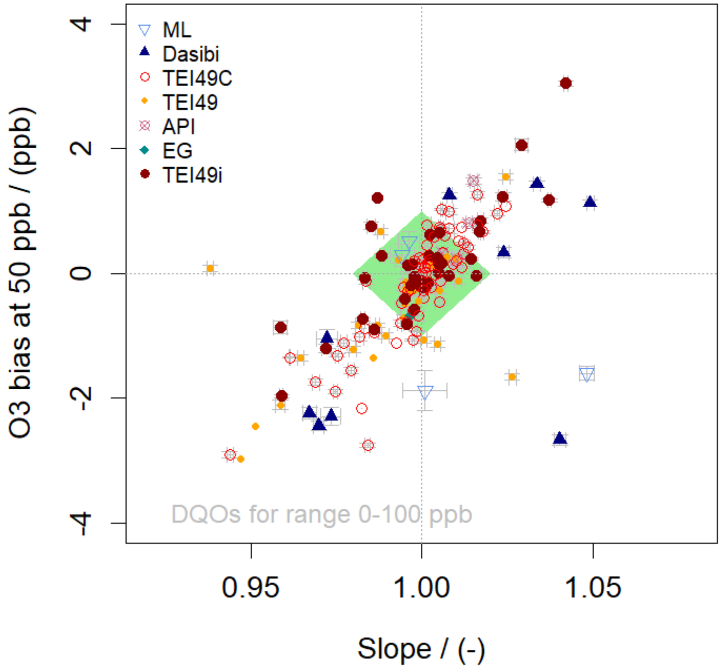
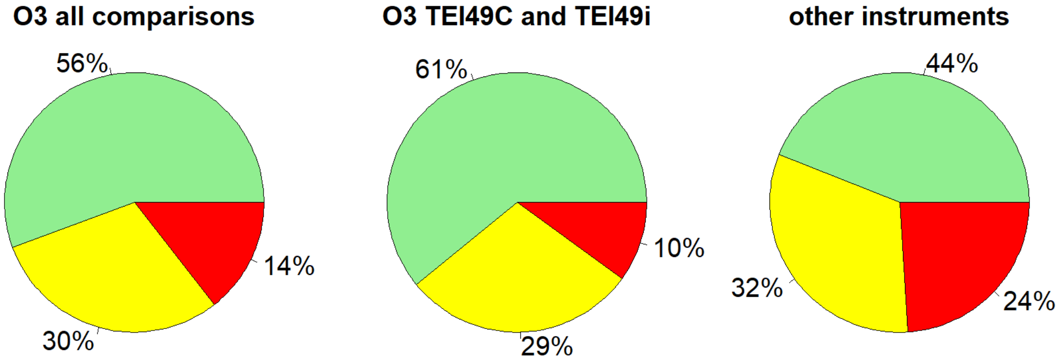
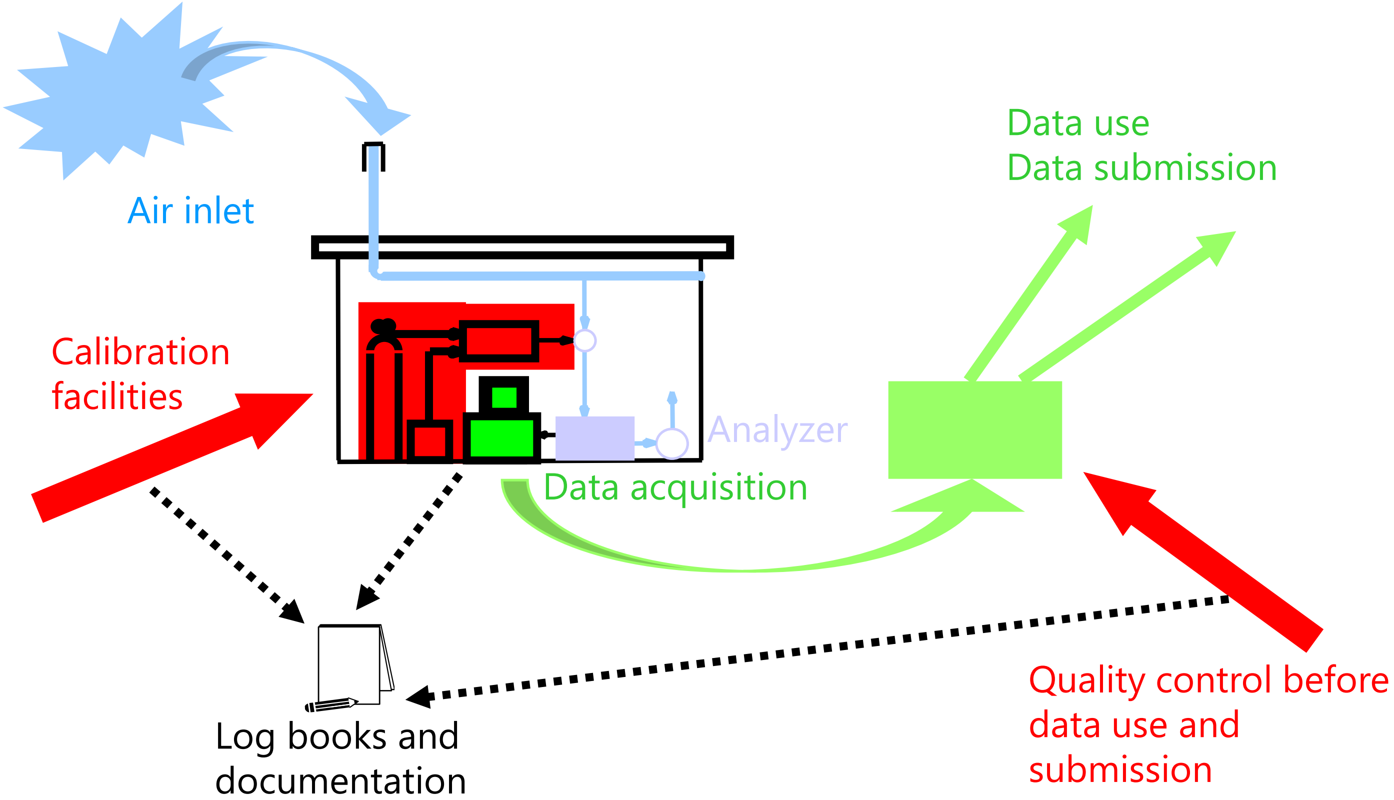




What else...

Successful measurements of air quality with good data (quality) needs

- Sufficient funding
- Adequate infrastructure
- Long term commitment
- Educated staff
- Enough staff
- Clear responsibilities and knowledge sharing
- Collaboration with national and international partners
- Efficient administration
- Ability to act



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Ian Galbally at the Cape Grim GAW station ©zc

What else…

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Izaña station staff, year/source unknown


©zc

What else...

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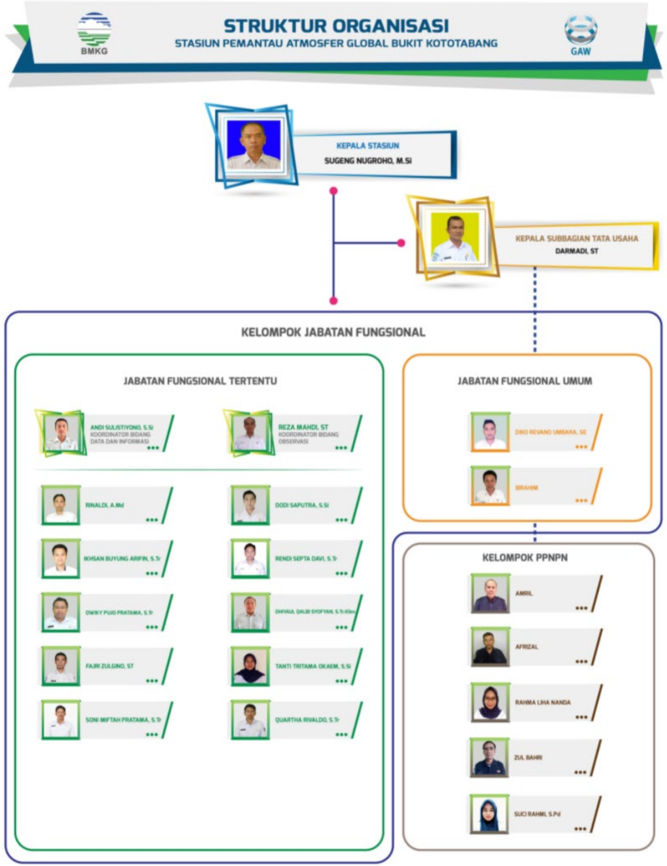

Source: https://gawbkt.id/index.php/c_profil/stuktur

What else…

Successful measurements of air quality with good data (quality) needs

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- Efficient administration
- Ability to act
- …

Ushuaia GAW station ©zc

Equipment delivery delayed by customs:

2019: 48 days

2017: 68 days

2015: 54 days

Further reading…

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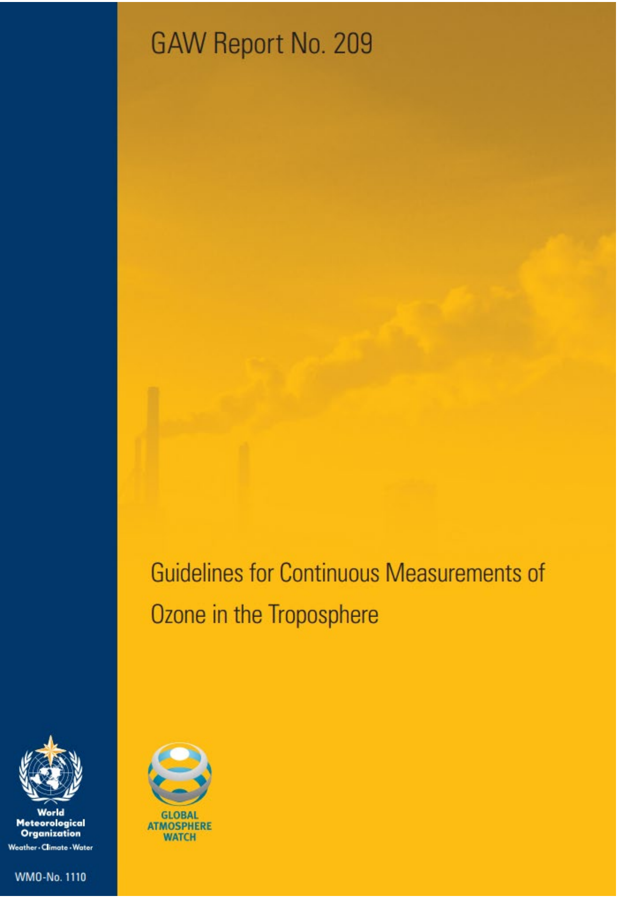

- Guidelines for the Continuous Measurements of Ozone in the Troposphere https://library.wmo.int/doc_num.php?explnum_id=7814

TABLE OF CONTENTS

Acknowledgments

Empa
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- Financial support of GAW activities by MeteoSwiss
- Staff at various GAW stations and Empa for their support