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Guidelines for continuous measurement of nitrogen oxide (NO) and nitrogen dioxide (NO₂) in the troposphere

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98 1 Introduction

99 Long term observations of the chemical composition and physical properties of the
100 atmosphere are crucial for understanding atmospheric chemistry and climate change. The
101 Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization
102 (WMO) has been established to provide reliable and high-quality data on a long-term basis
103 from regionally representative stations (Schultz et al., 2015). One major focus is the
104 monitoring of reactive gases such as nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) because nitric oxide
105 (NO) and nitrogen dioxide (NO_2) play key roles in tropospheric (photo)-chemistry controlling
106 tropospheric ozone formation, the atmospheric self-cleaning capacity and air quality; see
107 GAW Report- No. 195 (WMO, 2011a). However, within GAW there are only a few sites
108 performing continuous in-situ measurements of nitrogen oxides, most of them located in
109 Europe. Extension of the network is necessary and the need for data comparability between
110 these stations indispensable.

111 The WMO GAW program provides the following in support of measurements of nitrogen
112 oxides at GAW stations:

113

- 114 • An integrated framework for how these measurements of nitrogen oxides fit within the
115 WMO atmospheric observations program (WMO GAW Implementation Plan: 2016-
116 2023)
- 117 • Guidance for the setting up and conduct of measurements of nitrogen oxides (this
118 document)
- 119 • Training courses for scientists and technicians in the measurement of nitrogen oxides
120 through GAWTEC (GAW Training and Education Centre; <https://www.gawtec.de/>)
- 121 • Establishment and maintenance of primary NO reference and provision of laboratory
122 standards for GAW stations (not free of charge) through the Central Calibration
123 Laboratory
- 124 • A supply chain for certified calibration gases by the CCL and station audits via the World
125 Calibration Centre for Nitrogen Oxides (<https://www.fz-juelich.de/>)

- 126 • A repository for archiving and distributing the nitrogen oxides measurements (World
- 127 Data Centre for Reactive Gases (WDCRG <https://www.gaw-wdcrg.org/>).
- 128 • Scientific meetings organised by GAW for GAW participants to share their work

129 2 Rationale and Objectives

130 Measurements of nitrogen oxides have been made for decades using different techniques
131 and calibration scales. Harmonisation is essential to establish compatibility between the
132 measurements at different stations and for the achievement of a high-quality data set
133 representative for the globe suitable for the detection of global trends and other atmospheric
134 variations of nitrogen oxides. To fulfil these needs, long term stability of the reference scale,
135 reliable and robust measurement techniques as well as standard operation procedures to be
136 applied at the stations are required.

137 This report aims at documenting suitable *in-situ* measurement techniques for surface NO and
138 NO₂, and to give recommendations for the design of the measurements, the required
139 instrumentation and the data quality assurance and control. The Measurement Guidelines (or
140 equivalents) are to be applied at GAW sites and stations from contributing networks
141 (<https://community.wmo.int/activity-areas/gaw/research-infrastructure/contributing->
142 networks) with already existing NO_x measurement capabilities and at facilities where such
143 measurements have recently been added. The Guidelines should also be central to planning
144 where nitrogen oxides measurements are to be added in the foreseeable future. This report
145 follows up the initial work on this topic in the GAW Report- No. 195 (WMO, 2011a).

146 3 Data Quality Objectives for NO and NO₂ measurements at GAW 147 stations

148 The recent GAW Implementation Plan (WMO, 2017) defines data quality objectives (DQOs)
149 as "*qualitative and quantitative statements that clarify the objectives of observations, define*
150 *the appropriate type of data, and specify tolerable levels of individual measurement*
151 *uncertainty and/or network compatibility. DQOs will be used as the basis for establishing the*
152 *quality and quantity of data needed to support decisions.*"

153 Table 1 summarises the scientific needs, instrumental techniques, and sensitivity
154 requirements for NO_x measurement stations with different characteristics, including
155 continental, continental background, and pristine marine locations. The scientific needs refer
156 to (i) long-term monitoring to derive changes and trends in the atmospheric composition, (ii)
157 monitoring to enable analyses of source-receptor relationships and transport processes, (iii)
158 the investigation of photochemical processes, or the combination of these issues.

159 Considering the typical lifetime of nitrogen oxides (from a few minutes to days) and existing
160 knowledge of the climatology of nitrogen oxides which is related to the remoteness of the
161 station with respect to distance from source areas, it is useful to set 3 different levels of DQOs
162 according to the site characteristics, e.g., the typically encountered mole fractions of NO_x. The
163 levels are described as:

- 164 • continental basic (Level 1, "basic")
- 165 • continental background environments (Level 2, "enhanced")
- 166 • and pristine (Level 3, "high").

167 Despite clear scientific needs to achieve the data quality objectives, the above formulated
168 requirements will indeed present a measurement challenge given the low levels of NO and
169 NO₂ expected at many GAW sites. Further, the need to quantify trends accurately over time
170 at low ambient levels of NO and NO₂ places an additional burden on even the best
171 measurement techniques, so that careful operation by well-trained staff and thorough
172 attention to details is required to achieve the DQOs and the necessary input of measurements
173 of NO and NO₂ to wider decision making.

175 Table 1 Data quality Objectives (DQOs) for NO and NO₂ under differing conditions.

Level	1 (basic)	2 (enhanced)	3 (high) ¹
Site characteristics	Continental basic	Continental background	Pristine marine background, free troposphere
Mean mole fraction NO _x	> 1 nmol/mol	0.1 – 1 nmol/mol	< 0.1 nmol/mol
Scope (corresponding time resolution)	long term monitoring, trends (1 hour), source-receptor-relationship, transport processes (hour-minute), photochemical process studies (minute)		
Detection Limit (1 hour, 3σ)	NO: 50 pmol/mol NO ₂ :100 pmol/mol	NO: 10 pmol/mol NO ₂ :20 pmol/mol	NO: 1 pmol/mol NO ₂ :5 pmol/mol
uncertainty (1 hour, 2σ) ²	NO: 40 pmol/mol or 3% NO ₂ :80 pmol/mol or 5%	NO: 8 pmol/mol or 3% NO ₂ :15 pmol/mol or 5%	NO: 1 pmol/mol or 3% NO ₂ :3 pmol/mol or 5%
uncertainty (1 month, 2σ) ³	NO: 2.5% NO ₂ : 3%	NO: 2.5% NO ₂ : 3%	NO: 1 pmol/mol or 2.5% NO ₂ :3 pmol/mol or 3%
data coverage	66% (90% desirable)		
suggested method ⁴	CLD / PLC	CLD / PLC	CLD / PLC
Alternative / upcoming methods ⁵ (backup or QC reasons)	CAPS, LIF, DOAS, QCL	QCL, LIF	LIF

176 ¹ in pristine environments with NO_x levels below 10 pmol/mol, the required detection limits and uncertainties would
 177 be 0.1 pmol/mol for NO and 0.3 pmol/mol for NO₂.

178 ² whichever is the larger, e.g., for level 2 “enhanced” at NO₂ of 1 nmol/mol an uncertainty of 50 pmol/mol is required
 179 (5% of 1 nmol/mol), at 0.2 nmol/mol an uncertainty of 15 pmol/mol would be required.

180 ³ assuming that the random uncertainties are negligible compared to the calibration uncertainty

181 ⁴ see list of acronyms (Annex 1) for full method names

182 ⁵ methods that are either new and not yet fully tested for their long-term applicability or research type
 183 instrumentation that is demanding to operate, thus, prone to incorrect handling and therefore not fully suitable for
 184 long-term monitoring.

185

186 GAW stations are classified into several levels according to their measurement programs,
 187 purpose and to some extent location (WMO, 2017). These levels or types are:

188 Global Stations: These stations primarily observe GAW variables (at least 6) under background
 189 conditions, i.e., without permanent significant influence from local pollution sources.

190 Regional Stations: The station location is chosen such that, for the variables measured (at
 191 least 2), it is regionally representative and is normally free of the influence of significant local
 192 pollution sources or at least frequently experiences advection of pollution-free air from
 193 specific wind directions.

194 Mobile Stations: Mobile stations use moving platforms for atmospheric composition
 195 observations. The measurement techniques could be modified from the recommendations to
 196 ensure instruments accommodation at the platform. At present, the research vessel R.V.
 197 Investigator is the only mobile GAW station (Humphries et al., 2019).

198 Local Stations: Local Stations conduct measurements in urban environments and in other
 199 locations impacted by nearby emissions (e.g., from biomass burning). GAW local stations are
 200 to satisfy the same requirements as for regional stations except for the sitting requirement.

201 More details about the differences in GAW station types is given in (WMO, 2017)

202 Table 2 indicates the relationship between the Levels of DQOs and the types of GAW stations.
 203 There is not a one-to-one relationship between NO_x DQOs and GAW station types, which is
 204 acknowledged in a broader context in (WMO, 2017). Mobile stations could be of any of the
 205 three DQO levels depending on the environment they are intended to operate within. In the
 206 subsequent discussion there will be some separate sections to cater for the requirements of
 207 different NO_x DQO levels.

208

209 Table 2 The relationship between the Levels of DQOs and the types of GAW stations

NO_x DQO Level	1 (basic)	2 (enhanced)	3 (high)
Site characteristics	Continental basic	Continental background	Pristine marine background, free troposphere
GAW Station Type			

Global	X	✓	✓
Regional	✓	✓	✓
Mobile	✓	✓	✓
Local	✓	X	X

210

211

212 4 Essential requirements for planning and implementing a program for 213 monitoring surface NO and NO₂ at a GAW Station

214 4.1 Planning

215 This Guideline assumes that a GAW station is already established, and the step being
216 described is the selection and implementation at the existing GAW station of in-situ NO_x
217 measurements at one of the three levels (1 (basic), 2 (enhanced), 3 (high)). The essential
218 planning steps are (WMO, 2017):

- 219 • Securing resources necessary to purchase, maintain and provide scientific and technical
220 needs of the in-situ NO_x measurements program
- 221 • Identifying the level of in-situ NO_x measurements DQO to be adopted
- 222 • Obtaining training of scientific and technical staff on the in-situ NO_x measurements
223 through GAWTEC
- 224 • Obtaining additional support, as necessary, to help with the mechanical, electrical and IT
225 aspects of the in-situ NO_x measurements system setup
- 226 • Obtaining support from either the Nitrogen Oxides WCC or a twinning arrangement with
227 another GAW Station to assist with the setting up and the undertaking, analysing, and
228 archiving of the first several years of in-situ NO_x measurements
- 229 • Submitting data to the respective data centre on a yearly basis documenting Year N no
230 later than end of Year N+1
- 231 • Document relevant metadata with the data submission and in the GAW Station
232 Information System (GAWISIS)

233

234 4.2 Detail of Infrastructure Requirements

235 The list below is a compilation of the needed infrastructure for *in-situ* NO_x measurements at
236 GAW-stations. More detailed information can be found in the following sections.

- 237 1. Inlet (Sect. 5.2)
 - 238 a. Low residence time
 - 239 b. Shielded from UV light
 - 240 c. Free from condensation
 - 241 d. Material
- 242 2. Instrumentation (Sect. 5.3)
 - 243 a. Chemiluminescence analyser (CLD) for NO
 - 244 b. Photolytic converter for NO₂
 - 245 c. (Pump)
- 246 3. Calibration (Sect. 5.3.1)
 - 247 a. Gas Dilution System
 - 248 b. Gas phase titration unit with O₃ generator
 - 249 c. Zero gas generator and / or zero air supply
 - 250 d. Laboratory NO standard (certified, traceable to the WMO GAW NO Scale),
251 working standard, target gas
 - 252 e. (automated) plumbing system
- 253 4. Ancillary measurements (Sect. 5.3.5)
 - 254 a. Ozone
 - 255 b. Indicator of continental airmass (e.g., Carbon monoxide or black carbon)
 - 256 c. Meteorology
 - 257 d. Radiation
- 258 5. Data acquisition system (Sect. 5.4)
 - 259 a. Time accurate
 - 260 b. Robust
 - 261 c. Backed-up
- 262 6. Data processing system
 - 263 a. Includes instrument operating parameter checks

- 264 b. Utilizes GAW data reduction algorithms
- 265 c. Provides csv. File data output
- 266 d. Provides graphics, including using data from other instruments, suitable for
- 267 quality assurance
- 268 7. Quality management system
- 269 8. Skilled personnel

270 5 Measurement setup

271 5.1 Location and site local requirements

272 Location and site requirements have to be in compliance with GAW station standards (see
273 GAW Implementation Plan 2016-2023 (WMO, 2017)):

- 274 • Representativeness for the region: the station's location must be regionally
275 representative for the measured species, e.g., reflecting typical in population,
276 vegetation, weather conditions, etc.
- 277 • Unaffected from local contamination sources: the sample location must be upwind of
278 any buildings, garages, parking lots, generators, or other emission sources – any nearby
279 areas where fossil fuels or biomass may be combusted. Station personnel should remain
280 downwind of sample collection and refrain from smoking.
- 281 • Infrastructure: Measurements sites should provide facilities which allow sound
282 operation. This usually requires year-round access, sufficient electrical and reliable
283 power, a suitable data acquisition system and other supplies depending on the
284 instrumentation.

285 Furthermore, a controlled laboratory temperature (air-conditioning) is necessary for the
286 precision of most measurements and instrumentation should not be exposed to direct
287 sunlight. Network connection for (automated) data transfer to the data processing and
288 analysis centre as well as for remote access of the data acquisition system is highly
289 recommended in particular for stations with infrequent operator presence. This ensures a
290 timely backup of the measurement data, allows basic maintenance, and potentially provides
291 the opportunity for problem identification in case of instrumental issues.

292 5.2 Air inlet and sample line design

293 5.2.1 Materials

294 Inert materials should be used throughout any ambient air inlet to avoid modification of the
295 ambient air by sampling. Materials should be smooth (not prone to adsorption), non-porous

296 (low absorption & diffusion) and inert (little reactivity). In practical terms quartz/borosilicate
297 glass and PFA (Perfluoroalkoxy alkane) tubing are recommended. Materials such as brass,
298 copper, aluminium, PET etc. are not suitable as gas handling materials in NO_x measurement.
299 Other instruments measuring different species from a common inlet may place further
300 restrictions on the applicable materials. Other materials may be more appropriate in specific
301 applications e.g., quartz photolysis cells, etc. Silica lined tubing is appropriate for high
302 pressure gas lines including calibration gases. The use of NAFION sample driers is **not**
303 **recommended** for NO and NO₂ measurement due to their conversion of HONO to NO causing
304 bias in NO measurements (ACTRIS-GAW European NO_x-intercomparison at the observatory
305 Hohenpeißenberg 10.-21. October 2016).

306 5.2.2 Sample Lines

307 Special considerations for NO and NO₂ are reactions within the sample lines modifying the
308 ambient air concentration by (1) the exposure of any sample line to sunlight, and (2) the
309 reaction of O₃ and RO₂ with NO. Therefore:

- 310 1. It is recommended to shield the sample line against light. In dark conditions the ambient
311 photolysis reaction $\text{NO}_2 + h\nu \Rightarrow \text{NO} + \text{O}$ reaction is prevented
- 312 2. The residence time within the sample line should be minimised to reduce the effect of
313 the reactions $\text{NO} + \text{O}_3 \Rightarrow \text{NO}_2 + \text{O}_2$, and $\text{RO}_2^* + \text{NO} \Rightarrow \text{RO}^* + \text{NO}_2$ shifting NO towards NO₂
314 to a significant extent on second timescales. This is particularly important in the case of
315 alkylperoxy radicals (RO₂^{*}) as they are not typically measured, thus cannot be corrected
316 for. Practically, shortening the inlet residence time can be achieved by:
 - 317 a. Using a **sample line as short** as possible
 - 318 b. **Reducing the pressure** in the sample line.
 - 319 c. **Increasing the flow rate** in the sample line by e.g., using a secondary bypass
320 pump.
 - 321 d. Reducing the inner diameter of in the sample line.

322 Note that actions c and d above will cause a pressure drop at the instruments inlet and the
323 consequences of possible pressure drop on the instrument's performance must be
324 considered.

325 It is recommended that ambient O₃ concentration is measured, and the sample line is well
326 characterised in terms of residence time so that a correction may be applied for imperfect
327 sampling as detailed in the appendix E.

328 The performance of the inlet line can be tested by spiking the ambient air sample with a
329 constant calibration gas flow at the ambient inlet and the instrument inlet. The mole fractions
330 of NO and NO₂ are thereby determined at the inlet and instrument and changes in the
331 concentrations of NO or NO₂ in the inlet can be detected.

332 5.2.3 Sampling Height and Position

333 Sampling height should be chosen that ambient air measurements are not affected by local
334 contamination. An installation of at least **2 metres, preferably 10 meters**, away from the
335 closest surface is recommended. Roofs can be appropriate when the inlet is situated well
336 above its boundary layer. For a rooftop inlet, a height of inlet of a minimum of 2 metres above
337 the roof ridgeline is recommended.

338 It is recommended that the inlet **of appropriate material for NO and NO₂ observations (see**
339 **5.2.1) be downward facing**, directed into the **prevailing wind**, fitted with a **rain hood/ funnel**.
340 An inverted 500 ml PTFE beaker is used in some locations. Cleanliness of the hood and the
341 inlet needs to be checked regularly (see Chapter 8).

342 5.2.4 Heating

343 Controlled heating of the sample line to a few degrees (3 - 4 °C) above ambient temperature
344 is recommended to prevent condensation of water, organic and inorganic volatile
345 compounds. The temperature should not exceed 40 °C to avoid significant thermal
346 decomposition of other trace gases (e.g., PAN) leading to an interference in the NO and/or
347 NO₂ measurements.

348 5.2.5 Sample filtering

349 The NO and NO₂ analyser(s) should be equipped with an inlet line filter made of Teflon with
350 a pore size of 5 µm right at the entrance to the instrument. The filter should be changed

351 regularly, consummate with local conditions. The use of Nylon 6-6 sample filter which
352 efficiently removes (>95%) nitric acid is recommended.

353 5.3 Instrumentation

354 For NO, GAW recommends the NO chemiluminescence detection technique (CLD), and for
355 NO₂ photolytic conversion of NO₂ to NO, followed by the detection of NO (see [appendix 6](#)) for
356 use for measurement of nitrogen oxides at GAW Stations. Detailed recommendations for
357 instrumentation appropriate for the three levels of NO_x DQOs are described in Section 6.
358 Emerging techniques are promising for measurements of NO and NO₂, but, as of this report,
359 none are yet mature enough to be recommended by GAW due to the requirement for highly
360 skilled personnel and frequent maintenance to achieve high quality measurements (see
361 [appendix 6](#)). Whilst GAW encourages stations to exploit and develop these new techniques,
362 currently operational measurements should be performed using photolytic converters
363 coupled with CLD.

364 Calibration of the GAW recommended NO CLD technique and NO₂ photolytic converter
365 coupled to the NO CLD technique requires:

- 366 • a traceable source of nitric oxide (NO) calibration gas, generally in a cylinder containing
367 a standard gas mixture
- 368 • a gas dilution system
- 369 • a source of zero air or means to generate air free from NO and NO₂ (zero air) for the
370 dilution system and to determine instrumental offsets
- 371 • A gas phase titration (GPT) system, using an ozone generator to generate O₃ for reaction
372 with a metered amount of NO standard to generate a known concentration of NO₂ for
373 calibration of NO₂ converters (see appendix 6).

374 A gas dilution system is required to dilute the more concentrated calibration gases down to
375 lower concentrations that are closer to the level of ambient measurements. These systems
376 generally use two or more mass flow controllers, one for the calibration gas and one for the
377 zero gas. The specifications of the accuracy and drift of the flow measurements must be

378 sufficient that they contribute less than half of the accuracy required under the DQOs.
379 Commercial gas dilution systems are available that meet these requirements.

380 A gas phase titration (GPT) system, typically using a low-pressure mercury vapour lamp to
381 photolyze air or pure O₂ to generate a quantity of O₃ for reaction with a metered amount of
382 NO standard to generate a known concentration of NO₂ is required for calibration of NO₂
383 converters (Andersen et al., 2021;Galbally, 2020).

384 Air quality combined gas dilution – gas phase titration systems are commercially available
385 that are suitable for NO and NO₂ and incorporate a gas phase titration unit. This technology
386 can be used for all three levels of DQOs.

387

388 5.3.1 Calibration gases

389 Calibration gases, traceable to the Central Calibration Laboratory (CCL) scale and a calibration
390 unit with the possibility of gas phase titration (for calibration of NO₂) are required. The station
391 transfer standard which is a cylinder of a type approved by the CCL as a secondary or tertiary
392 level from the CCL Primary NO calibration gas standard. Dilute mixtures of NO and ultrapure
393 N₂ in the range 450 nmol/mol to 10 µmol/mol (450 ppb to 10 ppm) are recommended, stored
394 in specifically passivated cylinders. The amount fraction of NO in the cylinders determine
395 uncertainties and stabilities of the standard cylinders. Typical stabilities and expanded
396 uncertainties are 3 % expanded uncertainty and 1 year stability at 450 nmol/mol, 0.8 %
397 expanded uncertainty and 2-year stability at 10 µmol/mol and 0.5 % expanded uncertainty
398 and 5-year stability at 50 µmol/mol. Calibration gases should be within their certification
399 period when used and should be checked for drift/recertified when out of service.

400 It is advice to use the transfer standard for regular calibrations. For cost reasons or if a
401 different concentrations range is needed a working standard can be used in addition. This
402 working standard is a cylinder of NO calibration gas for day to day use at the Station. This
403 standard must be checked every 6-month against the station transfer standard. When station
404 transfer standard and/or the working standard is replaced, there should be a minimum of 5
405 direct comparisons via the measurement instrumentation of the old and the new cylinder.

406 Cylinder regulators for standards should be of high purity stainless steel type, dedicated for
407 use only with the NO standard, and being purged thoroughly before use taking care not to
408 introduce ambient air into the cylinder which can lead to conversion of NO to NO₂ and thus
409 invalidate the certification.

410 5.3.2 Introducing calibration gas into NO/NO_x analysers

411 The issue of how to introduce calibration gases into a gas analyser is generally dealt with only
412 briefly, if at all, when discussing atmospheric composition measurements. However, in the
413 case of NO and NO₂ and the CLD-PLC analyser, a more detailed approach is needed because
414 of the effect of NO to NO₂ conversion by O₃ in the inlet and the sensitivity of the detector
415 response to water vapour.

416 There are two logical points of introduction of the calibration gas to a CLD-PLC analyser, at
417 the ambient Inlet where the sampled air is sucked out of the atmosphere and at the analyser
418 inlet where the sampled air enters the analyser system. There are also two obvious diluents
419 for the calibration gas, ambient air and zero air (air treated to remove all NO and NO₂). In
420 Table 1 the set of combinations of these variables and the presence or absence of O₃ and
421 humidity in the diluent (called systems) are presented. The two systems most used are
422 System 1, the ambient air inlet with ambient air as the diluent and System 4 the analyser inlet
423 with zero air as the diluent. These two options are discussed in the following subsections. An
424 important consideration is the number of corrections that need to be made to the calibration
425 and ambient data after data acquisition. These corrections are inlet and analyser specific and
426 introduce additional uncertainty into the results. Therefore, a system of no or small
427 corrections for NO data is preferable. The examples of that are System 1 and System 6. To our
428 knowledge, System 6 has never been utilized. System 6 is an option that could be explored at
429 GAW stations with research programs. However, the conditions at which a correction is
430 neglectable must in any case be carefully investigated. E.g., changing ozone or water
431 concentration might still necessitate corrections.

432

433 Table 3 Possible configurations and diluents for NO and NO₂ analyser calibration.

System	Calibration gas injection Point*	Diluent	Analyte contains H ₂ O	Analyte contains O ₃	Corrections required for NO mole fraction
1	Ambient Inlet ¹	Ambient air	✓	✓	none
2	Analyser Inlet ²	Ambient air	✓	✓	ozone
3	Ambient Inlet	Dry Zero air	X	X	humidity and ozone
4	Analyser Inlet	Dry Zero air	X	X	humidity and ozone
5	Ambient Inlet	Humidified Zero air	✓	X	ozone
6	Ambient Inlet	Humidified and ozone added Zero air	✓	✓	none
7	Analyser Inlet	Humidified Zero air	✓	X	ozone
8	Analyser Inlet	Humidified and ozone added Zero air	✓	✓	none
9	Pre-dried ambient air*	Dried Ambient air ³	X	?	ozone

434 5.3.3 Zero Air

435 A source of NO_x free synthetic or zero air is required for determining detector artefacts and
436 offsets, as well as being required to calibrate in locations with high or variable background
437 NO_x concentrations e.g., continental.

438 *In-situ* systems of zero air generation generally rely on a combination of sorbent media such
439 as carbon/charcoal, potassium permanganate, nickel nitrate, precious and semi-precious
440 metal catalysts, possibly in combination with a broad band UV photolysis cell for generating
441 ozone to oxidise certain reactive gases before scrubbing. There may also be a pre-drying
442 system so that the dew point of the zero gas is low (< -15 T_d) which slows saturation of any
443 sorbents; however, the sorbents still have a finite life and must be replenished periodically to
444 maintain zero gas purity.

¹ The Ambient Inlet is where the sampled air is sucked out of the atmosphere

² The Analyser Inlet is where the sampled air enters the analyser system

³ System similar to that described by Andersen et al. (2021)

445 5.3.4 Gas phase titration systems

446 As the calibration by GPT requires the measurements of both NO and NO₂ standards recent
447 developments of spectroscopic instruments which measure only NO₂ have fostered research
448 into direct calibration sources of NO₂ (Worton, 2020). However, NO₂ in gas cylinders is less
449 stable than NO. The main impurity is HNO₃ whose concentration increases over time. Progress
450 has been made over recent years to develop stable NO₂ gas mixtures e.g., within the MetNO₂
451 project (<http://empir.npl.co.uk/metno2/>). Still, calibration cylinders of dilute mixtures of NO₂
452 and N₂ are not recommended yet.

453 Other calibration sources of NO₂ include permeation devices (Mitchell, 2000) or sources
454 where N₂O is photolyzed (Birks et al., 2020). Work must be done to ensure the traceability of
455 these sources. Therefore, GAW does not recommend these calibration methods yet.

456 In continental sites it is acceptable (and often necessary) to calibrate an instrument in zero
457 (synthetic) air. However, this changes the humidity of the sample gas unless specific
458 rehumidification has been implemented. The result in the absence of rehumidification is that
459 the instrument is more sensitive when calibrated than when operated in measure mode due
460 to the absence of water vapour in the calibration gas which would otherwise result in
461 quenching of excited state NO₂* in a chemiluminescence system. This results in an under-
462 estimation of NO_x which will also be variable when ambient humidity is changing which must
463 be corrected for (see 7.3.1). Thus, rehumidification of zero gas is recommended.

464 5.3.5 Calibration by spiking ambient air

465 The corrections for humidity and ozone effects might not be not required if calibration is done
466 by spiking ambient air at the ambient inlet with a calibration gas (Galbally, 2020). This
467 technique has been used by many research groups since the advent of CLD NO_x
468 measurements.

469 A slightly different setup is described by (Andersen et al., 2021) where the ambient air is dried
470 with a Nafion dryer In this system, see Section 5.2.1 this report. A NO gas standard with
471 5 μmol/mol (5ppm) is added with a flow of 8 ml/min to the flow of dried ambient air of 1000
472 ml/min. The calibration gas is injected right before the BLC. The resulting concentration during

473 calibration is three orders of magnitude larger than the ambient concentration, effects due
474 to changing NO concentration in ambient air can be neglected. The system corresponds to
475 system 9 in Table 3. There is still need for correction for NO conversion to NO₂ by ozone within
476 the inlet, upstream of and within the nafion drier.

477 The conversion efficiency is determined with GPT using zero air.

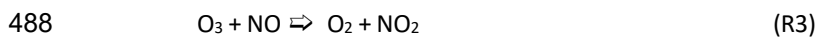
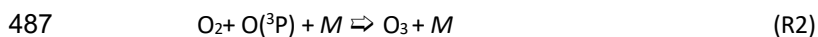
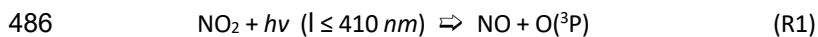
478

479 Figure 1 Setup for calibration by spiking ambient air. From (Andersen et al., 2021).

480 5.3.6 Ancillary instrumentation

481 Measurements of other reactive gases and meteorological parameters, whilst not essential,
482 can complement NO_x measurements, give greater context to data, and allow for more
483 sophisticated data processing.

484 Ozone (O₃), is invariably also measured when measuring NO_x due to the well know null cycle
485 between the two as in reactions R1 – R3:



489 Ozone instrumentation is ubiquitous and easily operated in the case of *in-situ* ozone
490 photometers (WMO, 2007a).

491 Other atmospheric pollution tracers such as carbon monoxide (CO) or black carbon (BC) can
492 help identify sources of elevated NO_x. At pristine sites radon is a valuable tracer of continental
493 exposure. Basic meteorological parameters such as ambient temperature, barometric
494 pressure, humidity, wind speed and direction are universally useful and are provided by most
495 automatic weather stations. They are required to report ‘dry’ data at standard temperature
496 and pressure and needed for the correction of humidity effects.

497 5.3.7 Instrumentation for Basic Level DQOs

498 The minimum requirement for an analyser to be classed as trace level measurements is that
499 the NO_x analyser should determine the chemiluminescent zero i.e., be equipped and
500 operating with a “pre-chamber”, “zero”, or “background” measurement mode. The
501 instrument should also be fitted with a photolytic convertor of either a lamp or LED light
502 source. The DQOs for basic level (Table 1) are at the limit of what is available from readily
503 available commercial trace gas level instruments. Some instruments may require or benefit
504 from a more powerful vacuum pump separate from the instrument.

505 The instrument output should include the following data streams:

- 506 • Zero reading – preferably signal from PMT
- 507 • NO reading – preferably signal from PMT
- 508 • NO_c reading – preferably signal from PMT
- 509 • ON/OFF of zero (pre-reactor)
- 510 • ON/OFF of photolytic convertor

511 It is desirable that the instrument output include the following additional data streams:

- 512 • Sample flow
- 513 • O₂ or air flow to the ozoniser
- 514 • Reaction cell pressure
- 515 • Reaction cell temperature
- 516 • PMT temperature

517

518 5.3.8 Instrumentation for Enhanced Level DQOs

519 The minimum requirement instrumentation for enhanced level DQOs is similar to but more
520 demanding than the instrumentation for basic level DQOs in terms of detection limit and
521 stability.

522 5.3.9 Instrumentation for High Level DQOs

523 Extra consideration must be made for measurements in pristine environments where
524 ambient concentrations of NO and NO₂ are typically at very low pmol/mol levels. Here
525 instruments are operated close to or at their limit of detection (LOD) and become very
526 sensitive to small offsets and changes in conditions.

527 Small instrumental zero offsets due to pressure changes, humidity changes and slight
528 temperature differences become increasingly important and must be accounted for. These
529 'artefact' signals can be measured and accounted for with very careful study of night-time NO
530 offsets and with humidified ultra-pure zeroing gas for NO₂.

531 There are only few instrument manufacturers who construct instruments to meet the High
532 Level DQOs. However, to reach and maintain the high quality of measurements for the
533 pristine atmosphere on a long-term basis requires a sustained research grade effort.

534 Stations may develop bespoke systems for generating zero air, especially those in pristine
535 environments, where commercial systems may not meet the data quality objectives. The
536 purity of zeroing gases is especially critical in pristine environments where instruments are
537 often operating very close to the limit of detection and small uncertainties in the zero
538 measurement can have a dramatic effect. Therefore, more than one method for calculating
539 the NO offset must be tested (Andersen et al., 2021;Galbally, 2020).

540 As converter interferences from higher atmospheric nitrates gain more importance at pristine
541 sites, extra efforts are required to characterize these interferences. At the station at Cape
542 Verde a BLC and a PLC are run in parallel to evaluate these interferences as well as to
543 determine artefacts in NO₂ (Andersen et al., 2021).

544 Further details can be found in the publications that describe the setup at Cape Verde
545 (Andersen et al., 2021), Cape Grim (Galbally, 2020) and of the IAGOS instrumentation (Berkes
546 et al., 2018).

547 5.4 Data acquisition, processing and storage

548 Reliable data collection and early data processing are paramount in ensuring return on
549 investment in measurement capability. Therefore, robust systems for (a) reliably recording
550 data collected and (b) subsequent processing are a priority for any site. It is recommended
551 that data recording software be implemented that removes any requirement for manual
552 retrieval of instrument data. Additionally, it is recommended to use integrating hardware
553 control of the system such that any action performed automatically, or manually is recorded.

554 Any data acquisition system should be designed to keep accurate time (e.g., by syncing to a
555 timeserver or GPS) and record at a fixed rate. The data collection rate should match or exceed
556 the desired reporting rate,. Hardware or software systems can both achieve good data logging
557 if implemented well.

558 Data which is collected should be stored securely preferably on two drives at the GAW station
559 and backed up to an off-site location regularly to avoid loss of data due to failed hardware at
560 a station, or corruption over time.

561 The data processing software should have four characteristics. All useable instrument data
562 output including logs etc should be utilized, preferably automatically, to provide quality
563 assurance and flags for the data. The data should be processed using the GAW data processing
564 algorithms that are included in Section 7 of this report. The software should produce output
565 in .csv files and even include the option to attach a header consistent with submitting the
566 data to the WDCRG. The software should also be able to access other data records from the
567 station and combine these with the NOx record to produce graphics for quality assurance and
568 data interpretation.

569 5.5 Calibration

570 The chemiluminescence technique for NO is not an absolute measuring method and
571 sensitivity depends on parameters like cell temperature or pressure, photon count efficiency
572 of the PMT, contamination or degradation of optical components, etc. which can change with
573 time. Therefore, periodic calibration of the device is required.

574 Depending on data quality objectives (DQOs), calibrations should be performed on regular
575 basis and with such intervals that the expected deviation between consecutive calibrations is
576 lower than the required uncertainty based on the DQO. In continental atmosphere ($\text{NO}_x > 0.1$
577 nmol/mol), zero checks are typically not as important as span checks for instruments
578 equipped with a pre-chamber. However, to ensure that zero air contains only traces of
579 nitrogen oxides causing a signal well below the DQO detection limit, zero checks should
580 always be performed together with span checks. According to the DQOs, recalibration should
581 be performed at least once per week for level 1 and every 3rd day for level 2 and 3 stations.

582 Chemiluminescence instruments operate linearly in theory with only slight deviation in
583 systems performing as designed. Calibration concentration is therefore not critical and factors
584 such as gas consumption, dilution range often dictate what concentration is used for
585 calibration. However, it is prudent to try and calibrate in the same range as which
586 measurements are made – this is not necessarily possible in pristine environments. The
587 instrument linearity should also be verified up to the maximum of the expected ambient
588 amount fraction range at least once a year. Nonlinear instruments indicate fundamental
589 issues which should be rectified.

590 It is further recommended that periodic calibrations be timed so that they occur at a different
591 time each day/week, in order that the dataset not be biased by having low data coverage for
592 a specific time every day. An additional linearity check with different calibration amount
593 ratios should be done once a year.

594 Different instruments may also provide different parameters or options, and the calibration
595 hardware may be integrated (automated), separate (automated), or manual.

596 In all cases it is imperative that a timestamped record of the various calibration states is kept
597 either in logging software or offline with the instrument. Artefact determination (e.g., due to
598 nitrate decomposition on hot surfaces in the instrument) may not be appropriate for
599 continental sites whilst being essential in pristine environments. Some instruments also may
600 not give visibility of the raw counts and/or zero data depending on manufacturer and
601 configuration. Some may automatically apply newly measured calibration parameters to the
602 data (resulting in an undesirable step change but can be corrected for) whereas others do not

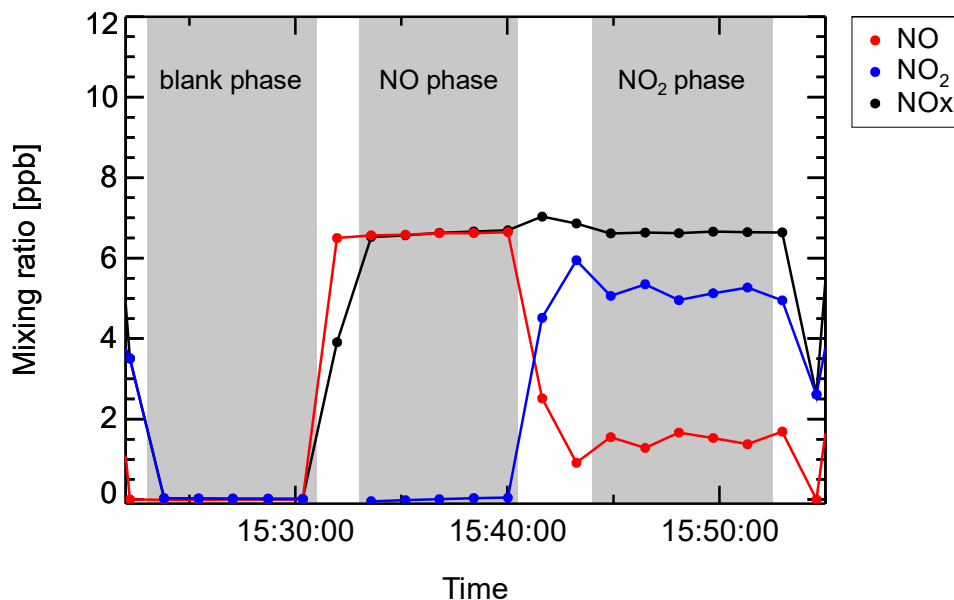
603 and are applied in post processing. For both approaches it is crucial that the calibration
604 parameters (zero, sensitivity and conversion efficiency) are recorded and stored.

605 The instrument sensitivity and conversion efficiency determined by calibrations are applied
606 to measured counts by interpolating them from the times calibration times to the
607 measurement times (see appendix C)

608 In any case, a calibration should include three steps:

- 609 1) a period when a NO standard is measured to determine the sensitivity (NO phase)
- 610 2) a period, when a NO₂ is measured to determine the conversion efficiency CE_{NO_2} (NO₂
611 phase)
- 612 3) a blank period to determine NO and NO₂ artefacts (blank phase).

613



614

615 Figure 2 Schematic of NO_x calibration

616

617 Calibrations should be performed under the same conditions as the ambient air
618 measurements. Generally, the NO₂ phase calibration should always immediately follow the
619 NO phase as it includes the NO chemiluminescence sensitivity.

620 5.6 Documentation

621 All actions taken on the instrument or related to the instrument (inlet, pump, data acquisition)
622 must be documented in a station logbook with the respective time and the responsible
623 person. The time zone of the logbook entries should also be clearly documented. Special care
624 must be taken for the documentation of the material, dimension, flow, temperature, and
625 pressure of all components of the inlet system from the inlet point to the NO analyzer. Any
626 change of the analyzer, e.g., instrument failures, maintenance and calibrations must be
627 recorded. Logbooks can be
628 Logbooks can be kept as hardcopy or electronically. As logbooks are part of the metadata,
629 they should be regularly copied for backup reasons and stored. An example can be seen in
630 (Galbally, 2020).

631 5.7 Personnel Qualification

632 Well trained personnel are essential. The officers in charge should be aware of the whole
633 complexity of the analysis system. The participation in dedicated training courses concerning
634 nitrogen oxides such as the GAWTEC (GAW Training and Education Centre;
635 <https://www.gawtec.de/>) training course on reactive gases is recommended for both the
636 scientists and technicians undertaking the NO_x measurements. Additional IT and data
637 processing help is required in the initial years of a new NO_x measurement program.

638 5.8 Health and Safety

639 GAW advises the participation in safety training depending on the site and the
640 instrumentation used, such as handling of toxic and compressed gases, chemicals and
641 electrical hazards., The detection of NO by CLD technique (see [appendix 6](#)) requires ozone in
642 toxic concentrations and it must be ensured that the ozone hazard is treated accordingly e.g.
643 ozone exhaust scrubbers, ozone alarms. High voltages (>1000 Vdc), ultraviolet light and high
644 temperatures (>300 °C) are other potential hazards to personnel and training and protective
645 actions/equipment are essential.

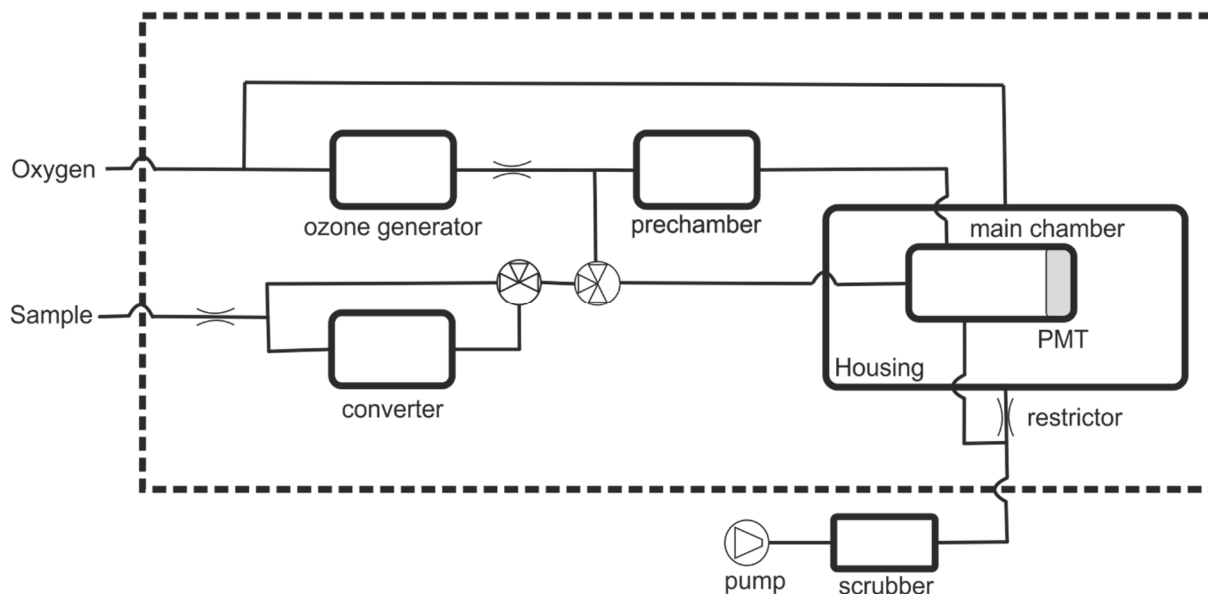
646 **6 Chemiluminescence Measurements for NO and NO₂**

647 GAW currently recommends only NO chemiluminescence for nitric oxide, and photolytic
648 conversion followed by NO chemiluminescence for nitrogen dioxide monitoring. These two
649 functions are usually combined into a single, relatively inexpensive (specification dependent),
650 commercially available instrument of which there are several options offering performance
651 which meet the data quality objectives for levels 1 and 2. For level 3 (pristine and free
652 troposphere) modified or custom-built instruments based on the same principles may be
653 required, though commercial systems may also be/become available.

654 These techniques are recommended due to the maturity of the technology, robustness of the
655 instruments, and abundance of manufacturers of these instruments. Other technologies may
656 also meet or exceed the required data quality objectives.

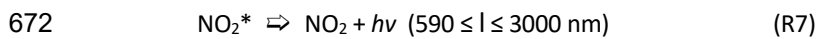
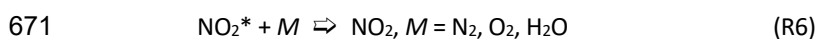
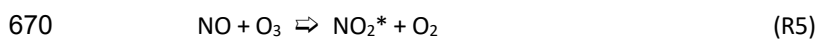
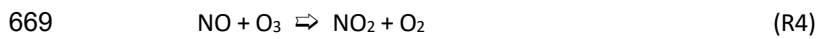
657 **6.1 NO Chemiluminescence detector (CLD)**

658 The NO chemiluminescence detector (CLD) is widely used for NO and NO₂ detection. It has
659 been invented in 1970 (Fontijn et al., 1970), has a long record of measurement in highly
660 polluted and pristine environments and has been characterised extensively.



661
662 Figure 3 Schematic of a CLD analyzer
663

664 The chemiluminescence technique detects nitric oxide (NO) via the gas-phase reaction of NO
665 with O₃ in high excess partially yielding to an excited NO₂* (²B₁) (R5) (Clough and Thrush,
666 1967; Clyne et al., 1964). The excited NO₂* is either quenched by N₂, O₂ and H₂O (R6) or emits
667 a photon in the red/infra-red wavelength (R7), which is then detected by a photomultiplier
668 tube (PMT):



673

674 The number of photons emitted by the decay of excited NO₂* to NO₂ is proportional to the
675 NO present before reaction with O₃ (Drummond et al., 1985). The photons emitted (R7) are
676 detected by a cooled PMT with the sample under low pressure (to minimise the quenching
677 rate of the excited of the NO₂* in order to yield a signal which is linearly proportional to the
678 number density of NO in the sample gas (Fontijn et al., 1970). Quenching (R6) is minimized by
679 operating at high vacuum to reduce collision probability. However, quenching still occurs;
680 thus, it is necessary to calibrate the detectors' response (sensitivity) to a known concentration
681 of NO regularly. A changing ambient humidity in the sample has a marked effect on drift in
682 sensitivity and needs to be corrected for (see 7.3.1)

683 The chemiluminescence reaction takes place in a reaction chamber, labelled as main chamber
684 in Figure 3. Ozone is produced from an ozonizer which can be fueled with oxygen or synthetic
685 air. Before entering the pump, the ozone is scrubbed. As water can condense at the PMT
686 window which will lead to a loss in sensitivity or can damage the electronics the PMT housing
687 is flushed with dry air.

688 For trace level NO detection CLDs are equipped with what is referred to as a pre-chamber,
689 zero, or background measurement mode. All three of these refer to the same measurement

690 of 'detector background' and are all implemented in basically the same way. A background
691 measurement is necessary in CLD instruments for three reasons:

- 692 (I) The detector signal is non-zero even in the absence of any analyte
- 693 (II) There is a detector signal due to chemiluminescence of ozone reacting on the cell
694 walls
- 695 (III) The detector is sensitive to gas phase reactions other than NO + Ozone

696 Point (I) is due to thermionic emission of electrons across the gain stages of the
697 photomultiplier tube (PMT) which is driven at >1000 Vdc and is intrinsic to CDL design. This
698 signal is often referred to as "dark current", "dark count", or "dark noise" and is reduced by
699 operating the detector (PMT) at low temperature; it should remain stable so long at the
700 temperature is stable. Point (II) is observed when the ozoniser is turned on and the detector
701 signal increases in the absence of any known gas phase contaminant, and Point (III) is due to
702 signal from reactions of atmospheric alkenes with ozone. These alkene + ozone reactions are
703 also chemiluminescent in the red/infrared region – same as NO + ozone. Other
704 chemiluminescent reactions which emit photons outside of the red/infra-red region are not
705 considered as a red band pass filter is generally present between the reaction chamber and
706 the PMT.

707 To determine the magnitude of the "dark current", surface reactions and alkene + ozone
708 reactions the contribution of NO + ozone must be removed. This is done by reacting NO with
709 ozone in a pre-chamber ahead of the main reaction chamber so that no nitric oxide is present
710 in the main reaction chamber. This works because alkene + ozone reactions are ~2 orders of
711 magnitude slower than that of NO + ozone so only those reactants are present in the reaction
712 chamber whilst in this pre-chamber zero measurement mode, all NO having been reacted
713 (Drummond et al., 1985).

714 In practice the pre-chamber zero measurement is achieved by diverting the reagent ozone
715 flow with a high conductance Teflon/PFA 3-way valve from being added directly to the
716 reaction chamber, to being added upstream before the pre-chamber as Figure 4.

717 The frequency of pre-chamber, zero, or background measurements should be set to capture
718 the drift of factors affecting the signal e.g., changing detector temperature or atmospheric

719 variability (e.g., 2 min). The duration of pre-chamber, zero, or background measurements
720 should be long enough to obtain a stable signal whilst not strongly impacting data coverage
721 (e.g., 1 min). Longer, less frequent zeroing maybe be appropriate, as also shorter, and more
722 frequent zeroing.

723 6.2 NO₂ Photolytic Converter

724 GAW recommends the photolytic conversion (PLC) of ambient nitrogen dioxide (NO₂) to NO
725 followed by CLD detection for measuring NO₂. Conversion is performed below 405 nm using
726 a light source such as broad band Xenon high pressure, metal halide lamps or narrow band
727 ultraviolet light-emitting diodes (UV-LEDs).

728 Subsequent to the conversion within the photolytic converter the sum of converted fraction
729 of NO₂ and ambient NO is detected by the CLD. Ambient NO₂ is calculated by the difference
730 of the total signal (NO_x) and ambient NO (Kley and McFarland, 1980) provided that the
731 conversion efficiency (CE) of the converter is known.

732 The residence time inside the photolytic converter increases the conversion efficiency but at
733 the same time enhances the back reaction of NO with O₃, therefore converters generally are
734 optimised to provide acceptable CE and time response given the sample flow requirements
735 of the coupled CLD.

736 Photolytic converters may be implemented into CLD systems in various ways depending on
737 design and the data needs:

- 738 1. A PLC can be switched in and out of the flow path of a single CLD to modulate the
739 NO/NO_x signal. A bypass pump may maintain flow through the PLC when out of
740 circuit.
- 741 2. A PLC can be illuminated periodically in the flow path of a single CLD to modulate
742 the NO/NO_x signal. This is generally applicable to UV-LED based implementations.
- 743 3. Two CLDs in parallel can be used, one with a PLC in its flow path so that one
744 measures NO, and the other NO_x. This provides the highest time resolution data
745 and generally fastest response.

746

747 The various implementations and variations require subtly different treatments of the data;
748 however, all can provide data to the standard required by all three levels of NO_x DQOs at GAW
749 stations.

750

751 6.3 Other techniques for NO_x measurements

752 In addition to chemiluminescence, spectroscopic techniques have been developed to
753 measure NO and NO₂. A direct spectroscopic measurement of NO₂ circumvents the
754 conversion of NO₂ and reduces the possibilities of interferences. The instruments to target
755 NO₂ by Cavity Attenuated Phase Shift Spectroscopy (CAPS) been introduced more than ten
756 ago (Ge et al., 2013;Kebabian et al., 2008). Other spectroscopic methods include iterative
757 cavity-enhanced DOAS (Horbanski et al., 2019) and Quantum Cascade Laser Absorption
758 Spectroscopy (Sobanski et al., 2021). . Only recently, single-photon laser-induced
759 fluorescence have been applied to measure NO at mixing ratios with a detection limit of
760 better than 1 pptv for a integration time of 1 s (Rollins et al., 2020). Although theses
761 instruments are used in campaigns and perform well in intercomparisons (Javed et al., 2018),
762 they are only rarely used for continuous measurements at remote or pristine sites and
763 experience in the long-term behavior of these instruments are lacking. This is why these
764 measurement guidelines do not yet include a SOP for spectroscopic systems.

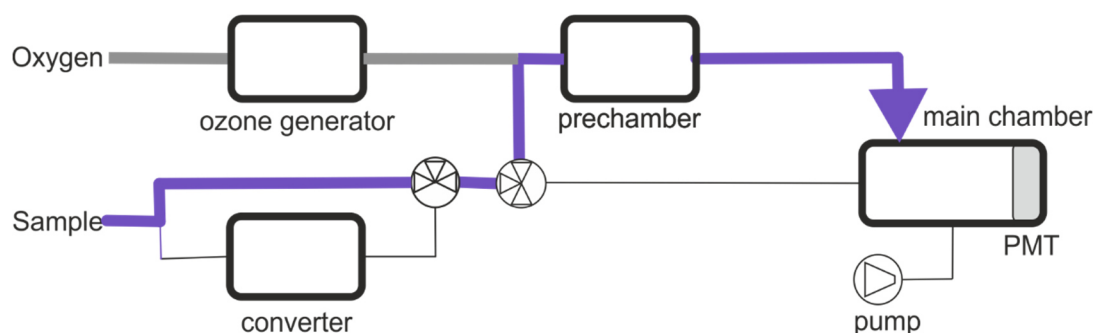
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766 7 Data processing algorithms

767 7.1 Raw signal processing

768 Besides NO, some hydrocarbons (e.g., alkenes) and other trace substances react with O₃
769 leading to an excited OH* radical which fluoresces at similar wavelength to NO₂*. These
770 reactions are generally slower than reaction (R5) and can be accounted for by adding a so-
771 called pre-chamber or zero mode to the NO measurement cycle. Within the pre-chamber the
772 reaction time is sufficiently long that the NO+O₃ reaction (R4, R5) and subsequent
773 deactivation of NO₂* (R6, R7) completes inside the pre-chamber before reaching the main
774 reaction chamber and the PMT. Only photons emitted from the slower reactions of O₃ with
775 alkenes and other interfering agents are detected (pre-chamber or zero mode). This
776 interference signal together with the dark current of the PMT and unspecific
777 chemiluminescence of ozone generated in the reaction cell or on the walls is called the
778 “detector background signal” (c_{zero}).

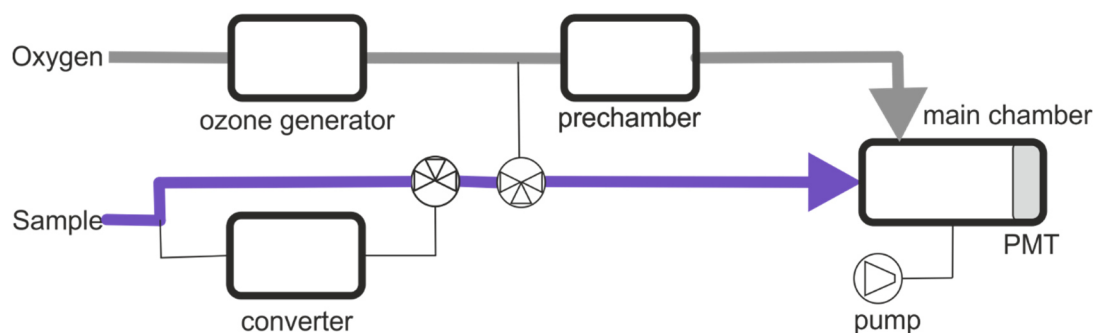
779 For measurements of NO₂ GAW recommends the photolytical conversion into NO followed
780 by CLD detection (See Appendix 6). The conversion is performed below 400 nm using an
781 adequate broad band light source like Xenon high pressure, metal halide lamps or small band
782 ultraviolet light-emitting diodes (UV-LEDs), latter referred as “blue light converter” (BLC).
783 After the conversion within the photolytic converter the sum of converted fraction of NO₂
784 and ambient NO is detected by the CLD.



785

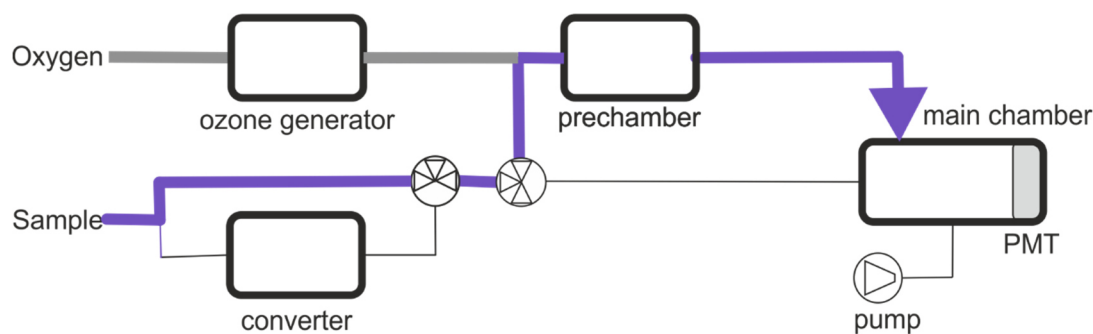
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787 By altering both the converter modes and the chamber mode in the modes a measurement
 788 cycle for NO_x consists of four steps.



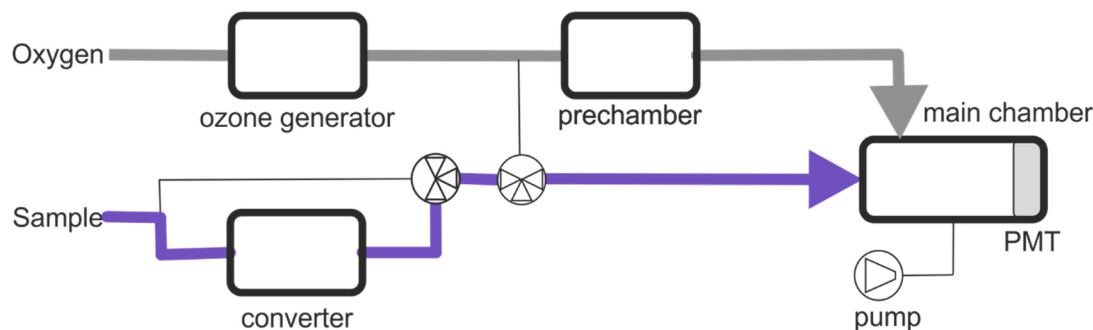
789
 790 Figure 4 Flow diagram of a chemiluminescence instrument in the NO mode. Gray line: Ozone Flow. Violet line:
 791 sample flow.

792 In the NO mode (Figure 4) the sample bypasses the converter and enters directly the main
 793 chamber (violet line) where it is mixed with the ozone. The number of raw counts observed
 794 during this mode are later referred as c_{NO} .



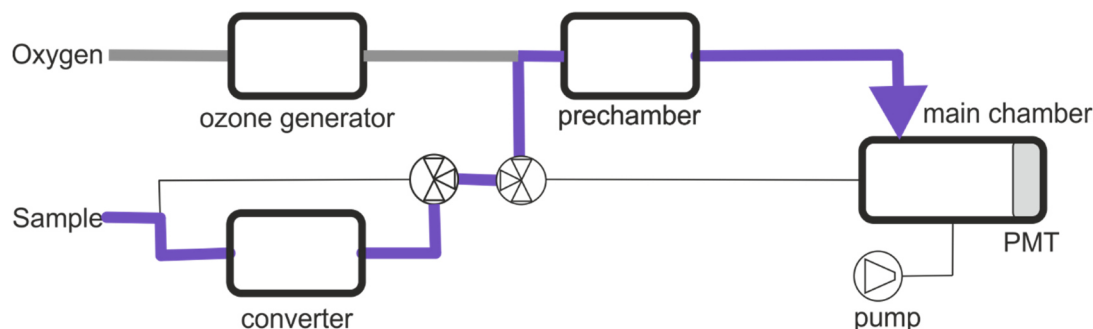
795
 796 Figure 5 Flow diagram of a chemiluminescence instrument in the NO zero mode. Gray line: Ozone Flow. Violet line:
 797 sample flow.

798 In the zero mode (Figure 5) ozone and the sample mix in the prechamber first entering the
 799 main chamber. The number of raw counts measured are later referred as c_{NOZero} .



800
 801 Figure 6 Flow diagram of a chemiluminescence instrument in the NO_x mode. Gray line: Ozone Flow. Violet line:
 802 sample flow.

803 In the NO_x mode the sample flow goes through the converter (Figure 6). The number of
 804 counts recorded during this phase are c_{NOc} .



805
 806 Figure 7 Flow diagram of a chemiluminescence instrument in the zero mode for NO_x. Gray line: Ozone Flow. Violet
 807 line: sample flow.

808 As for the NO mode, there is also a zero mode for the NO_x measurements. The counts are
 809 labelled as c_{NOzero} .

810 The NO amount fraction $[NO]_M$ in ambient air is calculated from the difference of the
 811 observed signal in the reaction cell (c_{NO}) and the signal including the pre-chamber (c_{NOzero})
 812 multiplied with the sensitivity of the CLD ($Sens_{CLD}$). A possible offset should be subtracted:

$$[NO]_M = \frac{c_{NO} - c_{NOzero}}{Sens_{CLD}} - Offs_{NO} \quad \mathbf{1}$$

Variable	Designation
$[NO]_M$	Amount fraction of NO measured
c_{NO}	Raw counts observed in the NO mode
c_{NOzero}	Raw counts observed in the NO zero mode
$Sens_{CLD}$	CLD Sensitivity
$Offs_{NO}$	NO Offset

813 The NO sensitivity is the response of the instrument per unit of calibration gas supplied e.g.,
 814 if 1000 counts per second (cps) are recorded whilst sampling a known concentration of 5
 815 nmol/mol gas, then the sensitivity is 200 cps/nmol/mol. Note that the inverse of this
 816 sensitivity, expressed in Equations 1 and 2, occurs in the literature (Galbally, 2020). If an
 817 instrument does not provide raw counts the sensitivity can be calculated also from other
 818 instrument output, e.g., in amount fraction.

819 The mixing ratio of ambient $[NO_2]_M$ is calculated from the difference of the signal (c_{NOc}) in
 820 the NO_x mode and the counts in the NO mode (c_{NO}) divided by the sensitivity of the CLD
 821 $Sens_{CLD}$ and the conversion efficiency (CE_{NO_2}). The conversion efficiency CE_{NO_2} denotes the
 822 yield of NO_2 photolyzed to NO (for more details see chapter 0). Possible offsets must be
 823 subtracted

824

$$[NO_2]_M = \frac{(c_{NOc} - c_{NOczero}) - (c_{NO} - c_{NOZero})}{Sens_{CLD} \times CE_{NO_2}} - Offs_{NO_2} \quad 2$$

Variable	Designation
$[NO_2]_M$	Amount fraction of NO_2 measured
c_{NOc}	Raw counts observed in the NO_x mode
$c_{NOczero}$	Raw counts observed in the NO_x zero mode
c_{NO}	Raw counts observed in the NO mode
c_{NOZero}	Raw counts observed in the NO zero mode
$Sens_{CLD}$	CLD Sensitivity
CE_{NO_2}	NO_2 Conversion efficiency
$Offs_{NO_2}$	NO_2 Offset

825 If the measurement of NO and NO_2 is sequential, data of c_{NO} , c_{NOc} and zero mode data might
 826 be synchronized prior to analysis by linear interpolation (see appendix C).

827 7.2 Calibration

828 CLD Sensitivity, conversion efficiency and offsets are regularly determined during calibration.
 829 The calibration procedure for chemiluminescence instruments comprises at least of three
 830 phases.

- 831 • A blank phase, when only synthetic air is added
- 832 • An NO phase when NO is added from a standard cylinder
- 833 • An NO_2 phase, when NO_2 is produced from NO after ozone is added.

834 The sensitivity of the CLD is determined by measuring a standard which is referenced to the
 835 primary standard (see Section 8). For calibration, the standard is diluted to typical ambient

836 concentrations or to concentrations slightly above ambient concentrations (e.g., for
 837 continental background calibration range $\sim [0, 30 \text{ nmol/mol}]$). The amount fraction after
 838 dilution $[NO]_{Dil}$ can be deduced from the amount fraction of NO in the standard $[NO]_{Ref}$,
 839 the flow of the gas standard $flow_{Cal}$ and flows of ozone $flow_{O_3}$ and synthetic air $flow_{SA}$
 840 used for dilution:

$$[NO]_{Dil} = [NO]_{Ref} \times \frac{flow_{Cal}}{flow_{Cal} + flow_{SA} + flow_{O_3}} \quad \mathbf{3}$$

Variable	Designation
$Sens_{CLD}$	CLD sensitivity
$[NO]_{Dil}$	Amount fraction of NO produced from the Dilution/GPT system
$[NO]_{Ref}$	Amount fraction in the standard cylinder
$flow_{Cal}$	flow of the gas standard into the Dilution/GPT system
$flow_{SA}$	flow of the synthetic air into the Dilution/GPT system
$flow_{O_3}$	flow of ozone in the Dilution/GPT system

841 It is crucial to accurately determine the dilution of the reference standard. The flows of the
 842 flowcontrollers should regularly be checked. In addition it is possible to determine the dilution
 843 by measurement of dilution tracer in the standard, e.g., by measuring CO₂ by a high-precision
 844 CO₂ analyzer (e.g., with a Cavity Ringdown Spectrometer). Gas standards which contain CO₂
 845 and NO are available from the Central Calibration Laboratory (CCL).

846

847 The sensitivity of the CLD $Sens_{CLD}$ is calculated where $c_{NO.NO}$ are the number of raw counts
 848 in the NO mode in the NO phase and $c_{NO.blank}$, the number of counts in the NO mode in the
 849 blank phase. The term $(c_{NO.blank} - c_{NOzero.blank})/Sens_{CLD}$ is the offset of for NO. At remote
 850 sites it might not appropriate to determine the offset with blank measurements in synthetic
 851 air (see 7.2.2)

852

$$Sens_{CLD} = \frac{(c_{NO.NO} - c_{NOzero.NO}) - (c_{NO.blank} - c_{NOzero.blank})}{[NO]_{Dil}} \quad \mathbf{4}$$

Variable	Designation
----------	-------------

$Sens_{CLD}$	CLD sensitivity
$[NO]_{Dil}$	Amount fraction of NO produced from the GPT system during NO phase
$c_{NO.NO}$	Raw counts in the NO mode observed in the NO phase of the calibration
$c_{NOzero.NO}$	Raw counts in the NO zero mode observed in the NO phase of the calibration
$c_{NO.blank}$	Raw counts in the NO mode observed in the blank phase of the calibration
$c_{NOzero.blank}$	Raw counts in the NO zero mode observed blank phase of the calibration

853 7.2.1 NO₂ conversion efficiency

854 The NO₂ conversion efficiency CE_{NO_2} is determined in the NO₂ phase. It is assumed that the
855 residence time of sample gas within the converter is constant throughout measurement for
856 CE_{NO_2} to be valid. If not, then the photolysis frequency and residence time must be known
857 instead. In gas phase titration NO₂ is produced by oxidation of NO from the standard cylinder
858 with ozone. As NO_x is constant the amount of NO₂ produced equals the amount of NO which
859 is lost. Hence $[NO_2]_{Dil}$ can be calculated from the difference of the raw count signals in the
860 NO $c_{NO.NO}$ phase and the NO₂ phase $c_{NO.NO_2}$ and the sensitivity of the CLD ($Sens_{CLD}$)

$$[NO_2]_{Dil} = \frac{(c_{NO.NO} - c_{NOzero.NO}) - (c_{NO.NO_2} - c_{NOzero.NO_2})}{Sens_{CLD}} \quad 5$$

861 With $c_{NOc.NO_2}$ and $c_{NO.NO_2}$ being the raw count rates in the NO_x and NO mode within the NO₂
862 phase of the calibration the conversion efficiency CE_{NO_2} is defined as

$$CE_{NO_2} = \frac{(c_{NOc.NO_2} - c_{NOczero.NO_2}) - (c_{NO.NO_2} - c_{NOzero.NO_2})}{Sens_{CLD} \times [NO_2]_{Dil}} \quad 6$$

863 Inserting formula into formula results in

$$CE_{NO_2} = \frac{(c_{NOc.NO_2} - c_{NOczero.NO_2}) - (c_{NO.NO_2} - c_{NOzero.NO_2})}{(c_{NO.NO} - c_{NOzero.NO}) - (c_{NO.NO_2} - c_{NOzero.NO_2})} \quad 7$$

Variable	Designation
CE_{NO_2}	NO ₂ conversion efficiency
$[NO_2]_{Dil}$	Amount fraction of NO ₂ produced from the GPT system during NO ₂ phase

$C_{NOc.NO2}$	Raw counts in the NO _x mode observed in the NO ₂ phase of the calibration
$C_{NOczero.NO2}$	Raw counts in the NO _x zero mode observed in the NO ₂ phase of the calibration
$C_{NO.NO2}$	Raw counts in the NO mode observed in the NO ₂ phase of the calibration
$C_{NOzero.NO2}$	Raw counts in the NO zero mode observed in the NO ₂ phase of the calibration
$C_{NO.NO}$	Raw counts in the NO mode observed in the NO phase of the calibration
$C_{NOzero.NO}$	Raw counts in the NO zero mode observed in the NO phase of the calibration

864 7.2.2 NO offset

865 The NO offset (Off_{SNO}) is any non-zero signal ($C_{NO.blank}$), in addition to the
866 chemiluminescent zero (prechamber mode), that is measured in the absence of NO in the
867 sample gas be it synthetic zero air that contains all other relevant species except NO, either
868 in the zero phase or in ambient air at night away from any sources of NO.

$$Off_{SNO} = \frac{C_{NO.blank} - C_{NOzero.blank}}{Sens_{CLD}}$$

8

Variable	Designation
Off_{SNO}	NO offset
$C_{NO.blank}$	Raw counts in the NO mode observed in the blank phase of the calibration
$C_{NOzero.blank}$	Raw counts in the NO zero mode observed in the blank phase of the calibration
$Sens_{CLD}$	Sensitivity of the CLD

869 NO offset signals can be positive or negative due to subtle difference in pressure and humidity
870 between zero and measure modes, imperfect zeroing (see appendix A.1), temperature
871 differences, etc. Perfectly NO free synthetic air can't generally be guaranteed so in case where
872 any offset signal is an appreciable proportion of any typical daytime measurement i.e.,
873 pristine environments, then the NO value at night can be more appropriate (see Zero offset
874 correction. Spurious artefacts may also be introduced by dry zero gas causing changes in
875 humidity within an instrument which is normally exposed to humid ambient air.

876

877 **7.2.3 NO₂ offset**

878 The NO₂ offset ($Off_{S_{NO_2}}$) is any positive signal above the NO offset signal whilst sampling
 879 zero air.

$$Off_{S_{NO_2}} = \frac{C_{NOx.blank} - C_{NO.blank}}{Sens_{CLD} \times CE_{NO_2}} \quad 9$$

Variable	Designation
$Off_{S_{NO_2}}$	NO ₂ offset
$C_{NOx.blank}$	Raw counts in the NO _x mode observed in the blank phase of the calibration
$C_{NO.blank}$	Raw counts in the NO mode observed in the blank phase of the calibration
$Sens_{CLD}$	Sensitivity of the CLD
CE_{NO_2}	NO ₂ conversion efficiency

880 NO₂ offset signals can arise from photolysis of adsorbed nitrates on the internal walls of the
 881 photolytic converter and can vary with time. The NO₂ offset can be caused by electronic
 882 interferences or impurities in the zero air. In either case the cause should be investigated and
 883 rectified.

884 **7.2.4 Zeroing efficiency**

885 Zeroing efficiency is a metric of how well the zero mode of an instrument operates i.e., how
 886 much of the NO supplied to the instrument is reacted to NO₂ with the zeroing volume during
 887 the zero measurement cycle. Practically the zeroing efficiency (ZE_{zero}) is easily determined
 888 during a calibration cycle by equation

$$ZE_{zero} = \frac{C_{NOzero.NO} - C_{NOzero.blank}}{C_{NO.NO} - C_{NOzero.blank}} - 1 \quad 10$$

Variable	Designation
ZE_{zero}	Zero efficiency
$C_{NOzero.NO}$	Raw counts in the NO zero mode observed in the NO phase of the calibration
$C_{NOzero.blank}$	Raw counts in the NO zero mode observed in the blank phase of the calibration
$C_{NO.NO}$	Raw counts in the NO mode observed in the NO phase of the calibration
$C_{NOzero.blank}$	Raw counts in the NO zero mode observed in the blank phase of the calibration
$C_{NOzero.NO}$	Raw counts in the NO zero mode observed in the NO phase of the calibration

889 Data can be corrected for zeroing efficiency if desired, however the discrepancy caused by
890 $Z_{E_{zero}} < 100\%$ effectively cancels out due to the sensitivity being underestimated (Galbally,
891 2020).

892 7.3 Interference corrections

893 7.3.1 Corrections for humidity interferences

894 Excited NO_2 is quenched more effectively by water than by nitrogen or oxygen (Matthews et
895 al., 1977). Accordingly, the humidity interference must be corrected using the water
896 concentration measured in parallel.

$$[NO]_{H_2O} = [NO]_M \times (1 + \alpha \times [H_2O]) \quad 11$$

897 Here, $[NO]_M$ is the uncorrected amount fraction of NO measured, calibrated in dry air,
898 $[H_2O]$ is the measured absolute water concentration in units per thousand [‰], α is the
899 correction factor and $[NO]_{H_2O}$ the amount fraction obtained after humidity interference
900 correction. The ambient water concentration $[H_2O]$ can be calculated from the relative
901 humidity and the measured temperature (See appendix D). Likewise, the measured NO_2
902 amount fraction must be corrected using equation

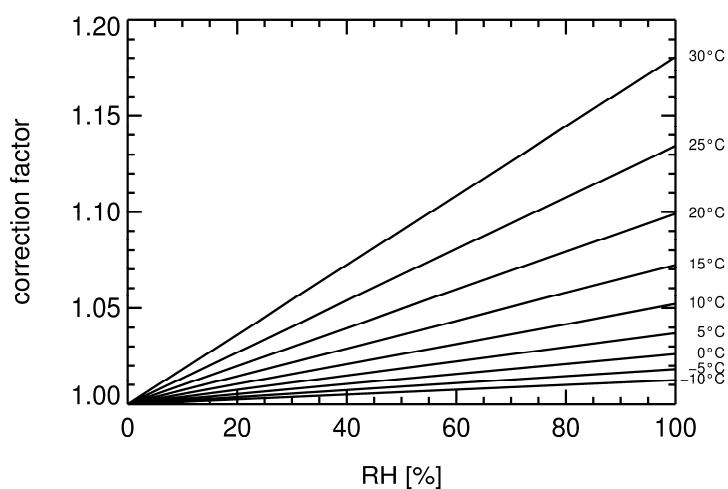
$$[NO_2]_{H_2O} = [NO_2]_M \times (1 + \alpha \times [H_2O]) \quad 12$$

Variable	Designation
$[NO]_{H_2O}$	Humidity corrected amount fraction of NO measured
$[NO]_M$	Uncorrected amount fraction of NO measured
$[NO_2]_{H_2O}$	Humidity corrected amount fraction of NO_2 measured
$[NO_2]_M$	Uncorrected amount fraction of NO_2 measured
α	Humidity correction factor
$[H_2O]$	Measured absolute water concentration in units per thousand [‰]

903 The correction factor α depends on the ratio of the sample flow and the sum of the sample
904 flow and (dry) flow of ozone into the reaction chamber. (Ridley et al., 1992) proposed the
905 equation **13** for calculation:

$$\alpha = (4.3 \pm 0.3) \times 10^{-3} \times \frac{flow_{sample}}{flow_{sample} + flow_{ozone}}$$

Variable	Designation
α	Humidity correction factor
$flow_{sample}$	Sample flow into CLD
$flow_{ozone}$	Ozone flow into CLD



906

907 Figure 8 Factors $(1 + \alpha \times [H_2O])$ to be applied for measurements at different temperatures and humidities.
 908 Values are calculated from equation 13.

909 An absolute humidity of 9 g/m^3 corresponding to 50% relative humidity at 20°C accounts for
 910 about 4% signal loss. It is recommended to determine α by comparison with a spectroscopic
 911 method which is not prone to interferences or by adding humidity during calibration. A
 912 comparison of five different CLDs yielded α values between 2.5 and 4 (Wegener and The
 913 MetNO₂ SAPHIR intercomparison team, 2020).

914 7.3.2 Corrections for ozone interferences for NO

915 NO reacts with ambient O_3 in the inlet manifold, in the photolytical converter and after
 916 passing the photolytical converter before the detection in the CLD. In addition, ozone is
 917 produced in the converter which can oxidize NO on its way to the detector. These processes
 918 should be minimised by reducing the residences times in the instrument. Although a large

919 fraction of the NO loss can be attributed to heterogeneous processes (Ridley et al., 1988)
 920 intercomparisons show that the overall loss process can be well described by homogeneous
 921 reactions (Fehsenfeld et al., 1990).

922 In the NO mode, when bypassing the converter (Figure 9, dashed line), NO is consumed by
 923 reaction with ozone and a reduced amount fraction $[NO]_{E1}$ would be observed. The amount
 924 fraction of ambient NO before entering the sampling line ($[NO]_0$) can be calculated from
 925 $[NO]_{E1}$ equation 14:

$$[NO]_0 = [NO]_{E1} \times e^{k_{O_3L} \times (t_L + t_B + t_D)} \quad \mathbf{14}$$

926 Here, $[NO]_0$ is the corrected NO amount fraction, $[NO]_{E1}$ is the uncorrected NO amount
 927 fraction measured, k_{O_3L} is the rate of the reaction between NO and O₃ in the sampling line
 928 ($k(O_3+NO) \times [O_3] \times 10^{-9} \times M$); t_L , t_B and t_D are the duration in the sample line, in the converter
 929 bypass and from the converter to the detector. The ozone correction is then calculated using
 930 the rate coefficient (k_{O_3}) at the temperature of the inlet line, e.g. $1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 931 at 298K (Atkinson et al., 2004).

932 7.3.3 Corrections for ozone interferences for NO_x

933 In the NO₂ mode, when passing the photolytical converter, NO is formed from NO₂ photolysis.
 934 NO and NO₂ will converge to a photostationary state which can be described as:

$$[NO]_{PSS} = \frac{J_C}{J_C + k_{O_3C}} \times ([NO]_0 + [NO_2]_0) \quad \mathbf{15}$$

935 J_C is the photolysis rate in the photolytical converter and $[NO]_{PSS}$ the amount fraction of NO
 936 in the photostationary state. Likewise, the amount fraction of NO₂ in the photostationary
 937 state is:

$$[NO_2]_{PSS} = \frac{k_{O_3C}}{J_C + k_{O_3C}} \times ([NO]_0 + [NO_2]_0) \quad \mathbf{16}$$

938 The level of NO approaches the photostationary state with a time constant of $(k_{O_3C} + J_C)$.
 939 $[NO]_{EC}$, the amount fraction of NO after the converter can therefore be described with

940 equation 17, where $[NO]_L$ is the amount fraction of NO at the end of the sampling line, and
 941 t_c the duration of stay in the converter.

$$[NO]_{EC} = [NO]_{PSS} - ([NO]_{PSS} - [NO]_L) \times e^{-(k_{O_3C}+J_C) \times t_c} \quad \mathbf{17}$$

942 Rearranging equation 17 gives:

$$[NO]_{EC} = [NO]_{PSS} \times (1 - e^{-(k_{O_3C}+J_C) \times t_c}) + [NO]_L \times e^{-(k_{O_3C}+J_C) \times t_c} \quad \mathbf{18}$$

943

944 The ambient NO₂ amount fraction of $[NO_2]_0$ can be calculated from the amount fraction of NO
 945 at the converter exit $[NO]_{EC}$:

$$[NO]_0 + [NO_2]_0 = \frac{J_C + k_{O_3C}}{J_C} \times \frac{[NO]_{EC} - [NO]_L \times e^{-(k_{O_3C}+J_C) \times t_c}}{1 - e^{-(k_{O_3C}+J_C) \times t_c}} \quad \mathbf{19}$$

946

947 After passing the converter the amount fraction of NO is reduced again before entering the
 948 detector at an amount fraction of $[NO]_{E2}$. This loss process is determined by the residence time
 949 from the converter to the detector t_D .

$$[NO]_{E2} = [NO]_{EC} \times e^{-k_{O_3L} \times t_D} \quad \mathbf{20}$$

950 Inserting 22 into 19 results in

$$[NO]_0 + [NO_2]_0 = \frac{J_C + k_{O_3C}}{J_C} \times \frac{[NO]_{E2} \times e^{k_{O_3L} \times t_D} - [NO]_L \times e^{-(k_{O_3C}+J_C) \times t_c}}{1 - e^{-(k_{O_3C}+J_C) \times t_c}} \quad \mathbf{21}$$

951

952 $[NO]_L$, the amount fraction of NO at the end of the sampling line can be derived from $[NO]_0$,
 953 the amount fraction of NO at the tip of the sampling line or from $[NO]_{E1}$, the amount fraction
 954 of NO at the end of the bypass line.

$$[NO]_L = [NO]_0 \times e^{-k_{O_3L} \times t_L} = [NO]_{E1} \times e^{k_{O_3L} \times (t_B + t_D)} \quad \mathbf{22}$$

955

956 $[NO_2]_0$ can then be calculated from $[NO]_0$ and $[NO]_{E2}$ using equation 23 which combines equation
 957 19 and equation 22:

$$[NO_2]_0 = \frac{J_c + k_{O_3C}}{J_c} \times \frac{[NO]_{E2} \times e^{k_{O_3L} \times t_D} - [NO]_{E1} \times e^{-(k_{O_3C} + J_c) \times t_C + k_{O_3L} \times (t_B + t_D)}}{1 - e^{-(k_{O_3C} + J_c) \times t_C}} - [NO]_0 \quad \mathbf{23}$$

958 or

$$[NO_2]_0 = \frac{J_c + k_{O_3C}}{J_c} \times \frac{[NO]_{E2} \times e^{k_{O_3L} \times t_D} - [NO]_{E1} \times e^{-(k_{O_3C} \times (t_C) - k_{O_3L} \times (t_B + t_D) + J_c \times t_C)}}{1 - e^{-(k_{O_3C} + J_c) \times t_C}} - [NO]_0 \quad \mathbf{24}$$

959

960 The system described above has a flow system with where the sample is guided through the
 961 PLC or through a bypass by means of two valves. If the system has a flow system with only
 962 one flow path, with PLC or LED lamp radiative flux is switched on or off then the residence
 963 time and the temperatures of the system in “bypass mode” are equal to the system in
 964 “converter mode”. As the residence times in bypass t_B and converter t_C and the reaction rates
 965 with ozone are equal the equation 24 will transform into

966

$$[NO_2]_0 = \frac{J_c + k_{O_3C}}{J_c} \times \frac{[NO]_{E2} \times e^{k_{O_3L} \times t_D} - [NO]_{E1} \times e^{(k_{O_3L} \times t_D - J_c \times t_C)}}{1 - e^{-(k_{O_3C} + J_c) \times t_C}} - [NO]_0 \quad \mathbf{25}$$

967

968

969 The amount fraction $[NO]_{E2}$ is the amount fraction of NO in the detector after passing the
 970 photolytical converter and corresponds to

$$[NO]_{E2} = [NO]_{E1} + [NO_2]_M \times CE_{NO_2} \quad \mathbf{26}$$

971

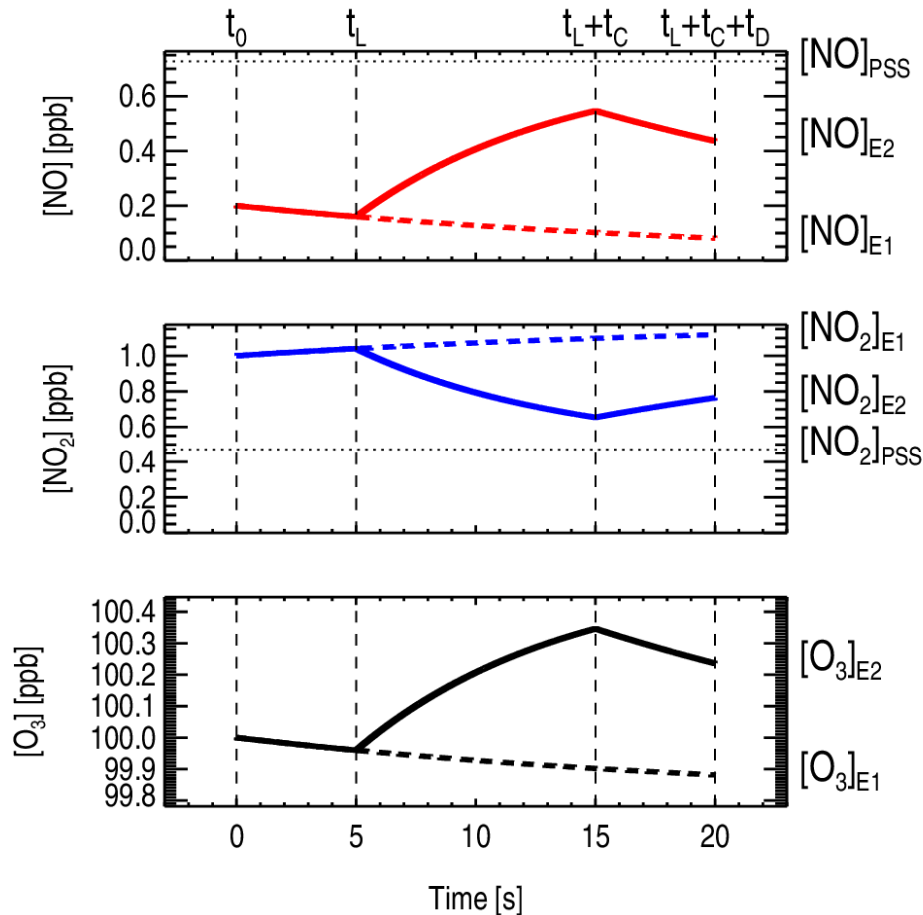
972 $[NO_2]_M$ is the amount fraction of NO_2 observed and CE_{NO_2} is the efficiency of the converter.

973

Variable	Designation
$[NO_2]_{PSS}$	Amount fraction of NO_2 at the photostationary state in the converter

$[NO_2]_M$	Amount fraction of NO_2 measured
$[NO_2]_0$	Amount fraction of NO_2 at the tip of the inlet line
$[NO]_{PSS}$	Amount fraction of NO at the photostationary state in the converter
$[NO]_{EC}$	Amount fraction of NO after the converter
$[NO]_{E2}$	Amount fraction of NO at the detector after passing the converter
$[NO]_{E1}$	Amount fraction of NO measured
$[NO]_L$	Amount fraction of NO before the converter
$[NO]_0$	amount fraction of NO at the tip of the inlet line
CE_{NO2}	NO_2 conversion efficiency
k_{O_3C}	Reaction rate of the between NO and O_3 in the converter
k_{O_3L}	Reaction rate of the between NO and O_3 in sampling line, bypass line or from converter to detector
J_C	Photolysis rate in the photolytical converter
t_C	Residence time in the converter
t_B	Residence time in the converter bypass
t_L	Residence time from the tip of the inlet line to the converter
t_D	Residence time from the converter to the detector

974 Even with small residence time the ozone interference can be significant. Performing the
975 ozone correction for NO and NO_2 data is mandatory before submission the data to the data
976 archive. An example calculation can be found in appendix E. The ozone correction assumes
977 that the ozone concentration is constant throughout sampling line and converter which is
978 valid under pristine conditions.



979

980 Figure 9: Simulation of the temporal behaviour of NO, NO₂ and O₃ in inlet line and photolytical converter. t_L:
 981 residence time in the sampling line, t_C residence time in the converter. The solid line marks time series with
 982 converter on, dashed line marks conditions when the sample air bypasses the converter.
 983

984 7.3.4 Zero offset correction

985 In remote (pristine) environments where ambient NO_x might be <100 pmol/mol it is
 986 recommended to use the measured night-time NO signal as the detector artefact (Lee et al.
 987 2009; Galbally 2020). Differences in moisture content between ultrapure air and the ambient
 988 air might manifest as a spurious offset, however, for measurement sites far from sources –
 989 including potential biogenic/soil sources of NO within a few meters of the inlet – ambient
 990 night-time NO concentrations are expected to equal zero due to reaction with ambient O₃.

991 To assess valid offset zero corrections, all these conditions must be met:

- 992 • a level of ozone > 20 ppb
- 993 • low ozone variability with a variation coefficient of < 0.1

- 994 • no local sources of NO
- 995 • the absence of sunlight
- 996 • steady meteorological conditions with wind speed > 2 m/s
- 997 • the absence of high levels of VOCs.

998 7.4 Measurement uncertainties

999 Measurement uncertainty is defined as the parameter associated with the result of a
 1000 measurement that characterized the dispersion of the values that could be reasonably
 1001 attributed to the measurement. The uncertainty is estimated following the “Guide for
 1002 expressing uncertainty in measurements” (Joint Committee for Guides in Metrology (JCGM),
 1003 2008).

1004 In ambient measurements the uncertainty contributions due to zero, span, and repeatability
 1005 of the measurements must be considered, additionally errors in corrections applied to the
 1006 data as described in section 7.3, especially for O3 in the inlet line and PLC and water vapor in
 1007 the CLD measurement chamber.

1008 The uncertainty analysis (Andersen et al., 2021; Berkes et al., 2018) should separately
 1009 determine systematic uncertainties and random uncertainties. Systematic uncertainties are
 1010 due to the laboratory standard and systematic effects of the dilution system applied. Other
 1011 uncertainties are typically evaluated in multiple determinations and thus random in nature.
 1012 Gaussian error propagation assuming independent errors is assumed.

1013 Each measurement needs to be supplemented by its total uncertainty (coverage factor $k=2$)
 1014 and the random part expressed by the standard deviation. This information is supplied to
 1015 WDCRG characterized the dispersion of the values that could be reasonably attributed to the
 1016 measurement.

1017 7.4.1 Uncertainties

1018 The combined uncertainty u_{CNO} for NO measurements is

$$u_{CNO} = \sqrt{u_{zero}^2 + u_{NO}^2 + u_{lin}^2 + u_{cal}^2 + u_{int}^2}$$

1019

Variable	Designation
u_{CNO}	Combined standard uncertainty
u_{zero}	Precision at zero
u_{NO}	Reproducibility of measurements
u_{lin}	Uncertainty due to deviations from linearity
u_{cal}	Uncertainty due to calibration
u_{int}	Uncertainty due to interferences

1020

1021 The combined uncertainty u_{CNO_2} for NO₂ measurements with CLD is

1022

$$u_{CNO_2} = \sqrt{2u_{zero}^2 + 2u_{NOc}^2 + u_{lin}^2 + u_{cal}^2 + u_{int}^2}$$

28

Variable	Designation
u_{CNO_2}	Combined standard uncertainty
u_{zero}	Precision at zero
u_{NOc}	Reproducibility of measurements
u_{lin}	Uncertainty due to deviations from linearity
u_{cal}	Uncertainty due to calibration
u_{int}	Uncertainty due to interferences

1023

1024 The reproducibility u_{zero} can be determined by measuring zero gas or, in case of NO,
1025 evaluating ambient data with time periods when NO is zero. The procedure shall evaluate all
1026 series of 10 consecutive measurements (both NO and NO₂) and determine their absolute
1027 scatter by means of the standard deviations in nmol/mol. Then, an average of those 10
1028 periods with the lowest standard deviation is built and used as the reproducibility of ambient
1029 measurements of NO or NO₂.

1030

1031 The reproducibility of measurements u_{NO} can either be determined by multiple
1032 measurements of a highly diluted calibration gas and assessing additional impacts due to

1033 fluctuations in the zero and due to interfering species in ambient air, or what is recommended
1034 here, by extracting appropriate periods from routine, continuous ambient air measurements.
1035 The latter has several advantages as (1) it characterizes the scatter for real ambient air, (2) it
1036 is available in the data sets and does not require additional measurements, and (3) it can be
1037 automatically withdrawn from the measurement series by statistical criteria. The procedure
1038 shall evaluate all series of 10 consecutive measurements (both NO and NO₂) and determine
1039 their absolute scatter by means of the standard deviations in nmol/mol. Then, an average of
1040 those 10 periods with the lowest standard deviation is built and used as the reproducibility of
1041 ambient measurements of NO or NO₂.

1042 The uncertainty due to deviations from linearity u_{lin} can be calculated by fitting a linear
1043 regression function of the measured amount fractions against calibrated amount fractions.
1044 At least 4 standard amount fractions should be available. They can be obtained by a set of
1045 calibrations gases covering the whole measurement range or dynamic dilution of a working
1046 standard.

1047 The uncertainty u_{cal} contributions in NO calibration measurements are the flow rates of
1048 mass-flow regulating devices, the uncertainty of certified reference material, the zero-gas
1049 purity, the repeatability of the analyzer, and drifts of the analyzer. Additionally, for NO₂ the
1050 photolytic converter efficiency must be included.

1051 The overall uncertainty U_{CNO_2} is calculated by using the coverage factor $k=2$

$$U_{CNO_2} = k \times u_{CNO_2}$$

29

Variable	Designation
U_{CNO_2}	Overall uncertainty for NO ₂
k	Coverage factor
u_{CNO_2}	Combined standard uncertainty for NO ₂

1052 **7.4.2 Limit of Detection**

1053 The limit of detection (LOD) is calculated from the 2σ statistical precision of blank
 1054 measurements in the NO mode and zero mode (Berkes et al., 2018). For this the standard
 1055 deviations of $S_{NO.blank}$ and $S_{NOzero.blank}$ for the NO and zero NO mode over the integration
 1056 time t are calculated. Standard deviation is calculated in [counts/s]; the integration time is in
 1057 [s].

$$LOD_{NO} = \frac{2 \times \left(\sqrt{\frac{S_{NO.blank}}{t}} + \sqrt{\frac{S_{NOzero.blank}}{t}} \right)}{Sens_{CLD}} \quad 30$$

Variable	Designation
LOD_{NO}	Limit of detection for NO
t	Integration time (seconds per measurement)
$Sens_{CLD}$	Sensitivity of CLD
$S_{NO.blank}$	Standard deviation of raw counts in the NO mode observed in the blank phase of the calibration
$S_{NOzero.blank}$	Standard deviation of raw counts in the NO zero mode observed in the blank phase of the calibration

1058

1059 Likewise

1060

$$LOD_{NO_2} = \frac{2 \times \left(\sqrt{\frac{S_{NOc.blank}}{t}} + \sqrt{\frac{S_{NOczero.blank}}{t}} \right)}{CE \times Sens_{CLD}} \quad 31$$

Variable	Designation
LOD_{NO_2}	Limit of detection for NO ₂
t	Integration time (seconds per measurement)
CE	NO ₂ conversion efficiency
$Sens_{CLD}$	Sensitivity of CLD
$S_{NOc.blank}$	Standard deviation of raw counts in the NO _x zero mode observed in the blank phase of the calibration
$S_{NOczero.blank}$	Standard deviation of raw counts in the NO _x mode observed in the blank of the calibration

1061 8 Operation and Maintenance, Quality Assurance and Quality Control 1062 (QA/ QC)

1063 8.1 Quality Assurance and Quality Control

1064 The general quality assurance and quality control (QA/QC) concept is laid out in the
1065 WMO/GAW Strategic Plan 2008–2015 (WMO, 2007b) and its addendum (WMO, 2011b). The
1066 GAW quality assurance (QA) system includes all aspects of atmospheric chemistry
1067 observations, as training of station personnel, assessment of infrastructures, operations, and
1068 the quality of observations at the sites. The documentation of data submitted to the WDCs is
1069 also part of the QA/QC process. The primary objectives of the GAW QA system are to ensure
1070 that the data in the WDCs are consistent, of known and adequate quality, supported by
1071 comprehensive metadata.

1072 Quality control (QC) is a measure to review all factors involved a process. While quality
1073 assurance is process oriented and focuses on defect prevention, quality control is product
1074 oriented and focuses on defect identification. Quality assurance (QA) is mainly ensured at the
1075 stations; quality control (QC) is mainly a task for the WCCs.

1076 To ensure continuity and repeatability of a measurement that measurement should be made
1077 following a standard set of operating procedures (an SOP). The SOP should set out the
1078 operating practices, valid parameters etc. of the instrument used and the entire sampling
1079 system leading to that instrument e.g., sample line or manifold. The SOP should be followed
1080 in a way that a malfunctioning instrument or sample line leak is easily identifiable from simple
1081 parameters and tests detailed in the SOP. These are specific to each instrument and site, but
1082 generally include calibration (and typical valid calibration parameters), leak checks and data
1083 quality checks.

1084 In addition to the SOP all actions, replacements, adjustments, etc of the measurement
1085 system should be documented in a logbook in sufficient detail. These records provide the
1086 critical information on the collected data and their traceability, e.g. a problem identified in
1087 future can be quickly traced back and related to the recorded actions.

1088 Thirdly, regular back-up of measurement data and logs should be performed, either
1089 automatically or manually and detailed in the SOP – whichever is appropriate for the site.
1090 Back-up of data should be as regular as is practical, and back-up copies should be stored
1091 safely, preferably off-site.

1092 Because of the different nature of the instrumentation, distinct SOPs will be required for
1093 stations operating with the three levels of DQOs.

1094 8.1.1 SOP for Stations with Basic Level DQOs

1095 A typical SOP may contain a checklist of maintenance items and data checks to be performed
1096 at regular intervals. As a basic example:

1097 **Daily:**

1098 *Gases and Electricity*

- 1099 • Is the instrument operating?
- 1100 • Electrical power / Data acquisition: Are the cable really fixed?
- 1101 • Inlet line: is the inlet line leak-proof? Is no room air pulled in? (Unusual spikes in data
1102 corresponding to presence of personal in lab are hints towards a leaky inlet line.) Are
1103 there any signs of condensation in the inlet line? Are the flow and temperature(s) of the
1104 inlet line in the allowed range (control unit of inlet line)? (Hint: Measure the inlet flow at
1105 the beginning of the line and compare to the sum of individual instrument flows.)
- 1106 • Dry air supply for flushing the PMT window: Is the dry air connected correctly? Is the
1107 drying unit working well, or does the silica gel cartridge need to be regenerated? It is very
1108 important to feed dry air into the CLD which is used for flushing the PMT window.
1109 Humidity leads to condensation at the PMT window followed by significant loss of
1110 sensitivity. Condensation from high humidity also can lead to failure of the PMT or
1111 connected electronics.
- 1112 • In case the CLD is operated with pure oxygen for supplying the ozonizer (Hint: To improve
1113 the sensitivity of CLD the ozone generator should be operated with pure oxygen): Is the
1114 oxygen supply correctly connected and is the pressure of the oxygen cylinder sufficient?
1115 Check for time to order a new oxygen cylinder (consider delivery time). Commercially

1116 available oxygen generators are also capable of producing oxygen of sufficient quality
1117 and are a viable alternative to using cylinder oxygen.

1118 *Instrument parameters*

- 1119 • Is the measurement system showing any errors / alarms / warnings?
- 1120 • Are the inlet flow and the chamber pressure in the expected range? Is there a drift in
1121 chamber pressure? Since chamber pressure directly affects the sensitivity of the
1122 instrument (quenching) it must be constant. Otherwise, recalibration is needed. Drift in
1123 chamber pressure or inlet flow might be a hint for a blockage of the inlet line or a
1124 weakening of the pump.
- 1125 • Are the temperatures (PMT, reaction chamber, photolysis cell, CLD) within the allowed
1126 ranges? Especially the PMT temperature is important since it directly affects the noise of
1127 measurement.

1128 *Data and metadata acquisition*

- 1129 • Is the clock of the data acquisition system accurate and/or synchronized with a GPS
1130 signal?
- 1131 • Do the data displayed at the instrument match with the respective data in the data file
1132 of the acquisition system? This is a simple and effective test whether the data flow from
1133 instrument to data storage is o.k.

1134 *Data checks*

- 1135 • Are the NO and NO₂ data in a typical range? NO₂ data are typically some 2-10 times
1136 higher than NO during daytime. If they are equal, this is a strong hint of defective
1137 conversion.
- 1138 • Is the background signal in the prechamber mode in the expected range (not all analyzers
1139 provide this information)? Problems might be a hint for a weakening of the ozone
1140 generator.
- 1141 • Are there “artefact signals” during night (in the presence of ambient O₃ > 20 nmol/mol)
1142 and during measurement with zero air?

1143 *Weekly*

1144 • Every 2nd day (depending on aspired precision of measurement): calibration (span
1145 check) and determination of conversion efficiency (see Chapter 5.5) and zero air
1146 measurement.

1147 • Do the calibration results vary within usual and acceptable limits?

1148 • Check NO₂ conversion efficiency. If NO₂ conversion efficiency falls below 40% or lamp
1149 intensity fluctuating excessively day to day: Change of Xe-photolysis lamp, (other
1150 conditions and limits for other types of converters e.g., Blue Light Converter).

1151 • How large is the enhancement of the zero mode by NO? This indicates declining O₃
1152 generator performance.

1153 • Does the sample filter need replacement?

1154 • Is there sufficient operating gas (air, O₂, calibration standard, etc.)?

1155 **Every 2nd week**

1156 • (depending on pollution level): Change of inlet line filter.

1157 **Every month**

1158 • Is the sample line contaminated?

1159 • Is there sufficiency data storage space?

1160 **Every 3rd month**

1161 • (depending on pollution level and - in case of use of drying cartridges for dry air
1162 generation - capacity of drying cartridge): change of filters at dry air and oxygen inlet;
1163 regeneration of drying cartridge. First the CLD is shifted to standby mode. Then the filters
1164 and cartridges are exchanged. (Hint: It is convenient to use a silica gel and a drierite
1165 (CaSO₄) cartridge in serial connection. The silica gel absorbs most of the humidity,
1166 subsequently the dew point is further lowered by the drierite. The silica gel can be easily
1167 regenerated by means of a microwave during some minutes. During that time the system
1168 can continue operation with the Drierite cartridge alone in this case the CLD does not
1169 need to be switched into stand-by mode. With this setup the Drierite cartridge must be
1170 regenerated only every third month in a cabinet dryer.)

1171 **Every 6th month**

1172 • Do a calibration comparison between the Laboratory standard and the working standard

1173 • Is the calibration comparison within usual and acceptable limits?

1174 **Yearly**

- 1175 • Service vacuum pump.
- 1176 • (depending on pollution level): cleaning of reaction chamber, cleaning of photolysis
- 1177 chamber; (persistent loss in counting rate is an indication of a dirty cell, loss in conversion
- 1178 efficiency even when using a new lamp is an indication of a dirty photolysis chamber).
- 1179 Refer to instrument manual for disassembling reaction, pre-reaction and photolysis
- 1180 chamber. (Different cleaning instructions exist from manufacturers for BLCs.) Warning:
- 1181 The PMT, if under electrical power, will be destroyed by incident light. Once
- 1182 disassembled it is recommended to use the following cleaning procedure for the reaction
- 1183 chamber, the pre-reaction chamber and the photolysis chamber: First rinse with
- 1184 deionized water. For more persistent deposits use a lint-free cloth. Avoid scratching the
- 1185 walls or any glass part. Do not use organic solvents or acids!
- 1186 • Calibrate flow controllers
- 1187 • Service O₂ generator (if used)
- 1188 • Perform a multi-point point calibration and a zero air measurement
- 1189 • Do the results vary within usual and acceptable limits?
- 1190 • Review the years processed data and submit the processed and quality assured NO and
- 1191 NO₂ data to The World Data Centre for Reactive Gases, WDCRG.

1192 Some instruments require periodic replacement of consumables, e.g., valves, or maintenance

1193 of the pump (e.g., regular membrane replacements). Refer to instrument manuals for details.

1194 In addition, Reference documents for air quality monitoring networks (AQEG, 2004;CEN,

1195 2005;EPA, 2002), may also be consulted for further information. However, caution is required

1196 as many regulatory monitoring networks still rely on heated surface converters for NO₂ to NO

1197 conversion. Moreover, these networks are largely focussing on measurements in more

1198 polluted environments, thus, higher levels of nitrogen oxides are usually observed resulting

1199 in less demanding QA/QC required.

1200

1201 **8.1.2 SOP for Stations with Enhanced Level DQOs**

1202 An SOP for enhanced level DQO would be like the SOP for basic level DQO see 8.1.1. The
1203 period between calibrations should be shortened (see chapter 7.2).

1204 **8.1.3 SOP for Stations with High Level DQOs**

1205 Most of the items of stations with high level DQOs can be found in the SOP for basic level DQO
1206 (see 8.1.1). Instead of weekly calibrations, the instrument must be calibrated every three
1207 days. Other tasks relate to the specific setup. The SOP for NO_x measurements at Cape Grim
1208 can be found in (Galbally, 2020).

1209 9 Data management including Archiving

1210 All final, quality-controlled data obtained as part of the GAW programme should be submitted
1211 without undue delay (attempts should be made to update the archives every year or more
1212 often) to the responsible World Data Centre.

1213 The global data archive for in situ nitrogen oxides data is the World Data Centre for Reactive
1214 Gases (WDCRG) maintained by the Norwegian Institute for Air Research (NILU,
1215 <https://www.gaw-wdcr.org/>). WDCRG accepts continuous data as hourly data as well as
1216 higher aggregates (daily, monthly averages) along with associated standard deviations. In
1217 addition to the NO/NO₂ data, WDCRG also encourages submission of meteorological data.
1218 Also, historic time series can be submitted.

1219 The process of data submission is described at the EBAS webpage ([https://ebas-](https://ebas-submit.nilu.no/)
1220 [submit.nilu.no/](https://ebas-submit.nilu.no/)). The normal data submission is the regular, annual data submission. Before
1221 the first data submission EBAS should be contacted via email to ebas@nilu.no. On contact
1222 stations should provide the GAWSIS station ID, see <https://gawsis.meteoswiss.ch/GAWSIS/>.

1223 Recorded time series need to be visually inspected and outliers due to maintenance,
1224 instrumental malfunctions, measurement artefacts, or local contamination need to be
1225 flagged. Examples are data when measuring laboratory air during maintenance actions, first
1226 data after power outages, erroneous data due to pump failures etc. Data flagging should be
1227 done consulting the station and instrument logbooks.

1228 Each station should develop a detailed procedure for evaluating the measurement data or
1229 use the procedure developed by WCC- NO_x. It contains statistical analysis of the span-factors,
1230 zero gas readings and converter efficiency analyses supported by visual inspection of the
1231 temporal development over longer time periods, e.g., typically a year. The time series are
1232 checked versus the instrument log and discontinuities in the time series should be associated
1233 to documented instrument changes. In case a discontinuity cannot be attributed to
1234 documented instrumental changes, other explanations for the behaviour of the instrument
1235 must be analysed by careful inspection of the metadata like chamber pressure or flow rate.
1236 In case no explanation for a discontinuity can be identified, an uncertainty contribution in the
1237 same magnitude as the discontinuity must be considered. Generally, the zero gas readings

1238 should be in the range of the expected detection limit and the standard deviation of span
1239 factors and converter efficiencies in the range of estimated uncertainties, e.g., typically a few
1240 percent.

1241 The calibration data are then used to determine a best fit to the span function of the
1242 instrument in time; usually, the scatter in the calibration data in frequent span and zero
1243 measurements is larger than the drift in running averages of these values and accordingly
1244 running averages of the span factors should be used in data evaluation.

1245 The instrument readings in ambient measurements are transformed to mole fraction values
1246 using the above- described averaged span factor functions in time. It is required to evaluate
1247 the mole fractions, repeatability of measurements and the uncertainty together with the flags
1248 in one step, e.g., by use of spread sheet calculations or dedicated scripts and using the
1249 information from the log. Thus, discontinuities in the time series are apparent and can directly
1250 be attributed to the log and be associated with higher uncertainties and corresponding flags.

1251 Data of NO and NO₂ are plotted together with ozone (and an anthropogenic tracer as black
1252 carbon or CO, if available) in quality-check-charts covering periods of typically 2 weeks These
1253 data are checked for NO periods at night which are obtained with ambient ozone present (>
1254 20 nmol/mol) and under conditions of low ozone variability, steady meteorological
1255 conditions, and absence of high level of VOC. If no local NO sources exist NO should be zero.
1256 If not, there is a zero off-set in the data and a correction must be applied covering the
1257 deviation from zero and a corresponding uncertainty must be considered in these
1258 measurements (see 7.3.4). Pollution episodes are characterized by elevated NO₂ and lower
1259 levels of ozone. In the case of local pollution, the NO and NO₂ signals are highly variable and
1260 anti-correlated with ozone, NO₂ may occasionally be negative. Such episodes should be
1261 flagged as polluted data but should be left in the data set.

1262 During the data evaluation process, it is also recommended to assess the results of the
1263 repeated target gas observations. If data processing and calibration of the data perform as
1264 expected, the calibrated target gas results need to show constant output, also in case of
1265 changes of the calibration gas or in case of changes of the instrument's sensitivity. If the
1266 calibrated target gas data show increases in variability or longer-term drifts, the instrument,
1267 the reference gases, and the QA/QC measures need to be carefully evaluated.

1268 Furthermore, annual cycles should be plotted and compared to corresponding cycles from
1269 recent years, wind roses should demonstrate no local or strongly inhomogeneous source
1270 patterns in the surrounding of the station, and percentile distributions of monthly values help
1271 to identify periods of unusual instrument operation.

1272 9.1 Ancillary data and metadata

1273 Ancillary data are instrument and station specific parameters that should be recorded along
1274 with the trace gas readings to keep track of the instrument performance and the
1275 environmental conditions which might be useful for data evaluation and flagging.

1276 Metadata should clearly identify:

- 1277 1. Station name, location, ID
- 1278 2. Originator, contact details
- 1279 3. Species, quoted unit
- 1280 4. Instrument and technique
- 1281 5. Averaging, statistical methods
- 1282 6. Sample height, inlet details
- 1283 7. Flag, missing values

1284 Other essential metadata are listed in the data submission manual at the EBAS data
1285 submission tool (<https://ebas-submit.nilu.no>). Other metadata or links to external sources
1286 can also be included. An example data file can be found in appendix F.

1287 9.2 Data archiving and submission

1288 The format used by WDCRG for the data is plain ASCII NASA-Ames 1001 encoded text in
1289 tabular form, preceded by a section containing metadata.

1290 An EBAS NASA Ames file consist of two parts; a metadata header and a column formatted
1291 data part. The header section contains several important metadata items describing the
1292 measurement site, data variable, instrument, measurement principle and operating
1293 procedure. If nothing changes in the measurement set up, the header will remain the same
1294 from year to year, and the measurement data will be visible as one continuous dataset in the

1295 database. The data section of an EBAS NASA Ames file consists of a fixed column number
1296 format ASCII table, including time stamp, data value and flag for each single measurement
1297 point or data average point. The data formatting templates give the user a detailed line-by-
1298 line explanation of what metadata that should be included on which line of the header, in
1299 terms of correct procedure and wording. Further information is available by clicking on the
1300 respective line number from the template. Flagging of data should be done according to the
1301 ACTRIS nitrogen oxides and EMEP guidelines. For the time being only flags from the tables at
1302 the format template pages are recommended, but a complete list of flags available in EBAS is
1303 located at <http://www.nilu.no/projects/ccc/flags/flags.html>

1304 The data center recommends to first create the data table and then add the header. Name
1305 the file over using the filename stated in the header.

1306 Quality checks performed by WDCRG currently include consistency checks as well as checks
1307 on data integrity. WDCRG uses “-9(99...)” with different numbers of digits depending on the
1308 field to indicate missing values. Data submitters are advised to consult the WDCRG data
1309 submission documents (available online; https://ebas-submit.nilu.no/getting_started) or to
1310 contact WDCRG prior to data submission.

1311 9.3 Data flagging

1312 **Three types** of flags exist for marking data

- 1313 • V (valid measurement): indicate a special condition at the station, but instrument has
1314 operated correctly, the data are therefore considered valid.
- 1315 • I (invalid measurement): showing that data are not available (not measured, deleted
1316 or if it is no precipitation)
- 1317 • M (missing measurement): mainly used for level 0 data to be able to exclude these
1318 data when being reprocessed to level 1 and level 2

1319 The following short list of the flags should be used with this template for or data
1320 harmonization across the network. It is possible to use several flags at the same time to give
1321 detailed information about the data.

1322 Data flagging should be traceable. If data is flagged invalid because of an instrumental
1323 problem, a corresponding entry should exist in the logbook. Although routines for automatic
1324 flagging based on e.g., windspeed exist it is recommended to manually check the correct
1325 flagging of data.

1326 Table 4 List of available flags. From <https://ebas-submit.nilu.no/templates/NOx/lev0>

Flag	Validity	Description
000	V	valid data, no flag. Checked by data originator. Overrides any invalid flags
147	V	Below theoretical detection limit or formal Q/A limit, but a value has been measured and reported and is considered valid. Used for accepted, irregular data
390	V	Data completeness less than 50% Used for aggregated datasets
559	V	Unspecified contamination or local influence, but considered valid
682	I	Unspecified contamination or local influence Used for mechanical or instrumental problem
999	M	Missing measurement, unspecified reason

1327 9.4 Data revisions

1328 Data which has been found to have an issue may be revised and re-submitted with an
1329 incremental revision/version number to indicate that it is the latest, most up to date version.

1330 Within the metadata the revision date and reason for revision should be present.

1331 10 Central Calibration Laboratory (CCL) and World Calibration Centre
1332 (WCC)

1333 10.1 Central Calibration Laboratory (CCL)

1334 The role of the Central Calibration Laboratory (CCL) is to maintain and disseminate primary
1335 standards to which measurement results within the GAW-network can be made traceable
1336 (WMO, 2007a) thus underpinning the long-term accuracy of data.

1337 The National Physical Laboratory (<https://www.npl.co.uk/>, NPL, United Kingdom) has been
1338 assigned as CCL for NO and NO₂. Furthermore, several other National Metrology Institutes
1339 (NMIs) also disseminate NO and NO₂ standards in nitrogen to meet the needs of the air quality
1340 monitoring community. The reference standards are gas standards. These reference gas
1341 standards are primary reference materials that are gravimetrically prepared independently in
1342 accordance with ISO 6142. They are directly traceable to the mole. Analysis of NO gas
1343 mixtures are performed by chemiluminescence or nondispersive ultraviolet (NDUV). Each set
1344 of mixtures are prepared in hierarchies where high concentration “parent” mixtures are
1345 diluted down to produce lower concentrations that are intercompared with previous
1346 hierarchies to ensure traceability and equivalence between them is demonstrated. New
1347 hierarchies are prepared from fresh materials every few years. NPL regularly participates in
1348 key comparisons organised by the Gas Analysis Working Group (GAWG) of the Consultative
1349 Committee on Amount of Substance (CCQM) with other NMIs. These key comparisons ensure
1350 comparability globally.

1351 The range and uncertainty in which these standards are available, have been peer reviewed
1352 and accepted, and are published together with the results of international comparisons to
1353 demonstrate their degrees of equivalence in the Key comparison database (KCDB) of the
1354 Bureau International des Poids et Mesures (Brewer et al., 2014;Perez et al., 2004).

1355 Transfer standards for calibrations at the stations are available from the CCL.

1356 **10.2 World Calibration Centre for NO_x (WCC-NO_x)**

1357 The main task of WCC is to assist the GAW sites to achieve the data quality objectives
1358 described in section 3 and to document the respective status of data quality. Additionally,
1359 the WCC links the *in-situ* observations to the primary standard. This should be done through
1360 regular calibrations, round robins, side-by-side measurements, and audits. The role of WCC is
1361 described in detail in WMO/GAW Report No. 172(WMO, 2007a).

1362 The Research Centre Juelich (<https://www.fz-juelich.de/>, Forschungszentrum Jülich,
1363 Germany) has been assigned by WMO to operate the WCC for NO_x in GAW.

1364 11 Quality control procedures conducted by the WCC

1365 Besides routine calibration and quality checks, comparisons, exchange of experience, and
1366 data control workshops are essential for compatible, quality proofed data. Main comparison
1367 procedures are round robin, side-by-side experiments in controlled environments (simulation
1368 chambers or manifolds) or in the field (many instruments at one site), and audits with
1369 comparison to reference instruments at a given station.

1370 11.1 Measurement guidelines

1371 The WCC- NO_x is responsible for updating the measurement guidelines, e.g., when new
1372 measurement techniques are developed, or SOPs needs to be revised. Interferences as the
1373 effect of ozone and humidity on the sensitivity of CLDs will be examined and measurement
1374 recommendations adapted.

1375 11.2 Round-robin exercises

1376 Calibration standard cylinders of NO in N₂ mixtures in the μmol/mol range will be used as test
1377 gases. Participants are asked to analyse the gas mixture following a well described procedure
1378 having been shipped the cylinder. Results are submitted by the participants using form sheets
1379 to achieve comparable methods of data and uncertainty evaluation. Such inter-comparisons
1380 ensure the traceability of the laboratory standards used. This is the basic requirement for
1381 comparable measurements. However, round-robins lack a check of the dilution systems and
1382 thus are not able to ensure traceable calibration factors.

1383 11.3 Target gases

1384 Target gases are calibration standard cylinders containing ~100 nmol/mol NO/N₂ mixtures
1385 purchased from gas suppliers, checked for stability, and certified by a reference laboratory.
1386 Target gases are treated as unknowns and are processed in the same way as the ambient air
1387 observations. By doing so, processed target gas data can be used to assess the
1388 quality/reproducibility of the data treatment. This process is overseen by the WCC. Such

1389 cylinders are shipped to the stations and used in monthly measurements, i.e., they are
1390 switched directly (manually or by automated valve) to the CLD and measured after a
1391 stabilization. Before empty or after maximum 2 years, they are replaced by new target gases.
1392 The used ones are sent back to the reference laboratory and re-checked for potential drift.
1393 Data from target gas measurements are flagged in the records and delivered together with
1394 ambient data to WCC and WDCRG for evaluation.

1395 **11.4 Side-by-side inter-comparisons**

1396 Side-by-side inter-comparisons take advantage of identical samples being analysed by co-
1397 located instruments. Instruments sample from a common manifold or are connected to an
1398 atmospheric simulation chamber. Complex sample gas matrixes can be analysed, and the
1399 mole fractions can be varied in a controlled manner such that a range from the detection
1400 limits of the instruments to polluted conditions is encountered. This enables a full
1401 characterization of the detection limit, the linear range, the span, and of potential artefacts
1402 of interfering gases which are present in the complex test gas mixtures used. Furthermore, it
1403 enables testing with both real ambient air measurements conditions and in spiked ambient
1404 measurements. It is task of the WCC to organize and oversee such inter-comparisons.

1405 **11.5 Station audits**

1406 Audits are the most powerful QA/QC tools. Station audits are performed by the WCC- NO_x,
1407 the FZ Jülich. Audits check for the conformity of a station to GAW QA system including
1408 recommendations of this Measurement Guideline, and the conformity of a measurement of
1409 test gases with targeted values within the DQOs. The reference for conformity of a station
1410 will evolve as the GAW QA system evolves, however, it will check all parts of the sampling and
1411 instrument set-up; the calibration and zero gas systems; the QA, training and instructions at
1412 the station; the calibration, zero gas, target gas, and standard addition data; the data delivery;
1413 the results from intercomparison exercises, the uncertainty evaluation; the logbook: the
1414 scientific use of the data; safety issues and the overall equipment of the station.

1415 [11.6 Data processing and QC tools](#)

1416 The WCC- NO_x has systematic data evaluation and visualization tools. These tools can either
1417 be used by the stations or stations can send their raw data including all necessary metadata
1418 to the WCC for this processing. It is recommended to be used by the stations supplying data
1419 to the GAW Datacentre for Reactive Gases (WDCRG) but not mandatory, i.e., stations can
1420 follow their own procedures if they are comparable.

1421 [11.7 Data workflow and issue tracker](#)

1422 Processed data are quality checked by GAW experts coordinated and overseen by WCC- NO_x.
1423 This initiates a review process. Issues indicating problems or questionable data are
1424 commented and sent to the station. The station re-checks instrumental conditions and
1425 questionable data and answers the raised issues. It proposes a procedure to overcome the
1426 issue, e.g., checked and ok, questionable and flagged, questionable and uncertainty enlarged
1427 and flagged, or rejected. The station answer and measures taken are again reviewed by WCC
1428 and experts, either settled or commented again. Usually, it is aimed for solving issues and
1429 have accepted data. If the process does not come to an agreement, WCC and experts have
1430 the right to flag the questionable data at the WDCRG. The review (issue-tracker) will be stored
1431 at the WDCRG and available to users.

1432 [11.8 Data control and evaluation workshops](#)

1433 It is planned that yearly data workshops will bring together the station PIs, WCC- NO_x and NO_x
1434 experts to evaluate and discuss station data with respect to quality and open issues.
1435 Generally, the workshop shall discuss data after data processing. It is central part of the data
1436 workflow and enables discussion of the issues identified so far and to raise new issues with
1437 the data.

1439 A. Artefacts and Interferences

1440 A.1 NO artefacts

1441 An “artefact”, or unwanted differences (positive or negative) in signal relative to the
1442 measured detector background, can often be observed in CLDs even when sampling NO-free
1443 air. Artefact signals can arise from spurious CLD pressure and humidity differences between
1444 these two modes (zero and measurement mode), outgassing of surfaces, or from real, non-
1445 zero amounts of NO in even ultrapure cylinder air.

1446 Artefact levels can be determined by overflowing the sample inlet with an excess of
1447 humidified ultrapure synthetic air and alternating between measurement and zero (pre-
1448 chamber) modes. Detector artefact levels must be determined routinely, approximately once
1449 every two days to make an accurate determination of ambient NO in the low pmol/mol (ppt)
1450 range.

1451 In remote (pristine) environments where ambient NO_x might be <100 pmol/mol (ppt) it is
1452 recommended to use the measured night-time NO signal as the detector artefact. expected
1453 to equal zero due to reaction with ambient O₃. In case of moderate ozone mixing ratios > 20
1454 nmol/mol (ppb), low ozone variability (variation coefficient of < 0.1), absence of sunlight,
1455 high levels of VOCs and local NO sources and under
1456 steady meteorological conditions with wind speed > 2 m/s a comparison of the detector
1457 background signal to the ambient signal measured during night-time should give a good
1458 measure of the detector artefact signal (Galbally, 2020; Lee et al., 2009).

1459 Spurious CLD signals can arise from several sources and can be mitigated somewhat.
1460 Examples of common sources of NO artefact and their mitigation are:

- 1461 1. Adding 2 – 3% absolute humidity (absolute volume mole fraction) to the sample or
1462 ozone flow prior to the detector is an effective method of reducing NO artefact signals
1463 (Ridley et al., 1992). Limits of detection are also improved as background level and
1464 stability is improved. Sensitivity to NO is reduced however due to increased quenching
1465 of NO₂* (see chapter 7.3.1). This humidity addition is not necessary at sites with higher
1466 humidity such as coastal and island sites.

- 1467 2. Ingress of dirt into the reaction chamber can present a positive or negative offset
 1468 depending on the specific contaminant. A decrease in sensitivity may be associated also
 1469 as the reflectivity of the cell, or transparency of the PMT window, is reduced. In this case
 1470 disassembly and careful cleaning of the cell is necessary.
- 1471 3. The reaction time in the pre-chamber is set sufficiently for the NO+O3 reaction and
 1472 subsequent deactivation of NO₂* to be completed (see 7.1). However, in practice
 1473 inefficient mixing in the pre-chamber, an undersized pre-chamber, or insufficient ozone
 1474 concentration inside the pre-chamber can lead to inefficient zeroing caused by
 1475 incomplete deactivation of NO₂* before reaching the main reaction chamber. This is
 1476 observed as systematic negative artefacts. The pre-chamber residence time should be
 1477 the same as that of the reaction chamber ideally though is often fixed by a manufacturer
 1478 or limited by packaging. However, the “zeroing efficiency” is easily determined with
 1479 access to NO free air and NO calibration gas thusly:

$$ZE_{\text{zero}} = \frac{C_{\text{NOzero.NO}} - C_{\text{NOzero.blank}}}{C_{\text{NO.NO}} - C_{\text{NOzero.blank}}}$$

32

1480

Variable	Designation
ZE_{zero}	Zero efficiency
$C_{\text{NOzero.NO}}$	Raw counts in the NO zero mode observed in the NO phase of the calibration
$C_{\text{NOzero.blank}}$	Raw counts in the NO zero mode observed in the blank phase of the calibration
$C_{\text{NO.NO}}$	Raw counts in the NO mode observed in the NO phase of the calibration
$C_{\text{NOzero.blank}}$	Raw counts in the NO zero mode observed in the blank phase of the calibration
$C_{\text{NOzero.NO}}$	Raw counts in the NO zero mode observed in the NO phase of the calibration

- 1481 Measured ambient signals can be corrected for zeroing efficiency if required and zeroing
 1482 efficiency can be determined regularly during normal calibration if needed. However this
 1483 correction is not necessary if the calibration is calculated (as it normally is) using the zero
 1484 measured during the calibration (Galbally, 2020).
- 1485 4. Differences in pressure between measurement and zero modes can lead to subtle
 1486 changes in sensitivity or outgassing of adsorbed contaminants within the system. Careful
 1487 design choices in plumbing schemes can eliminate pressure differences, however in

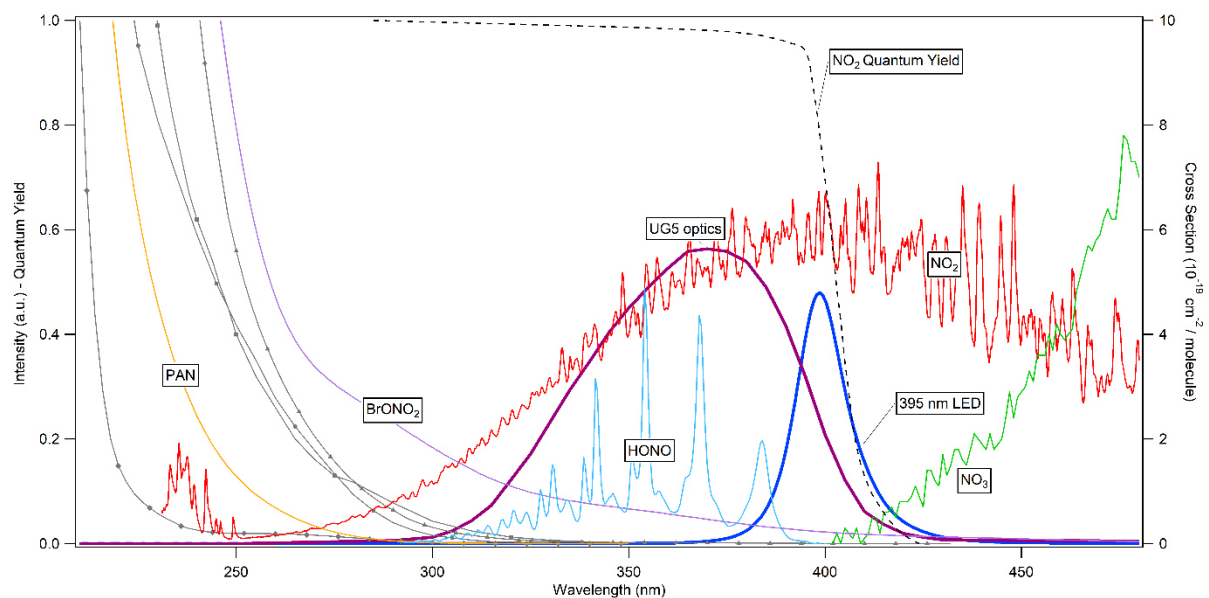
1488 commercial systems there may be no flexibility. In this case the artefact must simple be
1489 measured and corrected for.

1490 A.2 Converter Interferences

1491 Determination of NO_2 by photolytic conversion and detection as NO whilst robust, well
1492 characterised, and reliable is not perfect. Several well-known artefacts and interferences have
1493 been documented and must be considered, minimised, or else corrected for.

1494 A.2.1 Photolytic interferences

1495 Depending on the wavelength spectrum of the photolysis source, a fraction of ambient
1496 nitrous acid (HONO) can be photolyzed to NO interfering with the NO_2 measurement. For a
1497 broadband photolysis spectrum similar to sunlight (e.g. from a Xe high pressure lamp), the
1498 photolysis frequency of HONO relative to NO_2 has been calculated to be between 22% (Frey
1499 et al., 2013) and 37% (Ryerson et al., 2000). For the line spectrum of a UV-LED this
1500 interference is calculated to be 2.0, 12.6, and 25.7% for UV-LEDs with principle outputs of
1501 395, 385, and 365nm respectively.



1502

1503 Figure 10 - Cross-sections of various atmospheric nitrates and UV light sources.

1504 Bromine nitrate, BrONO_2 , is also considered an interfering species due to having an absorption
1505 cross-section which is overlapped to a greater or lesser extent by all UV light sources.
1506 However due to the very low abundance of BrONO_2 in the lower atmosphere (Yang et al.,
1507 2005) it is insignificant considered (Pollack et al., 2010).

1508 *A.2.2 NO₂ Artefacts - Thermal interferences*

1509 Positive interferences due to thermal decomposition of higher atmospheric nitrates (peroxy-
1510 acyl nitrates, alkyl nitrates, nitric acid ...) within photolytic converters has been documented
1511 (Reed et al., 2016). Whilst thermal decomposition can occur at any point within the sampling
1512 system if the sample gas is raised above ambient for any significant amount of time, it can be
1513 a particular issue inside the PLC due to necessarily putting significant energy into sample gas
1514 (from hot, bright light sources). Several precautions can be taken to minimise possible
1515 thermal interferences:

- 1516 1. Separating the gas flow from contact with the UV-emitting elements.
- 1517 2. Cooling the photolysis cell to ambient or lower.
- 1518 3. Maximise NO₂ ⇒ NO conversion efficiency, i.e., unity, to minimize uncertainty in NO₂.
- 1519 4. Reduce residence time in PLC through reduce pressure, increased flow rates.
- 1520 5. Use inert material for photolysis cells e.g., quartz.

1521 *A.2.3 Converter artefacts*

1522 Photolytic converters of all designs are known to present positive artefact signals when
1523 illuminated (Del Negro et al., 1999;Gao et al., 1994;Pollack et al., 2010;Ryerson et al., 2000).
1524 Spurious non-zero signals are often detected when sampling NO_x free zeroing gas.

1525 Much like for NO artefact signals from the CLD, PLC artefacts can be determined by
1526 overflowing the sample inlet with an excess of ultrapure synthetic air. NO artefact must be
1527 determined at the same time, so the procedure is a simple extension. Whilst sampling
1528 ultrapure synthetic air the analyser alternated between NO, NO_x and zero (pre-chamber)
1529 modes. NO artefact must be subtracted from NO_x signal to determine NO₂ artefact. As with
1530 NO detector artefact levels must be determined routinely, approximately once every two
1531 days to make an accurate determination of ambient NO₂ in the low pmol/mol (pptV) range.

1532 The source of artefact signal is purported to be photolysis of adsorbed nitrates on the walls
1533 of the photolytic converter and can be minimised in the following ways:

- 1534 1. Periodic cleaning of the photolysis cell.
- 1535 2. Choice of cell material, i.e., non-porous, inert, e.g., quartz.
- 1536 3. Lensing of UV light in order not to illuminate the photolysis cell walls.

1537 4. Use of Nylon 6-6 sample filter which efficiently removes (>95%) nitric acid.

1538 It is assumed that the possibility for leaks, and impure zeroing gas would also be eliminated.

1539 *A.2.4 Negative PLC artefacts*

1540 • It is possibly to experience both positive and negative artefact signals from photolytic
1541 converters. The first being measured easily by sampling ultrapure synthetic air and
1542 simply subtracted from the measured signal. The second is more insidious and more
1543 difficult to qualify. The procedure to determine if a PLC experiences negative artefact is
1544 as follows:

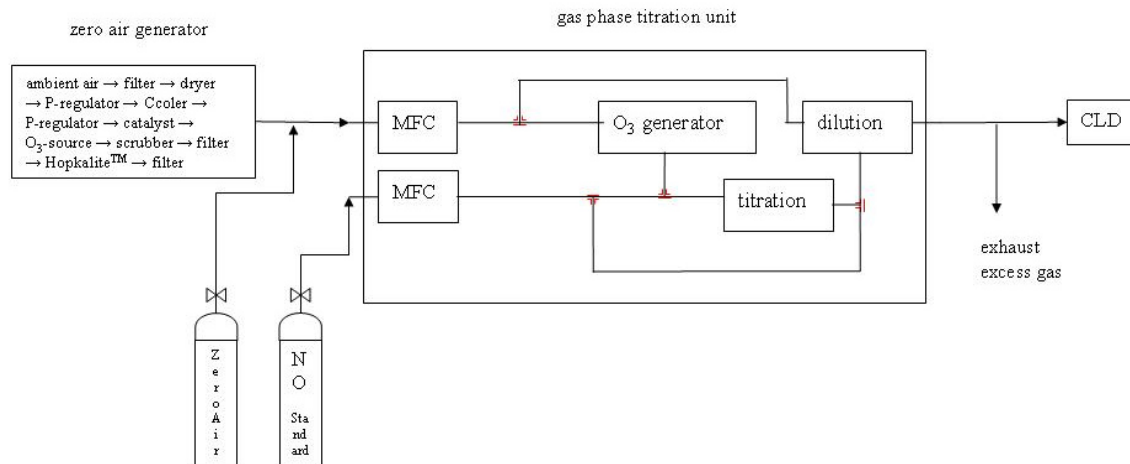
- 1545 1. Have the analyser sample an overflow of ultrapure synthetic air.
- 1546 2. Introduce a known flow of NO standard gas much like during calibration.
- 1547 3. Illuminate PLC and observe changes in the NO signal.

1548 If a decrease in NO, or an increase less than that of the NO₂ artefact, is observed then the PLC
1549 suffers from negative artefact with respect to NO. In this case correction is very uncertain and
1550 not advised, instead the PLC should be replaced.

1551 **N.B.** To determine if a PLC has negative artefact a truly NO₂ free source of air is required, and
1552 the NO standard gas (or NO source) must also be free of NO₂. Else an independent direct
1553 measure of NO₂ is required.

1554 **B. Calibration Procedure**

1555 Since the chemiluminescence technique is not an absolute measuring method and sensitivity
1556 depends on parameters like cell temperature or pressure, which can change with time,
1557 frequent zero and span checks are mandatory.



1558

1559 Figure 11 *Sketch of calibration configuration*

1560 For calibration, special equipment is needed and special care has to be taken to achieve
1561 reliable results: A zero air, i.e. air without significant amounts of NO in it, supply is needed (as
1562 the sketch indicates zero air in cylinders or alternatively a zero air generator should be used),
1563 which exceeds the gas consumption of the analyser by about a factor of 2 and has a
1564 sufficiently high purity such that the remaining nitrogen oxides concentrations are less than
1565 the detection limit of the respective Analyzer (Commercial zero air generators are available
1566 which provide nitrogen oxides free air (< 5 pmol/mol). An alternative is the use of adsorbent
1567 traps (activated charcoal and Sofnofil™ (Purafil) or Hopcalite™). The lifetime of these
1568 catalysts/absorbers strongly depends on the quality of air which must be cleaned. If zero air
1569 has been sufficiently clean and then shows increasing amounts of nitrogen oxides, change the
1570 cleaning cartridges. Each station should have at least one laboratory standard by the CCL or
1571 traceable to the CCL (transfer standard). The transfer standard or the NO working standard
1572 is used at the station for regular calibrations. The standard must be diluted with zero-air to
1573 achieve a suitable concentration range. For this, a dilution unit with flow controllers or passive
1574 elements like critical orifices or restrictors must be used which needs to be carefully

1575 characterized to achieve the required dilution factors and accuracy. From comparisons
1576 between working standard and laboratory standard it must be checked that no drift occurs.

1577 When first attached to the NO standard cylinder, pressure regulators must be flushed 4-5
1578 times with cylinder contents, in a way avoiding back-diffusion of residual air in the regulator,
1579 e.g., by initially evacuating the regulator. Then the regulators should remain under pressure
1580 for longer times, e.g., 24 hours, to achieve equilibrium. After another flushing for 4-5 times,
1581 they are ready for use. This procedure is required to prevent residual atmospheric O₂ in the
1582 regulator from reacting with NO and altering the cylinder mole fraction. The duration of the
1583 calibration procedure should be sufficiently long to observe a possible zero drift in the
1584 calibration signal.

1585 If NO₂ is measured at the site, the PLC-CLD system must also be calibrated for NO₂. Since NO₂
1586 is prone to instability in cylinders, it is recommended to produce NO₂ from NO standard gas
1587 by gas phase titration with ozone (it is not recommended to buy gas mixtures, which contain
1588 both NO and NO₂ since the O₂ added to stabilize NO₂ would react with NO to form NO₂). Thus,
1589 a gas phase titration (GPT) unit is needed, which consists of a dilution unit (which is also
1590 needed for the NO calibration, see above) and an ozone generator. The GPT ozone source
1591 must be stable over time. Irradiation of zero air with the 185 nm UV output from a
1592 temperature-controlled Hg pen-ray lamp has proved to be suitable. Silent electrical discharge
1593 is not appropriate for ozone production because it is not stable enough for GPT and generates
1594 small amounts of NO₂.

1595 Other methods for calibration of NO₂ include permeation sources or high-pressure cylinders
1596 with NO₂ concentrations in the high μmol/mol range. As the permeation device includes
1597 further error sources besides dilution, i.e., non-constant permeation rates and the need of a
1598 2-step dilution owing to the high NO₂ concentration involved, these methods generally have
1599 larger uncertainties than the method recommended above. Accordingly, these should only be
1600 used as an additional quality check. Procedures to use cylinders with NO₂ for calibration are
1601 under development.

1602 Calibrations should be performed under the same conditions as the ambient air
1603 measurements. Generally, the NO₂ calibration should always immediately follow the NO
1604 calibration as it includes the NO chemiluminescence sensitivity.

1605 The calibration procedure for chemiluminescence instruments comprises at least of three
1606 phases.

- 1607 • A blank phase, when only synthetic air is added. The raw counts observed in the different
1608 modes within this phase are designated here $c_{\text{NO.blank}}$, $c_{\text{NOzero.blank}}$, $c_{\text{NOc.blank}}$ and
1609 $c_{\text{NOczero.blank}}$
- 1610 • An NO phase when NO is added from a standard cylinder. The raw counts observed in
1611 the different modes within this phase are designated here $c_{\text{NO.NO}}$, $c_{\text{NOzero.NO}}$, $c_{\text{NOc.NO}}$
1612 and $c_{\text{NOczero.NO}}$
- 1613 • An NO₂ phase, when NO₂ is produced from NO after ozone is added. The raw counts
1614 observed in the different modes within this phase are designated here $c_{\text{NO.NO}_2}$,
1615 $c_{\text{NOzero.NO}_2}$, $c_{\text{NOc.NO}_2}$ and $c_{\text{NOczero.NO}_2}$

1616

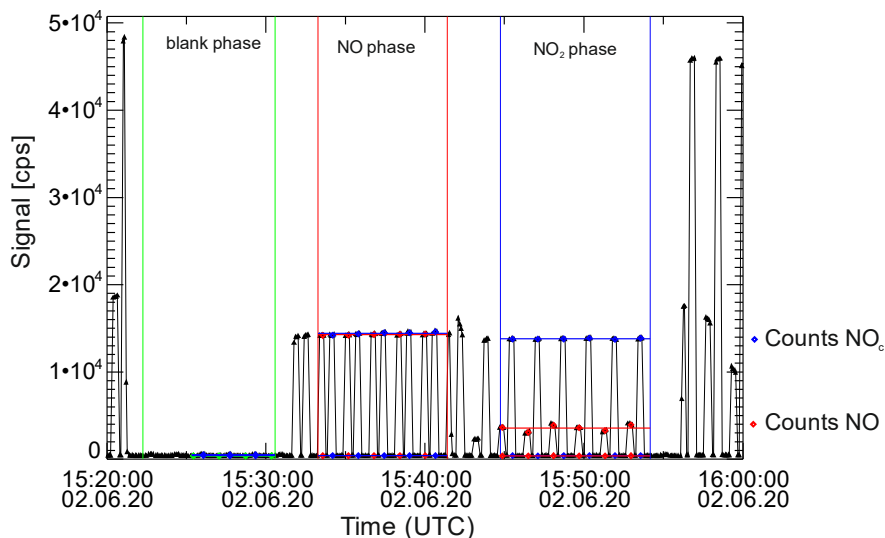


Figure 12: Time series a calibration showing counts observed from the NOc channel and NO channel.

1617 Practical procedure for manual calibration:

- 1618 1. Ensure that all instruments and tools needed for calibration are connected and
1619 working.
- 1620 2. Warm-up time of GPT with ozone generator should be at least 1 hour. Flush the
1621 calibration unit with a high mole fraction of ozone (e.g., 100 nmol/mol) during that time
1622 (warm up of ozone source and cleaning of tubing).

- 1623 3. Flow zero air for at least 20 min, connect calibration source to CLD and acquire
 1624 zero air counts for at least 10 minutes (depending on type of CLD). For CLDs displaying
 1625 the counts, compare the readouts (counts) of zero mode $c_{NOzero.blank}$ and
 1626 measurement mode $c_{NO.blank}$. Significantly higher levels during measurement mode are
 1627 an indication of NO impurities in zero air or leaks in the system, higher levels of $c_{NOc.blank}$
 1628 (sample flowing through PLC/BLC) are an indication of NO₂ impurities in zero air. If it is
 1629 not possible to look at the count rates change span to a high level and have a look on the
 1630 “mole fractions” at the respective modes.) These NO or NO₂ impurities in zero gas will
 1631 become critical if their amount exceeds the lower limit of detection of the instrument. In
 1632 this case resolve problems in your zero-air supply.
- 1633 4. Adjust the desired span point and allow the system to run for at least 20 minutes
 1634 until constant levels are achieved, then acquire the span air counts for at least 10
 1635 minutes. Calculate the sensitivity of the CLD using equation 5. Compare the
 1636 signals $c_{NOc.NO}$ and $c_{NO.NO}$ in the NO phase. Higher $c_{NOc.NO}$ signal compared to $c_{NO.NO}$ is
 1637 an indication of NO₂ impurities in the standard gas and/or zero air.
- 1638 6. After determination of the new calibration factors for NO, continue with NO₂
 1639 calibration.
- 1640 7. Choose an ozone concentration so that ~80% of the primary NO amount is
 1641 converted to NO₂. Allow at least 20 minutes for the instrument to stabilize.
- 1642 8. After stabilization acquire the data for the $c_{NOc.NO2}$ and $c_{NO.NO2}$ channel for at
 1643 least 10 minutes (each).
- 1644 9. Calculate the conversion efficiency. The effective produced NO₂ amount is the
 1645 difference from [NO] measured in the NO phase and in the NO₂ phase.

$$CE_{NO_2} = \frac{(c_{NOc.NO2} - c_{NOczero.NO2}) - (c_{NO.NO2} - c_{NOzero.NO2})}{(c_{NO.NO} - c_{NOzero.NO}) - (c_{NO.NO2} - c_{NOzero.NO2})}$$

33

Variable	Designation
CE_{NO_2}	Conversion efficiency of PLC or BLC
$c_{NOc.NO2}$	Raw counts in the NO _x mode observed in the NO ₂ phase of the calibration
$c_{NOczero.NO2}$	Raw counts in the zero NO _x mode observed in the NO ₂ phase of the calibration
$c_{NO.NO2}$	Raw counts in the NO mode observed in the NO ₂ phase of the calibration

$C_{NO.NO}$	Raw counts in the NO mode observed in the NO phase of the calibration
$C_{NOzero.NO}$	Raw counts in the zero NO mode observed in the NO phase of the calibration

1646

1647 10. Subsequently the NO_x analyser is reattached to the inlet line, GPT unit and zero
 1648 air supply are switched off and the pressure regulator of the standard gas cylinder is shut
 1649 off.

1650 **B.1 Automated calibration**

1651 The gas-phase titration unit and corresponding valves needs to be controlled by a computer
 1652 with control software. The metadata of the unit should be recorded. Zero gas and calibration
 1653 gas supply need to be switched by automated valves. The CLD inlet needs to be equipped with
 1654 appropriate automated valves (Material Teflon) switching between ambient air inlet and gas-
 1655 phase titration unit. Furthermore, an exhaust valve allowing purging of the GPT unit during
 1656 equilibration times is to be installed. Times when no ambient measurements are performed
 1657 must be automatically flagged in the data acquisition system of the NO_x Analyzer.

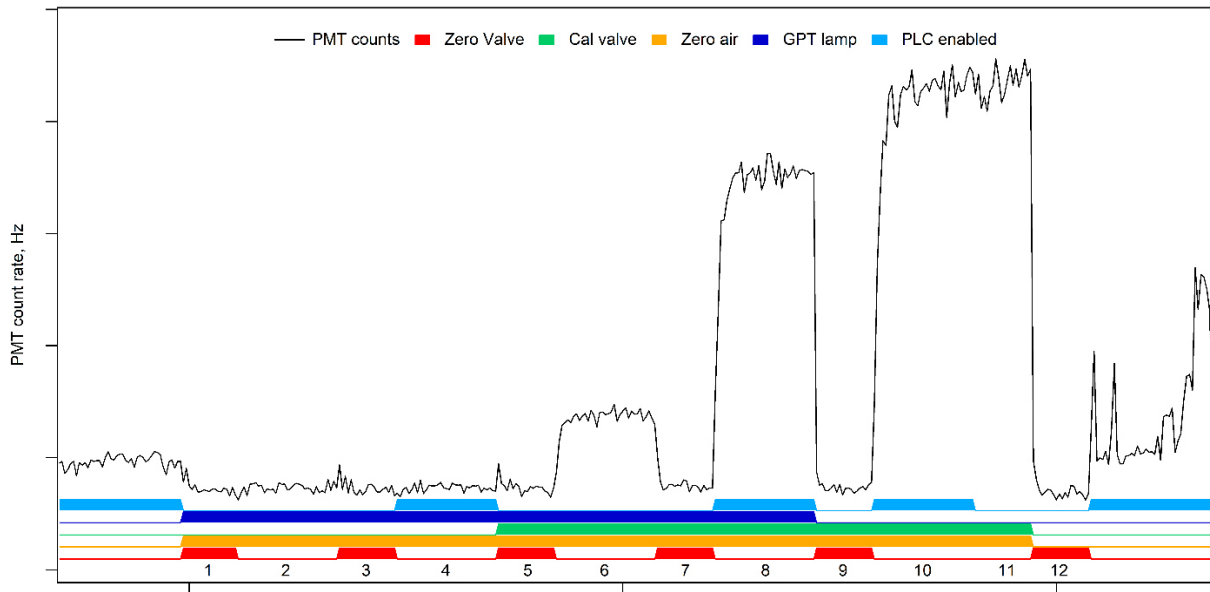
1658 Follow the above manual procedure with following modifications:

- 1659 • In step 2: Automated Valve switching will supply gases to GPT unit and purge them to
 1660 the exhaust valve.
- 1661 • In step 3: Open the valve from the gas-phase titration unit to the CLD, close the exhaust
 1662 and the ambient air supply valves. Specify the purge and measurement times according
 1663 to your specific set-up such that stable measurements are achieved in each mode.
- 1664 • In step 9: reverse automated valve switching to ambient measurements, switch off gas
 1665 supply to gas-phase titration unit and switch off unit.

1666 Zero, span and converter efficiency measurement data need to be evaluated and checked for
 1667 stable conditions during data analysis. Zero correction and span must be applied off-line to
 1668 the data.

1669

1670 B.2 Fast calibration procedure



1671

1672 Figure 13 – Example signal trace during a calibration for NO, NO₂ artefact, NO₂ conversion efficiency and NO
 1673 sensitivity.

1674 Figure 13 shows an example calibration cycle from an instrument calibrated in zero air which
 1675 reports raw counts and is being calibrated for (in chronological order):

- 1676
- 1677 1. NO artefact
 - 1678 2. NO₂ artefact
 - 1679 3. NO₂ conversion efficiency
 - 1680 4. NO sensitivity

1680 The states of the critical components such as valves, NO₂ converters, etc. is indicated by the
 1681 colour bars.

- 1682
- 1683 • 1 – 3; the NO artefact is determined between chemiluminescent zero measurements
 - 1684 • 3 – 5; the NO₂ artefact is determined between chemiluminescent zero measurements
 - 1685 ○ Whilst the artefacts were being determined the NO flow and GPT were stabilising and being dumped to waste i.e., the lines were being purged
 - 1686 • 5 – 7; the proportion of NO titrated to NO₂ by gas phase titration (GPT) is determined
 - 1687 • 7 – 9; the amount of NO₂ photolyzed back to NO by the photolytic converter (PLC) is
 1688 determined

1689 • 9 – 12; the NO sensitivity of the CLD is determined between chemiluminescent zero
1690 measurements

1691 ○ 10; a check of the NO₂ content of the NO cylinder is made – this check also verifies
1692 that the PLC is not consuming NO

1693 In this case the entire calibration cycle takes approximately 4 minutes, however the time
1694 taken should reflect the stabilisation time of the individual instrument and the uncertainty
1695 goals.

1696

1697 C. Linear Interpolation

Linear interpolation between two datapoints in a time series is done using the equation

$$y = y_0 \times \left(1 - \frac{t - t_0}{t_1 - t_0}\right) + y_1 \times \left(\frac{t - t_0}{t_1 - t_0}\right) \quad 34$$

1698 y_0 and y_1 are the values at the times t_0 and t_1 . y is the value to be calculated at time t .

1699

Variable	Designation	Example
t_0	Time t_0	2021-09-27 12:00:00
y_0	Value at t_0	1
t_1	Time t_1	2021-09-28 16:00:00
y_1	Value at t_1	5
t	Time t	2021-09-27 18:00:00
y	Value at t	1.857

1700

1701 D. Calculation of water concentration from relative humidity

1702

1703 For calculation of the water concentration the Antoine Equation can be applied

1704 The vapour pressure of water VP can be calculated from the relative humidity RH as follows

$$VP = \frac{RH}{100} e^{a-b/T} \quad 35$$

1705 Where RH is the relative humidity in [%] and T is the temperature in [K]

1706 A and b are constants with a= 21.36469 and b= 5339.66. The water concentration is

$$[H_2O] = \frac{VP \times MW_{H_2O}}{(P - VP) \times MW_{Air}} \times 100 \quad 36$$

1707 P is the air pressure in mbar, MW_{H_2O} is the molecular weight of water (18.015 g/mol) and MW_{Air} is the
 1708 molecular weight of dry air (28.949 g/mol).

1709

Variable	Designation	Example
RH	Relative humidity	50 %
T	Temperature	298.15 K
P	Ambient pressure	1013.25 mbar
a	Constant a	21.36469
b	Constant b	5339.66
VP	Partial water pressure	15.835 mbar
MW_{H_2O}	molecular weight of water	18.015 g/mol
MW_{Air}	molecular weight of dry air	28.949 g/mol
$[H_2O]$	Water mass fraction	0.987 %

1710 **E. Example for Ozone correction**

1711 NO can react with O₃ in the ambient air in the inlet and manifold before analysis giving an
 1712 overestimation of NO₂ and an underestimation of NO. This can be minimised by reducing the
 1713 residence time between the tip of any manifold to the instrument, however it must be
 1714 corrected in combination with equation 37:

$$[NO]_0 = [NO]_{E1} \times e^{k_{O_3} \times (t_L + t_B)} \quad \mathbf{37}$$

1715

Variable	Designation	Example
t_B	duration of stay [sec] in converter (BLC for LED off) or bypass line (PLC)	10s
t_L	duration of stay [sec] in sample line	5s
k_{O_3}	rate of the reaction between NO and O ₃ ($k(O_3+NO) \times [O_3] \times 10^{-9} \times M$)	0.045s ⁻¹
$[NO]_{E1}$	observed NO signal [nmol/mol] without photolytic converter (LED off in BLC, or bypass in PLC)	0.102 nmol/mol
$[NO]_0$	NO mole fraction at the entry of inlet line	0.2 ppb

1716

1717 The photolysis rate in the converter is calculated as

$$J_c = \frac{-\ln(1 - CE_{NO_2})}{t_c} \quad \mathbf{38}$$

1718

Variable	Designation	Example
CE_{NO_2}	conversion efficiency of PLC or BLC	0.5
t_c	duration of stay [sec] in converter (BLC for LED on) or PLC line	10 s
J_c	photolysis rate of NO ₂ in the converter	0.069 s ⁻¹

1719

1720 The amount fraction $[NO]_{E2}$ of NO at the end of the converter is calculated: $[NO]_{E2}$

$$[NO]_{E2} = [NO]_{E1} + [NO_2]_M \times CE_{NO_2} \quad \mathbf{39}$$

1721

1722 $[NO_2]_M$ is the measured NO₂ concentration and CE_{NO_2} is the efficiency of the converter.

Variable	Designation	Example
CE_{NO_2}	conversion efficiency of PLC or BLC	0.5

$[NO]_{E1}$	observed NO signal [nmol/mol] without photolytic converter (LED off in BLC, or bypass in PLC)	0.102 nmol/mol
$[NO_2]_M$	Measured NO ₂ concentration	0.55 nmol/mol
$[NO]_{E2}$	observed NO signal [nmol/mol] with photolytic converter	0.10 nmol/mol

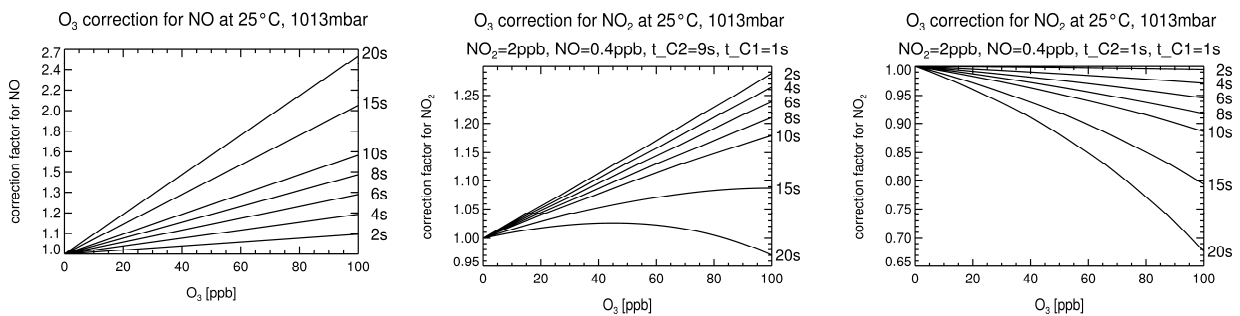
1723 With these parameters, the corrected NO₂ can be calculated according equation

$$[NO_2]_0 = \frac{J_C + k_{O_3}}{J_C} \times \frac{[NO]_{E2} - [NO]_{E1} \times e^{-(k_{O_3} + J_C) \times t_C + k_{O_3} \times t_B - (k_{O_3}) \times t_D}}{e^{-(k_{O_3}) \times t_D} - e^{-(k_{O_3} + J_C) \times t_C - (k_{O_3}) \times t_D}} - [NO]_0 \quad 40$$

1724 $[NO_2]_M$ is the measured NO₂ concentration and CE_{NO_2} is the efficiency of the converter.

Variable	Designation	Example
J_C	conversion efficiency of PLC or BLC	0.5
k_{O_3}	rate of the reaction between NO and O ₃ ($k(O_3+NO) \times [O_3] \times 10^{-9} \times M$)	0.045s ⁻¹
$[NO]_0$	NO concentration at the tip of sampling line	0.2 nmol/mol
$[NO]_{E2}$	Observed NO signal [nmol/mol] with photolytic converter	0.55 nmol/mol
$[NO]_{E1}$	observed NO signal [nmol/mol] without photolytic converter (LED off in BLC, or bypass in PLC)	0.10 nmol/mol
t_D	duration of stay [sec] in converter	10s
t_B	duration of stay [sec] in converter (BLC for LED off) or bypass line (PLC)	10s
t_D	duration of stay [sec] in from converter to detector	10s
$[NO_2]_0$	NO ₂ concentration at the tip of sampling line	1.0 nmol/mol

1725



1726

1727 Figure 14: Simulated correction factors for NO and NO₂ due to reactions with O₃ in the inlet line and in the
 1728 photolytic converter and in the converter bypass at different residence times and different initial ozone amount
 1729 fraction. Left panel: Simulated correction factor for NO at different residence time in sampling line and converter
 1730 bypass ($t_{C2}+t_L$). Central panel: Simulated correction factor for NO₂ at different residence times in sampling line
 1731 (t_L). and converter bypass ($t_{C2}+t_L$) simulated with $[NO]_0 = 2$ ppb, $[NO]_0 = 0.4$ ppb, $t_{C2} = 9$ s, $t_{C1} = 1$ s.
 1732 Right panel: Simulated correction factor for NO₂ at different residence times in sampling line (t_L). and converter
 1733 bypass ($t_{C2}+t_L$) simulated with $[NO]_0 = 2$ ppb, $[NO]_0 = 0.4$ ppb, $t_{C2} = 1$ s, $t_{C1} = 1$ s.

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end_time of measurement, days from the file reference point
nitrogen_monoxide, nmol/mol, Statistics=arithmetic mean, Calibration scale=NEL
nitrogen_monoxide, nmol/mol, Statistics=stddev
nitrogen_monoxide, nmol/mol, Statistics=percentile:15.87
nitrogen_monoxide, nmol/mol, Statistics=percentile:84.13
nitrogen_monoxide, nmol/mol, Statistics=expanded uncertainty 2sigma
nitrogen_monoxide, nmol/mol, Statistics=precision
nitrogen_monoxide, nmol/mol, Statistics=detection limit
numflag, no unit
nitrogen_dioxide, nmol/mol, Statistics=arithmetic mean, Calibration scale=NEL+GPT
nitrogen_dioxide, nmol/mol, Statistics=stddev
nitrogen_dioxide, nmol/mol, Statistics=percentile:15.87
nitrogen_dioxide, nmol/mol, Statistics=percentile:84.13
nitrogen_dioxide, nmol/mol, Statistics=expanded uncertainty 2sigma
nitrogen_dioxide, nmol/mol, Statistics=precision
nitrogen_dioxide, nmol/mol, Statistics=detection limit
numflag, no unit
NOx, nmol/mol, Statistics=arithmetic mean
NOx, nmol/mol, Statistics=stddev
NOx, nmol/mol, Statistics=percentile:15.87
NOx, nmol/mol, Statistics=percentile:84.13
NOx, nmol/mol, Statistics=expanded uncertainty 2sigma
NOx, nmol/mol, Statistics=precision
NOx, nmol/mol, Statistics=detection limit
numflag, no unit
0
60
Data definition: EBAS_1.1
Set type code: TU
Timezone: UTC
File name: M00001R.20190101000000.20201022000000.chemiluminescence_photolytic.NOx.air.2h.1h.M001L.NOx_42iTL_BIR.M001L_chem_photol.lev2.nas
Startdate: 20190101000000
Revision date: 20201022000000
Version: 1
Version description: initial revision, manually inspected
Data level: 2
Period code: 1y
Resolution code: 1h
Sample duration: 1h
Orig. time res.: 1mn
Station code: M00001R
Platform code: M00001S
Station WDCA-ID: GAWMO_BIR
Station GAW-ID: BIR
Station GAW-Name: Birkenes Atmospheric Observatory
Station other IDs: 201 (NILUDE)
Station land use: Forest
Station setting: Rural
Station GAW type: R
Station WHO region: 6
Station latitude: 58.38
Station longitude: 8.25
Station altitude: 220.0 m
Measurement height: 4.0 m
Regime: IMG
Component: NOx
Unit: ug N/m3
Matrix: air
Laboratory code: M001L
Instrument type: chemiluminescence_photolytic
Instrument name: NOx_42iTL_BIR
Instrument manufacturer: Thermo
Instrument model: 42i-TL
Instrument serial number: 12345
Method ref: M001L_chem_photol
Standard method: SOP=ACTRIS_NOxy_2014
Inlet type: Hat or hood
Inlet description: Downward facing with hood
Ozone correction: Not corrected for reaction with O3 in the inlet
Water vapor correction: Not corrected for water vapor quenching in CLD
Humidity/temperature control: None
Humidity/temperature control description: passive, sample heated from atmospheric to lab temperature
Volume std. temperature: 273.15 K
Volume std. pressure: 1013.25 hPa
Detection limit expl.: Determined by instrument counting statistics
Zero/negative values code: Zero/negative possible
Zero/negative values: Zero and neg. values may appear due to statistical variations at very low concentrations
QA1 measure ID: ACTRIS NOx s-b-s 2012
QA1 date: 20121116
QA2 measure ID: ACTRIS NO round robin 2012
QA2 date: 20120206
Originator: Fiebig, Markus, Markus.Fiebig@nilu.no, Norwegian Institute for Air Research, NILU, Atmosphere and Climate Department, Instituttveien 18, , N-2027, Kjeller,
Originator: Someone, Else, Someone@somewhere.no, Some nice Institute, WOW, Super interesting division, Street 18, , X-9999, Paradise, Noway
Submitter: Fiebig, Markus, Markus.Fiebig@nilu.no, Norwegian Institute for Air Research, NILU, Atmosphere and Climate Department, Instituttveien 18, , N-2027, Kjeller,
Acknowledgement: Request acknowledgement details from data originator
Comment: Data converted on import into EBAS from 'nmol/mol' to 'ug N/m3' at 273.15 K, 1013.25 hPa, conversion factor 0.6245228.
start_time end_time NO stdtdev NOperc16 NOperc84 NO_ac NO_pr NO_dl numflag_NO NO2 NO2stdtdev NO2perc16 NO2perc84 NO2_ac NO2_pr NO2_dl numflag_NO2 NOx NOxstdtdev NOxperc16 NOxperc84 NOx_
0.000000 0.041667 0.9222 0.0186 0.9222 0.9222 0.0800 0.0070 0.005 0.000000000 0.2224 0.0044 0.2224 0.2224 0.0300 0.0040 0.010 0.000000000 1.1546 0.0054 1.0522 1.2244 0.0700 0.0060 0.10
0.041667 0.083332 9999.9999 9999.9999 9999.9999 9999.9999 9999.9999 9999.9999 9999.9999 99.999 0.999000000 9999.9999 9999.9999 9999.9999 9999.9999 9999.9999 9999.9999 99.999 0.999000000 9999.9999

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1737 **G. Abbreviations and acronyms**

1738

1739 ACTRIS Aerosols, Clouds, and Trace gases Research InfraStructure Network

1740 ASCII American Standard Code for Information Interchange

1741 BIPM Bureau International des Poids et Mesures

1742 BLC Blue light converter

1743 CAPS Cavity attenuated phase shift (spectroscopy)

1744 CCL Central Calibration Laboratory

1745 CCQM Consultative Committee for Amount of Substance: Metrology in Chemistry and

1746 Biology

1747 CE Conversion efficiency

1748 CLD Chemiluminescence detector

1749 CRDS Cavity ring down spectroscopy

1750 DOAS Differential optical absorption spectroscopy

1751 DQO(s) Data quality objective(s)

1752 FT-IR Fourier transform infrared spectroscopy

1753 FZ Forschungszentrum

1754 GAW Global Atmosphere Watch

1755 GAWSIS GAW Station Information System

1756 GAWTEC GAW Training and Education Centre

1757 GPS Global Positioning System

1758 GPT Gas phase titration

1759 IAGOS In-service Aircraft for a Global Observing System

1760 ICAD Iterative cavity-enhanced DOAS

1761 ID Identifier

1762	ISO	International Standards Organisations
1763	JCGM	Joint Committee for Guides in Metrology
1764	KCDB	Key comparison database
1765	LED	Light-emitting diodes
1766	LIF	Laser induced fluorescence
1767	LOD	Limit of detection
1768	M	Avogadro constant
1769	MAX-DOAS	Multi-axis differential absorption spectroscopy
1770	NASA	North American Space Agency
1771	NILU	Norwegian Institute for Air Research
1772	NPL	National Physics Laboratory
1773	NMIs	National Measurement Institutes
1774	NO _x	nitrogen oxides (Sum of NO and NO ₂)
1775	NO _y	Sum of reactive nitrogen oxides
1776	PAN	Peroxy acyl nitrates
1777	PET	Polyethylene terephthalate
1778	PFA	Perfluoroalkoxy alkane
1779	PI	Principal investigator
1780	PLC	Photolytical converter
1781	PMT	Photomultiplier tube
1782	PS	Primary standards
1783	PSS	Photostationary State
1784	QA/QC	Quality Assurance and Quality Control
1785	SOP	Standard operating procedures

1786	TDLAS	Tuneable diode laser absorption spectroscopy
1787	TM	Trade mark
1788	UV	Ultraviolet
1789	WCC	World Calibration Centre
1790	WDC	World Data Centre
1791	WDCRG	World Data Centre for Reactive Gases
1792	WIGOS	WMO Integrated Global Observing System
1793	WMO	World Meteorological Organization
1794	ZE	Zeroing efficiency

1795 **References**

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