

# AirMonTech



## Quality needs Assurance: SOPs, Type Approvals, Equivalence Tests for Regulated Pollutants

Robert Gehrig, Christoph Hueglin and AirMonTech Consortium Workshop 'Current and Future Air Quality Monitoring', Barcelona, Spain







- Information on technologies and performance of available instruments for the measurement of regulated pollutants
- Guidance for optimal use of available instruments (measurement technologies)
- Provide easy access to this information through AirMonTech database
  - $\Rightarrow$  Harmonisation of air quality measurements in Europe





Collect and write documents relevant for persons involved in air quality monitoring (network operators) ...

... and make them easily accessible.



## **Document types**



- Documents collected from network operators and manufacturers (external suppliers)
  - Type approval test reports
  - Standard operating procedures (SOP)
  - Equivalence test reports (PM2.5/PM10 monitors)
  - Specification sheets/Application reports
- Basic documents on air pollutants and measurement technologies produced by the AirMonTech consortium
  - Metric Background Information (MBI)
  - Metric Measurement Technology Overview (MMTO)
  - Metric Measurement Technology Information (MMTI)
  - Model Standard Operating Procedures (SOPM)





Documents from network operators and manufacturers concerning WP 1 (existing technologies):

SOPs	97
Type approval test reports	21
(Partial) Equivalence test reports	9
Comparison raw data	8
Specification sheets / Application reports	34
Total documents	169



## **Received external documents (April 2012)**



### Documents from 16 countries:

- Austria
- Belgium
- Bulgaria
- Cyprus
- Denmark
- Estonia
- Finland
- France
- Flance
- Germany
- Ireland
- Italy
- Netherlands
- Slovenia
- Spain
- . Switzerland
- United Kingdom







### - Metric Basic Information (MBI)

includes definitions, sources (briefly), health relevance, regulations, reference methods, references

– Metric Measurement Technology Overview (MMTO)

table listing identified measurement technologies, typical operational characteristics, applicability to remote/rural/urban sites

– Metric Measurement Technology Information (MMTI)

details for each technology listed in the MMTO document

– Model Standard operating procedure (**SOPM**)

details for each technology listed in the MMTO document



## **AirMonTech Documents**



MBI, MMTO, MMTI, SOPM files

WP1 air pollutant
SO <sub>2</sub>
NO <sub>2</sub> (NO, NO <sub>x</sub> )
0 <sub>3</sub>
СО
PM2.5/PM10
Benzene

Available on database

In preparation



## MBI document for NO<sub>2</sub>



#### AirMonTech



Background Information on Air Pollutants and Air Quality Metrics

Pollutant Type: Gaseous Pollutants Pollutant Name: Nitrogen Dioxide (NO2)

#### Description of the metric

Nitrogen dioxide (NO2) is an important gaseous air pollutant as it is directly linked with a number of adverse effects on human health (see below). In addition, NO2 plays an important role in the formation of tropospheric ozone (O3) and is a precursor of nitrates which contribute to atmospheric fine particulate matter. As other N-compounds it contributes also to the eutrophication of soils and waters.

NO2 is directly emitted from various sources but also formed in the atmosphere from reaction of nitrogen monoxide (NO) with O3. NO2 can on the other hand photolyse to form NO and ozone, resulting in a cycling between NO and NO2 in the troposphere during daytime at time scales of minutes (Jacob, 1999). Consequently, current European legislative standards control the emissions of nitrogen oxides (NOx, the sum of NO and NO2) rather than of NO2.

The most important emission sector for NOx in Europe is transportation followed by combustion in power plants and industry. Commercial, residential and other stationary combustion sources and agricultural activities are other important sources of NOx (see EMEP emission data, available from http://www.emep-emissions.at/emissiondata-webdab).

Concentrations of NO2 are usually reported in  $\mu$ g/m<sup>3</sup> using the respective molar masses of 46 g/mol. Concentrations are reported with reference to standard pressure of 101,3kPa and standard temperature of 293 K.

#### Health Relevance

Adverse health effects of ambient NO2 have been reported through many epidemiological studies. Many studies reported short-term respiratory effects including the increase of respiratory symptoms, asthma exacerbations in children and adults, and increases in related emergency visits and admissions as well as respiratory mortality (Anderson et al 1997; 1998; Sunver et al 1997; Katsouvanni et al 2001; Stieb et al 2002: Galan et al 2003: Peel et al 2005: Samoli et al. 2006: Chiusolo et al. 2011: Tramuto et al. 2011: Mann et al. 2010). There is evidence that NO2 exposure increases symptoms and affects the infection defense mechanism among asthmatics (Mortimer et al 2002). There are also reports on the effects on the cardiovascular system and increases in cardiovascular admissions and mortality (Burnett et al 1999; Metzger et al 2004; Samoli et al. 2006; Chiusolo et al. 2011; Felber Dietrich et al. 2008), but not all evidence is consistent (Schwartz et al 1997; Roemer et al 1998). Recently there have been reports from Spanish cohorts associating prenatal exposure with decreased fetal growth (Estarlich et al. 2010; Estarlich et al. 2011). Several long-term studies assessed the effects of NO2 and reported effects on asthma incidence in children (Simons et al 2011), lung function decrements in children (Gauderman et al 2004) and adults (Schindler et al 1998), cardiac autonomic dysfunction (Felber Dietrich et al 2008) and mortality (Hoek et al 2002; Nafstad 2004; Filleul et al 2005) but the results across studies are not consistent (Forastiere et al 2006).



Background Information on Air Pollutants and Air Quality Metrics

In spite of the evidence, there is skepticism on whether the NO2 health effects are causal or are reflecting effects from other traffic related pollutants and in particular particles with which NO2 concentrations are highly correlated in time and space. NO2 results have been more inconsistent compared with the ones reported for particles and are also more dependent on the lag times examined as well as the susceptibility of the population. Evidence from toxicological studies suggests that there are NO2 effects in animals concerning lung metabolism, emphysema like structural changes, lung function, airway inflammation, bronchial hyperresponsiveness and decrease in host defense against pulmonary infections (Becker & Soukup 1999; Pathmanathan et al 2003; Forastiere et al 2006; Hodgkins et al. 2010). There is some evidence that NO2 acts synergistically with ozone or PM from controlled exposure human studies (Gong et al 2005). These can be considered in favor of independent NO2 effects but most have detected effects at higher than ambient level concentrations. However Koehler et al. 2011 demonstrated genotoxicity and DNA alterations at NO2 exposure of 200µg/m3 on nasal epithelial cells.

Compound	Toxicological Information	References	Epidemiological information	References
NO2	Effects on lung metabolism, emphysema like structural changes, lung function, airway inflammation, bronchial hyperresponsiveness and decrease in host defense against pulmonary infections	Becker & Soukup 1999; Hodgkins et al. 2010; Forastiere et al 2006	Short-term increase in respiratory symp- toms, asthma exacerbations in children and adults, increases in related emergency visits and admissions and respiratory mortality. Short-term increase in cardiovascular admissions and mortality	Anderson et al 1997; Sunyer et al 1997; Katsouyanni et al 2001; Stieb et al 2002; Peel et al 2005; Samoli et al. 2006; Chiusolo et al. 2011
	Genotoxicity and DNA alterations in human nasal epithelium	Koehler et al. 2011	Emergency room visits for acute respiratory symp- toms, asthma exca- cerbation in children	Anderson et al 1998; Galan et al 2003; Tramuto et al. 2011; Mann et al. 2010; Weinmayr et al. 2010
			Prenatal exposure affects fetal growth Long-term effects on asthma incidence in children, lung function decrements in children and adults; cardiac autonomic dysfunction in susceptible groups and mottality	Estarlich et al. 2010, Estarlich et al. 2011 Schindler et al 1998; Hoek et al 2002; Nafstad 2004; Gauderman et al 2004; Filleul et al 2005; Forastiere et al 2006; Felber Dietrich et al. 2008; Simons et al 2011



## MBI document for NO<sub>2</sub>



#### AirMonTech



Background Information on Air Pollutants and Air Quality Metrics



#### EC legislation, limit values (EU Directive 2008/50/EC)

Averaging period	Limit value	Date by which limit value
		is to be met
One hour	200 µg/m <sup>3</sup> (not to be exceeded more than 18 times in a calendar year)	1 January 2010
Calendar year	40 μg/m <sup>3</sup>	1 January 2010

#### Reference method for determination of the metric

The reference method for NO2 is based on the catalytic conversion of NO2 into NO and subsequent determination of NO by the chemiluminescence signal resulting from the reaction of nitrogen monoxide with ozone(EN14211:2005 "Ambient air quality — Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence"). The method is described in detail in the AirMonTech Technology Description File for NO2.

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## **MMTO document for NO<sub>2</sub>**



Dis	Air Mon Tech	Overview of Measurement Technologies for Air Pollutar Pollutant Type: Gaseous Pollutant Pollutant/Metric Name: Nitrogen Dioxide (NO2)	Overview of Measurement Technologies for Air Pollutants and Air Quality Metrics         'ollutant Type:       Gaseous Pollutant         'ollutant/Metric Name:       Nitrogen Dioxide (NO2)			
#	Technology	Characteristics and performance	Availability and current use of instruments	Suggested area of application		
1	Chemiluminescence com- bined with metal converter	<ul> <li>European reference method (EN14211; 2005).</li> <li>Robust instruments available from various manufacturers. Widely used in monitoring networks.</li> <li>Indirect method. NO2 is calculated as difference of NOx and NO.</li> <li>Not selective for NO2, because of interferences of other oxides of nitrogen [1]. This is especially important at rural and remote locations.</li> <li>Precision of typical instruments ±0.4 ppb or ±0.76µg/m<sup>3</sup> (1σ, 60min). Higher sensitivity for remote locations is possible.</li> </ul>	Commercial; moni- toring networks	Urban		
2	Chemiluminescence com- bined with photolytic con- verter	<ul> <li>Similar to Technology 1,</li> <li>but higher selectivity through photolysis of NO2, and</li> <li>slightly more complicated because correction of measured signal with converter efficiency required.</li> </ul>	Commercial; moni- toring networks	Urban Rural Remote		
3	Chemiluminescence with lu- minol	<ul> <li>Commercial instruments using this technique are no longer available.</li> </ul>	No longer commer- cially available			
ł	Cavity ringdown spectrosco- py (CRDS)	<ul> <li>Highly selective and sensitive method</li> <li>Currently no commercial instruments, only research instruments available [2, 3].</li> </ul>	Not commercially available, Research	Urban Rural Remote		
5	Cavity enhanced laser ab- sorption spectroscopy	<ul> <li>Highly selective and sensitive method</li> <li>High precision of around ±0.05 ppb or ±0.1µg/m<sup>3</sup> (1σ, 1sec), very high temporal resolution (e.g. 5Hz).</li> </ul>	Commercial; Re- search; monitoring networks	Urban Rural Remote		



## **MMTI document for NO<sub>2</sub> with CL method**





Pollutant Type:

Pollutant Name:

Description of Automated Technologies for Air Pollutants and Air Quality Metrics



Description of Automated Technologies for Air Pollutants and Air Quality Metrics



Flow schematic of a typical NO-NO<sub>x</sub>-NO<sub>2</sub> chemiluminescence monitor using a catalytic converter.



В.

#### Instruments with photolytic converters

An alternative to the above mentioned catalytic converters are photolytic converters, where conversion of NO\_2 is achieved by irradiation of NO\_2 with UV light (< 410nm) according to following reactions:

 $\begin{array}{ll} \mathsf{NO}_2 + \mathbf{h} \cdot \nu & \rightarrow \mathsf{NO} + \mathsf{O} \\ \mathsf{O} + \mathsf{O}_2 & \rightarrow \mathsf{O}_3 \\ \mathsf{NO} + \mathsf{O}_3 & \rightarrow \mathsf{NO}_2 + \mathsf{O}_2 \end{array}$ 

leading to following equilibrium:

 $NO_2 + O_2 + h \cdot v \leftrightarrow NO + O_3$ 

Instruments equipped with photolytic converters do not suffer from interferences to other oxidized nitrogen compounds and allow much more specific measurements of NO<sub>2</sub>. However, the conversion efficiencies of photolytic converters are around 50% and much lower than the requirements of the European standard (EN 14211:2005). The converter efficiency of photolytic converters needs to be regularly determined for the correction of the measured signal.

There are photolytic converters available on the market that can be integrated into conventional instruments equipped with catalytic converters, more or less simply by changing the converter type (see flow schematic below).

Measurement Technology:

Chemiluminescence method – detection of chemiluminescence from reaction of nitrogen monoxide with ozone

The measurement of NO<sub>2</sub> by detection of the chemiluminescence signal from the reaction of nitrogen monoxide with ozone is the reference method for ambient NO<sub>2</sub> measurements in Europe (EN 14211:2005). Monitors using this measurement principle measure the concentration of nitrogen monoxide (NO) and NOx (NO<sub>x</sub>=NO+NO<sub>2</sub>). The concentration of NO<sub>2</sub> is calculated by subtracting the measured NO<sub>x</sub> concentration.

**Gaseous Pollutants** 

Nitrogen Dioxide (NO2)

In a chemiluminescence analyser air is fed into the reaction chamber of the analyser, where it is mixed with an excess of ozone. All NO is oxidized to NO2 by following reactions:

 $\begin{array}{l} \mathsf{NO} + \mathsf{O}_3 \rightarrow \mathsf{NO}_2{}^* + \mathsf{O}_2 \\ \mathsf{NO}_2{}^* \rightarrow \mathsf{NO}_2 + h{\cdot}\nu \end{array}$ 

\* = excited state of species

Infrared light that is released from the decay of NO<sub>2</sub>\* from an excited state to the ground state is detected by a photomultiplier tube. The intensity of the detected light (chemiluminescence) is proportional to the concentration of nitrogen monoxide. For determination of nitrogen dioxide, the sampled air is fed through a converter where the nitrogen dioxide is catalytically reduced to nitrogen monoxide and analysed in the same way as previously described. The chemiluminescence signal is proportional to the sum of concentrations of nitrogen dioxide and nitrogen monoxide. The concentration of nitrogen dioxide is calculated from the difference of the measured NO<sub>x</sub> and NO concentrations.

#### A. Instruments with heated catalytic converters

Typical converters used for reduction of NO<sub>2</sub> into NO are made of a material such as stainless steel, copper, molybdenum, tungsten or spectroscopic pure carbon and are maintained at constant temperatures. The reference method for ambient NO<sub>2</sub> (EN 14211:2005) requires that the converter is capable of converting at least 95% of the nitrogen dioxide to nitrogen monoxide. A drawback of these converters is that other oxidized nitrogen compounds (e.g. HNO<sub>3</sub> and Peroxiacetyl nitrate) are reduced to NO with high efficiencies as well and can cause significant interferences (Steinbacher et al., 2007; Dunlea et al., 2007). These interferences are especially important at rural and remote sites.





### Aim of the model SOP

- Giving support to network operators in setting-up or updating an SOP.
- Giving example text for the necessary points which need to be addressed in an SOP.

*Important:* It can only serve as an extended template because an SOP needs to describe the actual circumstances of a network (site locations, exact type of an analyzer, organization and planning of the maintenance procedures etc.).

Example text is written in normal style, explanations and directions for needed specific input in *italic style*.





### **SOP version**

Give date and number of the current version of the SOP.

**Responsible person** *Name of the author of the SOP.* 

### Implementation of this SOP version

Date of the setting into force of the current version of the SOP and signature of the authorized person.

### **Measurement principle**

Nitrogen oxides (NOx) are measured continuously by chemiluminescence, after reaction of nitrogen monoxide with ozone. Nitrogen monoxide (NO) is measured directly; nitrogen dioxide (NO<sub>2</sub>) is first converted to nitrogen monoxide, after which the sum of the concentrations of both oxides is measured. By assuring that the conversion efficiency is above 98%, the concentration of nitrogen dioxide can then be calculated by subtraction of the independently measured concentration of nitrogen monoxide. The concentrations of nitrogen monoxide and nitrogen dioxide are measured in units of ppbv. For reporting these are converted to units of  $\mu$ g.m<sup>-3</sup> at standard temperature and pressure (20 °C, 101,325 kPa) using standard conversion factors.





### **Routine maintenance**

Perform the scheduled maintenance as required by the maintenance schedule. All performed maintenance steps have to be documented in the LOG-book together with date, time and name of the operator.

Here the different maintenance activities should be described. They may comprise e.g.: Flow controls, leak tests, cleaning processes, filter and scrubber replacements, check of sensors and status signals. A full list of required maintenance procedures and schedules can always be found in the instrument manual.





### NO<sub>x</sub>-Analyzer Thermo 42i TL









# Basic documents on air pollutants and measurement technologies produced by the AirMonTech consortium

- Proof-reading by members of the AirMonTech consortium.

# Documents collected from network operators and manufacturers (external documents)

- Unchanged files from source and/or authors indicated in the file.
- If appropriate, caveats and reservations of the AirMonTech consortium are expressed in the file description in the database.



## **Qualification of documents**



ies () JRC	<b>Document details</b>
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download
Document
Code: AMT9
Type: Standard operating procedures - Model ( SOPM )
Author: Empa, Robert Gehrig
Language: English
Title: Model of a Standard Operating Procedure (SOP) for NOx measurements with a chemiluminescence analyzer
Description: This model SOP aims at giving support to network operators in setting-up or updating a SOP for NOx monitoring. It gives example text for the necessary points which need to be addressed in a SOP. However, it can only serve as an extended template because a SOP needs to describe the actual circumstances of a network (site locations, exact type of an analyzer, organization and planning of the maintenance procedures etc.). Thus, these items have to be formulated for each monitoring network individually and in a specific way.
Created on: 20/03/2012 10.27.26

Updated on: 20/03/2012 10.28.16





## Currently 9 received and uploaded reports and 8 comparison data sets

- Collected by AirMonTech consortium and within a special project by JRC





### *Currently 21 received and uploaded documents*

- Not only complete reports
- Partly only certificates issued by testing agencies

More information on type approval tests and certification (EN 15267) in the next presentation by K. Pletscher





- Writing the remaining basic documents (MBI, MMTO, MMTI, SOPM)
- Second call for documents after going public with the database. The possibility to access the database might encourage additional network operators and manufacturers to provide documents.





- WP1 of AirMonTech is focused on collection and preparation of documents on regulated air pollutants.
- Approx. 170 documents on existing technologies (WP1) submitted by network operators and manufacturers are already accessible on the AirMonTech database.
- The basic documents of the AirMonTech consortium are currently in preparation. Examples for NOx measurements are already available on the database.
- Second call for ducuments after opening of the database.