
International Standard



7996

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Ambient air — Determination of the mass concentration of nitrogen oxides — Chemiluminescence method

Air ambiant — Détermination de la concentration en masse des oxydes d'azote — Méthode par chimiluminescence

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 7996 was prepared by Technical Committee ISO/TC 146, *Air quality*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

Ambient air — Determination of the mass concentration of nitrogen oxides — Chemiluminescence method

1 Scope and field of application

This International Standard specifies a chemiluminescence method for the determination of the mass concentration of nitrogen oxides present in ambient air.

The method is applicable to the determination of the mass concentration of nitrogen monoxide present in ambient air up to approximately 12,5 mg/m³ and of nitrogen dioxide up to approximately 19 mg/m³ respectively¹⁾ at 25 °C and 101,3 kPa.

For interferences, see 6.6.

2 References

ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Weighing methods*.

ISO 6144, *Gas analysis — Preparation of calibration gas mixtures — Static volumetric methods*.

ISO 6349, *Gas analysis — Preparation of calibration gas mixtures — Permeation method*.

ISO 6711, *Gas analysis — Checking of calibration gas mixtures by a comparison method*.

3 Principle

Passage of the air sample through a filter (to prevent mal-operation of the chemiluminescence analyser) at a constant flow rate into the reaction chamber of the analyser, where it is mixed with an excess of ozone. Filtering of the emitted radiation, proportional to the amount of nitrogen monoxide present in the air sample, by means of a selective optical filter and conversion of the filtered radiation into an electric signal by a photomultiplier tube.

Measurement of nitrogen dioxide in the air sample by reducing it to nitrogen monoxide by passage through a converter before it enters the reaction chamber.

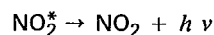
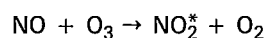
The electric signal obtained is proportional to the total amount of nitrogen oxides, and the nitrogen dioxide contribution is calculated from the difference between this value and that obtained for nitrogen monoxide only — when the air sample does not pass through the converter.

Analysers may be of the dual or cyclic type. In the dual type, the air flow is divided into two streams, one passing directly to the reaction chamber and the other via the converter. There are two reaction chambers and one or two detectors respectively monitoring the nitrogen monoxide and nitrogen oxides content of the air sample. In the cyclic type analyser, there is only one reaction chamber and detector and the output alternates between nitrogen monoxide and total nitrogen oxides measurements, i.e. the air sample alternately bypasses or passes through the converter.

4 Reactions

Luminescence is a characteristic of many substances from which light is emitted when they are excited. This phenomenon is called chemiluminescence when produced as a result of a chemical reaction.

This chemiluminescence method is based on the reaction



Excited nitrogen dioxide emits radiation centred around the near infra-red (1 200 nm).

5 Apparatus

Schematic diagrams of typical analysers are given in figures 1a) and 1b) (dual type) and figure 1c) (cyclic type). An apparatus consists of the following principal components (5.1 to 5.10).

1) At the temperature and pressure given, the following conversion factors apply.

NO: 1 mg/m³ $\cong$ 0,81 ppm (V/V)
1 ppm (V/V) $\cong$ 1,23 mg/m³

NO₂: 1 mg/m³ $\cong$ 0,53 ppm (V/V)
1 ppm (V/V) $\cong$ 1,88 mg/m³

5.1 Sample line.

The sample intake shall consist of a small inverted funnel connected to the sample line — the latter being as short as practically possible. Both shall be made of material which is inert to nitrogen monoxide and nitrogen dioxide. It is very important not to use any materials made from copper based alloys. From experience, the best materials to use are polytetrafluoroethylene (PTFE) or perfluoro(ethylene/propylene) (FEP). In order to avoid disturbance of the nitrogen monoxide-nitrogen dioxide-ozone equilibrium caused by reduced daylight intensity in the sample line, the residence time in the sample line should be as short as possible. The sample line may be moderately heated to avoid any condensation.

5.2 Particle filter.

The particle filter shall retain all particles likely to alter the performance of the analyser. At the same time, it and its support shall be made from material which will not retain nitrogen monoxide or nitrogen dioxide, for example PTFE or stainless steel. The particle filter shall be replaced or cleaned periodically as required by the dust loading at the sampling site. Overloading of this filter may cause loss of nitrogen dioxide by sorption on the particulate matter.

5.3 Control and regulation of sample flow rate.

The sample flow rate shall be maintained to $\pm 2\%$ of that specified by the manufacturer of the analyser. Flow rate control is usually maintained by a controlled pressure drop across restrictors.

5.4 Converter.

The converter shall consist of a heated furnace maintained at a constant temperature and is made of stainless steel, copper, molybdenum, tungsten or spectroscopically pure carbon. It shall be capable of converting at least 95 % of the nitrogen dioxide to nitrogen monoxide at a temperature not exceeding 400 °C.

The role of the converter is very important since it controls the determination of nitrogen dioxide.

5.5 Ozone generator.

Ozone is generated from oxygen by either ultra-violet radiation or by a high voltage silent electric discharge. If oxygen in ambient air is used for ozone generation by a high voltage silent electric discharge, it is essential that the air be thoroughly dried and filtered before entering the generator. If the ozone is generated using oxygen of recognized analytical grade from a compressed gas cylinder, this oxygen can be fed directly into the generator. The concentration of ozone produced shall be greater than the maximum concentration of nitrogen oxides being measured.

The flow rate of air or oxygen to the ozone generator shall be kept constant.

5.6 Reaction chamber.

This shall be constructed of an inert material. Its dimensions determine the characteristics of the chemiluminescence reaction (residence time, speed of reaction). The reaction chamber may be heated slightly to avoid condensation. The reaction is generally carried out at reduced pressure to minimize quenching effects and increase sensitivity.

5.7 Optical filter.

This filter shall remove all radiation at wavelengths below 600 nm, thus avoiding any interference produced by the chemiluminescence reaction with unsaturated hydrocarbons which radiate at these wavelengths.

5.8 Photomultiplier tube.

The output of the analyser is closely affected by the characteristics of the photomultiplier tube. In order to reduce background noise and the effect of temperature changes, the tube is usually housed in a thermostatically controlled refrigerated container.

5.9 Ozone filter.

The ozone shall be removed from the gas on leaving the reaction chamber by passage through activated charcoal. This prevents pollution of the immediate ambient air and protects the sampling pump.

5.10 Sampling pump.

Situated at the end of the circuit, the sampling pump draws air through the apparatus. It shall be capable of operating under the pressure conditions required for the reaction chamber.

5.11 Apparatus for checking the analyser converter efficiency (see 6.1).

5.11.1 Source of nitrogen monoxide, compressed gas cylinder containing nitrogen monoxide in nitrogen at a concentration of the order of 1 ppm (V/V). The actual concentration need not be known provided that it remains constant throughout the test.

5.11.2 Source of oxygen, compressed gas cylinder containing oxygen or air.

5.11.3 Ultra-violet lamp, capable of varying the size of the lamp window for producing varying amounts of ozone from oxygen.

5.11.4 Chemiluminescence analyser in which the temperature of the converter furnace is controllable.