

METHODS FOR MEASUREMENT, MONITORING AND CONTROL OF NO_x EMISSIONS

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ABSTRACT

European legislation requires that special aggressive pollutant gases (i.e. NO), must be measured continuously, particularly in locations with the suspected highest load risk.

There are a number of oxides of nitrogen, including nitrous oxide (N₂O), nitric oxide (NO), nitrogen dioxide (NO₂), nitrogen trioxide (N₂O₃), and nitrogen pentoxide (N₂O₅), that are referred to collectively as NO_x. The two oxides of nitrogen that are of primary concern to air pollution are NO and NO₂.

The monitoring of NO₂ for regulatory purposes requires methods suitable for concentrations measuring in the range relevant for Europe, i.e. 0 - 500 mg/m³, with a sufficiently high accuracy. Different methods have been developed for the measuring of NO₂ concentrations, some of which can only measure NO₂, while

others can also measure NO and/or NO_x. These methods are referring either to standard methods or to acceptable one, with simple chemical and physical principles, either to methods based on sophisticated electronic techniques.

In this paper are presented certain methods for measurement, monitoring and control of the nitrogen oxides, recommended at international level. Through these methods, can be known the quantity of NO_x emissions from ambient air. This is the first step to establish appropriate methods to prevent and reduce air pollution.

1. INTRODUCTION

To evaluate the large scale concentrations of nitrogen oxides, it is useful to measure at least NO₂ and O₃ in rural background air. Such measurements are made in most countries in Europe within the EMEP programme (Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air pollutants in Europe) [1].

There are a number of oxides of nitrogen, including nitrous oxide (N₂O), nitric oxide (NO), nitrogen dioxide (NO₂), nitrogen trioxide (N₂O₃), and nitrogen pentoxide (N₂O₅), that are referred to collectively as NO_x. The two oxides of nitrogen that are of primary concern to air pollution are NO and NO₂. NO is a colorless gas that is a precursor to NO₂ and is an active compound in photochemical reactions that produce smog. NO₂ is a reddish brown gas that gives color to smog and can contribute to opacity in flue gas plumes from stacks. By far the largest source of NO_x is combustion, although there are other industrial sources such as nitric acid manufacturing. The large amount of NO_x generated at coal-fired electric power plants is evident, and the very large contribution from motor vehicles and other forms of transportation is pronounced.

Preventing an increase in total NO_x emissions can be attributed to the increased use of NO_x controls, especially in automobiles and in industrial fuel consumption. NO_x is generated during combustion from three mechanisms: thermal NO_x, prompt NO_x, and fuel NO_x. Understanding these mechanisms enables one to utilize control methods for NO_x emissions [2].

2. METHODS FOR MEASUREMENT AND MONITORING OF NO₂

There are several well-established monitoring methods for NO₂, some of which can only measure NO₂, while others can also measure NO and/or NO_x. The methods differ with respect to chemical and technical principle as well as to temporal and spatial resolution. In some situations, only one monitoring method may be feasible, but where a choice of method is possible, the advantages and disadvantages of different methods need to be considered.

The most commonly used methods are briefly described below. Distinction is made between continuous and discontinuous methods, and between point measurements and remote sensing. The point measurements are representative for the monitoring site and for an area around the site, the size being determined by the emissions and other characteristics of the surroundings. The remote sensing methods measure the average concentration over the monitoring path in the atmosphere. Generally, only standardized and reliable methods should be used for environmental monitoring [1].

2.1. DISCONTINUOUS POINT MEASUREMENTS

Active and passive discontinuous methods are normally used for daily to monthly sampling. The manual discontinuous methods are relatively cheap and simple, but have several disadvantages including the need for manpower for sampling and analysis, the limited time resolution and the time delay until results are available. For the daily measurements of NO₂, there are two active methods, the potassium iodide and the Saltzmann methods [1].

The potassium iodide method is based on the absorption of NO₂ on a potassium iodide impregnated sintered glass filters. NO₂ is absorbed and reduced to nitrite by the iodide on the filter. The nitrite formed is extracted with deionised water and determined spectro-photometrically with the Griess method. This method can be used for measurement of nitrogen dioxide on a 24 h basis in ambient air within the range 0.1-10 µg NO₂-N/m³, assuming an air sample of 0.7 m³ and an extraction volume of 4 ml [3].

The Saltzmann/modified Saltzmann method is based on the direct Griess reaction during sampling (ISO, 1981). A pink colour is produced during sampling. The intensity is measured spectro-photometrically [4]. Diffusion denuders combined with an analysis by ion chromatography may also be used for the determination of NO₂. Carbon coated denuders allow for the simultaneous determination of NO₂ and PAN (peroxyacetyl nitrate) at concentration levels which approach 50 ppt (parts per trillion) on a 24 hour basis which makes the technique very suitable for the measurement of NO₂ in rural areas [5].

Diffusive, or passive, sampling methods are normally used for longer sampling periods, on weekly (usually in more polluted areas) or monthly (usually in less polluted areas) basis. The sampling technique is based on molecular diffusion of the gas molecules into the sampler, where they are quantitatively collected on an impregnated filter. No electricity, pump or other equipment (except for a rain shelter) is needed. The NO₂ collected on the impregnated filter is extracted from the filter with water and determined by chemical analysis. When calculating the concentration, the ambient air temperature must be taken into consideration, since the diffusion velocity is temperature dependent. Studies on the accuracy of diffusive samplers in comparison with other monitoring techniques for NO₂ show a good agreement with chemiluminescence's measurements, as well as with the potassium iodide method [1].

2.2. CONTINUOUS POINT MEASUREMENTS

Continuous monitoring methods cover various instrumental techniques. The chemiluminescence's method is most commonly used method and recommended as reference method for mandatory concentration measurements. The instrument signals are recorded continuously intervals and typically integrated to hourly means. The technique is based on the gas phase chemiluminescence's reaction of NO with O₃, which produces stimulated NO₂ emitting light at about 1200 nm wavelength (ISO, 1985). The air sample passes a heated catalytic converter where NO₂ is reduced to NO. The signal from the

air passing the converter gives the NO_x concentration, while the signal from the air drawn directly to the detector gives the NO concentration. NO_2 is determined as the difference between the two signals [1]. A traditional commercial monitor for NO_x is presented in figure 1. On a known fraction from air sample (1 from figure 1), all nitrogen dioxide is reduced at monoxide and after the reaction with ozone determine $\text{NO} + \text{NO}_2$. On other fraction (2), determines by the same method only the NO (the presented NO_2 , is not in excited state, so not presents luminescence). Then, by difference, the NO is determined [6].

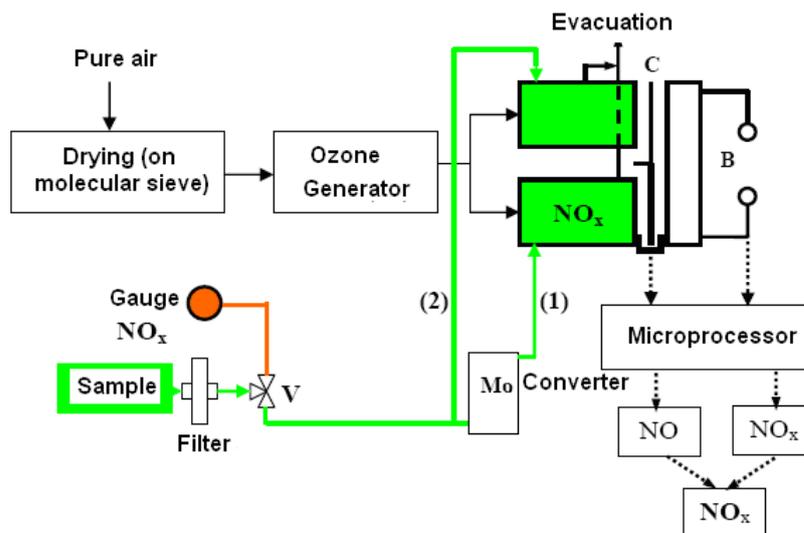


Figure 1 Schematic representation for utilization of the luminescence method for monitoring of the NO_x from air

2.3. REMOTE SENSING, DOAS

Differential Optical Absorption Spectroscopy is an open path optical measuring technique applicable for a number of gases, including NO_2 specifically, absorbing light in the UV and visible spectral regions. The technique is based on differential absorption, i.e. the difference between local maximums and minima in the absorption spectrum of the probed gas. The DOAS technique may also be used for NO, but a shorter path is required than for NO_2 . Light from a broad-band xenon high-pressure lamp is transmitted up to several kilometers through the atmosphere. The light is received and analyzed by the use of a fast scanning dispersive spectrometer to eliminate the influence of air turbulence. The DOAS technique is used today in a large number of applications, the most common being environmental monitoring of the main pollutants in urban areas, as a mean concentration over some distance in urban air. The major advantage of DOAS is that several compounds can be measured at the same time, i.e. HNO_2 , NO_3 radicals, benzene, toluene etc. However, the scattering of light by fog, heavy rain or snowfall may cause problems with data quality and availability. For aromatics significant interference must be taken into account. The technique is suitable for measurement of urban background concentration, where the small scale spatial variations from small local sources are not relevant or directly describing the information about the urban background air pollution.

Since automatic monitoring is very expensive, it will sometimes be preferable to use automatic monitoring in combination with indicative monitoring (passive sampling) and/or air quality modeling to more cost effectively assess the extent of high concentration areas and the spatial variability of pollutants.

The total description of local air quality by measurements requires many monitoring stations. However, many suitable models exist for the calculation of air pollution dispersion in local scale, and for fast chemical reactions, providing all relevant urban background air quality data and local meteorological parameters are available [1].

3. METHODS TO CONTROL NO_x EMISSIONS

Two primary categories of control techniques for NO_x emissions are (3.1) combustion controls, and (3.2) flue gas treatment. Very often more than one control technique is used in combination to achieve desired NO_x emission levels at optimal cost [7].

3.1. COMBUSTION CONTROL TECHNIQUES

A variety of combustion control techniques are used to reduce NO_x emissions. Some reduce the peak flame temperature; other reduces the oxygen concentration in the primary flame zone while other methods use the thermodynamic balance to reconvert NO_x back to nitrogen and oxygen.

3.1.1. LOW-EXCESS AIR FIRING

In the low air-fuel excess ratio firing techniques the principle is based on cutting back the amount of excess air, the lower oxygen concentration in the flame zone reduces NO_x production. In some cases where too much excess air has become normal practice, thermal efficiency is improved. However, low excess air in the resulting flame may be longer and less stable, and carbon monoxide emissions may increase. Applying advanced optimization systems at four coal-fired power plants resulted in NO_x emission reductions of 15 to 55% [2].

3.1.2. OVERFIRE AIR

The primary flame zone can be operated fuel rich to reduce oxygen concentration, and then additional air can be added downstream. This overfire air provides oxygen to complete combustion of unburned fuel and oxidizes carbon monoxide to carbon dioxide, creating a second combustion zone. Because there is so little fuel in this overfire zone, the peak flame temperature is low. Thus, NO_x formation is inhibited in both the primary and overfire combustion zones [7].

3.1.3. FLUE GAS RECIRCULATION

Another widely used method to control NO_x emissions is the flue gas recirculation technology, when some of the flue gas, which is depleted in oxygen, is re-circulated to the combustion air. This has two effects: the oxygen concentration in the primary flame zone is decreased, and additional nitrogen absorbs heat, and reduces the peak flame temperature [7].

3.1.4. WATER/STEAM INJECTION

Injecting water or steam into the combustion chamber provides a heat sink that reduces peak flame temperature. However, a greater effect is believed to result from the increased concentration of reducing agents within the flame zone as steam dissociates into hydrogen and oxygen. Compared to standard natural draft, in natural gas-fired burners, up to 50% NO_x reduction can be achieved by injecting steam at a rate up to 20 to 30% of the fuel weight [2].

3.1.5. LOW AND ULTRA LOW-NO_x BURNERS

Low-NO_x burners are designed to stage either the air or the fuel within the burner tip. The principle is similar to overfire air (staged air) or reburn (staged fuel) in a furnace. With staged-air burners, the primary flame is burned fuel rich and the low oxygen concentration minimizes NO_x formation. Additional air is introduced outside of the primary flame where the temperature is lower, thereby keeping the thermodynamic equilibrium NO_x concentration low, but hot enough to complete combustion. Staged-fuel burners introduce fuel in two locations. A portion of the fuel is mixed with all of the combustion air in the first zone, forming a hot primary flame with abundant excess air. NO_x formation is high in this zone. Then additional fuel is introduced outside of the primary flame zone, forming a low oxygen zone that is still hot enough for kinetics to bring the NO_x concentration to equilibrium in a short period of time. In this zone, NO_x formed in the primary flame zone reverts back to nitrogen and oxygen [8]. Ultra low-NO_x burners have been developed that incorporate mechanisms beyond simply staging air or fuel as designed in low-NO_x burners. They may incorporate flue gas recirculation within the furnace that is induced by gas flow and mixing patterns, and use additional levels of air and/or fuel staging [2].

All those methods are primary methods to reduce NO_x formation at the combustion chamber level.

3.2. FLUE GAS TREATMENT TECHNIQUES

3.2.1. SELECTIVE NON-CATALYTIC REDUCTION (SNRC) AND SELECTIVE CATALYTIC REDUCTION (SCR)

Other methods for NO_x reduction have been developed, like selective non-catalytic reduction (SNRC) and selective catalytic reduction (SCR). Selective non-catalytic reduction uses ammonia (NH₃) or urea (H₂NCONH₂) to reduce NO_x to nitrogen and water. The intermediate steps involve amine (NH_i) and cyanuric nitrogen (HNCO) radicals. The critical dependence of temperature requires excellent knowledge of the temperature profile within the furnace for placement of reagent injection nozzles. In the case that the SNCR process is not controlled efficiently, supplementary emissions will occur in exhaust gases, like CO, NH₃ or N₂O, called secondary emissions. In a typical application, SNCR produces about 30 to 50% NO_x reduction. In the SCR technology a catalyst bed can be used with ammonia as a reducing agent to promote the reduction reaction and to lower the effective temperature. An SCR system consists primarily of an ammonia injection grid and a reactor that contains the

catalyst bed. A variety of catalyst types are used for SCR: precious metals, vanadium pentoxide on titanium dioxide and various aluminum silicates.

3.2.2. LOW-TEMPERATURE OXIDATION WITH ABSORPTION

Other technology for NO_x removal is low-temperature oxidation of NO_x species to highly soluble N₂O₅, followed by absorbing the N₂O₅ in a wet absorption tower. An advantage of this process over other downstream treatment processes is very high NO_x removal efficiency, with 99% removal being reported for an industrial boiler [7].

All those are secondary methods for NO_x reduction.

4. CONCLUSIONS

By air quality monitoring can be known the levels pollutants discharged into the environment for assessment of pollution degree. Prevention, reduction and elimination of pollution are a continuous process, its purpose is to reduce or limit the pollutants to a level compatible with healthy, sustainable ecosystems.

In this paper are presented the main methods for measurement, monitoring and control of the nitrogen oxides, recommended at international level for the assessment of the environment quality.

Through the above methods can be known the concentrations of nitrogen oxides discharged in the alive and working environment. This is the first stage necessary to determine appropriate measures to prevent or reduce pollution degree.

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