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 (N$_2$O), nitric oxide (NO), nitrogen dioxide (NO$_2$), nitrogen trioxide (N$_2$O$_3$), and nitrogen pentoxide (N$_2$O$_5$), that are referred to collectively as NO$_x$. The two oxides of nitrogen that are of primary concern to air pollution are NO and NO$_2$.

The monitoring of NO$_2$ for regulatory purposes requires methods suitable for concentrations measuring in the range relevant for Europe, i.e. 0 - 500 mg/m$^3$, with a sufficiently high accuracy. Different methods have been developed for the measuring of NO$_2$ concentrations, some of which can only measure NO$_2$, while
others can also measure NO and/or NO\textsubscript{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\textsubscript{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 NO\textsubscript{2} and O\textsubscript{3} 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 (N\textsubscript{2}O), nitric oxide (NO), nitrogen dioxide (NO\textsubscript{2}), nitrogen trioxide (N\textsubscript{2}O\textsubscript{3}), and nitrogen pentoxide (N\textsubscript{2}O\textsubscript{5}), that are referred to collectively as NO\textsubscript{x}. The two oxides of nitrogen that are of primary concern to air pollution are NO and NO\textsubscript{2}. NO is a colorless gas that is a precursor to NO\textsubscript{2} and is an active compound in photochemical reactions that produce smog. NO\textsubscript{2} 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\textsubscript{x} is combustion, although there are other industrial sources such as nitric acid manufacturing. The large amount of NO\textsubscript{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\textsubscript{x} emissions can be attributed to the increased use of NO\textsubscript{x} controls, especially in automobiles and in industrial fuel consumption. NO\textsubscript{x} is generated during combustion from three mechanisms: thermal NO\textsubscript{x}, prompt NO\textsubscript{x}, and fuel NO\textsubscript{x}. Understanding these mechanisms enables one to utilize control methods for NO\textsubscript{x} emissions [2].

2. METHODS FOR MEASUREMENT AND MONITORING OF NO\textsubscript{2}

There are several well-established monitoring methods for NO\textsubscript{2}, some of which can only measure NO\textsubscript{2}, while others can also measure NO and/or NO\textsubscript{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\textsubscript{x} concentration, while the signal from the air drawn directly to the detector gives the NO concentration. NO\textsubscript{2} is determined as the difference between the two signals [1]. A traditional commercial monitor for NO\textsubscript{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 NO + NO\textsubscript{2}. On other fraction (2), determines by the same method only the NO (the presented NO\textsubscript{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\textsubscript{x} from air](image)

### 2.3. REMOTE SENSING, DOAS

Differential Optical Absorption Spectroscopy is an open path optical measuring technique applicable for a number of gases, including NO\textsubscript{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\textsubscript{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\textsubscript{2}, NO\textsubscript{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 effective 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\textsubscript{x} EMISSIONS

Two primary categories of control techniques for NO\textsubscript{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\textsubscript{x} emission levels at optimal cost [7].

3.1. COMBUSTION CONTROL TECHNIQUES

A variety of combustion control techniques are used to reduce NO\textsubscript{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\textsubscript{x} back to nitrogen and oxygen.

3.1.1. LOW-EXCESS AIR FIRING

In the low air-fuel excess ration firing techniques the principle is based on cutting back the amount of excess air, the lower oxygen concentration in the flame zone reduces NO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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% NOx 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-NOx BURNERS

Low-NOx 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 NOx formation. Additional air is introduced outside of the primary flame where the temperature is lower, thereby keeping the thermodynamic equilibrium NOx 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. NOx 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 NOx concentration to equilibrium in a short period of time. In this zone, NOx formed in the primary flame zone reverts back to nitrogen and oxygen [8]. Ultra low-NOx burners have been developed that incorporate mechanisms beyond simply staging air or fuel as designed in low-NOx 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 NOx 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 NOx 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 NOx to nitrogen and water. The intermediate steps involve amine (NH2) 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% NOx 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\textsubscript{x} removal is low-temperature oxidation of NO\textsubscript{x} species to highly soluble N\textsubscript{2}O\textsubscript{5}, followed by absorbing the N\textsubscript{2}O\textsubscript{5} in a wet absorption tower. An advantage of this process over other downstream treatment processes is very high NO\textsubscript{x} removal efficiency, with 99\% removal being reported for an industrial boiler [7].

All those are secondary methods for NO\textsubscript{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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