

Determination of Sulphur Dioxide by Pulsed UV-Fluorescence

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Abstract

We have investigated the cross-sensitivity of a commercially available SO₂ monitor (TEI 43 C-FG) with respect to the fluorescence of NO, CO and CO₂. Quenching of the NO and the SO₂ fluorescence by O₂ and CO₂ was also determined. The results were implemented in a set of equations and subsequently used to correct the monitor's output for possible interferences. For highly variable O₂ concentrations, quenching by molecular oxygen was controlled by dilution of the sample gas with synthetic air.

The response of an UV-fluorescence monitor to various gases is largely determined by the light spectrum used for excitation and detection. Therefore, absorption spectra of the main components were measured. Furthermore, fluorescence spectra of SO₂ and NO were obtained as a function of the excitation wavelength. Based on these data, the advantages and limitations inherent to the selection of filters are discussed and further improvements suggested.

1. Introduction

Sulphur dioxide (SO₂) is the most abundant anthropogenic sulphur compound in the troposphere, and is mainly emitted through coal and petroleum combustion, petroleum refining, and metal smelting operations. In Switzerland, SO₂ emissions were reduced by more than 75 % over the past twenty years. However, further improvements are necessary to meet international obligations and to avoid acidification of ecosystems. Therefore, continuing efforts on measurement and control of sulphur oxide emissions are needed [1].

Increasingly stringent emission limits for vehicle engines and industrial applications often require appropriate (catalytic) after-treatment systems. These systems are frequently sensitive to sulphur compounds. The precise determination of concentrations and reactions of sulphur oxides in (flue) gas treatments are therefore a novel application for sensitive SO₂ measurement techniques. This is e.g. illustrated by a study indicating oxidation and storage of sulphur oxides in a continuously regenerating trap (CRT)-system which is employed in diesel engines for the reduction of particulate matter emissions [2].

Commercial pulsed UV-fluorescence detectors offer an inexpensive and efficient way to measure SO₂, and are widely used both in ambient air and flue gases. In these instruments SO₂ is electronically excited by the radiation of an UV lamp, yielding an excited species which fluoresces in the UV.

This technique is very sensitive but other gaseous components may interfere. Quenching (e.g. by O₂ or H₂O) of the excited species can lead to an underestimation of the SO₂

concentration. Positive interference occurs by molecules which absorb radiation and fluoresce in the same region than SO₂ (e.g. NO and HC) [3]. In exhaust gases, nitric oxide (NO) is usually the main positive interferences, while oxygen is the most important quenching species if water vapour is removed by a Nafion dryer.

Materials and Methods

Interference studies

SO₂ measurements were performed with a SO₂ monitor from Thermo Environmental Instruments (TEI), Model 43 C-FG (Flue Gas) (detection limit approx. 0.02 ppm) [4]. A detailed description of the instrument is given in chapter 2.

NO, NO₂, CO and CO₂, were tested for positive interferences (fluorescence). CO₂, CO and O₂ were tested for negative interferences (quenching). The following gases were used: SO₂ in synthetic air: 19.0 ppm; SO₂ in N₂: 39.4 ppm, 9.8 ppm; NO in N₂: 10%, 890 ppm; NO₂ in N₂: 50.4 ppm; CO in N₂: 901 ppm; CO₂ in N₂: 10%; N₂ (60): 100%; synthetic air: 21% O₂ in N₂.

Gas mixtures were produced with a calibrated reference gas diluter (Panacon AG), Model 9103 0-100% and mass flow controllers (MFC), Sierra, Model PS1 0-50, 0-500 ml/min. All MFCs were calibrated with a high accuracy flowrate calibration standard (MKS Instruments), Model A-100 (Califlow) prior to their use. If mentioned in the text gas mixtures were diluted with synthetic air (21% O₂ in N₂) in a J.U.M. gas diluter, Model 108, approx. dilution ratio 1:12.

Absorption spectra

The absorption spectra of SO₂, NO and the bandpass filter (emission) were determined with a Varian UV-VIS-spectrophotometer, Model 1E. A 3 mm cell was used to measure the absorption spectra of SO₂ and NO (spectral bandwidth 0.2 nm). The transmission spectra of the excitation filter (interference filter) was measured with a Perkin Elmer UV-VIS-NIR-spectrometer, Model Lambda 900 [5].

Fluorescence spectra

Fluorescence spectra of SO₂ and NO were measured with a Perkin Elmer UV-fluorescence spectrometer, Model LS-3 in a 3 mm flow cell. Excitation and emission slits were both set to 10 nm.

SO₂ emissions of a diesel engine

To quantify the SO₂ conversion rates of a CRT system, a number of tests were performed on a engine test bench at EMPA using a Johnson Matthey CRT installed downstream of a modern heavy duty engine (displacement: 12 liter, rated power: 258 kW, 6 cylinder). The gaseous components SO₂, NO_x, NO, CO₂, CO and O₂ were continuously determined before and after the system in the diluted exhaust (dilution ratio 1:12). The effect of operating conditions on engine emissions was investigated by performing the measurements in three single modes (B100 (speed B; 100% load), C75, B25) and two steady state cycles (VERT: four stages of ISO 8178/4 C1-cycle for construction site engines, ESC: European Steady State Cycle). Every experiment was performed using a sulphur free (<1 ppm) and a low sulphur (42 ppm) fuel.

Gasfilter

A cylindrical quartz glass cell (suprasil QS) with an inner depth of 10 mm was used. The cell was filled with 30% NO in N₂.

2. Theory of Operation

Sulphur dioxide absorbs light in three primary UV regions. Out of these, the band between 190 nm and 230 nm is best suited for fluorescence measurements. Absorption of ultraviolet radiation at a frequency ν_1 by SO_2 yields an excited species SO_2^* with $h\nu_1$ being the quantum of energy absorbed by the molecules. SO_2^* can then release its excess energy by fluorescence at a different wavelength, typically between 240 - 420 nm, as given in reaction (1) with a rate constant k_f [6].



Negative bias

Two processes compete with fluorescence for the fate of the excited SO_2 intermediates: quenching (2) and photolysis (3).



Where k_q and k_p denote the rate constants for quenching and photolysis, respectively. Since k_q and k_p remain relatively constant over a wide range of temperatures the fluorescence intensity only depends on the concentration of the quenching compound M.

Quenching can be accounted for by calibrating with a standard that contains the same concentration of M as the sample. This is typically the case for measurements at ambient oxygen concentrations. If M is strongly variable, then stabilising its concentration by dilution with a gas containing high amounts of M is another option. This approach might e.g. be used by diluting the exhaust with synthetic air.

Positive bias

The SO_2 monitor will measure as SO_2 any species which absorbs at about 190 - 230 nm and fluoresces at 340 - 410 nm. Prior investigations of the fluorescence method point to positive interferences from nitric oxide (NO), carbon disulfid (CS_2) and ethylene (C_2H_2) [3, 6]. From these compounds in most exhaust gases only NO is present at significant concentrations. Figure 1 shows the absorption spectrum of SO_2 and NO in the region 190 – 260 nm. Both gases are showing several bands which belong to different vibronic states of the molecules [7]. Because the bands of nitric oxide are separated by several nm it should be possible to excite single vibronic states of sulphur dioxide without absorption (interference) of nitric oxide. If both gases are excited they fluoresce in a broad overlapping band continuum (Fig. 2). With a high resolution spectrophotometer about 250 lines can be resolved from the fluorescence spectrum of SO_2 [8], however, since the SO_2 monitor transmits a broad wavelength region sulphur dioxide fluorescence cannot be determined without interferences from nitric oxide. The ratio of SO_2 to NO fluorescence (Fig. 2) at least can help to find a wavelength region (emission) with a lower NO interference.

There are two main options to overcome positive interferences caused by fluorescence. Often it is possible to measure the concentration of the interfering compound in the exhaust gas and calculate its fluorescence out of this (chapter 3). Alternatively, the excitation or the emission filter of the SO₂ monitor might be modified to lower the excitation of the interfering compound or to preferentially filter its fluorescence radiation (chapter 4).

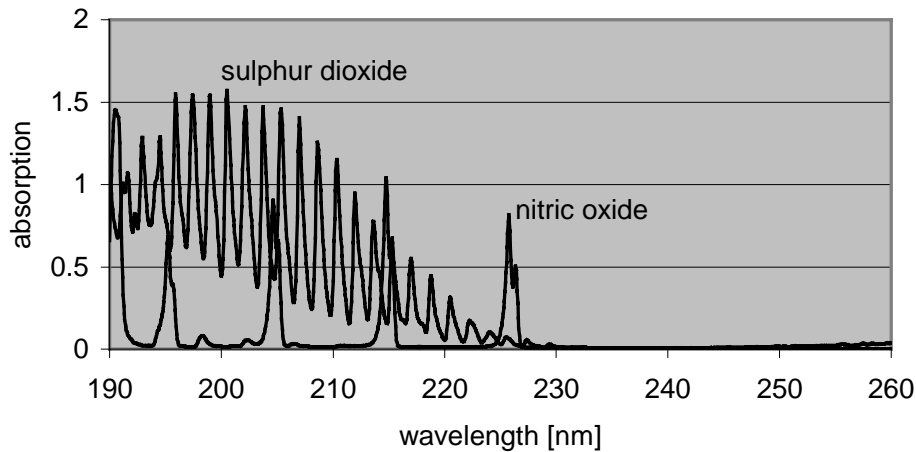


Figure 1: Absorption spectra of SO₂ (5% in N₂) and NO (30% in N₂) (spectral bandwidth 0.2 nm)

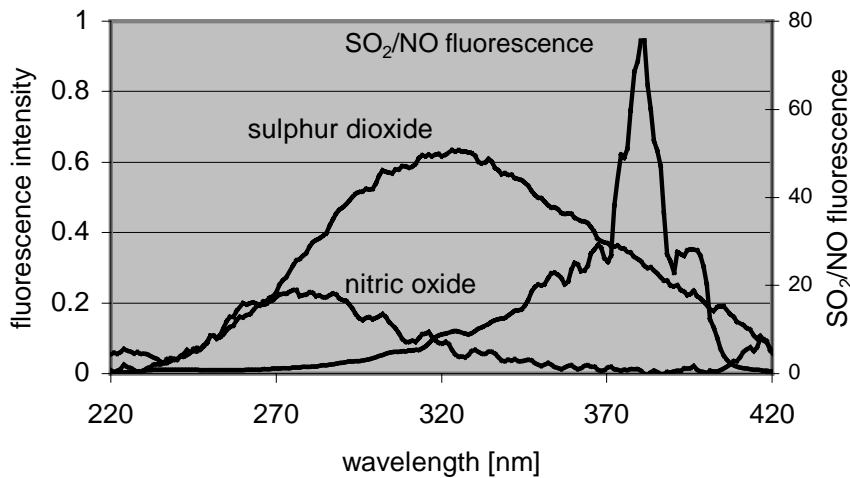


Figure 2: Fluorescence spectra of SO₂ (1.1% in N₂) and NO (0.9% in N₂) (excitation and emission slits 10 nm) (excitation wavelength 215 nm) and the ratio of SO₂ to NO fluorescence

Commercial monitor

The general set-up of the SO₂ monitor (TEI, Model 43 C-Flue Gas) [4] is shown in Figure 3. The gas flows through a "Kicker" which removes hydrocarbons from the gas stream through a selective permeation membrane. The excitation light is produced at 10 Hz by a pulsed xenon flash lamp and filtered by a set of four interference mirrors (excitation filter) which transmit light between 195 - 235 nm (Fig. 4).

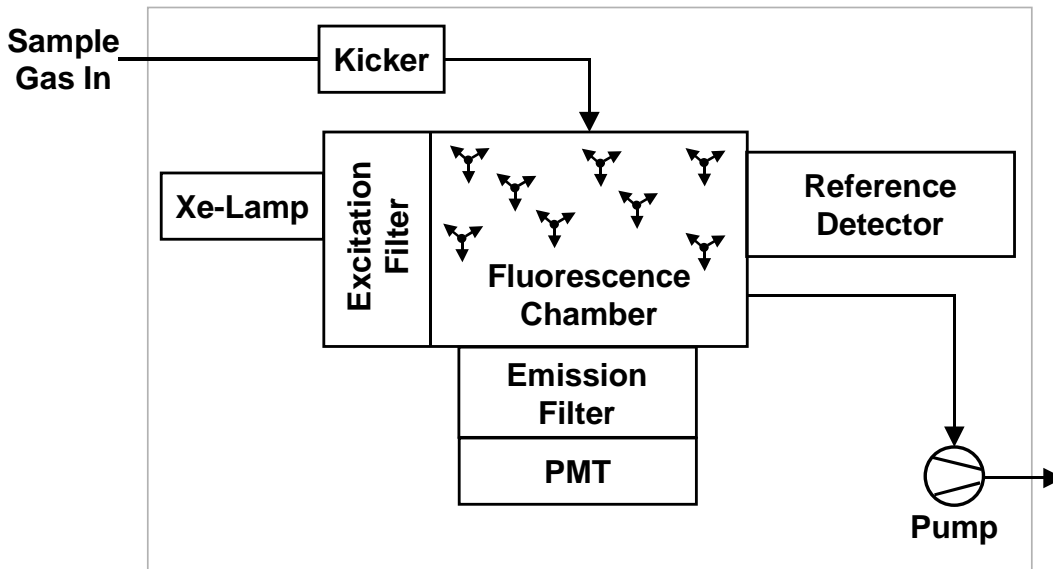


Figure 3: Schematic representation of the SO₂ monitor 43 C-FG (PMT: photomultiplier tube)

The emission filter is a combination of two bandpass filters (Fig. 5). It selects light between 340 and 410 nm before the emitted radiation reaches an orthogonally oriented photomultiplier tube. A photodetector monitors the light from the lamp. Its signal is compared to a reference signal and used to control the lamp intensity.

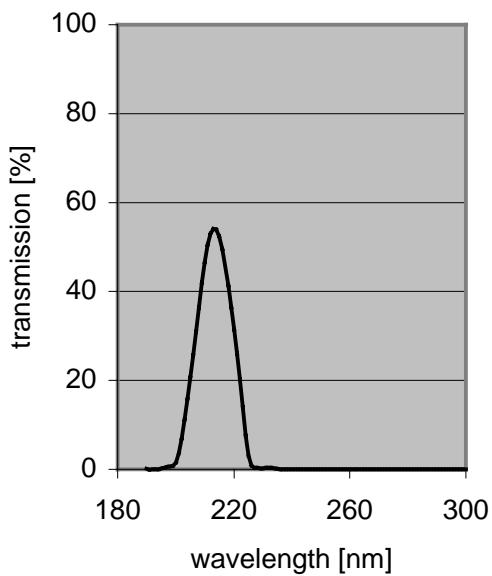


Figure 4: Transmission spectrum of the interference mirrors (excitation filter)

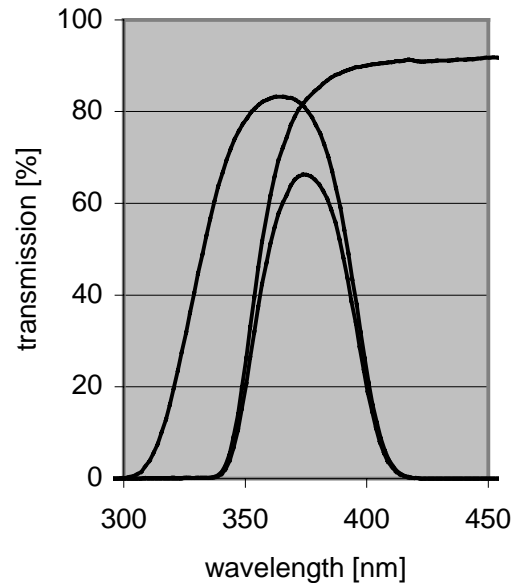


Figure 5: Transmission spectrum of the two bandpass filters and the resulting emission filter

3. Numerical corrections

To determine the SO₂ concentration in complex gas mixtures e.g. in the exhaust of a heavy duty engine, small concentrations of sulphur dioxide have to be determined in the presence of large concentrations of CO₂, O₂, H₂O, NO_x, CO, various hydrocarbons et cetera. Consequently the positive and negative interferences of these gases on the SO₂ fluorescence measurement have to be taken into account.

Therefore we investigated the cross-sensitivities of the SO₂ monitor (TEI 43 C-FG) with respect to the fluorescence of NO, NO₂, CO and CO₂ and the quenching of the SO₂ fluorescence by O₂, CO₂ and CO. Water vapour and the hydrocarbons were not taken into considerations since they can be removed from the exhaust gas with a Nafion dryer or a hydrocarbon kicker, respectively. For these experiments gas concentrations as expected in the exhaust of a diesel engine were chosen (Table 1).

	concentration	
	raw gas	diluted gas
O ₂	5-15%	19.5-20.5%
CO ₂	0-10%	0-0.8%
CO	0-600 ppm	0-50 ppm
NO	0-1000 ppm	0-80 ppm
NO ₂	0-300 ppm	0-25 ppm

Table 1: Gas concentrations used for the study of interferences (dilution ratio 1:12 with synthetic air)

Set-up

The excited SO₂ and NO molecules are quenched by oxygen, which leads to a decrease in fluorescence intensity (Fig. 7). Whereas this effect is strong for nitric oxide, oxygen quenching of sulphur dioxide fluorescence is smaller. To lower the NO fluorescence all measurements were executed at elevated oxygen concentrations in the diluted exhaust (Fig. 6). As a result the rejection ratio of NO, i. e. the number of NO molecules with the same fluorescence as one SO₂ molecule, can be increased from 5 (0% O₂) to 280 (19% O₂).

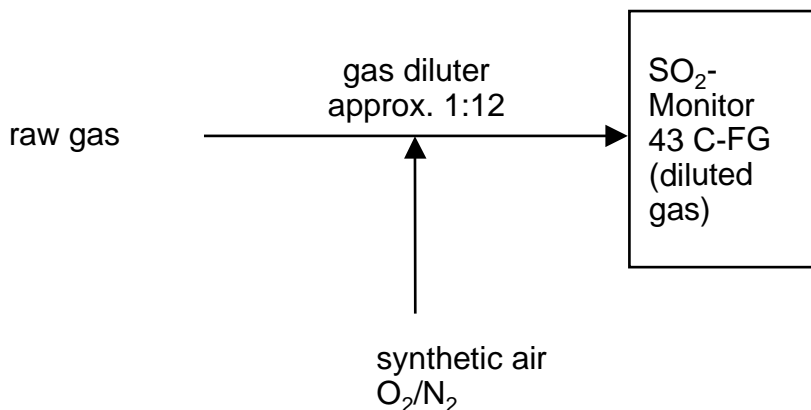


Figure 6: Set-up used for the interference studies and the SO₂ determination in an exhaust gas

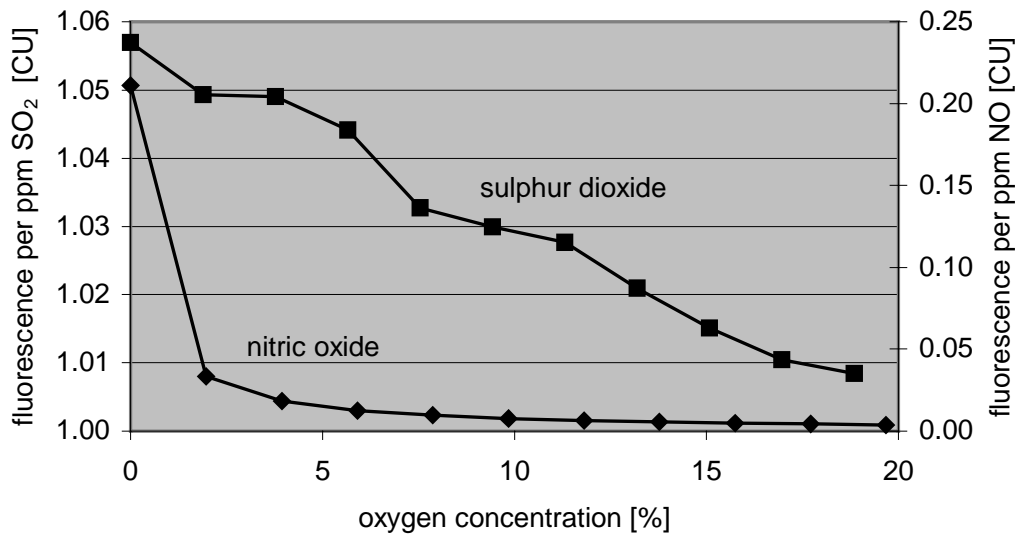


Figure 7: Quenching of sulphur dioxide and the nitric oxide fluorescence at different oxygen concentrations (CU: calibration units; i. e. relative to a SO₂ standard with an oxygen content of 21 %)

Negative bias

The negative bias of carbon monoxide (CO), carbon dioxide (CO₂) and oxygen (O₂) on SO₂ fluorescence was determined. The concentrations of CO, CO₂ and O₂ were varied within the concentrations expected for the diluted exhaust of a diesel engine (Tab. 1). By diluting the raw gas with synthetic air the oxygen concentration was stabilised (oxygen content in the diluted gas: 19.5-20.5% O₂). Therefore oxygen quenching was nearly constant and can be taken into account by calibrating the SO₂ monitor with a SO₂ standard in synthetic air. Quenching of the SO₂ fluorescence by CO and CO₂ in the diluted gas was less than 1%.

Positive bias

The flue gas components nitric oxide (NO), nitrogen dioxide (NO₂), carbon monoxide (CO) and carbon dioxide (CO₂) were tested for positive interferences.

In the concentration range examined (Tab. 1) fluorescence of NO (rejection ratio 280 at 19% O₂) and a weak NO₂ fluorescence (rejection ratio 3600 at 6% O₂) were detected. The SO₂ fluorescence can be determined from the total fluorescence measured with the SO₂ monitor by subtracting the NO fluorescence. The NO fluorescence can be calculated from the NO fluorescence coefficient $K(NO)^*$ and the NO concentration $c(NO)$ (4).

$$F(SO_2) = F_{tot} - K(NO)^* * c(NO) \quad (4)$$

$F(SO_2)$: SO₂ fluorescence

F_{tot} : total fluorescence

$K(NO)^*$: NO fluorescence coefficient

$c(NO)$: NO concentration in the exhaust gas

Additionally quenching of the NO fluorescence by O₂, CO₂ and CO was examined. NO fluorescence is quenched in the presence of O₂ and CO₂ (Fig. 8+9). Therefore the NO fluorescence coefficient $K(NO)^*$ has to be calculated from the NO fluorescence coefficient

$K(NO)$ (in the absence of O_2 and CO_2) and the oxygen and carbon dioxide quenching. If the oxygen and carbon dioxide concentrations vary in a small concentration range O_2 and CO_2 quenching of the NO fluorescence can be described as linearly depending on O_2 and CO_2 concentration (Fig. 8+9) (5).

$$K(NO)^* = K(NO) - q_{NO/O_2} * c(O_2) - q_{NO/CO_2} * c(CO_2) \quad (5)$$

$K(NO)^*$: NO fluorescence coefficient

$K(NO)$: NO fluorescence coefficient in absence of O_2 and CO_2

q_{NO/O_2} , q_{NO/CO_2} : coefficient for the O_2 , CO_2 quenching of the NO fluorescence

$c(O_2)$, $c(CO_2)$: O_2 and CO_2 concentration in the exhaust gas

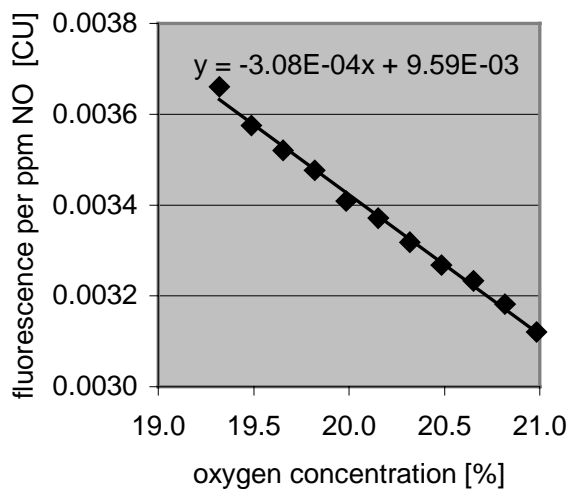


Figure 8: Quenching of nitric oxide fluorescence at different oxygen concentrations (CU: calibration units) ($K(NO)=9.59E-3$; $q_{NO/O_2}=-3.08E-4$)

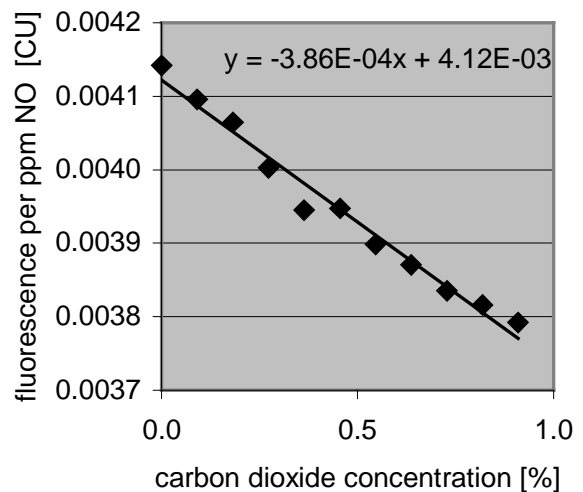


Figure 9: Quenching of nitric oxide fluorescence at different CO_2 concentrations (O_2 18%) (CU: calibration units) ($q_{NO/CO_2}=-3.86E-4$)

Limitations

- The NO interferences may change due to ageing of the Xe-flash lamp. Therefore the NO fluorescence coefficient $K(NO)$ and the coefficient for the O_2 and CO_2 quenching of the NO fluorescence q_{NO/O_2} and q_{NO/CO_2} have to be determined before each SO_2 measurement.
- Because NO fluorescence is quenched by O_2 and CO_2 all three gases have to be determined to correct the SO_2 fluorescence.

Example

SO₂ emissions of a diesel engine equipped with a CRT system

The developed numerical corrections were used to determine the SO₂ concentration in the exhaust of a diesel engine equipped with a continuously regenerating trap system (CRT). The CRT is comprised of an oxidation catalyst upstream of a particulate filter. The catalyst oxidises a proportion of NO in the exhaust stream to form NO₂, which is utilised to combust the soot trapped in the particulate filter [9]. SO₂ may be oxidised in a side reaction leading to sulphate, which can make a significant contribution to the particulate matter emission.

Numerical corrections

SO₂, NO, CO₂ and O₂ were continuously measured in the diluted exhaust (dilution ratio 1:12). NO, CO₂ and O₂ concentrations were used to calculate the NO fluorescence. The NO fluorescence was subtracted from the total fluorescence to calculate the SO₂ concentrations. The NO fluorescence coefficient and the coefficient for the O₂ and CO₂ quenching of the NO fluorescence were determined in the laboratory before.

Results

In front of the CRT-system SO₂ concentrations were mostly below the detection limit of 0.3 ppm using sulphur free fuel, but could easily be quantified when the engine operated on fuel with a higher sulphur content. The sulphur dioxide concentration was in good agreement with the values calculated from the sulphur content of the fuel. After the CRT-system the SO₂ concentration was generally low. This was probably due to the oxidation of sulphur dioxide to sulphuric acid on the oxidation catalyst.

Surprisingly, SO₂ concentrations were significantly higher downstream than upstream of the CRT system during the high temperature modes of one steady state cycle (VERT cycle). This indicates that SO₂ is accumulated on the particulate filter – possibly as sulphuric acid or sulphate - at moderate temperatures (420-430°C) and liberated as SO₂ at elevated temperatures (620-630°C) (Fig. 10) [2].

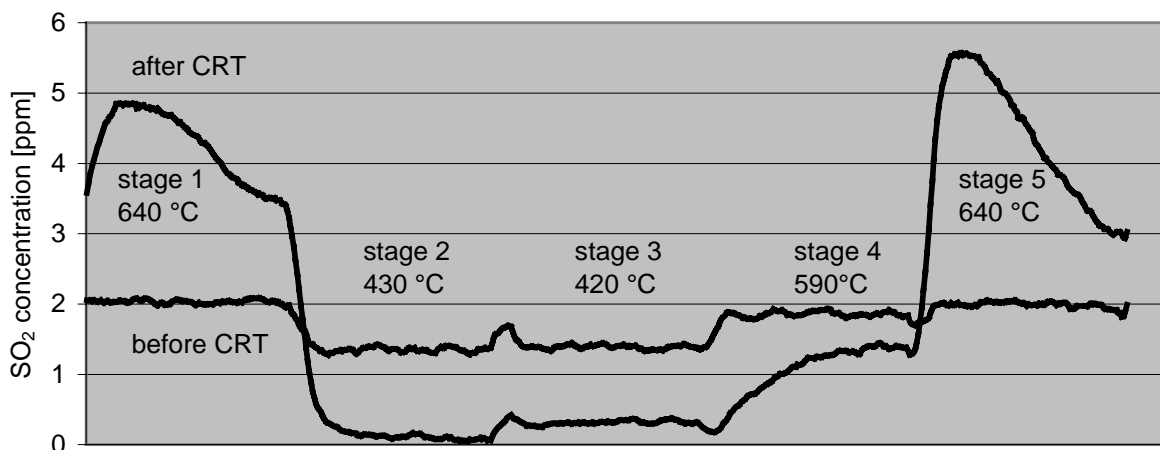


Figure 10: SO₂ concentration before and after the CRT system during the VERT cycle

4. Physical Modifications

Due to the limitations of the numerical correction mentioned it would be desirable to increase the selectivity of the SO₂ monitor. In general there are two possibilities by either improving the excitation or the emission filter. By changing the excitation filter of the SO₂ monitor it should be possible to lower the excitation of nitric oxide. By modifying the emission filter NO fluorescence emitted should be preferentially filtered.

Improvement of the excitation filter

The excitation filter of the SO₂ monitor 43 C-FG transmits light between 195 - 235 nm (Fig. 4). Both sulphur dioxide and nitric oxide absorb in this wavelength region and fluoresce in an overlapping band continuum (Fig. 1+2). Therefore it would be necessary to selectively excite single vibronic states of SO₂ without absorption (interference) of NO.

We constructed a gasfilter which was filled with nitric oxide (30% NO in N₂) and placed between the Xe flash lamp and the excitation filter. This filter selectively absorbed the radiation exciting the nitric oxide molecules. In laboratory experiments with this gasfilter it was possible to increase the rejection ratio of nitric oxide by a factor of ten. By this it is possible to measure low sulphur dioxide concentrations in the presence of high nitric oxide concentrations without a numerical correction.

5. Conclusions

UV-fluorescence is a very sensitive method to determine SO₂ concentrations in various gases and is widely used both in ambient air and flue gases. In the diluted flue gas of a waste incinerator, for example, sulphur dioxide concentrations can be determined with a sufficient precision to judge the observance of the emission limits. However, if small concentrations of sulphur dioxide have to be determined in complex gas mixtures the positive and negative interferences of these gases on the SO₂ fluorescence measurement have to be taken into account.

We have investigated the cross-sensitivity of a commercially available SO₂ monitor (TEI 43 C-FG) with respect to the fluorescence of NO, NO₂, CO and CO₂ and quenching of the NO and the SO₂ fluorescence by O₂ and CO₂. Oxygen was found to be the most important quenching species for SO₂ fluorescence. However, quenching of sulphur dioxide fluorescence can be overcome by diluting the raw gas and calibrating the SO₂ monitor with a SO₂ standard in synthetic air. Nitric oxide poses the most serious positive interference. NO fluorescence can be corrected by measuring the NO concentration and calculating the NO fluorescence. Since oxygen and carbon dioxide were found to quench the NO fluorescence their effect was also taken into considerations. By this approach it was possible to measure low concentrations of SO₂ (detection limit 0.3 ppm) at highly variable O₂ (4-19 Vol-%) and NO (30-1200 ppm) concentrations. The numerical corrections developed were applied in a project studying oxidation and storage processes of sulphur oxides in a continuously regenerating trap (CRT)-system.

Laboratory experiments to improve the excitation filter of the SO₂ monitor are promising. By installing a gasfilter in front of the excitation filter the rejection ratio of NO could be increased by a factor of 10. However, further experiments are needed in this respect.

6. Literature

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