

Continuous monitoring of the performance of a NO_x reduction system using electrochemical sensors

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Abstract

The efficiency of a NO_x removal system is continuously measured using a TÜV-approved analyser coupled to a high-temperature sampling system. Both NO and NO₂ are measured directly using electrochemical sensors without the need to convert NO₂ to NO. It is important to measure both components separately since the ratio of NO to NO₂ in stack gas is much smaller after NO_x removal. The sampling system has been designed to give fast response and to minimise the possibility of sample loss. Identical analysers are installed both before and after the NO_x removal system so as to reduce the likelihood of systematic errors.

Introduction

Stringent emissions legislation throughout the world requires operators of many combustion processes to monitor continuously the concentrations of a range of stack gases. Among the most important of these are NO and NO₂ (collectively NO_x). The very low levels of NO_x emissions now required cannot always be achieved by the use of low-NO_x combustion methods alone and so some form of scrubbing must be used to reduce NO_x levels. Selective catalytic reduction (SCR) is widely used in Europe and is gaining increasing acceptance in the USA. This method uses ammonia injection in the presence of a suitable catalyst to convert the NO_x to N₂ and H₂O. Depending on the application and the amount of ammonia slip that can be tolerated, NO_x reductions between 80% and 90% can be achieved (1).

A number of methods are available for measuring NO and NO₂, the most common being the chemiluminescent NO detector (2) which can be coupled to a thermochemical NO_x converter to give a total NO_x measurement. The typical efficiency of the NO₂ to NO conversion process is 90 to 95% when the converter is new, declining to 80% or less as the converter ages. The resulting error in total NO_x is small where the NO/NO₂ ratio is large, as in a traditional combustion application without deNO_x. However where the ratio is close to unity, as is the case after an SCR process, the error becomes unacceptably large and concern has been expressed (3) that NO_x converters cannot meet the accuracy requirements for low-level NO_x measurement.

For this reason, it is preferable to use a method which measures both NO and NO₂ directly. Optical methods using ultraviolet spectroscopy (4) have proved successful but are rather expensive. In-situ infrared measurements of NO and NO₂ are made difficult by the strong interference from water vapour at the principal absorption wavelength (5) whilst extractive IR measurements can suffer from baseline drift.

Continuous Electrochemical Analysis

Electrochemical cells are compact devices offering high reliability and good specificity. They are produced in large quantities and have been well-proven in a range of applications. Their principal limitation when used for continuous emissions measurement is that their responsivity starts to decline after a few hours exposure to typical concentrations of stack gas. This can be overcome by using a pair of electrochemical sensors for each species to be measured. One sensor in each pair is used to measure stack gas for a period, typically 30 minutes, after which it is purged with clean air to allow it to recover while the second sensor is exposed to stack gas. This recovery period ensures the cells remain stable over an extended timescale while at the same time allowing continuous measurement of gas concentration. This principle has been employed in a commercially-available instrument (6) which has proven successful with several hundred installations over a five-year period.

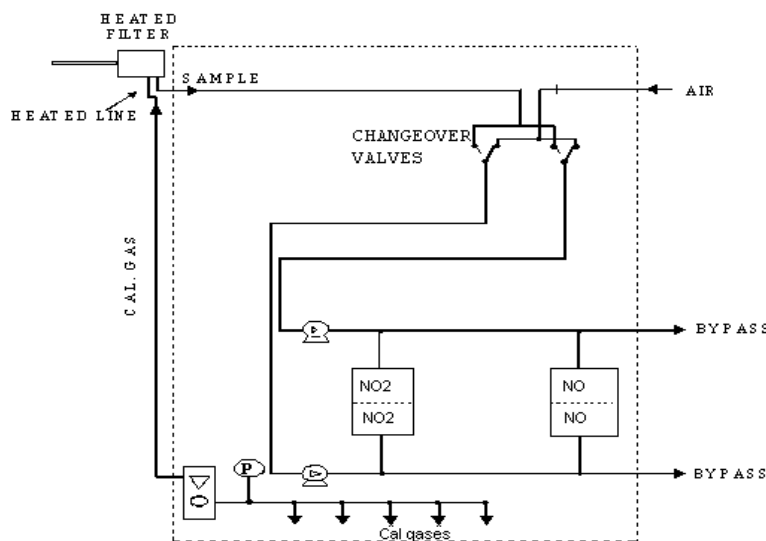


Figure 1 Schematic of FGA analyser

Automatic live-gas calibration through the sampling system is required for legislative compliance measurements in many areas and this can readily be incorporated into the instrument design.

Performance characteristics

Independent tests by the TÜV Rheinland (7) have shown that an instrument based on dual electrochemical cells can meet the stringent German standards for continuous emissions monitoring in both power generation (8) and incineration (9).

Measurement of NO was tested for accuracy and linearity over a specified range of 0-200mg.m⁻³ and for temperature stability over the range -20 to +50°C. Results are shown in Figures 2 and 3. Linearity was better than ±1% of the specified range whilst span drift with temperature was within ±3%; both values are easily within the specification limits. The zero point was stable to within 0.1% over the full temperature range.

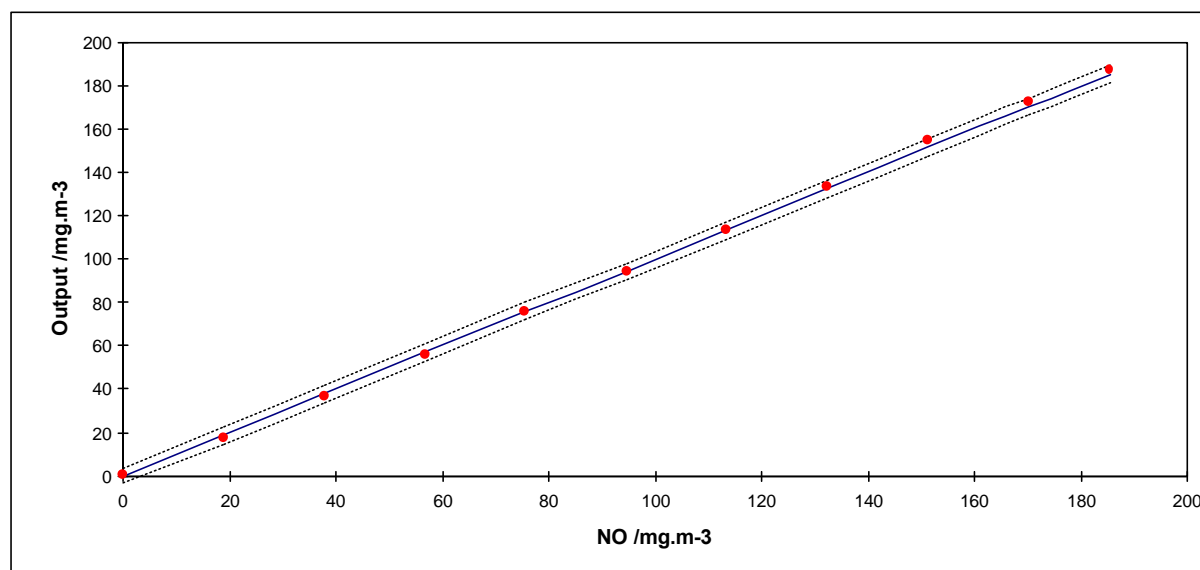


Figure 2 Linearity results for NO; permissible error limits are shown as broken lines

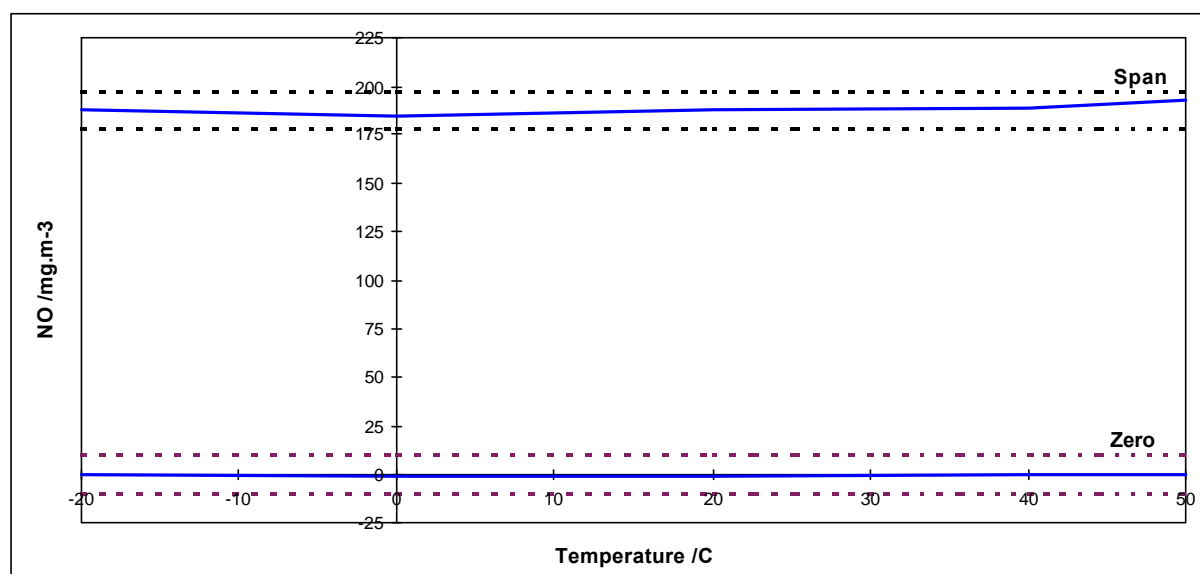


Figure 3 Temperature coefficient for NO; permissible error limits are shown as broken lines

Cross-interference was tested using a mixture of typical stack gases. The sum of all positive interferences was required to be less than +4% of the specified range and the sum of all negative interferences was required to be less than -4%. The results are shown in Table 1; the worst case error was less than 2%.

Species	Concentration	Zero shift	Span shift
CO ₂	15%	0	+1.3
CO	300 mg.m ⁻³	0	+0.6
SO ₂	1000 mg.m ⁻³	+0.8	0
NO ₂	30 mg.m ⁻³	0	0
NH ₃	20 mg.m ⁻³	0	0
N ₂ O	20 mg.m ⁻³	0	0
HCl	50 mg.m ⁻³	0	0
H ₂ O	30 %	0	0
CH ₄	50 mg.m ⁻³	0	0
Sum of +ve interferences		+0.8	+1.9
Sum of -ve interferences		0	0

Table 1 Cross-interference results for NO; all values are given as a percentage of the applicable measurement range of 200mg.m⁻³. Values less than ±0.5% are ignored

Approval has also been granted for measurements of CO and O₂ using the dual electrochemical sensor technique and it is expected that approval for NO₂ and SO₂ will be sought within the next 12 months.

Sampling System Design

In order to optimise the performance of an SCR system, NO and NO₂ concentrations must be measured both before and after the scrubber. A single analyser employing a sample switching system offers some advantages: as well as reducing the overall cost, such an arrangement can be more stable since any calibration drift will apply to measurements both before and after the SCR. However, the sequential nature of the switching means that this method cannot be applied where closed-loop control of the SCR process is required and so it is generally preferable to use separate analysers.

In order to minimise response time, the sample transport tubes must be kept as short as possible. In consequence, the analyser is generally installed close to the SCR and must therefore be sufficiently rugged to withstand this aggressive environment. It is also important to choose the sample point or points carefully so as to ensure a representative sample is taken. The SCR causes a large change in the flow patterns in the duct and, wherever possible, a survey should be undertaken with measurements made under a range of plant load conditions.

Sampling stack gases containing both SO_2 and NH_3 is complicated by the reaction between these species to form NH_4HSO_4 , a sticky, corrosive material. The reaction is favoured by temperatures below 250°C and so the sample probes and filters must be heated above this temperature.

High pressure blowback is used to remove deposits of fly ash and other solid material from the probe and filter. It is especially important in this application to use heated blowback air to avoid chilling the probe and filter since this will rapidly cause them to become blocked with NH_4HSO_4 .

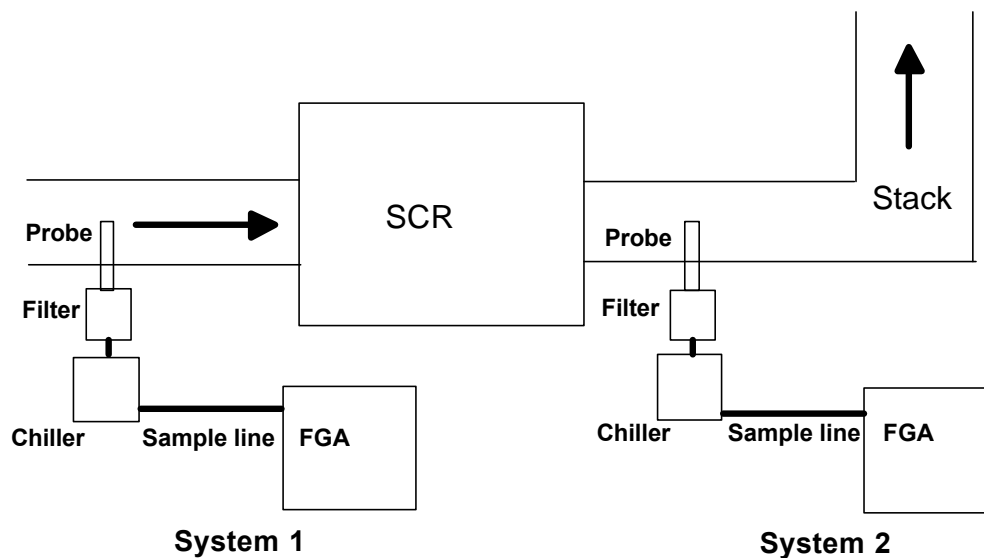


Figure 3 Sampling system design

Site Experience

A pair of FGA analysers has been installed at a site in the USA to monitor the performance of an SCR system. In order to ensure a representative sample of stack gas, each analyser draws a sample averaged across four points in the duct. The sample paths for the two analysers are identical so as to minimise the effects of phenomena such as time skew which could occur if one path were significantly longer than the other. The probe is heated to 280°C to minimise formation of NH_4HSO_4 . The sample is then cooled rapidly to remove water vapour; any NH_4HSO_4 formed at this stage is carried away with the condensate. Subsequent sample handling is at ambient temperature, with trace heating of the sample lines to prevent freezing of the residual water vapour at very low temperatures. A sample line length of 3m was chosen to minimise transport time from the probe to the analyser.

Initial results demonstrate that this technique is both a practical and an economically attractive method for measuring the efficiency of an SCR system.

Conclusions

The performance of a NO_x removal system employing selective catalytic reduction can be measured effectively and economically using an analyser employing dual electrochemical sensors. Key design features are the ability to measure both NO and NO₂ directly without the use of a NO_x converter, high-temperature sampling system to minimise formation of ammonium bisulphate and rapid response since the analyser is mounted close to the SCR. The Land FGA system has been widely used in stack gas analysis and, interfaced to a suitable sampling system, has shown that it is well-suited to this application. The analyser has been approved by TÜV for continuous emission measurements from both power plants and incinerators.

Biography

Derek Stuart is the senior research scientist at Land Combustion, and specialises in the design and development of instrumentation for stack gas analysis, using both optical and electrochemical techniques. He graduated in Physics from Edinburgh University in 1984 after which he spent six years working at the National Physical Laboratory on the development of methods for detecting trace gases in the atmosphere using tuneable diode laser spectroscopy and other high resolution techniques.

References

- 1 JE Cichanowicz, "What you should know before specifying SCR", *Power* 143(3), pp77-82 (1999)
- 2 Model AC21, Environnement SA, Poissy, France
- 3 CRTD 52: "Low NO_x measurement: Gas Turbine Plants; Final Report on Review of Current Measuring and Monitoring Practices", ASME, Washington DC, USA (January 1999)
- 4 D Stuart "Ammonia monitoring for advanced deNO_x applications", *CEM* 98, Teddington, UK
- 5 PL Hanst & ST Hanst "Gas measurement in the fundamental infrared region" pp335 - 470 in "Air Monitoring by Spectroscopic techniques" (MW Sigrist, ed) Wiley, New York 1994
- 6 Model FGA 950E, Land Combustion, Dronfield S18 1DJ, UK
- 7 TÜV Rheinland, report 936/808003/A, Cologne (August 1998)
- 8 TA Luft: BImSchV 13
- 9 TA Luft: BImSchV 17