PROCAL

Ammonia Monitoring

C B Daw - Managing Director Procal Analytics Ltd

www.procal.com

US EPA
40 CFR
Part 60&75
Compliant

sira
Certification Services
ISO 9001:2000

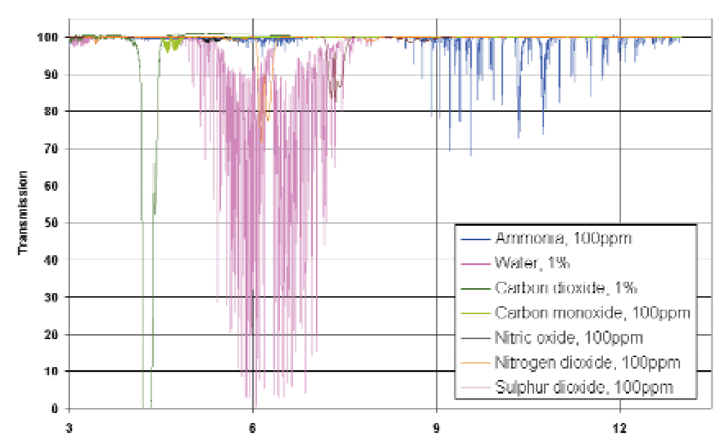
UKAS

1. Selection of Technique

1.1. Photometer

It is possible to monitor ammonia in-stack, using either infrared, or ultra-violet in-situ stack gas analysers. The cost effective method is to use a dual wavelength, single beam, multi-component analyser.

To avoid cross sensitivity from water vapour, ammonia can be measured at 10.4 microns (see Fig. 1). The absorption of ammonia at this wavelength gives a minimum range of approximately 0 - 200ppm. With this range, the analyser will meet the accuracy and repeatability required by performance standards such as MCERTS and US EPA 40 CFR, Part 60 and 75.



The drawback is that, to monitor at these wavelengths, the analysers optical system will have to use relatively expensive components, manufactured out of , for example, Zinc Selenide. This will obviously increase the cost, and if these components have to be replaced in the field, the cost of ownership.

The measurement can also be carried out using a dual wavelength, single beam, multi-component, ultra violet instrument. However, because of the relatively wide bands of absorption of the other gas species, it is very difficult to remove cross sensitivity between them.

To overcome these problems, and to make an instrument with the sensitivity to monitor low levels of ammonia from SCR plants, a more sensitive technique had to be developed.

The in-situ enveloped folded beam probe has been used very successfully for many years to monitor several combustion gas species, such as NO_X, SO_2, NH_3 and CO. These instruments have been shown to meet, relatively easily, the requirements of compliance sites. It was therefore decided to base the new instrument on the standard one metre, in-situ sample cell. As absorption in the UV is far greater for individual species than in infrared for a given path length, it was decided that a UV instrument that would overcome the drawbacks of the photometer should be developed.

2. Target Specification

Gas Species and Minimum Ranges

1.	NO	0-10ppm
2,	NO2	0-20ppm
3.	SO2	0-10ppm
4.	NH3	0-20ppm
5.	H2S	0-20ppm

Sample Temperature - Ambient to 350°C Comply with US EPA 40 CFR Part 60 & 75

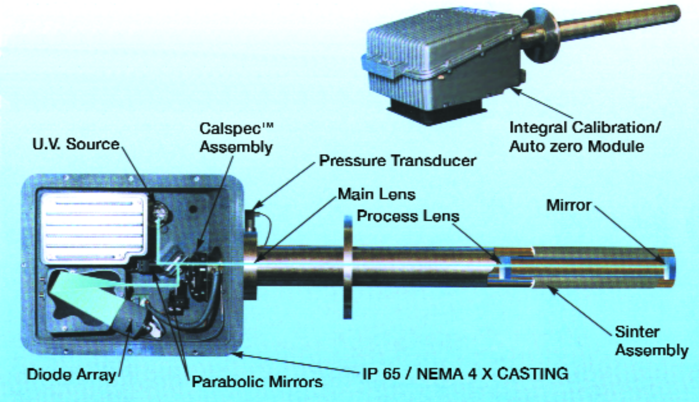
3. Development of a Suitable Analyser

One of the key criteria in designing an instrument suitable for continuous operation in a relatively hostile environment, is to design in reliability. In order to monitor low levels of pollutant gases and to remove the cross sensitivity of other gas species present, it was necessary to design a full spectrum analyser. The choice of selecting a UV array spectroscopy instrument, rather than an IR scanning technique, was that the UV full spectrum analyser is relatively simple, with the advantage that there is no need for a wavelength scanning mechanism. This was considered important in the design of a stable analyser which would be subjected to:

1. Vibration
2. Cycling of ambient temperature (mounted outdoors)
3. A high sample temperature

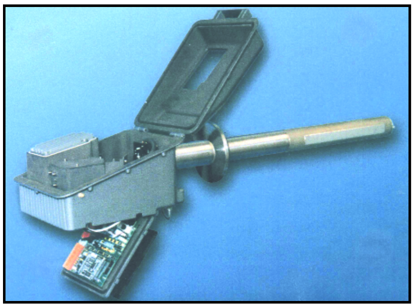
4. The Full Spectrum Analyser

The analyser is a one-piece instrument, with all the necessary components to carry out the analysis. The only part which isn't stack mounted, is the Analyser Control Unit, which can be up to one kilometre away from the analyser.



The instrument housing is manufactured from cast aluminium and rated to IP65 / NEMA 4X

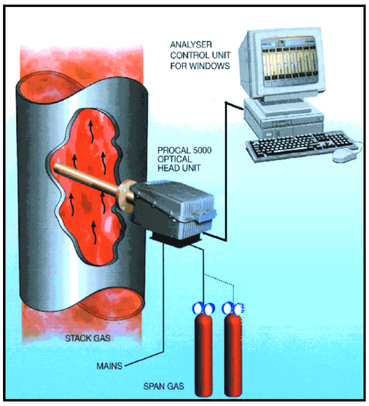
The housing consists of two separate compartments; ribbed cooling fins allow good heat dissipation and hinged covers allow easy access for maintenance.



The main upper compartment houses optical components, consisting of an ultraviolet source and a robust diode array spectrometer. The UV light, from a long life deuterium arc lamp, is collimated, and, utilising a beam splitter, the beam is directed through a main lens into the envelope folded beam stack mounted cell assembly.

The beam passes through the first portion of the assembly, which consists of a void containing air, before passing through a process lens and into the sample cell. The beam strikes a retroflector and is returned, down the same path, to the analyser housing, where it strikes the beam splitter assembly. An off-axis mirror then directs the beam to the spectrometer assembly. This consists of an entrance slit, a concave holographic grating and a diode array detector with linear multiple sensors. A narrow region of the spectrum is measured on each photodiode; the spectrum is recorded frequently and logged as a vector of intensities.

The sample cell, manufactured from 316SS, has sintered panels fitted to each side that allows flue gas to pass freely through the sample cell but excludes particulates.



The second deck of the housing contains the power supply, microprocessor, and auto zero and calibration solenoid manifold.

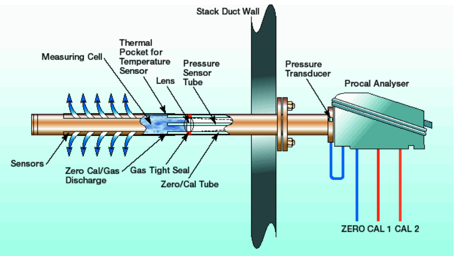
The stack mounted analyser is connected through an RS 485 interconnection to the analyser control unit or desktop PC.

5. Pressure and Temperature Compensation

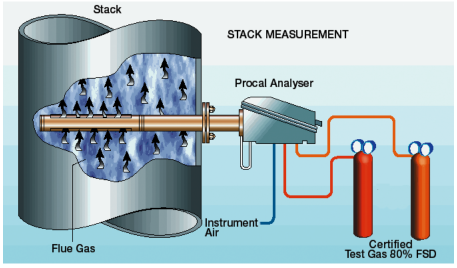
To ensure that the instrument is within ±2% accuracy, it is necessary to carry out automatic correction for changes in sample temperature and pressure. This is achieved by continually monitoring the temperature and pressure within the sample cell and compensating for any changes.

The pressure compensation deals with changes in barometric and flue gas pressure. In addition, if the certified test gas applied to the probe causes pressure increase, pressure compensation would remove the effect.

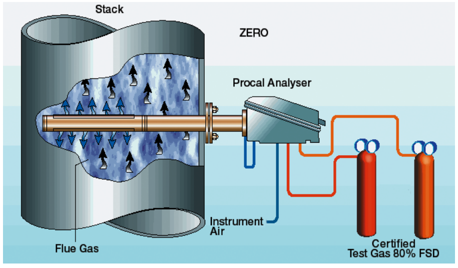
6. Automatic Zero & Calibration



To comply with various Environmental Agency requirements, in particular, US EPA 40 CFR Part 60 and 75, the instrument has to be challenged on a daily basis.



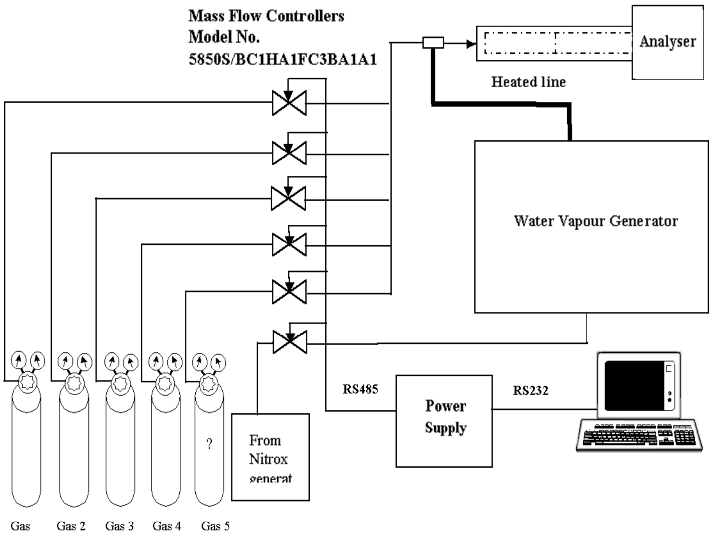
Normally, flue gas passes through the sintered panels, filling the in-situ gas cell, where the absorption of ultraviolet light takes place. Periodically, either automatically or on demand, a solenoid valve can be activated, allowing instrument air to be discharged into the in-situ cell, forcing out the flue gas and enabling the instrument to check zero and adjust as necessary.



In the same way, certified test gas, traceable to a National Standard, can be introduced into the sample cell, enabling the instrument to check, and, if necessary, adjust calibration.

7. Factory Calibration

To enable a thorough and accurate factory calibration of the full spectrum analyser, a technique had to be developed to calibrate for the individual gases, and, at the same time, remove cross sensitivity between the gases. To achieve this, a fully automatic gas mixing station was developed, which could mix the six main gas species present at the outlet of a de NOx Plant The gas mixing system, which is shown in the figure above, consists of six mass flow control devices, a series of cylinders containing calibration gas, a water vapour generator, and a heated jacket containing the sample cell of the instrument. The system is controlled by a computer, and during a normal calibration, 250 random mixtures are generated. The actual concentration of the individual gases in the mixture are obtained from flow rates measured by the mass flow controllers. The mixtures are fed in turn into the sample cell and an absorbance spectrum of each mixture is recorded by the computer.

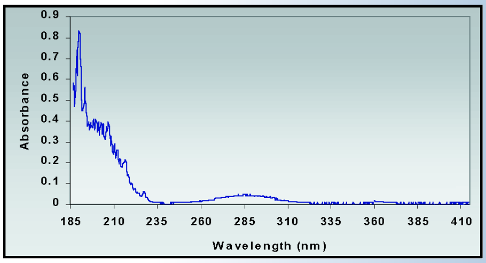


Using this data, stack gas samples can be analysed. By using chemometric mathematics, the individual concentrations of the gases can be determined. The factory calibration is good for the life of the analyser; the only consideration during normal operation is the sensitivity of each range. This can be verified by applying the certified test gas at pre-determined intervals.

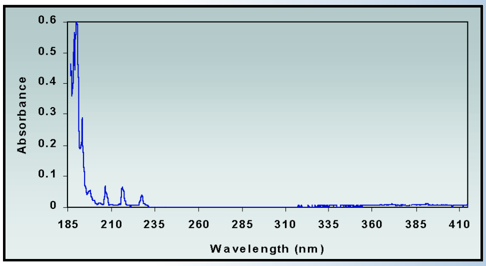
The sample temperature and pressure are also logged during the calibration and taken into account in the generation of the data set.

8. Calibration Results

Once the instrument was calibrated and verified, the following spectrum was taken from the instrument. This shows a gas mixture.

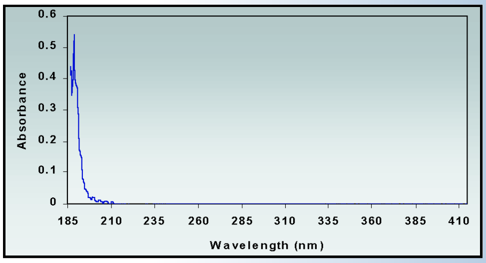


NH_3	19ppm
SO_2	545ppm
NO	553ppm
NO_2	90ppm
H_2O	9%



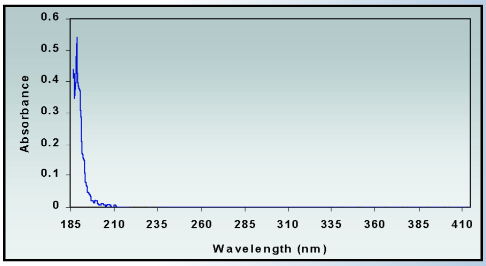
The data was analysed, and the spectra for SO_2 was retracted, giving the following concentrations.

NH_3	19ppm
NO	553ppm
NO_2	90ppm
H_2O	9%



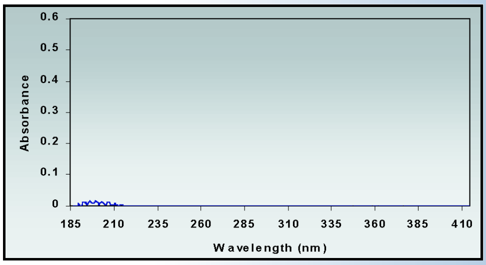
The same technique was used to remove NO, leaving the following gas mixture.

NH_3	19ppm
NO_2	90ppm
H_2O	9%

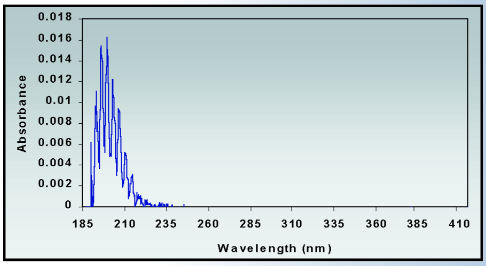


Similarly, the NO_2 was removed.

NH_3	19ppm
H_2O	9%



And finally, H_2O was removed, leaving 19ppm of NH_3



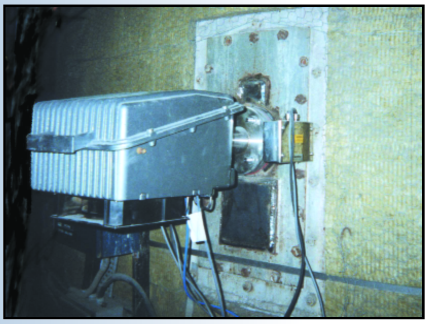
If the absorption axis is reduced, then clearly, the UV spectrum of NH_3 can be identified.

In effect, this is the way that the chemometrics mathematics is utilised to determine the concentration of the gases used. Knowing the absorption of individual gas species enables the concentrations to be calculated and displayed.

9. Field Experience

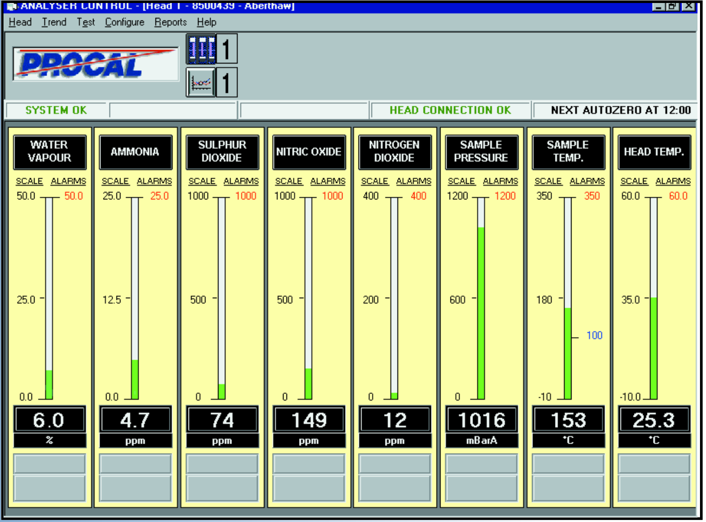
The power station used for the field trial was a coal fired power station, with an installed capacity of 1,500mw. It started operating in 1971.

The plant has three 500mw turbines, supplied by three boilers, each having an individual stack within an outer windshield. The full spectrum analyser was mounted at the 150 ft level on unit three.



The full spectrum stack gas analyser was installed in November 1999, and performs to specification.

The data from the analyser is displayed on a PC, which also data logs all the measured concentrations. In addition, the raw spectrum can be displayed.



SYSTEM OK | HEAD CONNECTION OK | NEXT AUTOZERO AT 12:00

	WATER VAPOUR	AMMONIA	SULPHUR DIOXIDE	NITRIC OXIDE	NITROGEN DIOXIDE	SAMPLE PRESSURE	SAMPLE TEMP.	HEAD TEMP.
SCALE	50.0 / 25.0 / 0.0	25.0 / 12.5 / 0.0	1000 / 500 / 0	1000 / 500 / 0	400 / 200 / 0	1200 / 600 / 0	350 / 180 / -10	60.0 / 35.0 / -10.0
ALARMS	50.0	25.0	1000	1000	400	1200	350 / 100	60.0
Value	6.0	4.7	74	149	12	1016	153	25.3
Unit	%	ppm	ppm	ppm	ppm	mBarA	°C	°C

Auto Calibration Log

Printed: 3/7/06 @ 02:00

Autocal report for OHU 1 - 8500439

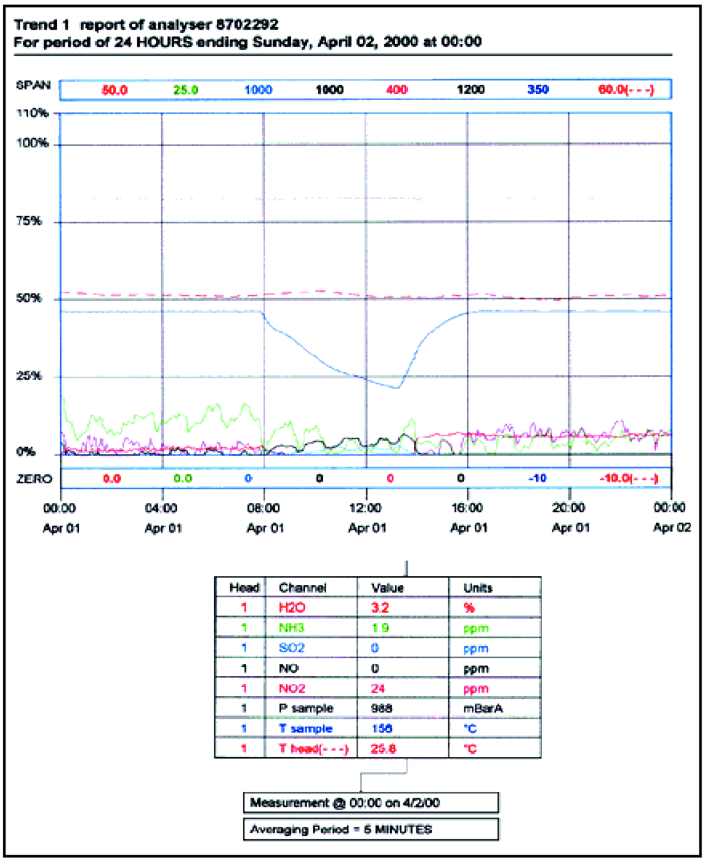
	NH3 (ppm)
Gas cyl. #	1

	3/6/06 @ 00:05	3/4/06 @ 00:05	3/2/06 @ 00:05	23/6/06 @ 00:05
Zero conc	0.0	0.5	0.6	0.0
Zero error (%)	0.0	2.1	3.3	0.0
Gas cyl. conc	24.7	24.7	24.7	24.7
Span conc	24.2	25.2	24.3	24.3
Span error (%)	-1.8	2.0	-1.6	-1.7
Status	OK	OK	OK	OK

	3/5/06 @ 00:05	3/3/06 @ 00:05	3/1/06 @ 00:05
Zero conc	0.2	0.8	0.0
Zero error (%)	0.9	3.1	0.0
Gas cyl. conc	24.7	24.7	24.7
Span conc	24.5	24.8	24.2
Span error (%)	-0.8	0.8	-2.0
Status	OK	OK	OK

The PC can also display auto zero and calibration log. The example shows seven days of calibration results.

11. Trend Display



Trend 1 report of analyser 8702292
For period of 24 HOURS ending Sunday, April 02, 2000 at 00:00

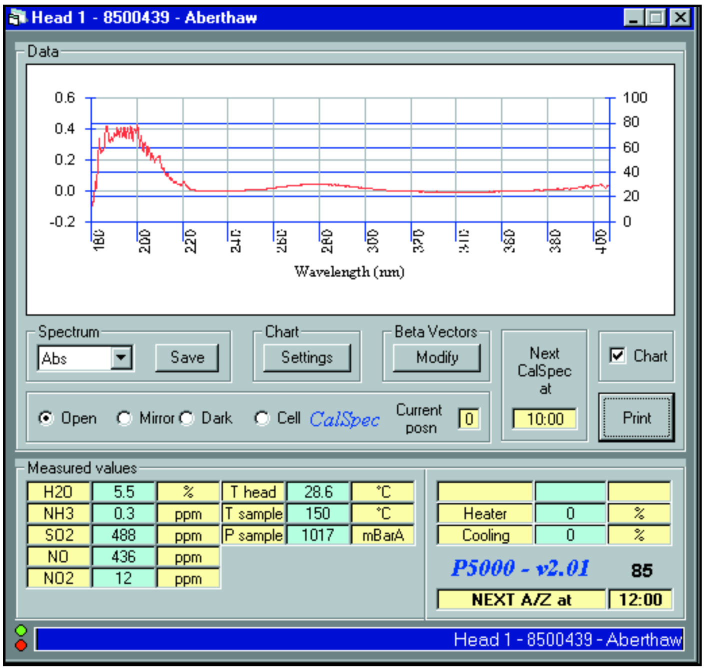
Head	Channel	Value	Units
1	H2O	3.2	%
1	NH3	1.9	ppm
1	SO2	0	ppm
1	NO	0	ppm
1	NO2	24	ppm
1	P sample	988	mBarA
1	T sample	156	°C
1	T head(- - -)	25.8	°C

Measurement @ 00:00 on 4/2/00

Averaging Period = 5 MINUTES

12. Spectrum Print

This is a very useful diagnostic tool, enabling other species of gases to be identified.



H20	5.5	%	T head	28.6	°C
NH3	0.3	ppm	T sample	150	°C
S02	488	ppm	P sample	1017	mBarA
NO	436	ppm			
NO2	12	ppm			

Heater	0	%
Cooling	0	%

It has been shown that, by using a stack mounted, high resolution spectrometer, low levels of ammonia can be measured, even with a background of relatively high levels of SO_2 and water vapour. With the use of the in-situ enveloped folded beam sample cell, it is possible to meet the performance standards laid down by Environmental Agencies for continuous emission monitoring.

The Procal 5000 full spectrum analyser has also been used in other demanding applications, such as total reduced sulphur (TRS) in the paper and pulp industry, and low level NO, NO_2 and SO_2 in the exhausts from gas turbine power stations.

References: **Hutchinson, RJ** **"Spectroscopy in Smoke Gas Stacks"**

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