PAPER AND PULP CONTINUOUS EMISSION MONITORING

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Chris Daw - Managing Director Procal Analytics Ltd
The performance and reliability of In-Situ Continuous Emission Monitoring (CEM) Analyzers have improved to such an extent that they are now a practical alternative to the traditional extractive systems. The advantages are not only associated with the lower cost of installation and ownership but also reliability and response of the monitored emissions. This is particularly true in the Paper & Pulp industry where the requirement to monitor and report emissions of Total Reduced Sulphur (TRS) has been challenging. To date the requirement has been met by extractive systems, which because of their complexity tend to require significant maintenance.

### Typical Extractive TRS CEM System

The typical system consists of a Dilution Probe mounted on the recovery boiler stack; the diluted sample is transported to an instrument shelter through a sample line. The sample which has been diluted, filtered, and in some systems had the moisture removed, passes into the TRS CEM’s system. The sample passes through a scrubber which removes the Sulfur Dioxide (SO2) then through a high temperature convertor which converts all the TRS components, Hydrogen Sulphide (H2S), Dimethyl-Disulfide (DMDS), Dimethyl-Sulfide (DMS) and Methyl Mercaptan (CH3SH) to Sulfur Dioxide. The SO2 concentration is measured using a UV Fluorescence Analyser. If required the sample can by-pass the scrubber / convertor and monitor the SO2 concentration. To demonstrate the system is in compliance, zero and span gas can be introduced through a calibration port into the dilution probe. The main drawback of this type of system is the high maintenance requirement which results in lower than acceptable availability.

### In-Situ TRS CEMs System

To overcome the problems associated with extracting the sample from the stack a system using proven In-Situ technology was developed for the Paper & Pulp industry. In addition the system overcame drawbacks associated with sample conditioning in particular sample filtration, dilution, SO2 scrubbing and conversion of the TRS gas species to SO2.

By continuously monitoring the absorbance spectrum between 180nm - 400nm it is possible to identify and display the concentrations of all the UV absorbing gas species present in the stack. This in addition to the gas species, which combined, represent TRS but also include NO, NO2, HCl and SO2. Uniquely this enables the concentration of TRS to be displayed as individual gas species (H2S, DMS, DMDS, CH3SH) or combined. This additional information can contribute to the plant control strategy. To avoid confusion the TRS concentration can be displayed speciated or as TRS.

### Compliance Requirements

To comply with US EPA 40 CFR 60.75 the analyser can automatically, adjust and report daily zero and span verifications. Three tubes enter the in-situ sample cell; the first is a thermo pocket, the second is connected to a pressure transducer mounted on the analyser flange. In any stack gas analyser, variations in both sample temperature and pressure can affect the measurement. By continuously monitoring both sample temperature and pressure these changes can be easily compensated for ensuring the accuracy of measurement required. A third tube allows instrument air (zero) and test gas (span) to be discharged into the sample cell forcing out the stack gas allowing automatic calibration verification / reporting.

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**Total Reduced Sulfur (TRS) Monitoring and other Paper & Pulp CEMs Requirements**

**Diode Array Spectroscopy**

This is a method of obtaining a full spectrum in the UV visible (VIS) and near infrared (NIR). A simple spectrometer with no continuously moving parts is used consisting of an entrance slit, concave diffraction grating and a detector consisting of linear array of sensors. The great advantage is that the wavelengths are measured in parallel therefore there is no need for a wavelength scanning mechanism. This gives the robustness required for site operation, combined with rapid response and a high signal to noise ratio.

Individual gas species although absorb in the 180 - 230 nm region have their own unique shape spectrum. The PROCAL 5000 principle of measurement is that an UV optical system sends light through an in-stack sample cell which is continuously refreshed with stack gases. The spectrum of the stack gas is measured and from this the concentration of individual gases is calculated.

**Procal 5000 Optical Unit**

A parabolic mirror collimates UV light from a long life deuterium arc lamp source and the beam is directed through a beam splitter to the end of the reflector tube assembly containing the in stack sample cell. The beam is returned by a retro reflector to the beam splitter which directs it to the second of axis mirror and then to the spectrometer housing. The spectrometer consists of an entrance slit, a concave holographic grating and a diode array detector.

Although UV gas spectra have been known for many years, UV gas analysis has only become widely used for stack gas analysis since the availability of chemometric calibration methods and suitable ways of mounting and operating reliably in industrial environments. In comparison with infrared (IR) spectra, UV spectra of gases are much more intense, therefore a more sensitive method allows lower levels of pollutants to be monitored.
The basic typical system comprises an analyser and a PC, which displays the monitored concentrations with data logging and reporting capability (MODBUS / 4-20mA) in addition the system is LAN & WAN ready. If required the system can be supplied with a modem enabling remote support from PROCAL customer service team.

A series of screens are available including panel display of all monitored concentrations, long term data logging and diagnostics.

If required an integrated system can be supplied which in addition to the pollutant gases can also monitor and report Flow, Oxygen and Opacity. The data can be used to calculate normalised pollutant concentrations to a level of Oxygen and if required, using a flow measurement, the levels of pollutant gases and dust can be reported in mass units.

Display all monitored ranges

Calibration Log Viewed and Printed

Trending of Data
To date the Procal CEM’s have been used on over 35 Paper & Pulp applications worldwide. The following examples are from compliant sites in North America.

### Dryden Pulp Mill Operated by Weyerhaeuser Paper Ltd

**Two Procal 5000**
- 0 - 30 ppm TRS
- 0 - 20 ppm H2S
- 0 - 10 ppm DMS
- 0 - 10 ppm DMDS
- 0 - 10 ppm CH3SH
- 0 - 200 PPM SO2
- 0 - 200 PPM NOX
- 0 - 25% H2O

Procal 5000 installed on a Low Odour Recovery Boiler

### Smooth Rock Falls Pulp Mill Operated by Tembec

**Procal 5000 installed on Recovery Boiler**

### Thunder Bay Mill Operated by Bowaters

**Procal 5000**
- Scrubber Control
- 0 - 100 ppm ClO2

**Bleaching Process**
The analyser is used in the bleaching process forming part of the control strategy. The application required a probe designed to resist the very aggressive process gas including a heater manufactured from Hastelloy. The analyser has been in service from February 02 the only significant or service required was to install an improved retroreflector. The output from the analyser is used to control the scrubbing process, ensuring that the vent Chlorine Dioxide (ClO2) emission is kept to a minimum.

### Other applications in the Pulp & Paper Industry

<table>
<thead>
<tr>
<th>Application</th>
<th>Analyser</th>
<th>Typical Ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiler House</td>
<td>Procal 200</td>
<td>0 - 500 ppm SO2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0 - 1000 ppm CO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0 - 250 ppm HCl</td>
</tr>
<tr>
<td>Lime Klin</td>
<td>Procal 200</td>
<td>0 - 250 ppm NOx</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0 - 50% H2O</td>
</tr>
<tr>
<td>Recovery Boiler</td>
<td>Procal 200</td>
<td>0 - 1500 ppm CO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0 - 250 ppm CH3OH</td>
</tr>
</tbody>
</table>

### Conclusion

It has been demonstrated that the In-situ analyser is a reliable, low cost of ownership technique for the continuous emission monitoring needs of the Paper & Pulp Industry, meeting the requirements of US EPA 40 CFR Parts 60 & 75.

### Other publications

**Data Sheets**
- Procal 5000 Data Sheet
- Pulsi 200 Data Sheet
- ACWn Data Sheet

**Papers**
- CEM of Sulphide gases (TRS)
- CEM - In-Situ
- CEM: A Practical Approach to TRS

**Reference Number**
- 7-3601-03 R J Hutchinson - Procal
- 7-4670-04 J Potter - Procal
- 7-3904-01 C B Daw - Procal

**Author**
- Jim Stachowich - Hydroflo

Procal reserves the right to alter these specifications without prior notification.