

## ON-LINE ANALYSIS OF COPPER FOUNDRY'S STACK GAS COMPOSITION BY LOW RESOLUTION FT-IR GAS ANALYSER

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### ABSTRACT

Stack gases of a copper foundry's after-burner were measured on-site by low resolution FT-IR gas analyser.

Concentrations of carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), methane (CH<sub>4</sub>) and water vapor (H<sub>2</sub>O) were continuously measured for a period of three days.

Validation of the method included laboratory determination of the detection limit, linearity and measuring range for each gas component. In addition, the uncertainty of the field measurement results was obtained by using the performance data in the laboratory. Applicability of the method has been demonstrated earlier in several comparative measurement campaigns against single component methods and against other measurement groups. Additionally, the method has been successfully used for emission measurements from varying emission sources.

The method was accredited on 10.12.1997 by FINAS (Finnish Accreditation Service) for sulfur dioxide (SO<sub>2</sub>) concentration measurement. The scope of accreditation was extended on 24.9.1998 to cover carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) concentration measurements.

### 1. INTRODUCTION

Multi-component gas analysers utilizing FT-IR (Fourier Transform Infrared)-spectrometry have been recognized for a long time as potential instruments to be used for monitoring emissions of combustion gases. Nowadays several FT-IR Continuous Emissions Monitors (CEMs) are in routine use measuring emission gases like HCl, NH<sub>3</sub> and HF, in addition to criteria pollutants. Both low spectral resolution and traditional high spectral resolution spectrometers are used in modern FT-IR combustion gas analysers.

In field measurement campaigns it is necessary to use rugged instrumentation which can withstand the demanding environmental conditions of industrial plants. Ambient temperature swings and factory floor vibration can severely distort an improperly designed FT-IR spectrometer and render measurement results unusable. In field campaigns, unlike in continuous applications, it is usually not feasible or even possible to install the analyser in a climate conditioned and vibration-isolated cabinet. Additionally, a field instrument has to be easy to use and set-up within a short time. Specifically, the time required for analytical method development has to be very short in order for the measurement technique to be competitive in respect to other analytical methods. It is usually preferred as well, that no liquid nitrogen is needed to cool the detector of the FT-IR spectrometer.

Due to the factors presented above, low resolution FT-IR spectrometry is a very suitable gas analysis method especially for demanding industrial applications. The advantages of low resolution FT-IR spectrometry in gas analysis have been presented in greater detail in, for example, Jaakkola *et al.*

Low resolution FT-IR spectrometry has proven its applicability in the field conditions in several comparative measurement campaigns. For example Larjava *et al.* have reported comparison

measurements performed with low resolution FT-IR gas analyser against several single component analysers.

## 2. EXPERIMENTAL

### 2.1 Analyser

A GASMET FT-IR gas analyser, manufactured by Temet Instruments, Finland, was used in the field measurements presented here. Experimental parameters included  $8\text{ cm}^{-1}$  spectral resolution,  $\text{BaF}_2$  optics, a Peltier-cooled semiconductor detector. The measured spectral range was from  $950\text{ cm}^{-1}$  to  $4200\text{ cm}^{-1}$ . The gas cell was a temperature-controlled ( $150\text{ }^\circ\text{C}$ ) multiple-reflection gas cell, with a volume of 1.1 litres. The absorption path length was 2.4 meters. The gas cell material was Teflon coated aluminum. CALCMET for Windows control and spectral analysis software was used to perform multicomponent analysis of the collected FT-IR spectra. This software utilises patented multicomponent analysis algorithm for simultaneous analysis of a maximum of 30 different components.

### 2.2 Laboratory measurements

Laboratory tests were conducted to determine experimentally the detection limits of all monitored gases. The matrix detection limits (DLs) were calculated using the following definition

$$\text{DL} = c_0 + 3\sigma,$$

where  $c_0$  is the average measured concentration at 0 ppm analyte level and  $\sigma$  is the standard deviation of the analysis results during the monitoring period.

Table 1 displays the experimental matrix detection limits of the FT-IR gas analyser. The detection limits were defined for a gas matrix that consisted of 15% water vapour and 10% carbon dioxide. The calibration ranges used in the measurements reported here are presented in Table 1. The calibration ranges were corrected for non-linearity and the largest relative deviation from the calibration curve is less than 1%.

**Table 1.** Calibration ranges of the monitored gases and FT-IR matrix detection limits.

Component	Calibration / measurement range	Matrix detection limits
Carbon dioxide	0.05 – 25 vol-%	-
Carbon monoxide	3 – 3000 ppm	5.5 ppm
Sulphur dioxide	1 – 1000 ppm	2.4 ppm
Nitric oxide	1 – 1000 ppm	8.0 ppm
Nitrogen dioxide	1 – 300 ppm	3.3 ppm*
Methane	1 – 200 ppm	2.0 ppm
Water	1 – 25 vol-%	-

\* measured from the  $2915\text{ cm}^{-1}$  band

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## 2.3 Field measurements

The sample gas transportation and conditioning for the FT-IR gas analyser consisted of a heated probe, heated sample lines and a heated pump. The temperature of all sample transport components was set at 150 °C. The probe material was 316 stainless steel and it contained a 20 micron in-duct filter. The heated pump was a Teflon membrane pump made of stainless steel. The sample line material was Teflon. The overall length of the sampling line was 15 meters from the probe to the analyser. The sample gas was not dried and the gas flow rate was 2 litres per minute.

The measuring system was calibrated using single component calibration gas both before and after the measuring session. The calibration gas was injected through the in-duct filter in the heated probe. The calibration was considered to be successful if the analysis result for each component did not deviate more than  $\pm(x^2 + 1^2)^{1/2}$  % from the certified cylinder concentration. The x stands for the relative uncertainty of the calibration gas provided by the gas supplier.

## 3. RESULTS AND DISCUSSION

### 3.1 Field measurements

The results of the three-day emission measurement period are displayed in Figures 1 and 2 for carbon dioxide, water vapour and carbon monoxide and in Figures 3 and 4 for sulphur dioxide, nitric oxide, nitrogen dioxide, nitrous oxide and methane. The summary of the results is expressed in Table 2 as period average, minimum and maximum concentrations. Measurement uncertainty is presented after the period as an average at 95% confidence level. All results are reported on wet basis.

Due to the operation of the process, concentrations vary considerably during the monitoring period. In particular carbon monoxide concentration fluctuates strongly due to the batch-like copper feed of the process. The resulting wide dynamic range is accurately covered by the FT-IR analyser. The concentrations of the other emission components were rather low but were nevertheless above the respective matrix detection limits of the analyser and thus successfully detected and quantified. From the evening of 13.5.1998 until the morning 14.5.1998, copper was not fed to the process, which can clearly be seen from the Figures 1 and 2.

**Figure 1.** Concentrations of carbon dioxide (CO<sub>2</sub>), water vapor (H<sub>2</sub>O) and carbon monoxide (CO) as a function of time during the three day emission measurement period.

**Figure 2.** Heavy fluctuation is due to the batch-like copper feed of the process. Concentrations of carbon dioxide (CO<sub>2</sub>), water vapor (H<sub>2</sub>O) and carbon monoxide (CO) as a function of time during one 8-hour period.

**Figure 3.** Concentrations of sulfur dioxide (SO<sub>2</sub>), nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>) and methane (CH<sub>4</sub>) measured as a function of time during a three day emission measurement period.

**Figure 4.** Heavy fluctuation is due to the batch-like copper feed of the process. Concentrations of sulfur dioxide (SO<sub>2</sub>), nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>) and methane (CH<sub>4</sub>) measured as a function of time during one 8-hour period.

**Table 2.** Summary of the results as period average, minimum and maximum concentrations. Measurement uncertainty included. Uncertainty is calculated for the maximum measured range of each component.

Component	Average Concentration	Min – max	Uncertainty (k=2)	Relative uncertainty (%)
Carbon dioxide	6.31 vol-%	2.5 – 8.69 vol-%	± 0.4 vol-%	± 4.6
Carbon monoxide	158 ppm	7 - 2970 ppm	± 110 ppm	± 3.7
Sulphur dioxide	14 ppm	< 1* - 35.8 ppm	± 5 ppm	± 14.0
Nitric oxide	45 ppm	< 1* - 134 ppm	± 6 ppm	± 4.5
Nitrogen dioxide	37 ppm	< 1* - 200 ppm	± 12 ppm	± 6.0
Methane	13 ppm	< 1* - 30 ppm	± 4 ppm	± 13.3
Water	6.3 vol-%	< 1* - 10.9 vol-%	± 0.7 vol-%	± 6.4

### 3. CONCLUSIONS

Low-resolution FT-IR spectrometry has shown its applicability as a powerful field emission measurement method. The method has been tested in comparative measurement campaigns world-wide against traditional single component methods and no significant differences between the results of FT-IR and other methods have been detected.

During routine emission measurement, valuable additional information on the process can be obtained by using FT-IR spectroscopy. The need to study fast process changes by continuously monitoring the process gas with FT-IR gas analyser, brings the most of the analytical power and speed of FT-IR in use. Used for this purpose, the FT-IR method is very useful to try to understand and solve problems in processes. Another important advantage of FT-IR is the possibility to save all the spectra collected on-site for post-analysis. In this way it is possible to verify any contemplated or unreliable measurement data and detect unknown components in the gas stream.