

# Feature Article

## Modification of HORIBA's ENDA-5000 Continuous Emission Monitoring System in order to fulfill requirements of European standard EN 15267-3

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HORIBA's ENDA-5000 Continuous Emission Monitoring System (CEMS) is used for continuous monitoring of NO<sub>x</sub>, SO<sub>2</sub>, CO, CO<sub>2</sub> and O<sub>2</sub> in stack gas, produced by stationary sources like power plants, boilers, gas turbines, furnaces, chemical plants, etc. Prior to the introduction of new CEMS to the European Market, the whole system must be tested and approved by the European certification agency, for example TÜV in Germany or MCERT in the U.K. There are lots of test procedures, which are applied to CEMS during the certification process in the laboratory as well as in the field under real process conditions. CEMS units must comply with the conditions that are specified in European standard EN 15267-3.<sup>[1]</sup> One of the most important items is the test for resistivity of CEMS system against disturbing or interfering chemical components.

### Introduction

The industrial combustion of coal, oil, gas, waste and other combustion materials does not provide just energy, but also generates emission, gases like NO<sub>x</sub>, SO<sub>2</sub>, CO, CO<sub>2</sub>, HCl, HF, and dust particles. These gases as well as the dust particles are subject of continuous monitoring. In present time, HORIBA provides several analyzer systems for the continuous monitoring of most important emissions gases, which are NO<sub>x</sub>, SO<sub>2</sub>, CO, CO<sub>2</sub>, and of course O<sub>2</sub> as the reference component. In this year, HORIBA brings the ENDA-5000 analyzer system for continuous monitoring of NO<sub>x</sub>, SO<sub>2</sub>, CO, CO<sub>2</sub>, and O<sub>2</sub> to the European market. The heterogeneous components NO, SO<sub>2</sub>, CO, are determined by Non Dispersive Infrared (NDIR) combined with HORIBA's Cross Flow Modulation technology, while the oxygen concentration is measured by a magneto-pneumatic analyzer. Prior to entering the European market, the entire monitoring system, consisting of sampling probe, heated sampling line, sample conditioning unit and analyzer, must be approved by European certification agency. As mentioned in the preface, there are many test procedures that have to be conducted to CEMS during the certification, in

laboratories as well in the field under real process conditions. The entire certification procedure is described by the European Standard EN15267-3 and includes tests of parameters like: response time, detection limit, standard deviation for zero and span point, linearity, zero and span drift, NO converter efficiency, influence of ambient temperature, sample flow rate and sample pressure, influence of vibration, fluctuation of voltage supply, and, probably the most important, the influence of specified disturbing and interfering components.

Combustion and various other production processes do not only generate gaseous emissions of NO, SO<sub>2</sub>, CO, CO<sub>2</sub> as mentioned above, but also other gases like N<sub>2</sub>O, HCl, NH<sub>3</sub>, CH<sub>4</sub>, and H<sub>2</sub>O, according to fuel type and technology. The presence of these gases can have a significant influence for measurement of NO/NO<sub>x</sub>, SO<sub>2</sub>, CO, CO<sub>2</sub>. This is the reason why any CEMS system is being approved by European Certification agency according to EN 15267-3 and must be resistive to the above mentioned, specified disturbing and interfering components. The infrared optical bench of the ENDA/CMA-5000 system is equipped with gas filters and compensation detectors to prevent the interferences

caused by  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Problems to overcome are not only caused by interfering components, but also by the  $\text{SO}_2$  and  $\text{NO}_2$  loss in the sample conditioning system. According to EN 15267-3 the total influence of interfering and disturbing components, including the loss of any tested component in sample conditioning system, must not exceed 4% of the measurement range. This is one major issue for all kinds of extractive analyzers and sample conditioning systems, which operate under dry (cold) conditions. In general they use electrical coolers (Peltier or compressor) to cool down the sample gas down to +5 °C dew point and remove the moisture. As  $\text{SO}_2$  is well soluble in the water, we can expect a high loss of  $\text{SO}_2$  in the electrical cooler, while cooling down wet sample gas containing up to 30 Vol.% of  $\text{H}_2\text{O}$ . As the standard configuration of the HORIBA ENDA-5000 sample conditioning system did not fulfill the requirements of EN 15267-3 at the German TÜV Certification agency, especially not the application of humid  $\text{SO}_2$  test gas containing 30 Vol. % of  $\text{H}_2\text{O}$ , HORIBA Austria has decided to modify the sample conditioning system of ENDA-5000 in order to fully comply.

## Materials and Methods

The ENDA-5000 is extractive analyzer system, measuring  $\text{NO}/\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{O}_2$  at dry condition, i.e. the very first element of sample conditioning system is electrical cooler, which has to remove the moisture from the sample gas down to +5 °C dew point. As  $\text{SO}_2$  is very well soluble in the water, we must expect high loss of  $\text{SO}_2$  in the electrical cooler, while cooling down wet sample gas, containing up to 30 Vol.% of  $\text{H}_2\text{O}$ . The assembly of the primary cooler unit, used in the sample conditioning, should minimize the contact between sample gas and condensing water as much as possible. But there is still a big loss of  $\text{SO}_2$  inside the cooler, significantly exceeding 4 % of measurement range. This is a critical issue especially in case of low concentration measurement for  $\text{SO}_2$ . The EN 15267 requires to test the  $\text{SO}_2$  analyzer operating at measuring range 0 to 75 mg/m<sup>3</sup> (= 0 to 26.2 ppm).

One solutions to prevent the loss of  $\text{SO}_2$  and  $\text{NO}_2$  in first sample gas cooler is to establish a sufficient acidulous environment inside the cooler's heat exchanger, in order to replace the water condensate with weak acid.  $\text{SO}_2$  and  $\text{NO}_2$  as well as acid gases will not be affected in acidulous environment and will pass through the cooler without loss. A suitable acid for this purpose is diluted Orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ), injected in front of the primary cooler. Hence we have developed a special, electrically heated injection system, incorporated in front of first electrical cooler. A very small amount of weak orthophosphoric acid solution is injected by a peristaltic pump

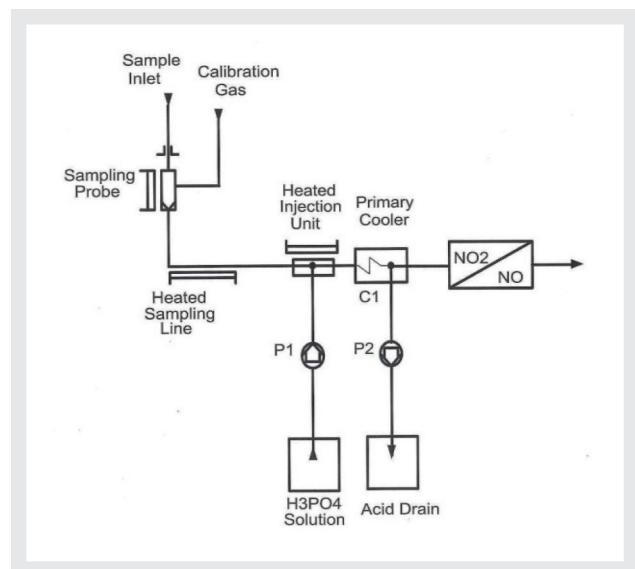


Figure 1 ENDA-5000 - front part of sample conditioning system – flow schematic with electrical cooler ECP1000-G, temperature set to +5 °C and heated  $\text{H}_3\text{PO}_4$  injection section.

(Figure 1, P1) into the sample gas stream. The essential prerequisite is to inject the acid at a high temperature, at least 80 to 90 °C. Immediately after injection, the sample gas together with ortho-phosphoric acid flows into the primary cooler. Due to sufficiently acidulous environment inside the cooler's heat exchanger, saturated with ortho-phosphoric acid, the  $\text{SO}_2$  and/or  $\text{NO}_2$  cannot be additionally dissolved or absorbed. All the ortho-phosphoric acid solution is consecutively removed as acid condensate from the bottom part of electrical cooler by peristaltic pump (Figure 1, P2).

The heated acid injection unit is connected directly behind the sample line inlet port, inside of ENDA-5000 analyzer cabinet. (Figure 2) (The outlet of acid injection unit is connected directly to the primary cooler, which is set to +5 °C. The ortho-phosphoric acid solution is injected by the peristaltic pump, delivering 0.3 L/hour. The acid drain at the bottom of cooler is removed by similar peristaltic pump with capacity of 0.6 L/hour.

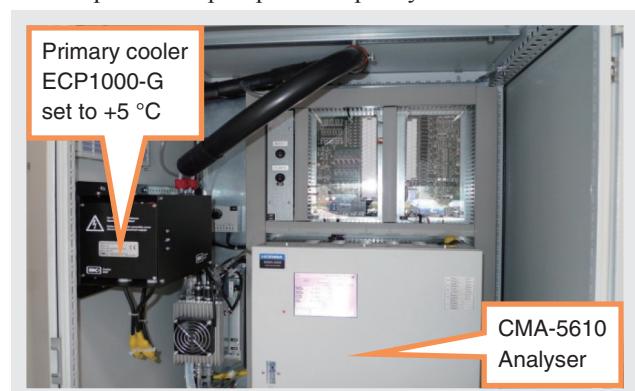


Figure 2 ENDA-5000 cabinet - upper part with electrical cooler ECP1000-G, temperature set to +5 °C and heated  $\text{H}_3\text{PO}_4$  injection section.

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Once the acid injection unit is started, the acidulous environment inside the primary cooler is created within several minutes. The measured loss of SO<sub>2</sub> is minimized to less than 1%.

If the acid injection is switched OFF, the acidulous environment remains for about 10 minutes, but then the SO<sub>2</sub> concentration will start to drop, as SO<sub>2</sub> starts to dissolve in the water condensate inside the cooler.

## Results

In Figure 3 you can see the response characteristic of the ENDA-5000 analyzer, if dry sample gas (span gas containing 25 ppm SO<sub>2</sub> in N<sub>2</sub>) is applied to ENDA-5000 Analyzer's inlet port. In this case, as sample gas is absolutely dry, the phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) is not injected. The response efficiency is very high and this can be used for ZERO and SPAN calibration for the ENDA-5000. Dry sample gas therefore meets the requirements of EN 15267-3, as ZERO and SPAN gas must flow through the entire sample conditioning system during the calibration procedure. Under real process conditions the calibration gas must always be applied to the sampling probe.

The next chart (Figure 4) shows the behavior of the ENDA-5000 Analyzer, if the sample gas (same concentration of 25 ppm SO<sub>2</sub> in N<sub>2</sub>) is applied under humid condition. In this case, sample gas contains additionally 13 to 15 Vol. % of H<sub>2</sub>O.

As you can see in Figure 4, the response characteristic is, although a little noisy, similar to the one with dry gas application. This is caused by injection of acid in form of drops. However, the amplitude of the noisy signal is only 0.2 – 0.3 ppm of SO<sub>2</sub>. Also the response time T90 is

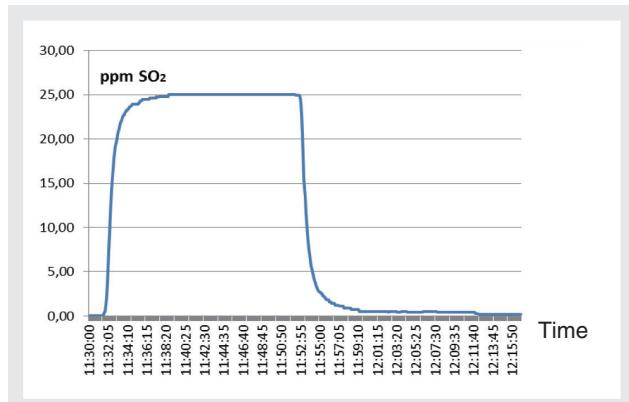


Figure 3 Response characteristic of ENDA-5610 Analyzer to 25 ppm SO<sub>2</sub>—dry gas, dry conditions, H<sub>3</sub>PO<sub>4</sub> not injected.

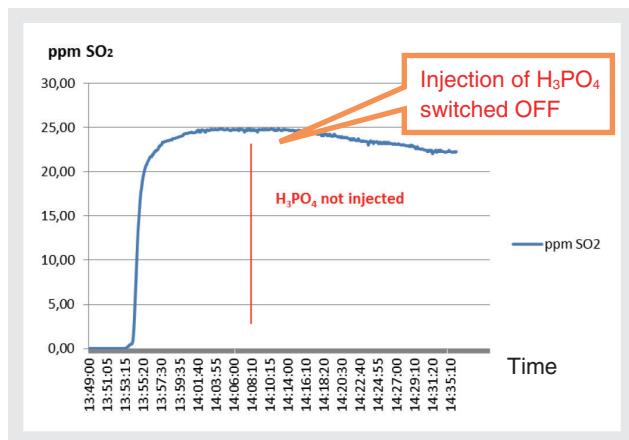


Figure 4 Response characteristic of ENDA-5000 Analyzer to 25 ppm SO<sub>2</sub>—humid sample gas, containing approx. 15 Vol. % of H<sub>2</sub>O.

practically the same like the dry gas application.

## Conclusions and Perspective

The modification of the ENDA-5000 sample conditioning system with above described phosphoric acid injection into the sample gas stream, has strongly improved the technical features of ENDA-5000 Analyzer System in case of low SO<sub>2</sub> concentration measurement. In the last few years we are facing the situation, that SO<sub>2</sub> concentrations, which are to be monitored, are strongly reduced. Due to restrictive laws, each production facility is presently equipped with flue gas desulfurization (FGD). 10 years ago, the situation was completely different and the combustion contained up to 1000 ppm. SO<sub>2</sub> is also measured in gas turbines powered by CNG (Compressed Natural Gas), where the SO<sub>2</sub> concentration is also very low, depending on the resource quality. Therefore the most requested measurement range for SO<sub>2</sub> lies within 20 to 50 ppm SO<sub>2</sub>. Under the utilization of this application, ENDA-5000 Analyzer system as approved system for emission monitoring according to EN 15267-3 can be used for any technological application, where low SO<sub>2</sub> concentration measurement is required.

## Reference

- [1] World Health Organisation EN 15267-3 Air quality – Certification of automated measuring systems



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