



Long-term test of VTT's high temperature sampling probe and analysis of cations and anions by CE-prototype

Authors: Olli Antson, Stella Rovio, Hannu Vesala

Confidentiality: Public

Report's title Long-term test of VTT's high temperature sampling probe and analysis of cations and anions by CE-prototype		
Customer, contact person, address MMEA Research Program		Order reference
Project name In-Furnace studies		Project number/Short name 71091-1.2/Cleen tunnit
Author(s) Olli Antson, Stella Rovio, Hannu Vesala		Pages 10
Keywords in-furnace studies, high-temperature sampling, online analysis, alkali analysis, capillary-electrophoresis		Report identification code VTT-R-057000-15
Summary This report summarizes the main results from a long-term stability and operation test of VTT's high temperature sampling probe, and the results from the test of real-time element analysis by VTT's CE-prototype. The operation of the probe was tested by continuously analysing the sampled gas by FTIR from the superheater section of a furnace. We also collected particles to a filter twice during the long-term test for laboratory analysis. The probe was observed to be fully operational after seven months' operation at about 600°C temperature in biofuel power plant. The probe was also used for collecting sample flow for VTT's CE-prototype. However, the temperature stabilization of the CE-prototype was inadequate for stable operation near the furnace, and analyses were continued at laboratory conditions. CE-prototype gave quite similar results for Cl ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , K ⁺ , Ca ²⁺ , Na ⁺ , Mg ²⁺ , Mn ²⁺ ions from a filter sample in comparison with a reference laboratory method.		
Confidentiality		Public
Espoo		
Written by	Reviewed by	Accepted by
Olli Antson Senior Scientist	Tuula Pellikka Principal Scientist	Jukka Lehtomäki Research Team Leader
Stella Rovio Research Scientist		
Hannu Vesala Senior Research Technician		
VTT's contact address P.O.Box 1000, 02044 VTT, Finland		
Distribution (customer and VTT) MMEA Research Program		
<i>The use of the name of the VTT Technical Research Centre of Finland (VTT) in advertising or publication in part of this report is only permissible with written authorisation from the VTT Technical Research Centre of Finland.</i>		

Contents

Contents.....	2
1. Introduction	3
2. Sampling system and long-term measurement	4
3. CE-analysis results	8
4. Conclusions	9

1. Introduction

VTT's high temperature sampling probe has been extensively used in several field campaigns in power plants during MMEA research program /1, 2, 3/. The sampling probe has been utilized for the collection of particle and gas samples from furnaces at 600-1000°C temperature. Particle samples have been collected onto impactor plates or to a filter, and the gas samples have been analysed by FTIR and by other gas analyzers. The main application of the impactor samples has been the determination of total element concentrations in superheater section.

In this study the durability and functionality of the sampling probe was tested for continuous operation in a furnace.

As a further test the sampling probe was connected to a Capillary Electrophoresis-prototype (CE-prototype) for online or at-site analysis of cations and anions (Cl^- , SO_4^{2-} , NH_4^+ , K^+ , Ca^{2+} , Na^+ , Mg^{2+} , Mn^{2+}).

2. Sampling system and long-term measurement

The structure of the sampling probe is shown in Fig.1. The probe materials are designed to withstand temperature up to 1200°C.

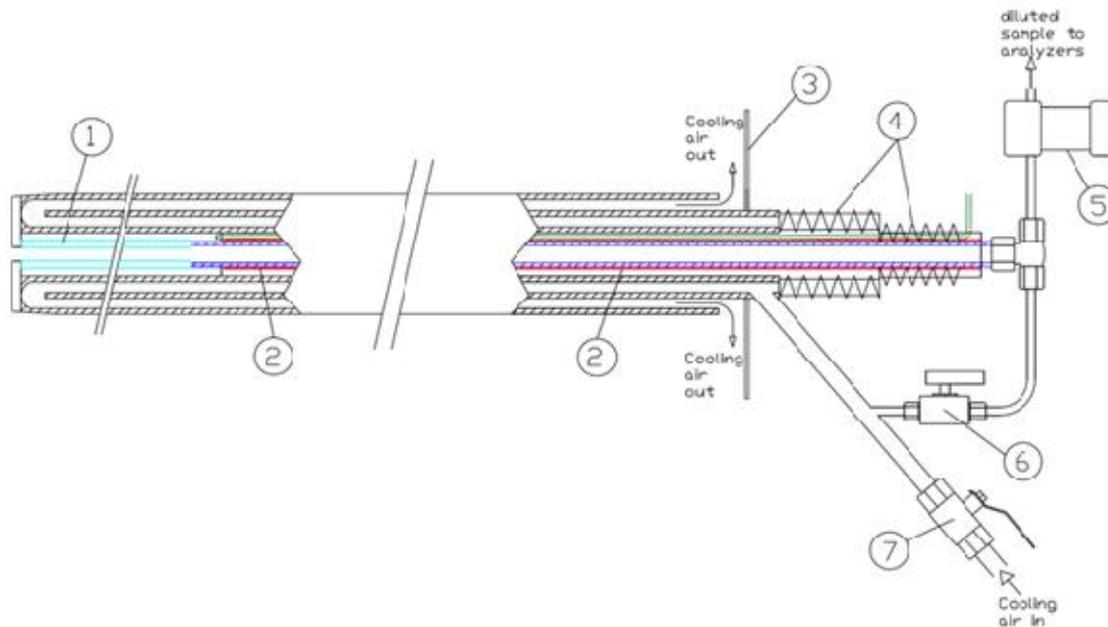


Figure 1. Cross-section of the gas sampling probe. (1) Dilution section in the probe tip, (2) Heated center pipe, (3) Steering plate for cooling-air, (4) Expansion springs, (5) Heated fine filter, (6) Back purge valve, (7) Cooling-air valve

Fig. 2 shows the connection of the sampling device to furnace at Anjalankoski biomass power plant.



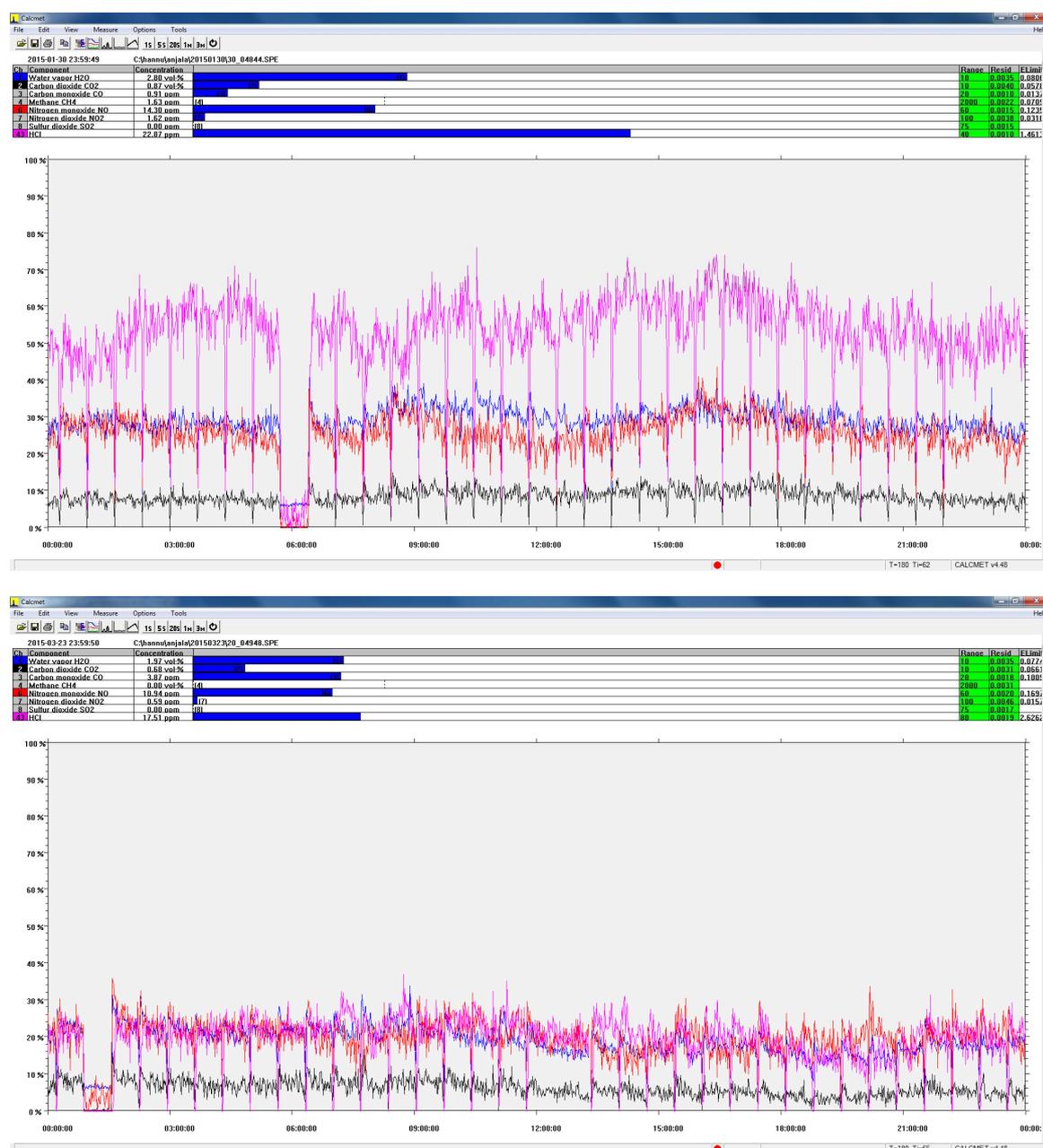
Figure 2. The sampling probe connection to the furnace (left), and the tip of the sampling probe in the beginning of the test (right).

The long-term test was implemented during 15.1.-30.8.2015 at Stora Enso Oyj Anjanlankoski biomass power plant.

The sampling probe is kept open and operational by using back-flush of pressurized N₂ through the center pipe. It seems that back-flush with 40 min. period is enough for long-term operation.

The functionality of the sampling system was continuously controlled by measuring gas phase concentrations and by collecting particle samples to filter.

Continuous FTIR data shows that gas concentration changes are within the normal variation of the boiler. Fig. 3 shows three examples of FTIR data on 2015-01-30, 2015-03-23 and 2015-06-23.



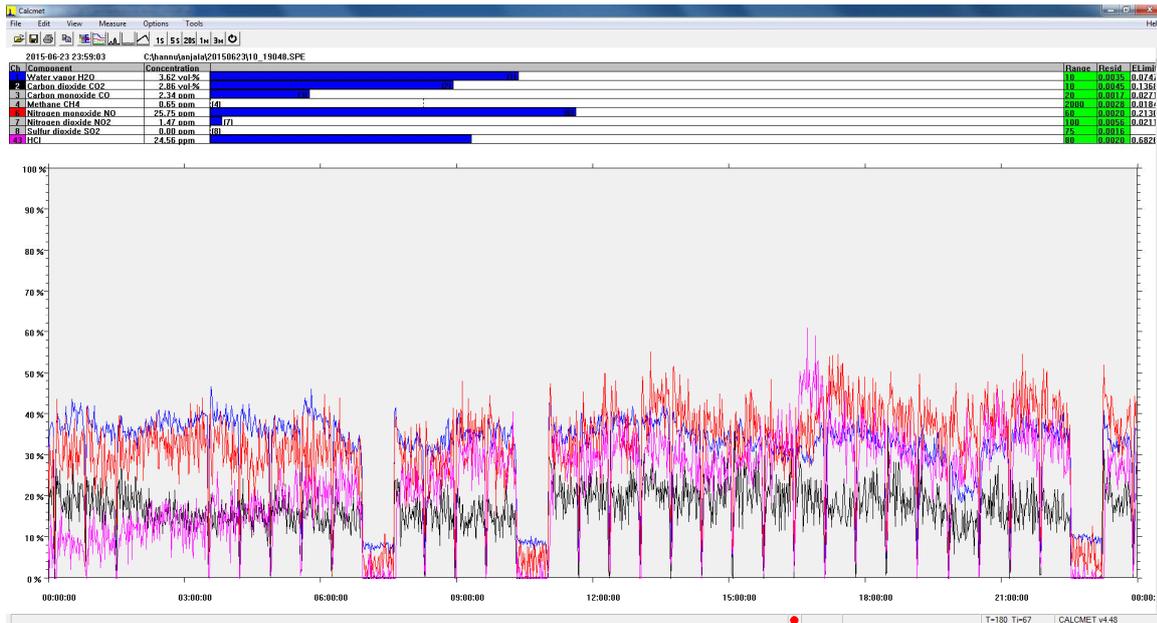


Figure 3. Example graphs of gas concentrations during the long-term test. The back-flush decreases concentrations to zero with 40 min period. The three low concentration periods in the last example graph indicate an error in the back-flush valve operation.

We tested the particle formation capability of the sampling system by comparing filter samples taken before the long-term test (4.6.2014) and after two months continuous operation of the probe (operation start 15.01.2015, filter sampling during 18.-20.3.2015). The Cl⁻, SO₄²⁻, K⁺, Ca²⁺ and Na⁺ ions were analysed from the filter samples and converted to element concentrations in the furnace. The data is also compared to experimental results in our earlier field experiment at Anjalankoski in 2011 /2/.

We observed that the variations of element concentrations between 4.6.2014 and 2011 experiments are such that the results after two months' operation are mainly within these variation limits. Only for Cl some of the filter samples had larger concentrations* than the variation limit. The comparison results are shown in Table 1.

Table 1. Comparison of element concentrations at Anjalankoski power plant in 2011, 2014 and 2015

Year	Analyzed elements / mg/m ³ (n)				
	Cl ⁻	SO ₄ ²⁻	K ⁺	Ca ²⁺	Na ⁺
Comparison data 2011	21-44	20-95	10-45	6-12	6-32
Comparison data 2014	31-44	120-175	31-39	42-65	29-38
After two months' sampling 2015	23-65*	36-106	25-38	24-44	17-29

The tip of the sampling probe after the operation in the furnace is shown in Fig. 3. The temperature was about 600°C during the whole measurement period.



Figure 3. Fouling of the probe after 7 months' operation in furnace.

3. CE-analysis results

The target of this study was to carry out real-time analysis of certain ions (Cl^- , SO_4^{2-} , NH_4^+ , K^+ , Ca^{2+} , Na^+ , Mg^{2+} , Mn^{2+}) collected from the superheater section. In this study we connected the high temperature sampling probe and CE-prototype developed at VTT (Fig. 4).

The idea of the measurement was to inject the sample flow from the sampling probe first to impinger sampling unit and then to CE-prototype. We also collected particle samples to a filter. However, during the field test the temperature near the boiler was too high for a stable operation of the CE-prototype (about 35°C), and so we could not carry out real-time analysis as planned.

The collected liquid and filter samples were reanalyzed later in laboratory conditions by CE-prototype. The comparison of CE-prototype results to the laboratory analysis results shows that CE-prototype gives quite similar results for Cl^- , SO_4^{2-} , NH_4^+ , K^+ , Ca^{2+} , Na^+ , Mg^{2+} , Mn^{2+} ions.

Further development of the CE-prototype is needed especially for the thermal stabilization of the system.



Figure 4. Online CE-prototype (left). Experimental setup for the sampling unit (right).

4. Conclusions

These tests finish the 5 year measurement program connected to in-furnace studies in MMEA program. These prototype tests give valuable information for further R&D studies of a real-time element analyser dedicated to the control of a furnace.

References

1. Antson O., Kauppinen J., Taipale R., Vainikka P., Vesala H., Tulipesämittaukset BFB kattilassa, VTT Report VTT-R-07625-11, 2011
2. Antson O., Mustikkamäki H., Vesala H., Wemberg A., In-furnace measurements at Rauman Voima Oy biomass power plant and at Stora Enso Oyj Anjalankoski power plant, VTT Report VTT-R-04453-13/EN, 2013
3. Antson O., Vesala H., In-furnace measurements at Jordbro power plant in March, VTT Report VTT-R-01644-14, 2014