



**Project acronym:** HEATSTACK  
**Project full title:** Production Ready Heat Exchangers and Fuel Cell Stacks for Fuel Cell mCHP  
**Grant agreement no:** 700564

# Deliverable 4.1 - Report on Establishment of Cr Evaporation Test Rig

**Version:** 2 .1

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Dissemination Level		
PU	Public	<input checked="" type="checkbox"/>
PP	Restricted to other programme participants (including the Commission Services)	<input type="checkbox"/>
CO	Confidential, only for members of the consortium (including the Commission Services)	<input type="checkbox"/>



## Version History

Version	Date	Author	Organisation	Description
1	19/12/2016	Kun Zhang	University of Birmingham	Initial draft
1.1	09/01/2017	J Craven	PNO	Quality review and formatting
2.0	01/07/2020	RSW	UoB	funding acknowledgment
2.1	02/07/2020	RSW	UoB	funding acknowledgment

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### Acknowledgment:

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No 700564. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme, and from Hydrogen Europe and Hydrogen Europe Research.





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## Glossary

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**Table 1:** Glossary

Terms	Definitions
Denuder technique	The denuder technique uses small capillaries for sampling and analysing volatile Cr content in a gas stream at sub ppb levels.
CAPH	Cathode Air Preheater
SOFC	Solid Oxide Fuel Cell



## 1 Introduction

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Solid oxide fuel cell (SOFC) systems that require the cathode air is pre-heated prior to entry into the cathode. They produce exhaust gas containing a high level of thermal energy which can be recovered and transferred elsewhere within the system. The cathode Air Pre-Heater (CAPH) functions as a heat exchanger, recovering heat from the exhaust gas to heat up the inlet air. The latest generation of the CAPH design uses Cr-containing steel alloys to provide improved oxidation resistance under isothermal and cyclic conditions and good high temperature strength. Chromia forming stainless steels are commonly used in high temperature processes such as heat exchangers, furnaces, automotive exhaust systems, and as bipolar plates in SOFC. The HEATSTACK project aims to develop a production-ready CAPH for the residential mCHP market and associated manufacturing capacity for volume production. However, stainless steel pre-heaters have been identified as important Cr sources in current SOFC designs [1, 2]. The volatilised Cr has been identified as a key fuel cell cathode degradation mechanism, since released Cr species react with the perovskites in the fuel cell cathode and cause phase separation and decomposition of the cathode materials [3]. The predominant volatile species of Cr are  $\text{CrO}_3$  and  $\text{CrO}_2(\text{OH})_2$  [4]. The latter requires the presence of  $\text{H}_2\text{O}$  to form and is for most practical applications the dominant volatile compound. While a number of researchers have focussed on the effects of cathode poisoning, few research groups have attempted to quantitatively evaluate the Cr evaporation from the stainless steel surface in a time resolved manner.

The primary aims of the present research are the following:

- Establish the test rig for collection of Cr volatiles basis on the theory of Denuder technique.
- Detect the most probable Cr-containing gaseous species over  $\text{Cr}_2\text{O}_3$  pellets in dry and humid air at high temperature.
- Confirm the accuracy of the Denuder test rig.



## 2 Denuder Technique Establishment and Testing

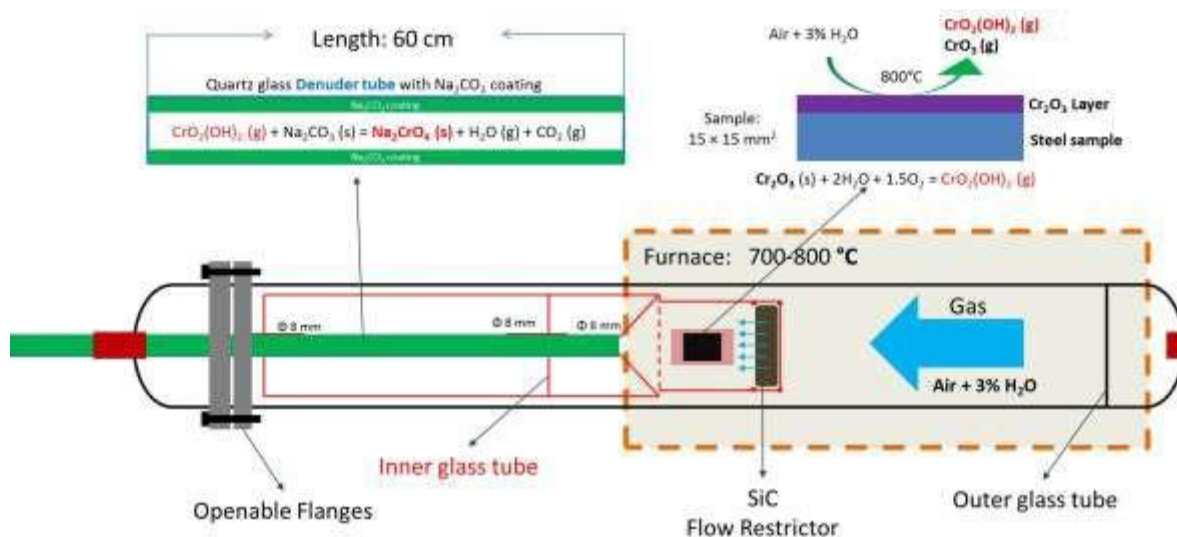
### 2.1 Vapour collection and analysis techniques

**Table 2:** Summary of analytic techniques used to quantify Cr volatiles.

Techniques	Efficiency	Disadvantages	Analysis Method	Detection Limit	Available Information
Transpiration	Assumes 100%	<ul style="list-style-type: none"> <li>Complexity of equipment.</li> <li>Formation of <math>Cr_2O_3</math> on tube wall.</li> <li>Highly concentrated acid for dissolving <math>Cr_2O_3</math>.</li> </ul>	ICP-MS	1-0.01 ppb	Total Cr and other elements
			ICP-AES	3 ppb	Total Cr and other elements
Denuder	95±5%	<ul style="list-style-type: none"> <li>Incomplete reaction between <math>CrO_2(OH)_2</math> and <math>Na_2CO_3</math>.</li> <li><math>CrO_3</math> is not collected.</li> </ul>	Photo spectrometry	1 ppm	Total Cr
Ionic conductivity method	100%	<ul style="list-style-type: none"> <li>Influence of conductivity by other dissolved ions.</li> </ul>	Conductivity Probe	10 ppm	Total Cr
Silicon wafer Collector	10%	<ul style="list-style-type: none"> <li>Several variable affect the collection efficiency.</li> <li>Low collection efficiency.</li> <li>RBS requires access to a particles accelerator for analysis.</li> </ul>	RBS	1 ppm	Relative Cr and other element
Ceramic plate collector	NA	<ul style="list-style-type: none"> <li>Incomplete quantitative analysis of Cr containing species.</li> </ul>	EDS	100 ppm	Relative Cr and other element
Quartz Wool Collector	80%	<ul style="list-style-type: none"> <li>Formation of <math>Cr_2O_3</math> on tube wall.</li> <li>Highly concentrated acid for dissolving <math>Cr_2O_3</math>.</li> </ul>	ICP-MS	1-0.01 ppb	Total Cr and other elements
TGA-Mass spectrometry	100%	NA	TGA-MS	100 ppb	Total Cr, Cr species and other elements

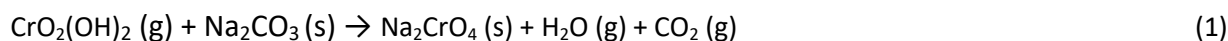
There are a number of methods to investigate high temperature vaporisation processes. The ultimate precision of the transpiration method depends upon the experimental collection efficiency, and the type of quantitative analysis used. Table 2 provides a summary of collection efficiencies and analytical precision for the different techniques used to quantify Cr vapours. Traditional transpiration technique [5] which condenses Cr vapours in fused quartz can reach almost 100% collection efficiency of Cr volatiles. However, accurate evaluation of vaporised Cr requires highly concentrated acid rinses to remove condensed Cr from the quartz surface, making complete Cr collection and analysis difficult. The ionic conductivity method [6] which dissolves soluble  $CrO_2(OH)_2$  and  $CrO_3$  in a DI water bath is capable of analysing 100% Cr species by measuring the conductivity of the resulting solution. Nevertheless, complications can arise when ions other than Cr are collected, since the conductivity measurement does not distinguish between different ionic species. For other techniques [7-9], such as silicon wafer collector, the relatively low Cr collection efficiency prohibits the application of these techniques in this work. The denuder technique [10] is one of the most effective ways to quantify a vapour evolving from a solid when large quantities of other gases persist in the gaseous environment. Cr species are collected at high temperature using a denuder tube, allowing continuous isothermal operation and avoiding disassembling the equipment for every measurement. Furthermore, Cr species are collected as chromate (IV), which is water-soluble and easily analysed.

## 2.2 Denuder setup



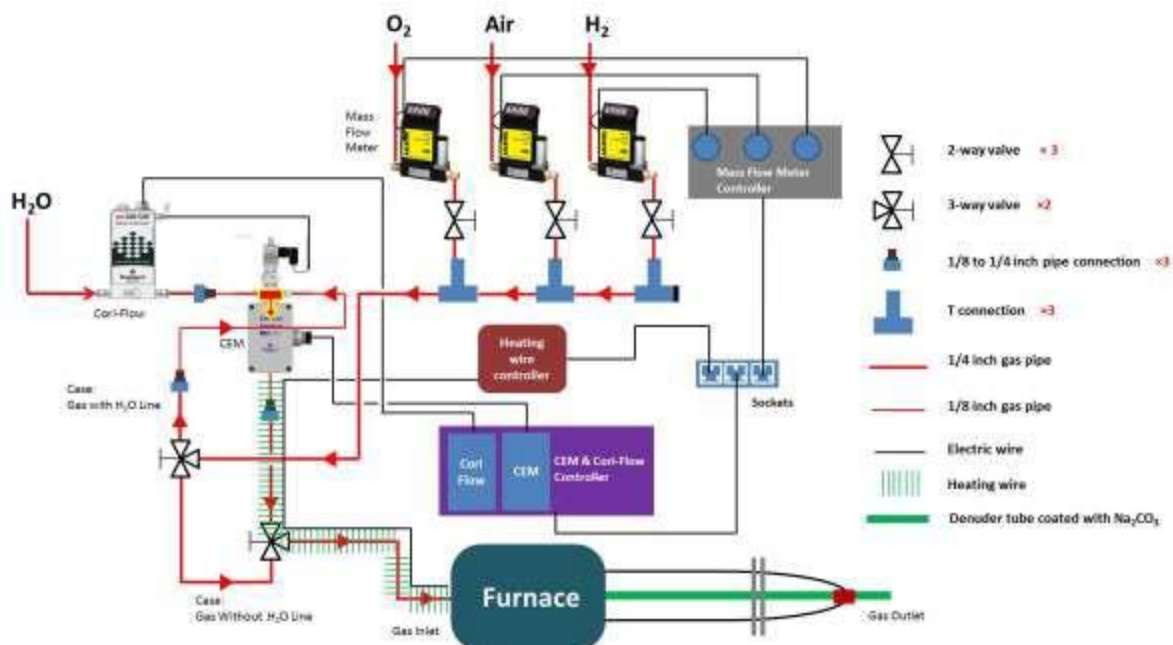
**Figure 1:** Schematic diagram of the Denuder Setup.

Vapour collection in small capillaries, known as denuder tubes, has been applied to investigate a variety of vapour species. Figure 1 illustrates the schematic of denuder technique for quantitative analysis of Cr volatility by analysing coatings inside denuder tube. Denuders are usually made of quartz glass tubes. In a denuder setup, the outer quartz glass tube (black line in Figure 1) with an internal diameter of 50 mm allows the humidified air to pass through, and is sealed with openable flanges to ensure gas tightness. The inner glass tube (red line in Figure 1) serves as sample holder and support for the denuder tube. The denuder tube (inner diameter: 5 mm and length 700 mm) is inserted into the inner glass tube. The stainless steel samples which have been cut into small metal coupons are placed over the inner glass tube and exposed to a high temperature in a furnace. Directly upstream of the samples, a flow restrictor consisting of porous SiC was placed to minimise natural convection and to obtain a more uniform flow pattern. Downstream of the samples, the humidified gas was fed through the quartz glass denuder tube, which has an internal diameter of 5 mm. The inner wall of the denuder tube is coated with  $\text{Na}_2\text{CO}_3$  which is used for Cr collection. The Cr-containing gas ( $\text{CrO}_2(\text{OH})_2$ ) produced in the simulated SOFC environment reacts with the  $\text{Na}_2\text{CO}_3$  to produce  $\text{Na}_2\text{CrO}_4$  on the basis of Equation (1):



After collection, the inside wall of the denuder tube was subsequently washed with 20 ml DI water. The Cr species inside the solution are then quantitatively analysed using a UV-vis spectrophotometer [10].

## 2.3 Process flow chart



**Figure 2:** The process flow chart for the entire test rig with Denuder technique.

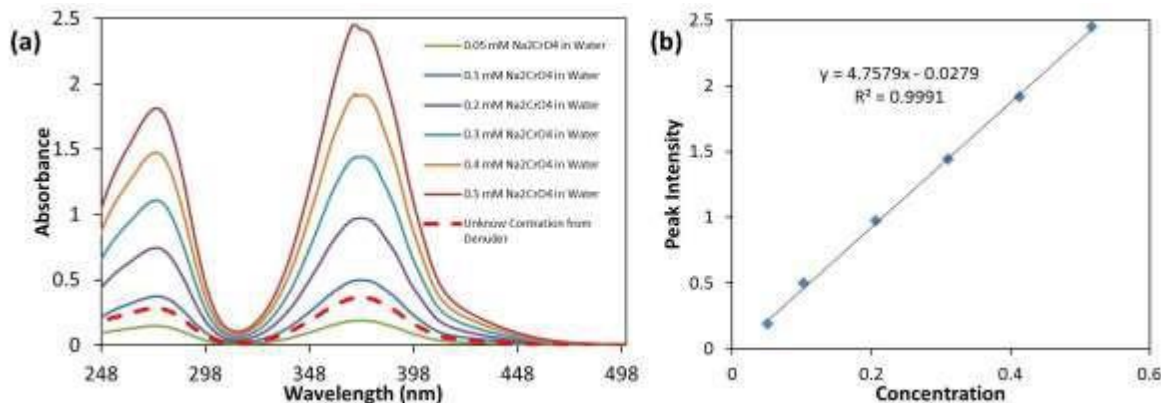
The process flow chart for the entire test rig attached with a denuder set-up is shown in Figure 2. Compressed air is used for the experiments. Water is injected through a Coriolis mass flow meter (Bronkhorst mini CORI-FLOW 50 g/h) and the volume of air is introduced with a GFC mass flow controller (AALBORG, GFC17, N<sub>2</sub>, 0-10 std L/min). The injected air and water are directed to the gas inlet and liquid inlet of the Controlled Evaporation and Mixture (CEM) (Bronkhorst W202A, maximum 10 L/min), respectively. The air/steam mixture is heated to 150 degree inside the CEM to ensure the vaporisation. A rope heater is warped over the stainless steel pipe between CEM and furnace so as to keep the temperature of steam higher than 100 degree. The mixture of 3% water vapour and air finally enters the Denuder glassware in order to simulate the SOFC cathode inlet gas.

## 2.4 Denuder tube coating

The sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) denuder has been used earlier for sampling of HNO<sub>3</sub> [11]. The inside wall of a hollow quartz glass tube with an internal diameter of 5 mm, an external diameter of 8 mm and a length of 700 mm, is coated with a thin layer of Na<sub>2</sub>CO<sub>3</sub>, in the following manner: A saturated solution of sodium hydroxide (NaOH) in methanol is sucked up through the tube to a height of 600 mm, thus leaving 100 mm of the Denuder tube uncoated at one end. The solution is drawn off and the wall is dried with a heat gun. The liquid methanol evaporates quickly and a smooth coating of NaOH is obtained, which is rapidly converted to Na<sub>2</sub>CO<sub>3</sub> by a CO<sub>2</sub> stream within one minute. Both ends of the denuder are then sealed until being used for Cr-containing gas sampling.



## 2.5 The accuracy of the denuder technique



**Figure 3:** (a) The UV-vis spectra of sodium chromate solution with different concentration; (b) Extraction and analysis of the peak values of UV-vis spectra.

As mentioned before, the  $\text{Na}_2\text{CO}_3$  coating is washed off with DI water and then quantified using a spectrophotometer. However, the concentration of the solution obtained from the denuder coating is unknown. In order to find out the concentration for this solution, commercial sodium chromate from Sigma-Aldrich was prepared into solutions with different concentrations, ranging from 0.05 mM to 0.5 mM. UV-vis spectrophotometer was conducted on these solutions and their corresponding spectra are shown in Figure 3a. As can be seen from Figure 3b, the intensity of the peaks increases with the increase of concentration. Obviously, there is a relatively strong linear relation between the peak intensity and the solution concentration. The UV-vis spectra for the solution with unknown concentration (red dash line) collected from the denuder tube is also shown in Figure 3a. The concentration can be calculated from the calibration function (Figure 3b) with the peak intensity of the unknown solution. Thus, the concentration was calculated as 0.13 mM for the unknown solution collected from Denuder tube. In addition, the actual weight loss of the  $\text{Cr}_2\text{O}_3$  pellet was measured by weighing the  $\text{Cr}_2\text{O}_3$  pellet before and after Cr evaporation test with a Cubis Micro Balance. The efficiency of the denuder setup for Cr volatiles collection is confirmed to be 98%. This high efficiency indicates that the denuder technique is applicable for quantitative analysis of Cr species evaporated from stainless steels.



### 3 Conclusions

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A technique for quantifying chromium volatilisation from materials at high temperature in an oxidising environment is presented. The described sodium carbonate denuder technique offers a simple and cheap method with a low detection limit for measuring Cr-containing gas evaporated from stainless steel in simulated SOFC cathode environment. The technique uses a denuder tube coated with sodium carbonate to collect chromium species in the form of chromate (VI) at high temperature. The denuder technique has high sensitivity and allows for continuous isothermal operation. In the present work,  $\text{Cr}_2\text{O}_3$  pellets are used as Cr volatile source to confirm the accuracy of the denuder setup under SOFC environment. The Denuder setup exhibits an efficiency of 98%. The efficiency can be affected by the gas tightness of the setup but it is possible to make corrections for these interferences. Thus, the Denuder technique built is adopted measurements of Cr evaporation of stainless steels under SOFC operating conditions.



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