

Bridging the Analytical Gap Between Gas Treatment and Reactor Plants in Carbon2Chem[®]

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The use of purified process gases as feedstock for subsequent processes requires a detailed verification of the gas purity to ensure long lifetimes of applied catalysts. Herein, the analytical infrastructure for the measurements of the cleaned gases is presented. An overview of all sampling points for the off- and on-line analysis is given. The detailed description of the composition of the cleaned blast furnace gas, its main components as well as its traces are presented. Thereby, over 99 % of the overall signal strength of this complex gas matrix measured with a proton transfer reaction mass spectrometer with H_3O^+ as reagent ion could be revealed. Furthermore, by the example of the catalyst poison H_2S , the necessity of monitoring continuously the gas matrix for certain compounds was proven.

Keywords: Carbon2Chem, Gas analysis, Mass spectrometry, Steel mill gases, Sulfur

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1 Introduction

The utilization of CO_2 , produced during steel manufacturing processes, through chemical conversion to, e.g., methanol is a major goal of Carbon2Chem[®] [1, 2]. This collaborative project between 18 partners of industry and academia connects different sectors like chemistry, steel and energy to build up a renewable carbon cycle, in which CO_2 is not waste, but indeed a resource. This approach of carbon capture and utilization (CCU) of metallurgical gases can help decreasing the net greenhouse gas emissions. Even if several case studies already have shown the possibility of using steel mill gases as feedstock for catalytic processes [3–7], several challenges for a reliable and performing synthesis process have to be mastered. Besides the main components, a variety of trace components including metals, polyaromatics and aliphatic hydrocarbons, oxygen-, nitrogen-, sulfur-containing and halogenated compounds are present in the raw metallurgical gases [8–14]. Without a comprehensive and time adapted gas treatment of the three metallurgical gases, namely coke oven gas (COG), blast furnace gas (BFG) and basic oxygen furnace gas (BOFG), catalyst poisoning and, therefore, a disruption of the downstream processes cannot be excluded. Furthermore, as operation modes in a steel mill can change, fluctuations in the concentrations of the main as well as the trace components, are expectable. To address these highly complex challenges, it is essential to build up a precise and flexible analytical system upstream, which answers the question of the design of a gas-treatment unit. This was done by Salazar Gómez et. al. [15] by the

realisation of the so-called HüGaProp-Container, a mobile container equipped with a state-of-the-art mass spectrometer, which can monitor traces and fluctuations in the raw gases down to the ppt-range as well as the course of the main components via gas chromatography (GC).

Whereas COG is an excellent hydrogen source, usage of BFG would decrease the CO_2 output the most. BFG has not only a high amount of CO_2 (Tab. 1), but it also offers the greatest volume fraction of all steel mill gases and is produced with $1\text{--}7 \times 10^5 \text{ Nm}^3\text{h}^{-1}$ [16]. Therefore, usage of BFG as feedstock for the catalytic synthesis of methanol and other basic chemicals is most promising [17, 18].

While a detailed knowledge on the main components is required to develop adequate process routes for utilization, the knowledge on the trace components is mandatory to judge on the catalyst lifetime in the subsequent process. For example, to ensure the long-term activity of the Cu-based methanol synthesis catalyst $\text{Cu/ZnO/Al}_2\text{O}_3$, it is highly

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Table 1. Typical composition of raw blast furnace gas (BFG) and after two-stage treatment [16].

Component	Raw BFG	BFG after two-stage treatment
Carbon Monoxide	20–28 vol %	20–28 vol %
Carbon Dioxide	17–25 vol %	17–25 vol %
Hydrogen	1–5 vol %	1–5 vol %
Ammonia	10–40 mg Nm ⁻³	NA
Cyanide Compounds	0.26–1.0 mg Nm ⁻³	NA
Hydrocarbons	67–250 g Nm ⁻³	NA
H ₂ S	NA	14 mg Nm ⁻³

NA = Data not available

recommended to keep the overall sulfur concentration below 0.1 ppm [19]. But even after a conventional two stage treatment at a steel mill, a certain amount of H₂S (Tab. 1) is present in the BFG, making a thorough gas treatment unavoidable to prevent catalyst poisoning in downstream processes [20, 21]. Therefore, one of the key processes in Carbon2Chem[®] is the gas treatment unit at the technical center in Duisburg, which tests different options for gas purification on a technical scale [22, 23]. The main components in the purified gases are determined and the gases are further converted in different reactor plants at the center following the process routes envisaged in the project. However, there is a need of an analytical system after the gas treatment unit and before the reactor plants, which is able to measure all main components as well as trace components. This system should provide valid information about the detailed gas composition in real time and act as an early warning system to impede catalyst poisoning in case of a component breakthrough. Applying such a system in a laboratory would not only protect the catalysts in downstream processes and therefore the reactor plants, but also being an essential source of information to further optimize the gas treatment unit. This task is tackled in a laboratory installed at the technical center.

2 The Laboratory

The Laboratory is equipped with fixed installations, like gas cabinets, pressure reducers and a water separator as well as a mobile unit, the so-called mobile analytical system (Masy)

consisting of a proton transfer reaction-quadrupole interface time-of-flight mass spectrometer (PTR-QiTOF-MS), two micro GCs, and a dilution system (Fig. 1). A detailed flow scheme of the installation is given in Fig. 2. It is possible to measure all purified gases provided at the technical center in Carbon2Chem[®] inside the laboratory in both, a high-pressure as well as a low-pressure variant. Furthermore, every gas can be analyzed at different treatment stages in and outside the technical center of Carbon2Chem[®] using the mobile analytical system Masy. To give further insights into the laboratory, the virtual lab tour is also highly recommended (www.cec.mpg.de/de/projekte-und-foerderungen/carbon2chem-reg).

2.1 Gas Flows in the Laboratory – Water Separator and Dilution System

Due to different pressure stages, expansion/compression steps and temperature fluctuations inside the gas treatment processes, the cleaned gases offer a high humidity. Therefore, condensation of water and water droplets inside the pipelines can be expected. In order to protect the analytical instruments in the laboratory, it is necessary to separate all liquid water traces from the gas stream before the measurement. Therefore, the individual gas streams are guided through a stainless-steel water separator (M&C TechGroup) separating water droplets through the force of gravity. Afterwards, the gas is either led into the exhaust pipe or into the analytical system Masy. The bypass to the exhaust enables a continuous flow of the gases guaranteeing a measurement of the actually provided gas in the laboratory. Furthermore, a sampling point is attached after the water separator for off-line sampling with, e.g., gas bags or sampling tubes and further analysis by thermal desorption gas chromatographic mass spectrometry (TD-GC-MS) in the Carbon2Chem[®]-Laboratory [24].

The centrepiece of the laboratory is the mobile analytical system. It is equipped with a PTR-QiTOF-MS, which will be discussed later on, and a dilution unit with two ports for the sample gases. By dilution with nitrogen, the gases can be transformed into more nitrogen-likely gases, resulting in a more precise measurement as highly concentrated compounds are lowered into the linear quantification range of the PTR-QiTOF-MS. This feature enables also more precise quantification, as calibration curves for certain compounds can be obtained based on dilution series with calibration gases.

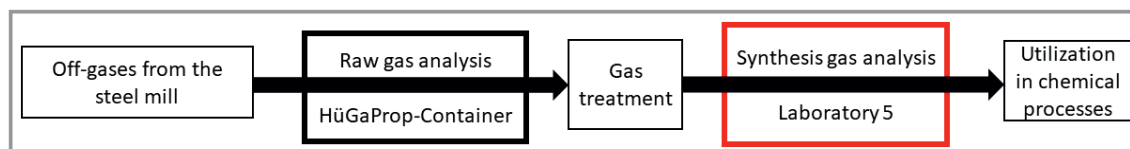


Figure 1. The integration of the analytical laboratory at the technical center (red) within the workflow of Carbon2Chem[®].

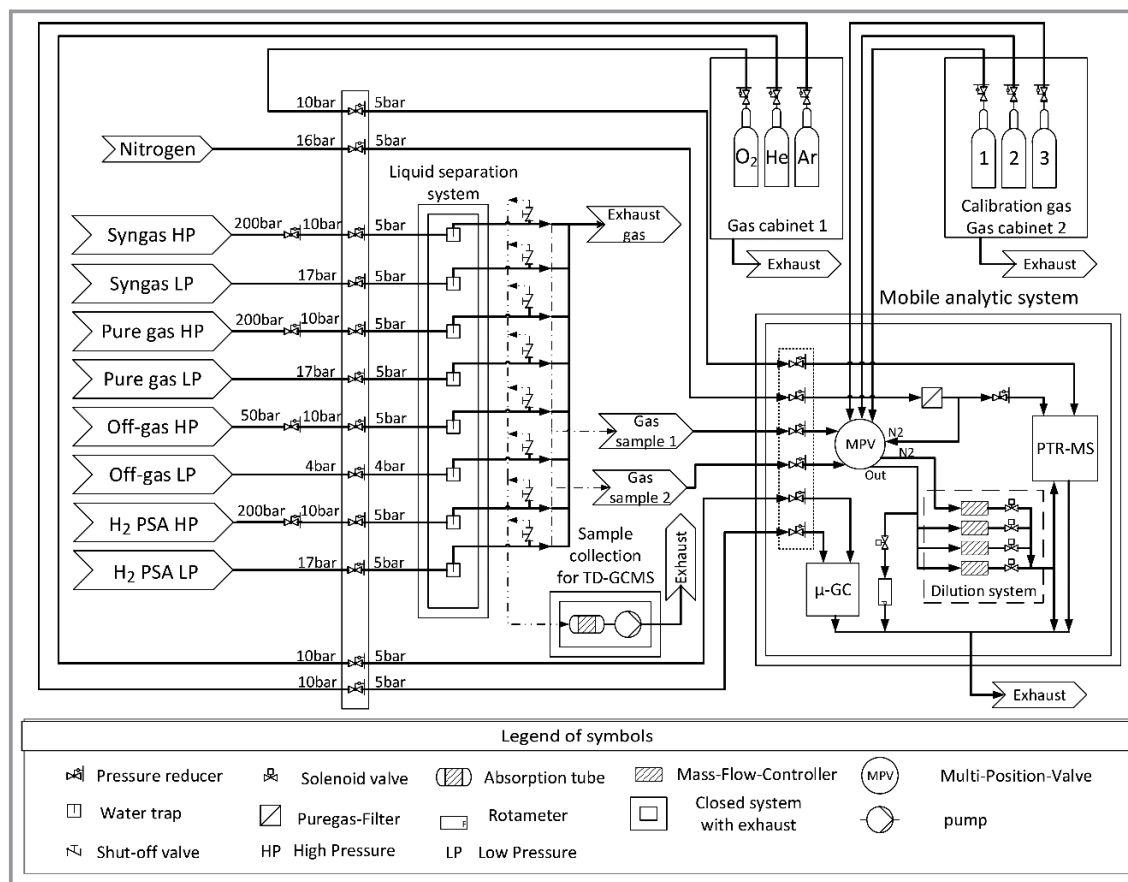


Figure 2. P&ID of the laboratory and its analytical infrastructure.

Selected via a multiport valve, the sampling gas is enclosed in parallel to three mass flow controllers (MFC, Bronkhorst®) with partially overlapping flow range ($0.1\text{--}5\text{ mL min}^{-1}$; $1\text{--}50\text{ mL min}^{-1}$; $10\text{--}500\text{ mL min}^{-1}$). The adjusted sample volume is afterwards diluted with N_2 with a fourth MFC ($50\text{--}1000\text{ mL min}^{-1}$) enabling a dilution up to 1:1000. The dilution unit is controlled by a computer applying the LabVIEW® control software.

2.2 Analysis of Main and Trace Compounds – Micro Gas Chromatography

The composition of the main components of the cleaned gases is determined via two micro GC Fusion instruments (INFICON GmbH, Bad Ragaz, Switzerland) [25], which enable an analysis down to the ppm range. The instruments are based on the MEMS (microelectromechanical systems) technology resulting in a faster component separation, a smaller sample volume and a shorter analysis time. Each individual module is a closed miniature gas chromatograph consisting of a MEMS sample injector, a resistively heated, temperature-programmed capillary column (up to $300^\circ\text{C min}^{-1}$), an electronic pressure control system and a MEMS-

based μTCD (thermal conductivity detector) as well as embedded chromatography software. The advantage of these integrated modules is the parallel distribution of the sample into all GC modules at the same time and enabling the measurement of a larger spectrum in a shorter time compared to a conventional GC.

The instrument is connected via bypass to the sampling line and the gas is distributed simultaneously to each injector via a sample inlet system to all GC modules within the device. The integrated sample conditioner reduces the sample gas pressure to approx. 83 kPa (12 psi) and heats the sample to a constant temperature in order to optimize the repeatability of the analysis. The carrier gases He , H_2 , Ar , N_2 transports the gas into the column for analysis. In contrast to the first micro GC, which is equipped with four modules and a water filter to protect the instrument from water droplets, the second micro GC offers only one module without a filter and is used explicitly for the determination of the water content.

To analyze the cleaned gases, the following columns are used:

Module 1-A: 10-m RT-Molsieve 5A [3-m Rt-Q-BOND] backflush injector

Module 1-B: 12-m RT-Q-Bond, variable volume injector

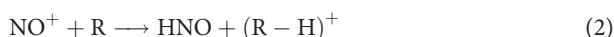
Module 1-C: 20-m CP-Molsieve, variable volume injector
Module 1-D: 8-m RT-U-Bond [1-m RT-Q-Bond] back-flush injector

Module 2-A: 8-m RT-U-Bond [1-m RT-Q-Bond] back-flush injector

Thereby, it is possible to separate small molecules like N_2^+ , Ar^+ , H_2^+ , O_2^+ , H_2O , CO^+ , CO_2^+ , HCN , COS^+ , H_2S^+ , and NH_3^+ , small hydrocarbons like methane[†], ethane[†], ethene^{*}, propane^{*} and propene^{*}, which covers the most important main and minor compounds for Carbon2Chem[®]. The determination of the volume percentage is based on a one-point calibration (*) or a two-point calibration (†).

2.3 Analysis of Trace Compounds – Proton Transfer Reaction-Quadrupole Interface Time-of-Flight Mass Spectrometer

The PTR-QiTOF-MS is a state-of-the-art mass spectrometer (IONICON Analytik GmbH, Innsbruck, Austria) which is able to measure trace components in the concentration level < 10 ppb due to its high mass resolution and sensitivity [26]. Equipped with a selective reagent ionisation (SRI) add-on [27], it is possible to switch between H_3O^+ , NO^+ , and O_2^+ as reagent ions for the ionisation of the different compounds and therefore, enables to detect the whole variety of components included in the cleaned metallurgical gases. Basically, the ionisation is made through either proton transfer (H_3O^+ , Eq. (1)), hydride abstraction (NO^+ , Eq. (2)), and charge transfer (NO^+ , Eq. (3); O_2^+ , Eq. (4)).



Whereas a successful proton transfer (Eq.(1)) depends on the proton affinity of a certain compound, which has to be higher compared to water ($\sim 691 \text{ kJ mol}^{-1}$), charge transfer reactions (Eqs. (3) and (4)) are based on the ionisation energies of the certain components, which in comparison has to be lower than NO^+ (9.26 eV) and O_2^+ (12.07 eV). Thus, only the combination of the results received using each reagent ion gives a complete picture of all trace components inside the gas, since every reagent ion only covers a certain number of compounds [28].

The reactions take place at a certain ratio of the electrical field E to the gas density number N , the reduced electrical field strength (E/N) inside the drift tube. The higher the ratio, the more fragmentation is observed, however, clustering processes, e.g., with water molecules, are suppressed. Therefore, an $E/N = 131 \text{ Td}$ was chosen as a good compromise for soft ionisation with less fragmentation and sparsely

water clustering [29]. Nevertheless, further insights into clustering and fragmentation processes can only be won by running simulation experiments [30].

A determination of the exact concentration of a certain trace compound with a PTR-MS is only possible via an external calibration [31]. Nevertheless, the instrument offers the possibility to calculate the concentration of a certain analyte $[A]_{\text{ppbV}}$ by:

$$[A]_{\text{ppbV}} = 1.6938e^{-11} \frac{U_d T_d^2 [AH^+]_{\text{cps}} T(H_3O^+)}{k_A p_d^2 [H_3O^+]_{\text{cps}} T(AH^+)} \quad (5)$$

With U_d , T_d , and p_d being the applied drift tube voltage, temperature, and pressure, respectively, and T being the instrumental response function (transmission). The transmission was measured using a commercial gas standard TO-14A Aromatics Mix (14 Components, Restek GmbH) with a nitrogen dilution of 1/10 through the dilution system. However, as this calculation is based on several approximations, e.g., an estimated k_A reaction rate constant and no fragmentation, this quantification gives only an idea ($\pm 50\%$) of the exact concentration.

3 Synthesis Gas Measurement

The use of off-gases from the steel mill plants as feed gas for catalytic processes reveals new challenges, as there might be many potential impurities included in the feed gas that might act as catalyst poison, as it is the case for the raw gases [3, 32]. Therefore, it is of high importance to reveal the composition of traces included in the synthesis gas and their concentration range. Especially sulfur-containing compounds, which are present in the ppm and ppb range of the raw metallurgical gases [16] cause irreversible damage to the catalyst by blocking the active sites of the Cu/ZnO/Al₂O₃ methanol catalyst. Thereby H₂S, COS, thiols, and SO₂ are the most studied cases. Besides sulfur containing compounds, halides, heavy metal carbons, P-containing compounds, and AsH₃ can also cause irreversible deactivation. Furthermore, nitrogen containing compounds, although causing reversible deactivation, may end up in the produced methanol and deteriorate the product quality [32]. To protect the reactor plants in Carbon2Chem[®] and to control the gas treatment, it is indispensable to monitor continuously the concentration range of these compounds.

3.1 Calibration and H₂S Quantification

To determine the exact concentration of H₂S in the synthesis gas, calibration measurements with a calibration standard (Messer Industriegase GmbH) were performed. The calibration standard contains H₂S in a concentration of 1.01 ppm ($\pm 2\%$) in nitrogen. Eleven concentration steps for the calibration from 1.01 ppb up to 1010 ppb were made

through dilution with nitrogen using the dilution system (Tab. 2). As every PTR-MS is handmade and unique, it is necessary to normalize the obtained corrected counts to the obtained values of the reagent ion for further comparison:

$$NCPS(H_2S) = \left[\frac{\text{Corrected Counts}(H_2S)}{\text{Corrected Counts}(H_3^{18}O)} \right] \times 10^6 \quad (6)$$

Thereby, the average value of 200 measurement cycles (1 cycle per second) was calculated. As it is possible that H_2S strongly adsorbs on the metallic surfaces of the tubing and the instrument, the measurement cycles were selected after the equilibrium was achieved and a stable signal of the substance could be determined. H_2S can only be detected quantitatively using H_3O^+ as reagent ion [28].

A linear approximation covering the whole concentration range from 0 ppb up to 1000 ppb is insufficient. For the obtained data two linear approximations can be applied (Fig. 3). First, from 0 ppb to 40 ppb (black) and second from 40 ppb to 1000 ppb (red), which also includes zero. As shown in Fig. 3, the calibration y_1 (black) might be applied up to a concentration of 40 ppb H_2S when dilution of the gas is required, whereas the calibration y_2 (red) can be used to determine the concentration of H_2S up to 1000 ppb. A possible explanation for the deviation at low concentrations is the dilution error, which is unavoidable and results from the error range of the MFCs in the dilution system, offering a higher weighting at low sample volumes. Therefore, the calibration y_2 is more reliable in a broad range, but for small concentrations a higher error range has to be considered.

To determine the correct H_2S concentration calibration y_2 was used, due to the high number of NCPS (>240). As presented in Fig. 4, the concentration calculated based on the external calibration is nearly doubled compared to the values given by the PTR-MS software. This deviation is somehow not surprising, as PTR-MS is only a semi-quantitative method with a specified error range of about 50 % [31]. Furthermore, PTR-MS is usually used for air analysis, which is a less complex gas matrix as it is in the case for treated BFG. This complicates the determination of the concentration of a certain analyte in the given gas matrix through the PTR-MS software in addition. However, it has to be highlighted that besides the high sensitivity this technique enables a reasonable quantification even without a detailed calibration which is not possible with other analytic techniques like conventional mass spectrometry.

As mentioned above, sulfur concentrations, even in the low ppb range, can cause catalyst deactivation due to poisoning. Therefore, such high H_2S con-

Table 2. Calibration of the PTR-QiTOF-MS for H_2S with H_3O^+ as reagent ion.

Concentration [ppb]	Normalized Counts	Normalized Count standard deviation
1.01	0.69448	1.43791
2.02	2.69934	2.27221
4.04	8.60833	3.8945
10.1	33.30783	6.38303
20.2	83.38726	9.88641
40.4	190.72453	13.32203
101	500.5737	25.03139
202	1130.01633	39.40872
404	2233.51867	51.76923
757.5	4132.52155	64.01258
1010	5581.97492	87.92107

centrations point to an insufficient sulfur removal for subsequent catalytic processes. In comparison, a thorough sulfur removal is shown in Fig. 5, which exhibits only very small concentration fluctuations in contrast to the top case.

3.2 Gas Composition in the Cleaned Blast Furnace Gas

Measured online via micro GC, Fig. 6 shows the composition of the main components H_2 , N_2 , Ar, CO, and CO_2 in the cleaned BFG. Both, CO and CO_2 are nearly equal and

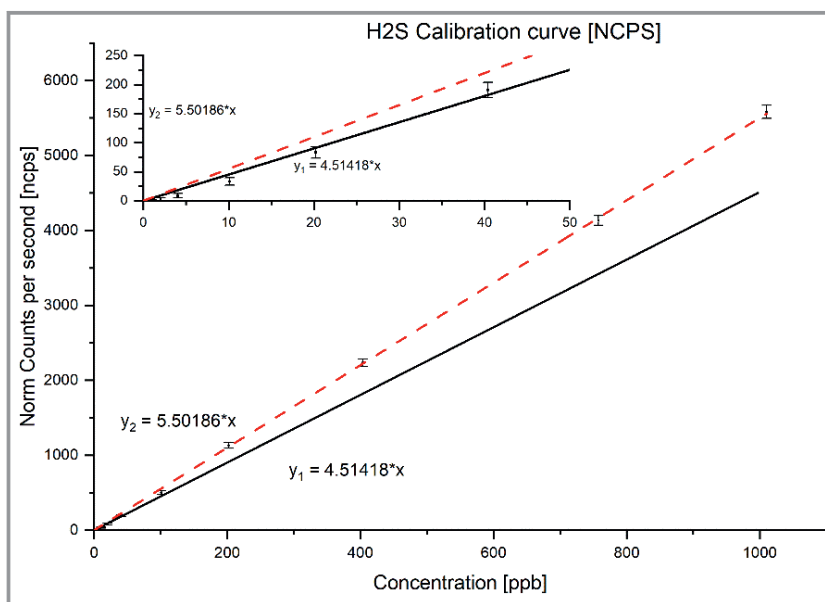


Figure 3. Calibration curves y_1 (black) and y_2 (red) for the PTR-QiTOF-MS with H_2S applying H_3O^+ as reagent ion.

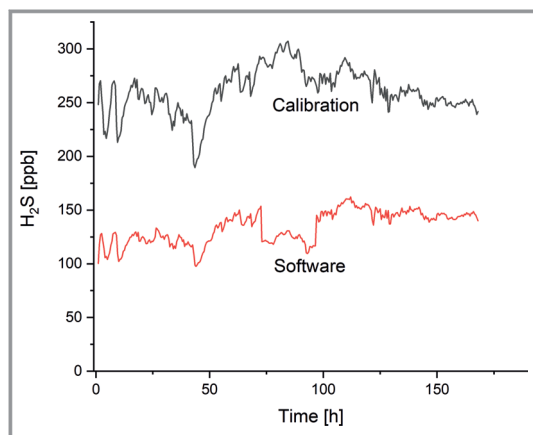


Figure 4. Comparison of the H_2S concentration over time calculated by the PTR-MS software (red) and the external calibration (black).

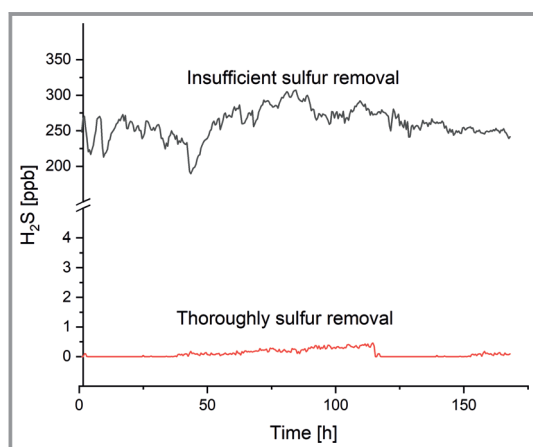


Figure 5. Concentration profile of H_2S for a time period with insufficient sulfur removal based on calibration y_2 (black) and concentration profile of H_2S for a time period with thoroughly sulfur removal based on calibration y_1 (red).

oscillate at ca. 22–24 vol%. In comparison, H_2 has about 5 vol%, Ar about 0.5 vol%, whereas N_2 shows 48 vol% in the cleaned BFG. All five main components offer an almost constant course. The information on these concentrations and their stability is required for the mode of operation and further process development of the subsequent catalytic reactions.

To give a full overview of almost all gaseous traces inside the cleaned BFG by PTR-MS, the gas was measured for several days without dilution. Thus, a pure impression of all compounds with a higher proton affinity compared to water ($\sim 691 \text{ kJ mol}^{-1}$) was received. Furthermore, it was possible to determine the percentage of the different classes of compounds depending on their signal intensity in a 24-h measurement (Fig. 7). Thereby, over 99% of the overall signal intensity could be revealed (Tab. 3). A mass spectrometer only enables the determination of a mass-to-charge ratio and, therefore, a sum formula. Without further validation, e.g., through offline sampling it is only possible to assume a concrete molecule in some cases. For further simplification, the contained elements ($\text{CH} < \text{O} < \text{N} < \text{S} < \text{Si} < \text{Metal}$) in the

Table 3. Signal intensity [%] and number of signals [%] in the cleaned BFG measurable with H_3O^+ as reagent ion.

Class of components	Signal intensity [%]	Number of signals [%]
Hydrocarbons	46.9	28.1
Oxygen containing	29.8	16.5
Nitrogen containing	19	4.9
Sulfur containing	2.9	4.5
Silicon containing	0.3	5.8
Halogen containing	0	0.7
Metal containing	0.9	7.0
Unknown	0.3	32.5

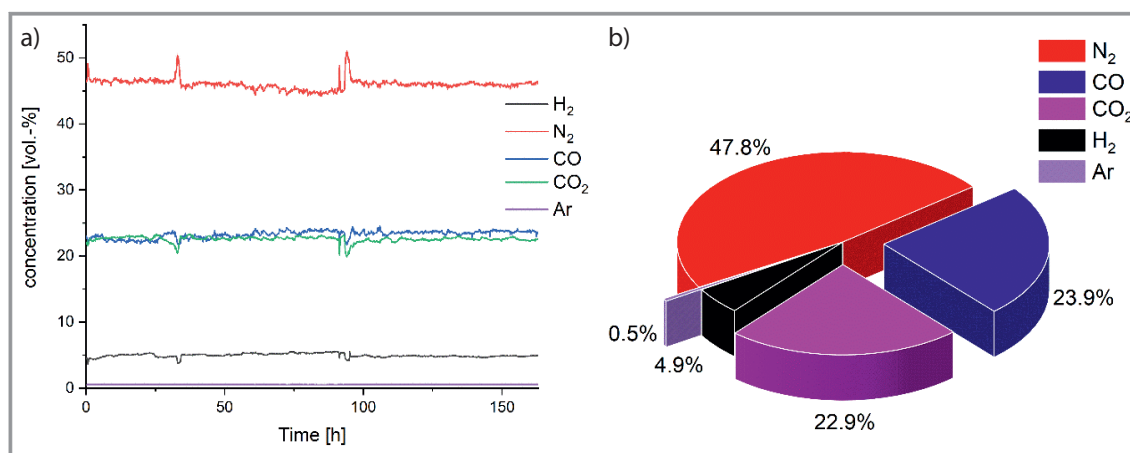


Figure 6. Concentration profile (a) and cake plot (b) of the main components in the cleaned BFG.

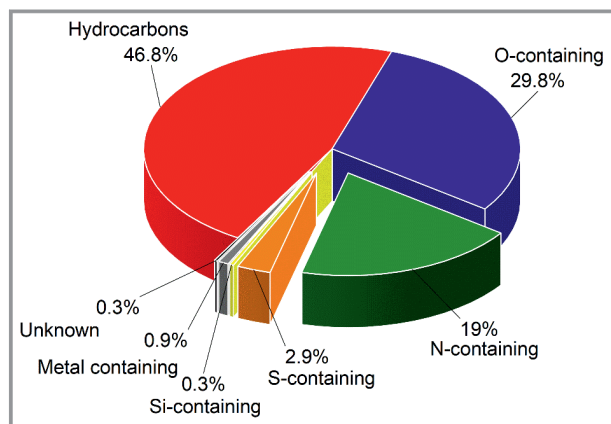


Figure 7. Cake plot (signal intensity, norm counts per second) of all components, which are measurable with H_3O^+ as reagent ion.

sum formula leading to the different classes of compounds are prioritized. For example, $\text{Fe}(\text{CO})_5$ counts for Metal containing and not for Oxygen containing.

To determine roughly the overall concentration of the detected traces, every compound was set in relation to toluene assuming a similar behavior inside the PTR-MS, as toluene was calibrated within the transmission measurement described above. Based on this approximation an overall concentration of 4.5 ppm ($\pm 100\%$) can be determined. However, as catalyst poisons are included inside the gas matrix, it is essential to consider the detailed composition. The main part of the signal intensity is produced by hydrocarbons. Thereby, aromatic substances, like benzene and toluene, and shorter aliphatic hydrocarbons, like propane and butane, owe the lions share. The heaviest detectable hydrocarbon was $\text{C}_{30}\text{H}_{50}$ with $m/z = 410.39(+1)$. Oxygen containing substances like alcohols, aldehydes, ketones and carboxylic acids produce nearly 30% of the overall signal intensity. Altogether, sulfur components, including H_2S as strongest signal, represent 4.5% of all signals with an overall intensity of 2.5%. Even with signal number of about 7.0%, metal containing compounds offer only 0.9% signal strength. However, as highly volatile complexes like $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$ are included, these compounds need permanent monitoring, as even a low concentration might be sufficient to cause irreversible catalyst deactivation. In summary, the signal strength of all identified compounds is below any critical level which might cause catalyst poisoning.

However, PTR-MS is a semi-quantitative method and can only give an idea of the concentration level. Furthermore, analysis with H_3O^+ as reagent ion is limited by the proton affinity of the analyte. Therefore, it is inevitable to validate the given results by off-line measurements, e.g., via TD-GC-MS, to get more detailed insight into the quantitative composition of all traces.

4 Conclusions

Regarding the high claim in Carbon2Chem[®] and its difficult task, the utilization of steel mill gases, it is shown that a detailed analysis of the gases is a crucial building block in the project concept. Within this work the installed infrastructure to tackle this task is described in detail. By applying this infrastructure the main as well as the trace components can be measured online in the analytical laboratory via two micro GCs and a PTR-QiTOF-MS, respectively. Thereby, over 99% of the overall signal intensity of the traces in the cleaned BFG were revealed. Furthermore, by external calibration the exact number of critical components can be obtained and compared to the values given by the PTR-MS software as semi-quantitative method. Extending this comparison in future measurements will allow a deeper insight in the reliability of the more general quantification provided by this method. The obtained results were already used within Carbon2Chem[®] for further optimization of the gas treatment to prevent catalyst poisoning and a more effective usage of the cleaned BFG. Therefore, a continuous monitoring of the main as well as the trace components, as it is been executed in the analytical laboratory, is essential for the road to success in the project Carbon2Chem[®].

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Symbols used

$[\text{A}]_{\text{ppbv}}$	[ppbv]	concentration of the analyte A
E/N	[Td]	reduced electrical field strength
k_A	$[\text{cm}^3\text{s}^{-1}]$	reaction rate constant
m/z	[-]	mass to charge ratio
p_d	[mbar]	pressure inside the drift tube
T	[-]	instrumental response function (transmission)
T_d	[°C]	temperature inside the drift tube
U_d	[V]	applied drift tube voltage

Abbreviations

BOFG	basic oxygen furnace gas
BFG	blast furnace gas
COG	coke oven gas
Masy	mobile analytical system
MFC	mass flow controller
MicroGC	micro gas chromatograph
MEMS	microelectromechanical Systems
NCPS	norm counts per second
ppb	parts per billion
ppm	parts per million
PTR-QiTOF-MS	proton transfer reaction-quadrupole interface time-of-flight mass spectrometer
SRI	selective reagent ionisation
TCD	thermal conductivity detector
TD-GC-MS	thermal desorption gas chromatographic mass spectrometry

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