


# The HüGaProp-Container: Analytical Infrastructure for the Carbon2Chem<sup>®</sup> Challenge

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DOI: 10.1002/cite.202000101

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The utilization of industrial off-gases as raw material requires a detailed knowledge on their time-depending composition, especially with regard to trace components. Within the framework of the HüGaProp project (Hüttengas Properties) a measuring container and the analytical methods for the characterization of trace components in the three raw metallurgical gases was developed. The mobile container is deployed in the project Carbon2Chem<sup>®</sup> to characterize the available off-gases at a steel mill and provide fundamental data to determine the required gas cleaning as well as the background for the further process design.

**Keywords:** Blast furnace gas, Coke oven gas, Converter gas, Proton transfer reaction time-of-flight mass spectrometry, Trace compounds

*Received:* April 30, 2020; *revised:* July 20, 2020; *accepted:* July 23, 2020

## 1 Introduction

The application of process or exhaust gases from steel industry as a raw material for the production of chemicals represents a major challenge as their composition is different compared to the usually applied raw materials used in the chemical industry. This challenging goal is addressed in the Carbon2Chem<sup>®</sup> project [1, 2]. One aim within the scope of the project is, e.g., the production of methanol from steel mill gases. Although the feasibility of methanol synthesis from such CO<sub>2</sub> sources has been shown recently [3, 4], until now very little information is available in literature about trace components in the ppb or even ppt concentration range in the three metallurgical gases coke oven gas (COG), blast furnace gas (BFG) and basic oxygen furnace gas (BOFG) [5, 6]. If not thoroughly removed these components can disrupt the use of downstream catalytic processes by reducing the catalyst lifetime due to poisoning. Therefore, there is a need for a profound qualitative and quantitative characterization of the raw and purified gases.

Tab. 1 shows typical average compositions of the three metallurgical gases. While the determination of the main components can be easily addressed by, e.g., gas chromatography, the determination of the other components including traces is up to now an unsolved issue. Regarding traces in COG, most of the literature focuses on fugitive emissions [7, 8] and workplace analysis [9], but for the process gas data are scarce [10]. Among aliphatic and aromatic (BTEX, PAHs, PCBs, and PCDD/Fs) hydrocarbons, also nitrogen-containing compounds (e.g., ammonia, amines, amides, etc.), sulfur-containing compounds (e.g., H<sub>2</sub>S, COS, CS<sub>2</sub>,

and mercaptans) and halogenated compounds may be present in these gases. However, substances such as metal organic compounds and arsine derivates can also be expected. Besides the scarce information on the nature and concentrations of these trace compounds, there is no information available on their temporal fluctuations in the metallurgical gases and their possible dependence on the main components CO and CO<sub>2</sub>. Such information is required for the custom-made design of gas cleaning processes with respect to the subsequent synthesis process.

Preliminary investigations showed the need for on-line monitoring of traces in the low ppb-range. Many substances could not be identified due to low recoveries associated using off-line sampling like, e.g., gas bags [11–13]. This indicated that there are unknowns in the gas matrix, which needed to be addressed. Furthermore, it turned out that on-site analysis and continuous measurements are necessary, since the multiple off-line analyses produced very different results and considerable fluctuations in the gas composition were found, which were attributed to the

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**Table 1.** Typical composition of steel mill gases [1].

Main components	Coke oven gas (COG) [%]	Blast furnace gas (BFG) [%]	Basic oxygen furnace gas (BOFG) [%]
Hydrogen (H <sub>2</sub> )	63	4	5
Carbon monoxide (CO)	7	25	64
Carbon dioxide (CO <sub>2</sub> )	2	23	17
Nitrogen (N <sub>2</sub> )	6	47	14
Others (incl. traces)	22	< 1	< 1

different operating stages during the steel production. Therefore, the determination and monitoring of possible gas fluctuations of trace components in the metallurgical gases and their correlation to the concentration variation of the main components is an important task, which requires a high-performance analysis. Applying an extremely sensitive commercial PTR-QiTOF (proton transfer reaction quadrupole interface time-of-flight mass spectrometer) from IONICON Analytik GmbH, Innsbruck, Austria, which is a prototype with enhanced resolution and sensitivity in comparison to other commercial instruments, may help to fill this knowledge gap. A detailed description of this kind of instrument has been given by Sulzer et al. [14]. Proton Transfer Reaction Mass Spectrometry (PTR-MS) is a technique originally developed to determine volatile organic compounds (VOCs) in air [15]. The main condition for the proton transfer reaction according to Eq. (1) to occur is that the analyte gases must possess a larger proton affinity than water (691 kJ mol<sup>-1</sup>):



where R is a gas phase analyte. This reaction is exothermic and proceeds at reaction rates which are close to the rate of collision (approximately: 10<sup>-9</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). Additionally, the main components of air such as nitrogen, oxygen, carbon dioxide and methane exhibit lower proton affinities than water and thus, are not measurable under standard conditions. This means VOCs in these gases can be analyzed without dilution, which enhances the detection limit of the method. The main drawback of PTR-MS is the presence of parasitic ions, such as NO<sup>+</sup>, O<sub>2</sub><sup>+</sup>, water clusters [(H<sub>2</sub>O)<sub>n</sub>]H<sub>3</sub>O<sup>+</sup>, [NH<sub>3</sub>]H<sup>+</sup>, and [N<sub>2</sub>]H<sup>+</sup>, which have to be minimized prior to the measurements. For instance, the presence of small amounts of NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> has been ascribed to back diffusion of air from the drift tube region [16]. Therefore, the insight from additional method development has to be considered to differentiate instrumental artefacts, e.g.; parasitic ions or memory effects, thus, helping the elucidation of complex mass spectra [17].

One of the main advantages of PTR-MS is the rather “soft” ionization of molecules by the primary ion H<sub>3</sub>O<sup>+</sup>. Therefore, the proton transfer can be considered to be almost non-dissociative with some exceptions (alcohols

[18] and terpenes [19]). Due to the low fragmentation, this technique allows the detection of molecules at their molecular mass plus one H<sup>+</sup> and, thus, it enables the analysis of complex gas mixtures without the need for previous separation methods. With this measuring principle, even isobaric can be identified, if the mass resolution is above 4000 m (Δm)<sup>-1</sup> [20].

In order to address the detailed analysis of the three metallurgical gases, a container setup including a PTR-QiTOF as central element was designed and built up within the framework of the project HüGaProp (Hüttengas-Properties, metallurgical gas properties), so that the usual problems associated with offline sampling [11, 21, 22] such as incomplete trapping of material, tedious and time-consuming sample preparation, evaporative losses, chemical degradation or incomplete recovery could be avoided by the direct on-site online measurement.

## 2 The mobile HüGaProp-Container

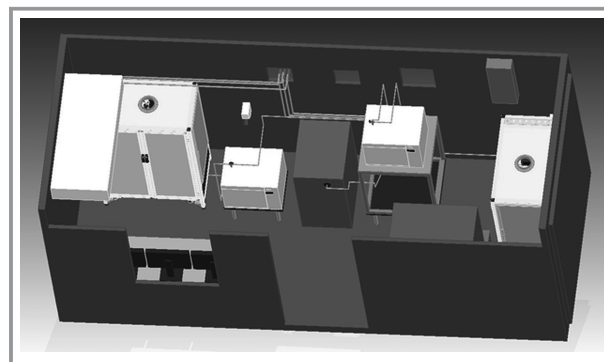
The HüGaProp project was a joint research project of the Max Planck Institute for Chemical Energy Conversion in Mülheim an der Ruhr and ThyssenKrupp AG in Essen funded by the Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung, BMBF). As a pre-project to Carbon2Chem<sup>®</sup> its major aim was to provide the necessary infrastructure and the development of a methodology to assess the compositional and temporal fluctuation of trace substances contained in the off-gases of the steel industry down to the ppt-level before and after a purification process, with special regard to their damaging effects for downstream catalytic processes. To enable the detailed time-depending characterization of the metallurgical gases including the so far not sufficiently known trace components mass spectrometry by a state-of-the-art PTR-QiTOF will be established for the analysis of complex gas mixtures. Since the chosen analytical system is highly sensitive, two isolated and climatized containers (a laboratory and a supply container) were considered for the on-site application in order to protect the analytical instruments as well as to obtain reliable data independent of the external conditions in summer and winter. The construction of the containers was divided into four phases (Fig. 1). First, all



**Figure 1.** Schedule of the HÜGaProp project from conception phase to implementation at the steel mill plant.

aspects of the required equipment were defined with respect to the functionality of the analytics as well as for the integration and safe operation of the containers at an industrial site. In the second phase, the infrastructure for the containers was constructed including the further equipment. Following the construction functionality tests of the gas supply, of the electrical and IT infrastructure as well as the first method development with the installed PTR-QiTOF were carried out. Finally, after concluding the construction at the MPI CEC, the containers were transported to the steel mill site in Duisburg and connected to the pre-conditioning unit at the sampling point. This pre-conditioning of the raw gases is required before feeding them into the laboratory container, as the gases are only available at around atmospheric pressure. To ensure a continuous gas flow through the devices in the container, a pump system delivers a flow of  $5 \text{ L min}^{-1}$  from which a bypass is used for the measurements with the mass spectrometer. Furthermore, the pre-conditioning unit includes a filter as well as a cold trap for condensing liquid components at  $5 \text{ }^\circ\text{C}$  to avoid their deposition within the piping and/or equipment. The main purpose of the pre-conditioning unit is to remove eventual dust particles and excess water in summer to avoid blocking or condensation in the gas lines at critical transfer points. As these steps anyway have to be performed before a thorough gas cleaning they will not influence the validity of the results obtained for the subsequent online gas analysis. Eventually, polar compounds could partially be absorbed in the condensate water, but in general, the gas composition remain unchanged after conditioning. Moreover, the applied filter as well as the condensate can be subsequently analyzed in more detail to obtain further insights in the overall composition of the metallurgical gases.

Fig. 2 shows an external 3D-view of the laboratory container. It was conceived to mainly carry out analytical tasks using the PTR-QiTOF. However, the laboratory container was additionally equipped with two catalytic reactor setups for material testing, each coupled with a gas chromatograph, which can also alternatively be used for direct analysis of the main and minor components of the metallurgical gases. These reactor setups can be used in parallel to the characterization analysis of the three metallurgical gases for direct exposure measurements on catalysts for syngas chemistry, like, e.g., methanol synthesis or further testing of gas cleaning materials to validate the feasibility of the chosen materials or processes. For this purpose, comparison experiments with pure gases from gas cylinders and the metallurgical gases can be realized in the test reactors.



**Figure 2.** 3D-Sketch of the Laboratory container.

Fig. 3 shows the P&ID inside the laboratory container. Its interior can be divided into three parts:

- The pretreatment and calibration part, where the dilution of highly concentrated gases takes place and custom-made or commercial gas standards for calibration purposes can be applied.
- The analysis part with the analytical instruments for the characterization of main and trace compounds in the metallurgical gases.
- The catalysis part, where gas cleaning materials can be tested and deactivation experiments for synthesis gas reaction with real or synthetic gases can be performed.

In order to ensure a constant temperature in the laboratory container throughout the year, it is equipped with a split air conditioning system (11.2 kW, Mitsubishi). Furthermore, an exhaust air system ensures an adequate air change. A gas alarm system from MCS (Medium-Control-Systems, Altenburg) is provided for monitoring possible leaks of flammable and toxic gases as well as smoke and the lack of oxygen in both containers. The gases required in the laboratory container are made available by the supply container. They are conducted to the laboratory container by means of permanently installed pipelines to ensure a continuous operation, where the bridge between the containers is enclosed in a tempered metal box. Pressurized air is provided by an air compressor from Dürr Technik. In the case of an error in one of the containers, solenoid valves in the supply container shut off the flammable and toxic gases and an alarm message is given. Furthermore, an uninterruptible power supply unit (UPS) from Emerson is housed in the supply container to protect the analytical devices in the laboratory container against possible current fluctuations. By considering and implementing the general safety aspects, the installed infrastructure comprising both containers

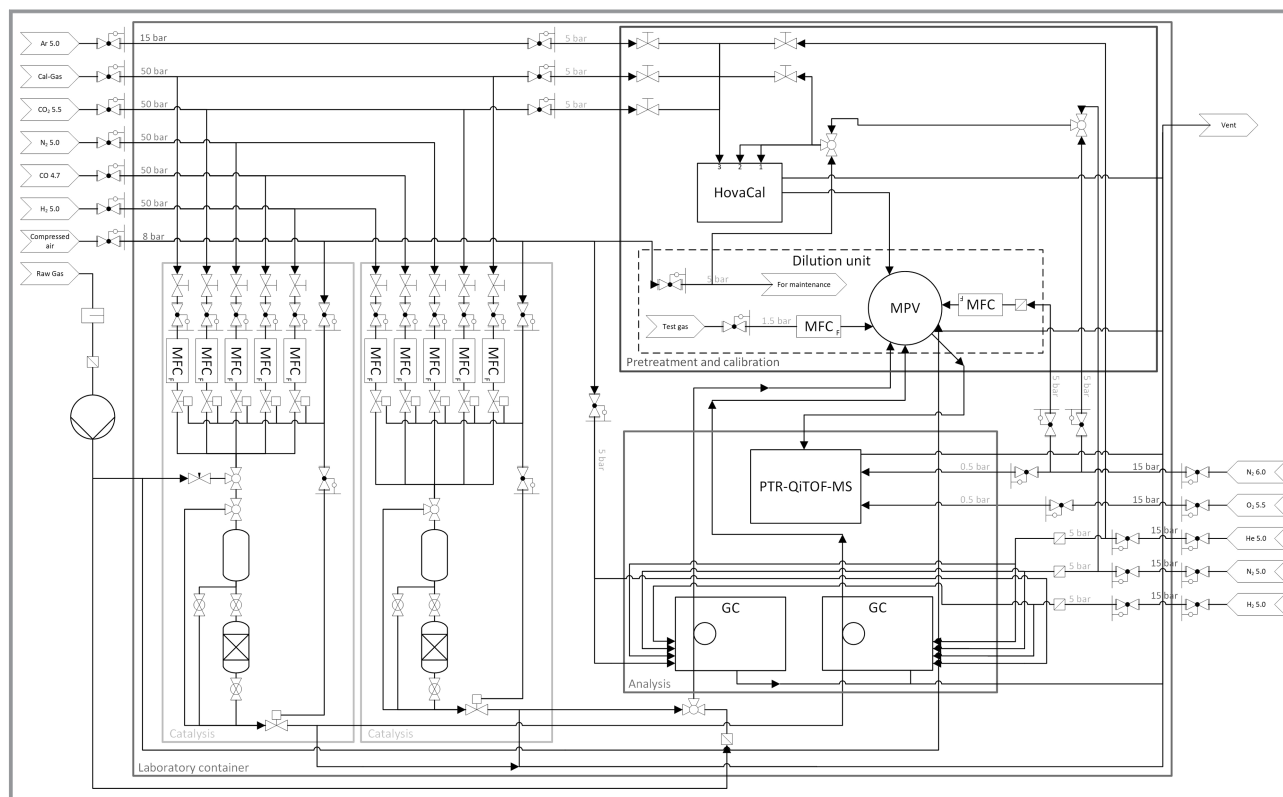


Figure 3. P&ID of the HÜGaProp container.

allows the independent and mobile application of the gas characterization on-site at industrial facilities. The investment for both containers counting the analytical instruments and the whole infrastructure (air conditioning, exhaust-air system, gas alarm system, etc.) was around 1 million Euros. All components and analytical instruments are commercially available, while the installation was performed predominantly in-house. Only the usual consumables are required for operation. These are primarily the gases for the supply of the equipment as well as the regular maintenance or replacement of wearing components, such as GC columns, sealing materials, filters etc. Here, for the maintenance - compared to a regular laboratory application - a slightly higher effort has to be considered due to the complex matrix of the gases of interest reducing the lifetime of some spare parts.

### 3 Main equipment of the Laboratory Container

#### 3.1 Process Mass Spectrometer (PTR-QiTOF)

A state-of-the-art process mass spectrometer (IONICON Analytik GmbH, Innsbruck, Austria) with high mass resolution and sensitivity for the measurement of trace compounds in the concentration range < 100 ppb is applied for

the characterization of the metallurgical gases. This prototype, the so-called proton transfer reaction quadrupole interface time-of-flight mass spectrometer (PTR-QiTOF, Fig. 4a) [14], is additionally equipped with a FastGC (Fig. 4b) [23], CO/CO<sub>2</sub> sensors and a so-called selective reagent ionization (SRI) add-on [24]. This process mass spectrometer is suitable for online measurements due to the good time resolution (<1 s), so that the smallest changes in the gas composition can be detected. However, the identification of isomeric compounds is not possible since they have the same nominal mass for the protonated molecule.

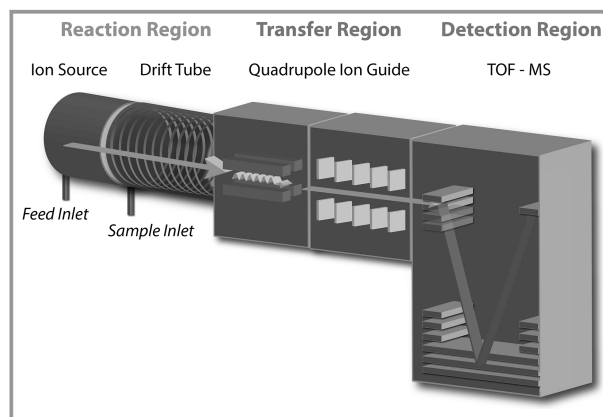


Figure 4. Schematic view of the PTR-QiTOF according to [12].

Therefore, the FastGC feature can be used to determine isomeric substances with a time resolution <60 s using a separation column [23].

Because not all possible substances contained in the metallurgical gases have a higher proton affinity than water, with the add-on SRI primary ions such as  $\text{NO}^+$  (9.26 eV) and  $\text{O}_2^+$  (12.07 eV) can be used so that substances that are invisible with protonated water can be measured by charge transfer according to Eqs. (2) and (3). Nitrogen and oxygen are used to produce these primary ions. The disadvantage of this is the increased fragmentation of the molecules, which makes the interpretation of the obtained mass spectra difficult.



When measuring gas samples with the PTR-QiTOF, the gas samples at the inlet are passed into the drift tube through a capillary (1/16"), which is heated to 100 °C with a heating hose. The proton transfer reaction takes place in the drift tube and the generated ions are collimated in the quadrupole ion guide and then detected in the TOF-MS (Fig. 4). The smallest flow at the inlet is around 106 mL min<sup>-1</sup> as standard, but higher flows up to around 800 mL min<sup>-1</sup> can be achieved. All exhaust gases produced in the device are passed on to the exhaust system.

In normal operation, the three metallurgical gases are connected in the dilution box to a flow through multipoint valve (MPV) from VICI, so that the various gases can be selected at predefined intervals. Furthermore, the outlet of the reactor setups, a calibration line as well as an additional line for a gas after purification are also connected to the MPV. In order to avoid condensation, the MPV is heated to approx. 150 °C. All connected gases flow continuously through the MPV. By this, it can be guaranteed that the selected gas sample for the analysis is always fresh and representative. In preliminary tests, it was found that direct measurement of the metallurgical gases may be difficult due to the differences in density or viscosity in comparison to air. Therefore, before the selected raw gases are measured with the process mass spectrometer, they are usually diluted with nitrogen to avoid saturation of the detector.

### 3.2 Calibration Gas Generator

As not all components can be calibrated using premixed gases, a multi-component calibration gas generator (HovaCAL® 3435-VOC) from IAS GmbH, Oberursel, Germany [25] is applied for calibration purposes of the analytical devices in the laboratory container, in particular the process mass spectrometer. The calibration gas generator is an extended version of [25], which is a dosing and evaporator system with controlled humidity. It dynamically generates

calibration gases by vaporizing pure organic and inorganic components, but also mixtures into a carrier gas. Additionally, further dilution steps of the gas vapor mixture are possible. This enables to calibrate for the most of the trace components in the metallurgical gases quantitatively without the need of commercial gas standards. One advantage of such a calibration gas generator is the possibility to customize gas mixtures also from substances that usually are not commercially available as calibration gases. In addition, it enables the optimization of measurement parameters of individual substances under controlled conditions (e.g., at specific relative humidity), which will facilitate the characterization of the metallurgical gases.

The calibration gas generator consists of an evaporation chamber, a dosing and a temperature control as well as a dilution part (Fig. 5). In the first stage the desired liquid is injected into a heated evaporator via a syringe pump module and mixed with a defined carrier gas flow (MFC 1 in Fig. 5), which can be adjusted within a flow range of 2.0 and 5.0 NL min<sup>-1</sup>. The syringe pumps operate in push-pull mode. Continuous operation is possible by the automatic switching of low-volume valves. The dosing range for the liquid is depending on the syringe size used. Usually, a syringe size of 12.5 µL is used, resulting in a dosing range between 0.25 and 100 µL min<sup>-1</sup>. For further dilution, a partial stream of the premixed gas is sent through capillary 1 and mixed with a defined dilution gas stream (MFC 2 in Fig. 5). A larger dilution ratio can be set via a second capillary, whereas the mixture from stage 2 is mixed with an additional gas stream (MFC 3 in Fig. 5) in stage 3. The flow rate through the capillaries is kept constant by controlling the pressure in the heated capillary part via back-pressure regulators taking into account the pressure drops caused by the heated capillaries as well as the additional restriction capillaries. The outlet of the restriction capillaries can be used to apply the gas mixtures at the several stages. Optionally, all stages can be humidified using separate dosing and evaporation systems. With the two additional stages, dilution ratios of up to 1/1000000 can be achieved. Similar to the metallurgical gases, the line of the calibration gas generator is connected to the analytics via the MPV to realize an automatized high flexibility.

### 3.3 Kinetic Reactor Setups and GC

Besides the analytics the laboratory container is equipped with two equal kinetic reactor setups from Premex Reactor GmbH, Lengnau, Switzerland. The flow diagrams of these are shown in Fig. 3. They are consisting of three main parts: a gas supply, a reactor part and a pressure control system. The gas supply enables the production of various gas mixtures from the pure gases as well as the supply with a real metallurgical gas. For the pure gases CO (4.7, 99.997 % purity), CO<sub>2</sub> (5.5, 99.9995 % purity), H<sub>2</sub> (5.0, 99.999 % purity), N<sub>2</sub> (5.0, 99.999 % purity) and a supply line for

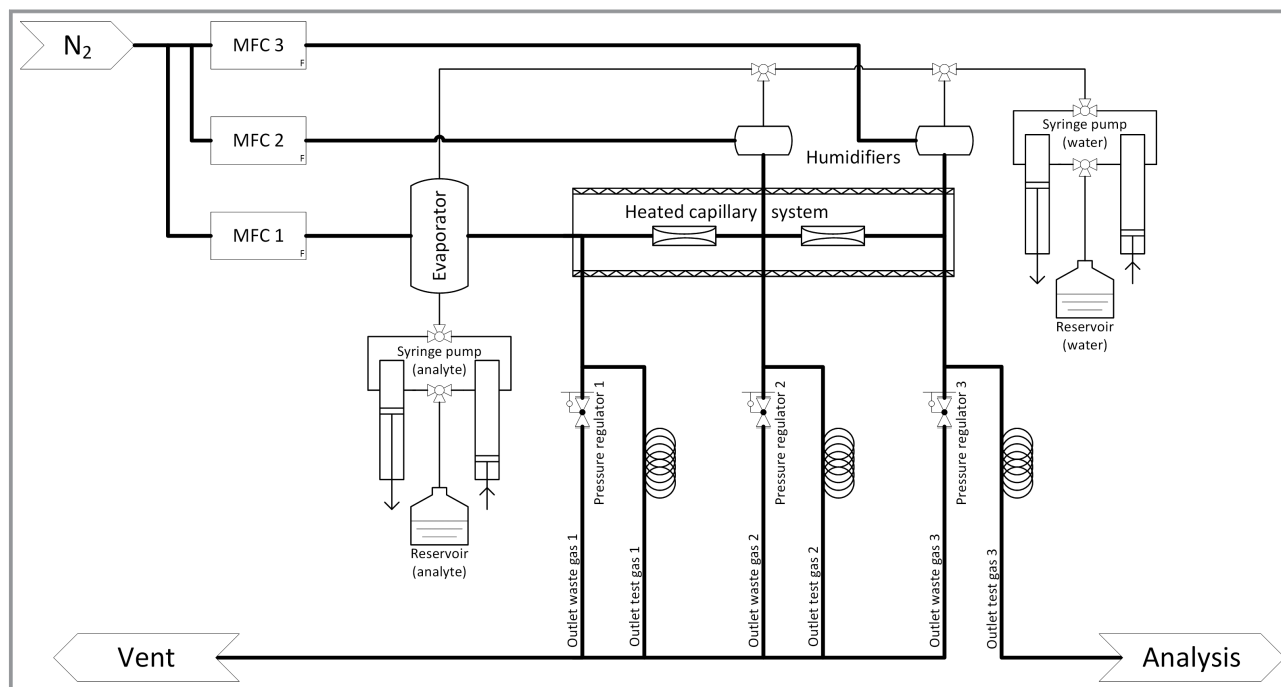


Figure 5. Scheme of the gas calibration generator HovaCAL® 3435-VOC.

calibration gases are available for performance tests in synthesis gas reactions. The desired partial pressures in the educt gas mixture and the corresponding total volume flow can be set for each gas line using separate mass flow controllers (MFC) from Bronkhorst Deutschland GmbH. The stainless-steel fixed-bed reactor is placed in an oven from HTM Reetz GmbH. The usual operating temperatures are in the range of 200–300 °C and the operating pressures are in the range of 30–50 bar realized by a Badger control valve. The fixed bed reactor has an inner diameter of 6.23 mm with a wall thickness of 1.65 mm. Shut-off valves are located at both ends of the reactor to allow the removal of the reactor at the end of an experiment under an inert atmosphere. This enables the characterization of the tested catalyst without contact to air to avoid the oxidation of the catalyst and therefore, to obtain a more realistic information on the catalyst structure during synthesis conditions. The tubing after the reactor is heated to 120 °C to avoid condensation of the products. For catalyst testing with the metallurgical gases an additional temperature-controlled reactor upstream to the synthesis reactor for the investigation of materials for gas cleaning can be applied. By this, a feasibility test of the gas cleaning can be realized in direct comparison to the detailed composition of the applied metallurgical gas determined with the PTR-MS technique. Furthermore, the application of two identical reactor setups allows performing investigations with both, pure gases from gas cylinders as well as metallurgical gases simultaneously under similar conditions for a direct comparison.

The product gas streams of the catalytic reactor setups are analyzed by means of gas chromatography. The gas

chromatographs (GC) from Agilent (7890B Series) are equipped with a custom-made method for separation and quantification of all components in the product gas stream with respect to synthesis gas reaction like, e.g., methanol synthesis. They are equipped with two sample loops, four separation columns, which are connected by several switching valves for adjusting the separation method as well as a flame ionization detector (FID) and two thermal conductivity detectors (TCDs) for detection and quantification of the components. The first sample loop is flushed with a HP PLOT U and a Molsieve 5A column. Here, helium is used as a carrier gas. While the permanent gases  $N_2$ , Ar,  $H_2$ , CO, and  $CH_4$  are set in bypass on the Molsieve column,  $CO_2$  and  $H_2O$  as well as the organic substances such as methanol are separated on the Plot column and determined with the FID detector. Afterwards, the Molsieve column is switched online again for the separation of the permanent gases, which are determined by a TCD detector. Because of similar heat capacities of He and  $H_2$ ,  $H_2$  cannot be quantified at this stage. Therefore, for the second sample loop  $N_2$  is used as carrier gas. When the permanent gases passed a HayeSep column, this column is switched to the vent to avoid strong adsorbing substances entering the Molsieve column. Again, the permanent gases are separated on Molsieve column and quantified by means of a TCD detector, but with special respect to  $H_2$ .

Besides the analysis of the product gas streams from the catalytic reactor setups, the GC is integrated in the overall interconnection of the laboratory container. This allows also the analysis of predominantly the main components of the metallurgical gases to increase the flexibility of the analytical devices installed in the laboratory container.

#### 4 Installation on the Steel Mill and First Measurements

After completion of all construction work, the HüGaProp containers were installed at the steel mill plant of thyssenkrupp Steel Europe AG in Duisburg. The sampling point shown in Fig. 6 was chosen because at this point coke oven gas and blast furnace gas are directly available and basic oxygen furnace gas can be made accessible by the installation of a connection gas line. Furthermore, general safety issues at the steel mill as well as the distance to the railways were considered for the determination of the optimal sampling point to avoid high vibration effects and, therefore, disturbance of the measurements.

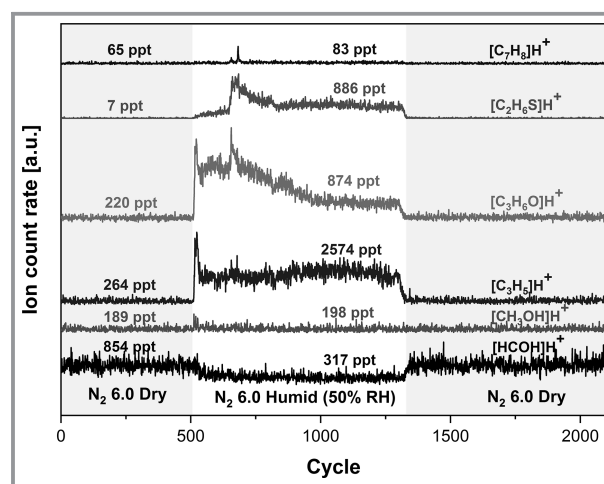


**Figure 6.** HüGaProp containers at the steel mill plant of thyssenkrupp Steel Europe in Duisburg.

Prior to the online measurement of the metallurgical gases the functionality of all components in the laboratory container was tested followed by method optimization and calibration of the PTR-QiTOF. Here, for the first online measurement with coke oven gas the main parameters of the PTR-QiTOF were optimized to figure out the best parameters for the measurement of these complex gas mixtures. In addition, the characterization of selected trace components was evaluated. The individual components are determined and quantified based on their isotopic pattern and their precise protonated mass. However, this requires extensive calibration experiments and knowledge of the reaction rate constants of the proton transfer reaction, at least for about 100 essential substances.

For calibration, commercial test gases with a concentration of 1 ppm for all components are used. During the calibration, the background is first measured with nitrogen (6.0, 99.9999 % purity, pre-filtered) and then the test gases are diluted with nitrogen, so that different concentration levels are obtained (e.g., 5 point calibration). Because some substances could strongly adsorb on the metallic surfaces of tubing and instrument, at each concentration level a waiting time is necessary until an equilibrium is achieved and a

stable signal of such substances can be determined. Fig. 7 shows time series of common VOCs of a background measurement using nitrogen under dry and humid conditions with the PTR-QiTOF. It can be seen that the background signals are humidity dependent, which complicates the typical background subtraction procedure and may result in misinterpretations and especially in misestimations. Therefore, prior to the measurements of the metallurgical gases a careful study of the background was carried out and a straightforward method for the differentiation of possible artefacts such as parasitic ions, memory effects and real gas contaminants and their humidity dependency was developed [17]. Only after having a good understanding of the dynamic of background signals in PTR instruments, estimations of real gas measurements could be safely made.



**Figure 7.** Time series of a background measurement using nitrogen 6.0 under dry and humid conditions with the PTR-QiTOF.

Tab. 2 shows the calibration results measured with the PTR-QiTOF using  $\text{H}_3\text{O}^+$  as primary ion for some substances contained in the commercial gas standard TO-14A Aromatics Mix (14 components). The sensitivities observed are roughly in accordance with previous results [24] and show an excellent linearity response until 300 ppb. However, a good linearity can be achieved up to 1000 ppb. Although for the characterization of the metallurgical gases a complete screening of the mass range up to  $m/z = 800$  is necessary for a non-target analysis, the observed limit of quantification values (LOQ) are good and enable also the online measurement of small concentration fluctuations of the metallurgical gases. Since PTR-MS is a semi-quantitative technique, calibration is not necessary for quantification if the collision reaction rate constant for a specific compound under specific E/N and humidity conditions is known, thus, avoiding the use of expensive commercial gas standards, which might even not possible for some exotic and highly toxic compounds.

During the method development of the PTR-QiTOF additional offline measurements using clear and aluminum-

**Table 2.** Calibration results of the gas standard TO-14A Aromatics Mix using  $\text{H}_3\text{O}^+$  as primary ion under dry conditions.

Component	Chemical formula	Protonated mass [ <i>m/z</i> ]	LOD [ppt]	LOQ [ppt]	Sensitivity [ncps/ppbv]	R <sup>2</sup>
Benzene	$[\text{C}_6\text{H}_6]\text{H}^+$	79.05428	41.57	138.58	549.21	0.9988
Toluene	$[\text{C}_7\text{H}_8]\text{H}^+$	93.06988	52.65	175.51	317.91	0.9987
Styrene	$[\text{C}_8\text{H}_8]\text{H}^+$	105.06988	34.39	114.62	466.95	0.9973
Ethylbenzene	$[\text{C}_8\text{H}_{10}]\text{H}^+$	107.08552	13.85	46.17	1298.92	0.9985
m-Xylene	$[\text{C}_8\text{H}_{10}]\text{H}^+$	107.08552	13.90	46.35	1286.31	0.9985
p-Xylene	$[\text{C}_8\text{H}_{10}]\text{H}^+$	107.08552	13.98	46.60	1286.31	0.9985
o-Xylene	$[\text{C}_8\text{H}_{10}]\text{H}^+$	107.08552	13.75	45.84	1311.79	0.9985
Chlorobenzene	$[\text{C}_6\text{H}_5\text{Cl}]\text{H}^+$	113.01528	31.18	103.92	316.72	0.9987
1,2,4-Trimethylbenzene	$[\text{C}_9\text{H}_{12}]\text{H}^+$	121.10117	25.90	86.34	806.03	0.9985
Mesitylene	$[\text{C}_9\text{H}_{12}]\text{H}^+$	121.10117	25.54	85.12	822.17	0.9985
1,2-Dichlorobenzene	$[\text{C}_6\text{H}_4\text{Cl}_2]\text{H}^+$	146.97629	8.41	28.04	1129.82	0.9986
1,3-Dichlorobenzene	$[\text{C}_6\text{H}_4\text{Cl}_2]\text{H}^+$	146.97629	7.96	26.53	1151.13	0.9986
1,4-Dichlorobenzene	$[\text{C}_6\text{H}_4\text{Cl}_2]\text{H}^+$	146.97629	7.86	26.19	1151.16	0.9986
1,2,4-Trichlorobenzene	$[\text{C}_6\text{H}_3\text{Cl}_3]\text{H}^+$	180.93732	30.35	101.15	336.32	0.9982

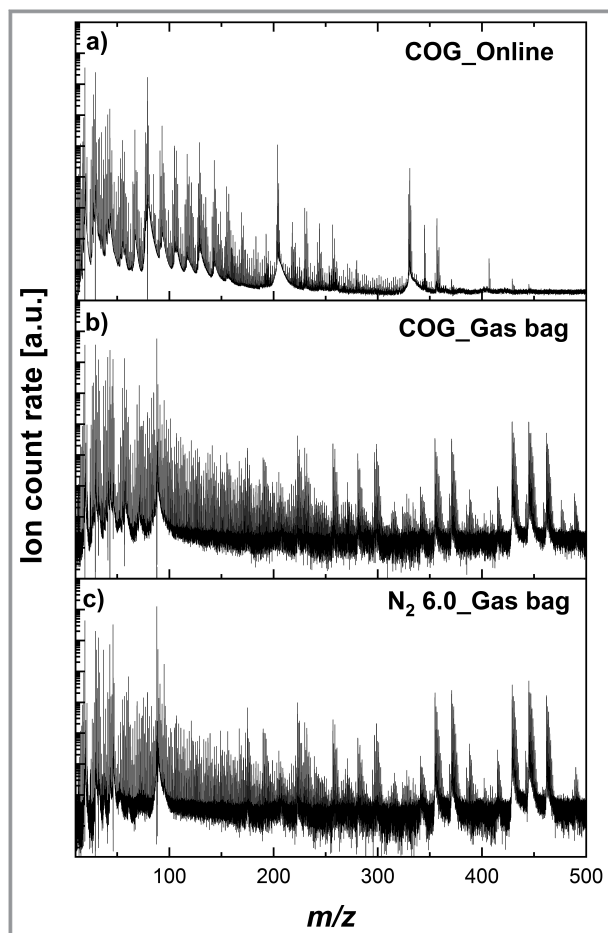
coated Tedlar<sup>®</sup> gas bags were carried out and compared to the online measurements. Due to the high sensitivity of the PTR-QiTOF, it was found that both types of Tedlar<sup>®</sup> gas bags exhibited relatively high background signals (Fig. 8), although a recommended time-consuming conditioning procedure [11] was followed before sampling. The main background signals were assigned to typical siloxanes, but many nitrogen-containing compounds were also found. Even though the background signals of the coated gas bags were in general lower than those of the clear gas bags, both kind of bags showed signals for compounds, which could interfere with compounds of interest in the three metallurgical gases. These findings are in contrast to previous results carried out with landfill gases [26] and breath gas matrices [27], where this kind of interferences were not reported, most likely due to the lower sensitivity of the analytical instruments used in comparison to the here applied PTR-QiTOF. Although the samples with the Tedlar<sup>®</sup> gas bags were undiluted in comparison with the online measurements where dilution factors between 600–800 were used, significant losses were observed. In the *m/z* region 100–200 the signals of many compounds exhibited significant reduction compared to the online analysis, which results in poor recoveries, even at short storage times (about 2 h). Therefore, this kind of sampling was discarded and only online analyses will be applied in the future. Here, in long-term measurement campaigns the three raw metallurgical gases are continuously measured, so that changes in operating conditions and the related fluctuations in the concentration of selected substances can be recorded. This information will serve as the basis for the optimization of the gas clean-

ing to provide suitable gases for the envisaged synthesis gas processes.

As an example for a long-term campaign with the PTR-QiTOF the time-depending concentrations of toluene and acrylonitrile in coke oven gas are shown in Fig. 9 for a selected period. In a 4 h section with a time resolution of 1 s the concentrations of both compounds were relatively constant (Fig. 9a). Due to the high temporal resolution, even small fluctuations can be determined. On the other hand, Fig. 9b shows the time series of average measurements of 4 h each for toluene and acrylonitrile over a period of 52 h. This concentration trend can be assigned to changes in the steel making process and give valuable information for the subsequent utilization of this kind of off-gases. The determination of substances like acrylonitrile are of paramount importance since this kind of nitrogen compounds can easily polymerize on the surface of materials applied in the gas cleaning or on a catalyst in a subsequent chemical process. So far, in our measurements with the three primary ions  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$ , and  $\text{O}_2^+$ , acrylonitrile shows to be measurable only with  $\text{H}_3\text{O}^+$ . This finding confirms also the milder conditions during the protonation process in comparison to the charge transfer processes and, therefore, the use of the three primary ions expands the measurement range of the applied instrument. By applying the developed method for the online measurements on-site, a more reliable information can be obtained compared to offline sampling with gas bags, where unreproducible effects might lead to misinterpretations of the trace concentrations in the metallurgical gases.

The information gathered in the HüGaProp container with the real gases about individual trace components and



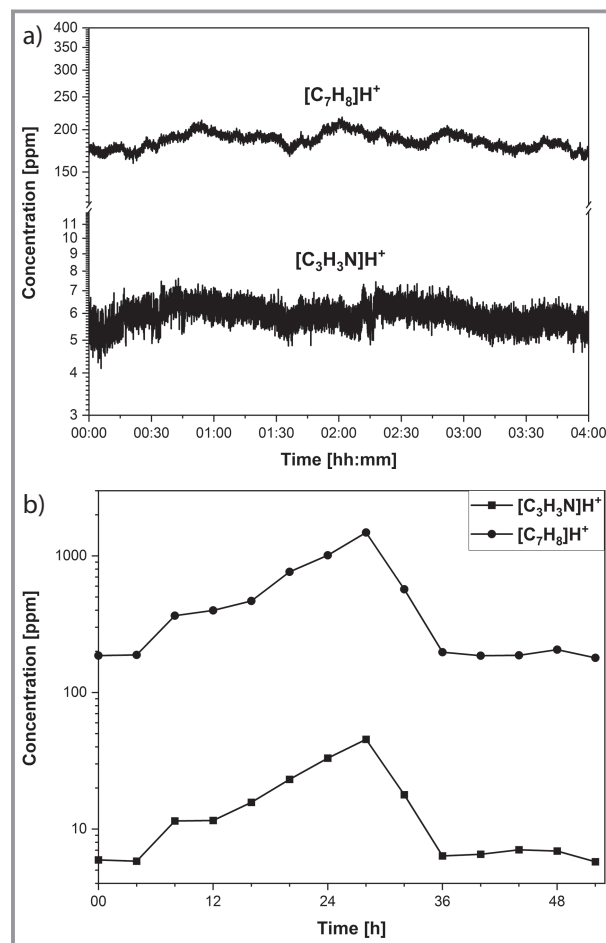


**Figure 8.** Mass spectra of coke oven gas measured online (a), with a Tedlar® gas bag (b) and a background spectrum of a Tedlar® gas bag filled with nitrogen 6.0 (c) using  $\text{H}_3\text{O}^+$  as the primary ion with the PTR-QiTOF.

trace component groups, together with instrument parameters, e.g., ionization conditions, sensitivity factors and mass spectra, will help to build up a spectra database. For this purpose, a new type of gas mixing plant is being built in addition [28], which can be simultaneously used as a gas calibrator for the study of model compounds under dry and humid controlled conditions to better understand the fragmentation patterns of compounds of interest found in the online measurements. This additional method development will help to further improve the PTR-QiTOF measurements performed in the HüGaProp container on-site and solve upcoming issues coming along with the detailed analysis of those complex gas mixtures.

## 5 Conclusions

The lack of detailed information on the composition of metallurgical gases especially with respect to trace components and their time-depending concentrations as well as their dependence on the overall gas composition requires



**Figure 9.** a) Time series with 1 s resolution of acrylonitrile and toluene in a 4 h measurement of coke oven gas using  $\text{H}_3\text{O}^+$  as primary ion with the PTR-QiTOF. b) Time series of 4 h averages for acrylonitrile and toluene in coke oven gas using  $\text{H}_3\text{O}^+$  as primary ion.

detailed online measurements to determine the feasibility of a further utilization of these gases as raw material. Their possible application as feedstock for chemical industry will have a high potential to reduce the  $\text{CO}_2$  emissions from steel industry and, therefore, to essentially contribute to a global sustainable strategy. Within the project HüGaProp the necessary infrastructure was developed to measure gas traces at the ppt-level in complex gas matrices online without the need of previous separation methods. With the high-end PTR-QiTOF technique unknown compounds can be identified without the need of spectral libraries. Based on an optimized method for the PTR-QiTOF regarding instrumental artefacts, possible interferences with artefacts are avoided. By knowing the dynamics of the background in the PTR-QiTOF and its humidity and collision energy dependency, misestimations of critical substances can be minimized as these would have a direct impact in over- or underestimations of, for instance, expensive purification systems. Simultaneously, the main gas components are determined via gas chromatography to obtain a whole picture

about eventual gas fluctuations and possible dependencies. This information will allow the design of processes on an industrial scale for the utilization of these gases as raw material. Furthermore, with the presented infrastructure direct exposure measurements can be performed on-site to check the feasibility of gas cleaning strategies or the subsequent application of synthesis gas processes for the production of, e.g., methanol. This online gas characterization in combination with the catalytic test setups is now applied within the project Carbon2Chem<sup>®</sup> to determine the feasibility of metallurgical gases as raw material. As the presented infrastructure is not directly related to steel industry, it also can be used generically for all applications in which complex gases, e.g., from stationary CO<sub>2</sub> emission sources such as coal power generation plants, waste incineration plants, cement industry or biogas plants are considered as feedstock for chemical industry.

The authors would like to thank the Max Planck Society for financial support as well as the Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung, BMBF) for funding the projects HüGaProp (Hüttengasproperties – wissenschaftliches Projekt zur Problematik der Verwendung von CO<sub>2</sub>-Abgasströmen aus dem Hochofen (Hüttengas) bei der Katalyse, Grant No. 03EK3546) and Carbon2Chem (Subproject L0, Grant No. 03EK3037C). The authors would also like to thank all the colleagues from the electrical, electronic, IT and purchase department for the support during the construction phase of the containers. A special thanks to Mr. Lesch, our gas fitter for the valuable feedback regarding the construction of gas infrastructure. Open access funding enabled and organized by Projekt DEAL.

### Symbols used

$m/z$	[-]	mass-to-charge ratio
R	[-]	gas phase analyte
[R]H <sup>+</sup>	[-]	protonated gas phase analyte

### Abbreviations

BFG	blast furnace gas
BMBF	Bundesministerium für Bildung und Forschung
BOFG	basic oxygen furnace gas
BTEX	benzene, toluene, ethylbenzene, xylene
COG	coke oven gas
cps	counts per second
E/N	reduced electric field
FastGC	fast gas chromatography
GC	gas chromatograph

GC-FID/TCD	gas chromatography flame ionization detector/thermal conductivity detector
HüGaProp	Hütten-Gas-Properties
LOD	limit of detection
LOQ	limit of quantification
MCS	Medium-Control-Systems
MFC	mass flow controllers
MPI-CEC	Max Planck Institute for chemical energy conversion
MPV	multiport valve
PAHs	polycyclic aromatic compounds
PCBs	polychlorinated biphenyls
PCDD/Fs	Polychlorinated dibenzodioxins/dibenzofurans
P&ID	Piping and instrumentation diagram
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
PTR-MS	proton transfer reaction mass spectrometry
PTR-QITOF	proton transfer reaction quadrupole interface time-of-flight mass spectrometer
PTR-TOF-MS	proton transfer reaction time-of-flight mass spectrometry
SRI	selective reagent ionization
TO-14A	toxic organic compounds method Aromatics Mix (14 components)
TOF	time-of-flight
UPS	Uninterruptible power supply
VOCs	volatile organic compounds

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