Design and Implementation of a Gas Generating System for Complex Gas Mixtures and Calibration Gases

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A test gas generation system for complex gas mixtures designed to mimic real industrial gas matrices with traces raging from low pptv to high ppmv level and minor and main components ranging from low to high percentage levels with variable relative humidity levels (0–80 % RH) is presented. It combines different gas generation methods to study fragmentation patterns under controlled conditions by means of a proton transfer reaction time-of-flight mass spectrometer, the application of alternative feedstocks in catalytic processes as well as the performance of gas purification and conditioning processes.

Keywords: Carbon2Chem®, Flue gas characterization, Gas generator, Gas traces, Metallurgical gases

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1 Introduction

The global framework set out by the Paris Agreement to mitigate greenhouse gas (GHG) emissions and limit global warming is a predominant socioeconomic challenge for many high-emission industries. In recent years, technological improvements and the development of more efficient processes have steadily reduced the energy demand and the emission of GHG [1, 2]. Meanwhile, the thermochemical efficiency of some of the current technologies is almost optimal. There is virtually no scope to reduce GHG emissions by introducing process innovations [3]. Therefore, further reduction may only be obtained by radical new production processes or by integrated production networks where inevitable flue gas emissions from one production serve as raw material of another chemical production [1, 4, 5].

In the envisioned concept of the Carbon2Chem® project [1, 2], emissions from steel industry are envisaged as raw material for the production of useful chemicals including ammonia (NH_3), methanol (CH_3OH), higher alcohols and polymers using electricity and energy generated from renewable sources [6–10]. Steel mill flue gases are exhaust gases generated during coking and combustion processes. Their composition depend on the type of raw materials and process conditions, e.g., the fuel/air ratio, fuel feed rate, temperature, mix of solid reagents applied, the interactions among different trace elements both during combustion and post-combustion [11]. Three different process stages from coal to steel provide three different gas types: coke oven gas (COG), blast furnace gas (BFG) and basic oxygen furnace gas (BOFG) which differ in their composition [1]. The main components of blast furnace and basic oxygen gases are CO_2, CO, and N_2. Coke oven gas mostly contains H_2 and CH_4 [1]. Some minor traces of catalyst poisoning compounds such as sulfur-, nitrogen- and halogen-containing compounds, metals, cyanide compounds, polycyclic aromatic hydrocarbons (PAHs), BTEX-aromatics (benzene, toluene, ethylbenzene, and xylenes), etc. can be present [12, 13]. The successful control and use of steel mill flue gases essentially depends on the proper understanding of their chemical and physical nature and of the concentration at the source of emission [14]. Furthermore, the impact of all components present in these gases on gas purification as well as catalytic processes has to be considered for their application as feedstock for the synthesis of bulk chemicals. Therefore, a crucial task in the Carbon2Chem® project is to provide simulated complex gas mixtures under well-controlled conditions mimicking these steel mill flue gases to develop an adequate enhanced gas purification as well as

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performing feasibility studies for the envisaged catalytic processes with respect to the available feed gases and process concepts. Feasibility studies of gas purification as well as catalytic processes, such as methanol synthesis [9, 10, 15, 16] using such carbon sources require a thorough analysis of possible poisoning mechanisms with model substances under similar conditions as in industrial plants. This poses the challenge of mimicking highly complex gas matrices with temporally fluctuating concentrations. Here, one important task will be more detailed deactivation studies considering trace compounds that might be present even in the purified feed gases. Most studies regarding catalyst deactivation mainly focus on the mechanisms of deactivation of single substances but competing effects occurring in complex gas mixtures are often ignored [17–20]. Additionally, the influence of the gas matrix on the physical and chemical properties affecting the mechanism of the catalyst deactivation is normally neglected. Therefore, the ability of providing corresponding complex feed gases including minor and trace components of interest will enable more detailed studies on the poisoning and matrix effects of these components and component mixtures as well as will allow a further judgement on the applicability of the chosen concepts and help to optimize these for realization.

Besides the direct investigation of process concepts applying realistic gas mixtures, these defined gas mixtures are required to optimize and calibrate the analytical techniques applied for the detailed characterization of the real steel mill flue gases before and after a purification. Conducting a systematic study on crude gas composition of steel mill process gases in combination with the direct application of these gases in gas purification as well as catalytic processes can deliver important insights and knowledge toward design of stable and active catalysts and also efficient flue gas purification technologies. The information of the characterization of traces in the three metallurgical gases gathered on-site at a steel mill plant [21] served as a basis for the design of the complex gas generating system.

The main advantages of the chosen analytical method for analyzing complex gas mixtures, a proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS) in comparison to conventional gas chromatography are high sensitivity, high mass resolution, high time resolution (100 ms) and low ionization-induced fragmentation. In contrast, for the analysis of volatile organic compounds (VOCs) by, e.g., GC-methods, a pre-concentration step is often necessary to increase sensitivity [22]. The most common pre-concentration methods are cryogenic trapping [22], impingers [23], and sorbent enrichment [24, 25]. This pre-concentration methods result in more time consuming procedures and less flexibility for the deployment at site where online measurements are required. One drawback applying proton transfer reaction mass spectrometry (PTR-MS) is the differentiation between isomers, e.g., between ethanethiol and dimethylsulfide, both with the chemical formula C_2H_6S [26, 27]. However, if the mass resolution is higher than 4000 $m/\Delta m$ isobaric compounds with the same nominal mass can be separated and, as pointed out by Graus et al. [28], with a resolution $m/\Delta m$ of at least 4000–5000 the identification of unknown substances by sum-formula assignments is possible. An additional drawback is that ions from different compounds (fragment ions) can overlap in PTR-MS and prevent an unambiguous identification of VOCs in a complex mixture [29]. On the other hand, PTR-MS is an online technique and the instruments are deployable to the sample source, so that no sampling with for instance Tedlar® gas bags is required, thus, avoiding typical losses of labile compounds and low recoveries [30–32]. Moreover, PTR-MS is a semi-quantitative technique, which means that if the collision reaction rate constant (k_i) for a specific compound is known a quantification can be carried out without the need of gas standards, which for exotic and highly toxic compounds is a big advantage. Concentrations in PTR-MS instruments can be calculated according to Eq. (1)

$$VOC_{[\mathrm{ppb}]} = \frac{\begin{array}{c}[VOC]\mathrm{H}^{+} \cdot 10^{9}U[\mathrm{V}] \cdot 2.8\left[\dfrac{\mathrm{cm}^{2}}{\mathrm{V_s}}\right] \cdot 22400 \cdot \\ 1013^{2}[\mathrm{mbar}^{2}](273.15 + T_\mathrm{d})^{2}[\mathrm{K}^{2}]Tr_{\mathrm{H_3O^+}}\end{array}}{\begin{array}{c}k_\mathrm{i}\left[\dfrac{\mathrm{cm}^{2}}{\mathrm{s}}\right]9.2^{2}[\mathrm{cm}^{2}] \cdot \mathrm{H_3O^+} \cdot p_\mathrm{d}^{2}[\mathrm{mbar}^{2}] \cdot \\ 6.02210^{23} \cdot 273.15^{2}[\mathrm{K}^{2}] \cdot Tr_{([\mathrm{VOC}]\mathrm{H}^{+})}\end{array}} \tag{1}$$

To enable the application of PTR-MS for the online analysis of complex gas mixtures, it is crucial to understand the fragmentation patterns under controlled conditions e.g. at different humidity levels to validate the obtained analyses of the steel mill flue gases. As it has been shown [33–35], humidity has a significant influence on the protonation reaction in PTR instruments. As until now no PTR mass spectra databases are available, it is necessary to build up an own database in order to retrofit the estimations made on-site to avoid under or overestimations, which may a have a severe impact on the design of purification systems and thus on investment costs. A correlation of the results from on-site gas analysis with catalytic and purification data from lab-scale experiments will allow to identify the optimal catalyst and process conditions for the industrial-scale application. Herein, strategies for fabrication of a gas generating system will be elaborated, which will mainly cover the following aspects required for a validation of the applicability of the chosen concepts:

1) evaluate process feasibility and catalyst poisoning due to exposure to certain compounds in flue gases;
2) assess gas purification technologies;
3) optimize and calibrate analytical techniques, particularly proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS) for analyzing low detection limit concentration (10-100 pptv) of compounds in steel mill flue gases.

2 Test Gas Generation Systems

In the gas generating system introduced here, gas mixtures of main and minor components can be enriched with VOCs at trace levels (pptv to ppbv) under dry or humid conditions to simulate gases after a purification process and in order to mimic the measurements conditions at the technical center of Carbon2Chem®[8]. This will enable the study of more realistic deactivation scenarios and help the optimization of the PTR-TOF-MS analysis. Therefore, the gas generating system provide gases with a highly defined composition, which can also be used as gas standards. As it has been established [36, 37], a gas mixture can be called standard if at least the following requirements are met:

- constant concentration of the analyte;
- knowledge of concentration of the analyte in a mixture with an accuracy greater than the accuracy of a device being calibrated;
- ready availability because of a large number of determinations during the device calibration;
- error sources are known.

There are generally two major classes of techniques to generate standard gas mixtures under controlled conditions: static techniques and dynamic techniques [36, 38, 39]. In static techniques various gases are dosed gravimetrically, monometrically and volumetrically, and added successively one component after another into close housings such as high-pressurized gas cylinders with previous wall treatment [40]. In dynamic mixing techniques, gases are mixed continuously on site from pure gases. Dynamic gas mixing techniques are applied when there is a need to produce precise standard gas mixtures based on the desired process conditions and frequent adjustments of the composition of the gas mixture are required [38]. Furthermore, dynamic methods inherently produce more homogeneous gas mixtures [40].

Fig. 1 shows an overview of common techniques of preparation of gaseous standard mixtures. A detailed description of the advantages and disadvantages of the techniques shown in Fig. 1 can be found in [36, 40, 41]. From all possible dynamic methods the injection method, which can be carried out by injecting liquids (pure or multicomponent solutions) with syringes, motor-driven syringes or syringe pumps into a diluting gas, offers several advantages. The main advantage is the preparation of test gases with a well-known concentration which can be varied in short time by applying different flow rates of the diluting gas [42]. An alternative way is to vary the injection speed of the syringes but care needs to be taken to avoid overloading in the vaporizers, especially for substances with high boiling points. Additionally, if several multicomponent solutions are injected in parallel, the number of compounds that can simultaneously be analyzed is huge. These kinds of systems have been proven to give reliable results even for concentrations at ppb level [43].

Permeation devices provide an excellent method of producing low concentrations of a broad variety of compounds (> 400) in gas mixtures. They usually consist of a short

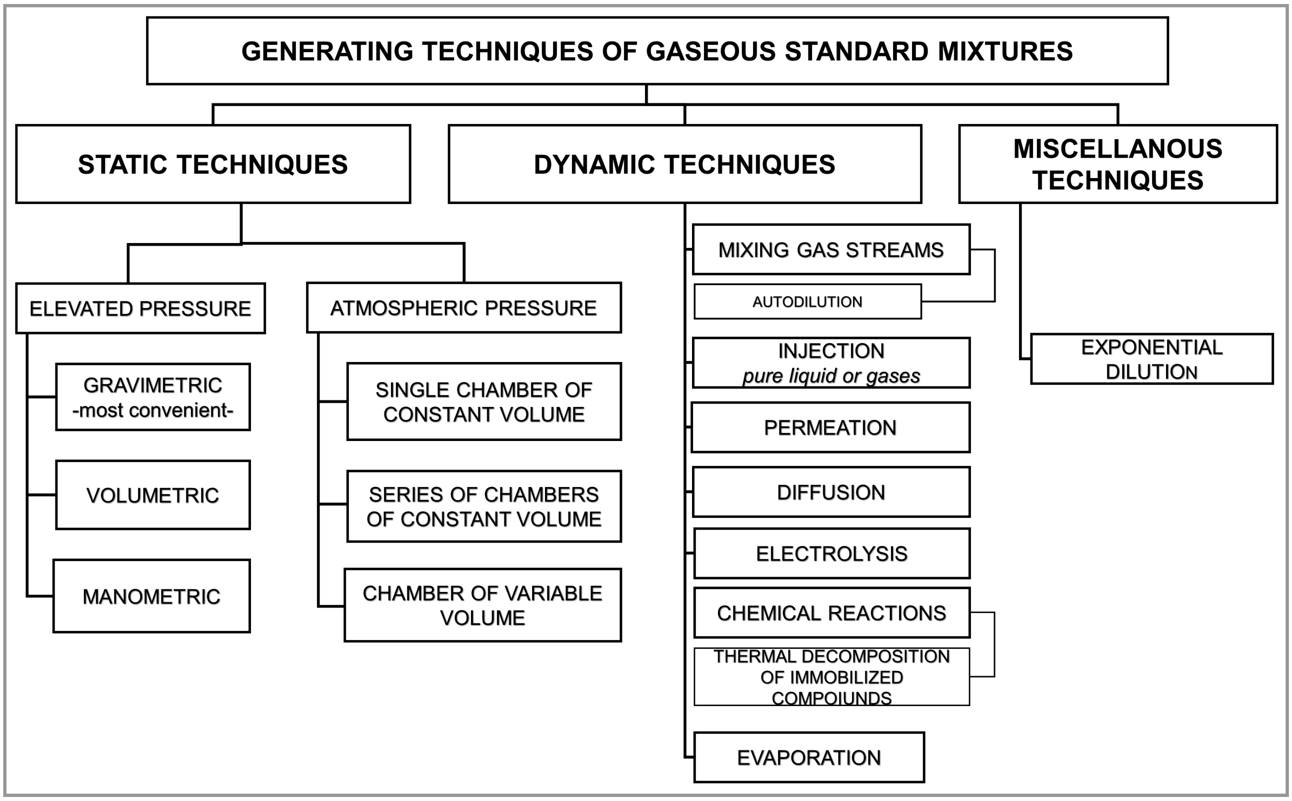

Figure 1. Techniques for preparation of gaseous standard mixtures according to [36].

polymeric tube containing a hermetically sealed desired analyte. The permeation rate of analytes strongly depends on the temperature applied [44]. Generally, for every degree Celsius of temperature increase, the permeation rate increases by 5–10 %. The temperature dependence of the permeation rate (P) is govern by an Arrhenius behavior (Eq. (2)) [45].

$$P = P_0 \exp\left(\frac{E}{RT}\right) \quad (2)$$

The difference in partial pressure between the inner and outer walls is the driving force for the process. In theory, the dissolution of gas into the polymer is governed by Henry's Law of Solubility, and Fick's Law of Diffusion, which can be used to describe the flux of gas through the tube wall. The permeation rate of any gas through a permeation tube of length, L, and radius, r, can be expressed by Eq. (3) [46].

$$q_s = 3\pi r L P_0 \exp\left(\frac{\Delta \mathrm{E_P}}{\mathrm{RT}}\right) \frac{(P_\mathrm{i} - P_0)}{d} \quad (3)$$

where q_s = sample emission rate, P_i = pressure of desired analyte inside the tube, P_0 = pressure of desired analyte outside the tube, d = thickness of the tubes wall.

3 Gas Generating System

The design of the gas generating system is based on data obtained by stoichiometric calculations of steel making flue gases, which suggest more than 250 potential components. These can be classified based on their concentration in three categories: main (5–99 %), minor (0.1–5 %) and trace components (< 0.1 %). The trace component group is the largest category regarding the number of compounds with more than 500 members. It only represents 0.1–1 % of the flue gases compounds and accounts for chemicals including sulfur- and nitrogen-containing organic compounds, alkanes, olefins, aromatics and PAHs. Tab. 1–3 represent some examples for the three categories.

Table 1. Assumed main still mill flue gases components based on [1, 2].

Compound	Chemical formula	Min	Max
		Concentration [%]	Concentration [%]
Hydrogen	H_2 (g)	1	70
Methane	CH_4 (g)	0.01	3.5
Carbon monoxide	CO (g)	4	70
Carbon dioxide	CO_2 (g)	0.2	25
Nitrogen	N_2 (g)	1	60
Oxygen	O_2 (g)	0.01	3

Table 2. Assumed minor still mill flue gases components based on [47, 48].

Compound	Chemical formula	Min	Max
		Concentration [%]	Concentration [%]
Ethene	C_2H_4 (g)	0.001	3
Hydrogen sulfide	H_2S (g)	0.001	2
Hydrogen cyanide	HCN (g)	0.001	2
Ethane	C_2H_6 (g)	0.001	2
Ammonia	NH_3 (g)[a]	0.001	1
Sulfur dioxide	SO_2 (g)	0.001	0.5
Nitric oxide	NO (g)	0.001	0.5
Nitrogen dioxide	NO_2 (g)	0.001	0.5
Benzene	C_6H_6 (l)	0.001	0.5
Toluene	C_7H_8 (l)	0.0001	0.5
o,m,p-Xylene	C_8H_{10} (l)	0.0001	0.5
Ethylbenzene	C_8H_{10} (l)	0.0001	0.5
Styrene	C_8H_8 (l)	0.001	0.5
Hydrogen chloride	HCl (g)[a]	0.001	0.5
Trichloroethylene	C_2HCl_3 (l)	0.0001	0.5

[a] Could alternatively be introduced in an aqueous solution.

The challenge in the design of the gas generating system was essentially to accurately measure and control the flow of gases of the minor and trace components. For example, to add carbonyl sulfide (COS) into gas streams, a mass flow controller (MFC) is needed that can provide a flow of 0.010 mL $\mathrm{min^{-1}}$. Also producing gas streams containing trace amounts of dimethyl sulfide ($(CH_3)_2S$) requires a flow controller that can control 0.0024 g $\mathrm{h^{-1}}$ of this component. No available commercial flow controller can deliver these desired flow rates. Additionally, some of the trace components are solid at ambient conditions. This factor also adds to the complexity of the design. One approach to tackle this technical challenge is to prepare mixtures of the compatible liquid feedstocks. To inject the liquid mixtures into gas streams, flow controllers with lowest flow range of 0.014 mL $\mathrm{min^{-1}}$ can be used. Also, small amounts of organic compounds can be injected into a vaporizer by choosing syringes of defined volumes. An alternative method is the application of permeation devices. Careful selection and engineering of these methods with respect to the compounds of interest enables the production of complex gas mixtures with VOCs concentrations ranging from a few ppt to high ppm level.

A flow diagram of the gas generating system is given in Fig. 2. Additionally, a photograph of the system is shown in Fig. 3 The gas generating system introduced here is a fully automated dynamic gas generating/mixing system, which

Table 3. Examples for assumed trace still mill flue gases components based on [47, 48]. The considered concentration range for these components is 0.00001–10 ppmv each of the total gas flow.

Compound class	Compound
Sulfur-Organic compounds	Methanethiol (CH_3SH), Dimethyl sulfide (C_2H_6S), Ethanethiol (C_2H_6S), Carbon disulfide (CS_2), Thiophene (C_4H_4S), Carbonyl sulfide (COS)
Nitrogen-organic compounds	Acetonitrile (C_2H_3N), Acrylonitrile (C_3H_3N), Methylamine (CH_5N), Formamide (CH_3NO), Acetamide (C_2H_5NO), Pyrrole (C_4H_5N), Pyridine (C_5H_5N)
Alkanes	n-Hexane (C_6H_{14}), n-Decane ($C_{10}H_{22}$), Cyclopentane (C_5H_{10}), Cyclohexane (C_6H_{12})
Olefins	*trans*-1,3-Butadiene (C_4H_6), *trans*-2-Pentene (C_5H_{10}), 1-Hexene (C_6H_{12}), Cyclopentene (C_5H_8), Cyclohexene (C_6H_{10})
Alcohols/Ethers/Phenols/Furans	Methanol (CH_4O), Ethanol (C_2H_6O), Phenol (C_6H_5OH), o,p-Cresol (C_7H_7OH), Dimethylether (C_2H_6O), Furan (C_4H_4O), Tetrahydrofuran (C_4H_8O), 1,4-Dioxane ($C_4H_8O_2$)
Aldehydes/Ketones	Formaldehyde (CH_2O), Acetaldehyde (C_2H_4O), Acetone (C_3H_6O), 2-Butanone (C_4H_8O)
PAHs	Anthracene ($C_{14}H_{10}$), Pyrene ($C_{16}H_{10}$)
Halogenated	1,2-Dichlorobenzene ($C_6H_4Cl_2$), 1,3-Dichlorobenzene ($C_6H_4Cl_2$)
Aromatics	*p*-Cymene ($C_{10}H_{14}$), 1,2,4-Trimethylbenzene (C_9H_{12}), *o,m,p*-Ethyltoluene (C_8H_{10})
Metallic/Organometallic compounds	Nickel tetracarbonyl ($Ni(CO)_4$), Carbonyl selenide (COSe), Thiocarbonyl selenide (CSSe), Mercury (Hg)

was designed and fabricated to satisfy most complex gas mixing requirements in terms of the described feeding criteria (number of components, their concentrations, back flow formation and corrosive compounds), relative humidity (% RH), pressure and temperature (θ). It is a unique and versatile setup, which enables a variety of studies in catalytic reactions, gas purification methods and calibration as well as method development of analytical instruments. The performance and control ranges of the fabricated system are summarized in Tab. 4.

Table 4. Technical specifications of the gas generating system.

Parameters	Value
Flow [L min^{-1}]	0.5–1.0
Temperature Pipelines [°C]	30–250
Temperature evaporator [°C]	60–180
Relative Humidity [%]	0–80
Pressure [bar]	1–60
possible components	>250

A core section of the system for the generation of calibration gases with VOCs traces was developed in collaboration with Inspire Analytical Systems (IAS) GmbH, Oberursel, Germany resulting in the HovaCAL® N 17837-VOC. The multi-component gas generator system for the injection of liquid components is based on a 3-stage dilution concept [43]. By this, also humidification of the generated gas mixtures can be achieved, which is crucial for the method development of the applied PTR-MS technique. Previous studies [33–35, 49–51] indicated that relative humidity (RH%) is a key affecting factor in the behavior of gas measuring systems. It may change measurement sensitivity, offset measurements values, affect peak location in chromatograms and interfere with actual measurements. Furthermore, real steel mill flue gases contain relative humidities. Thus, it is crucial to perform multiple calibration points using the same concentrations, but at various levels of RH%. For gas streams containing mixtures of trace concentrations, the divided dilution flow is superior compared to the direct injection [52]. Here, the water vapor is mixed with the highest flow rate gas stream (dilution gas). Splitting the dilution flow before addition of the component allows one portion of the dilution gas to be saturated with water vapor avoiding contact of the component with liquid water. Rejoining the streams creates a humidified gas stream. The RH% of the final mixture can be adjusted by the wet-to-dry gas flow ratio, adjusting the saturation temperature of the wet gas and adjusting the saturation pressure of the wet gas.

In addition to the injection of liquid components, for challenging cases like highly corrosive substances, liquids with a high boiling point or solids, a permeation gas unit from VICI, Switzerland is applied. Besides providing designed feed gases for performance tests in catalytic reactor setups and gas purification units one focus of the overall setup is to mimic the three metallurgical gases in order to study the fragmentation patterns of relevant VOCs in different gas matrices under dry and humid conditions. This will help the analysis of the real gases carried out on-site at the still mill plant from ThyssenKrupp Steel Europe in Duisburg, Germany, using a PTR-TOF-MS instrument [21]. All these experiments will be carried out in the Carbon2Chem®

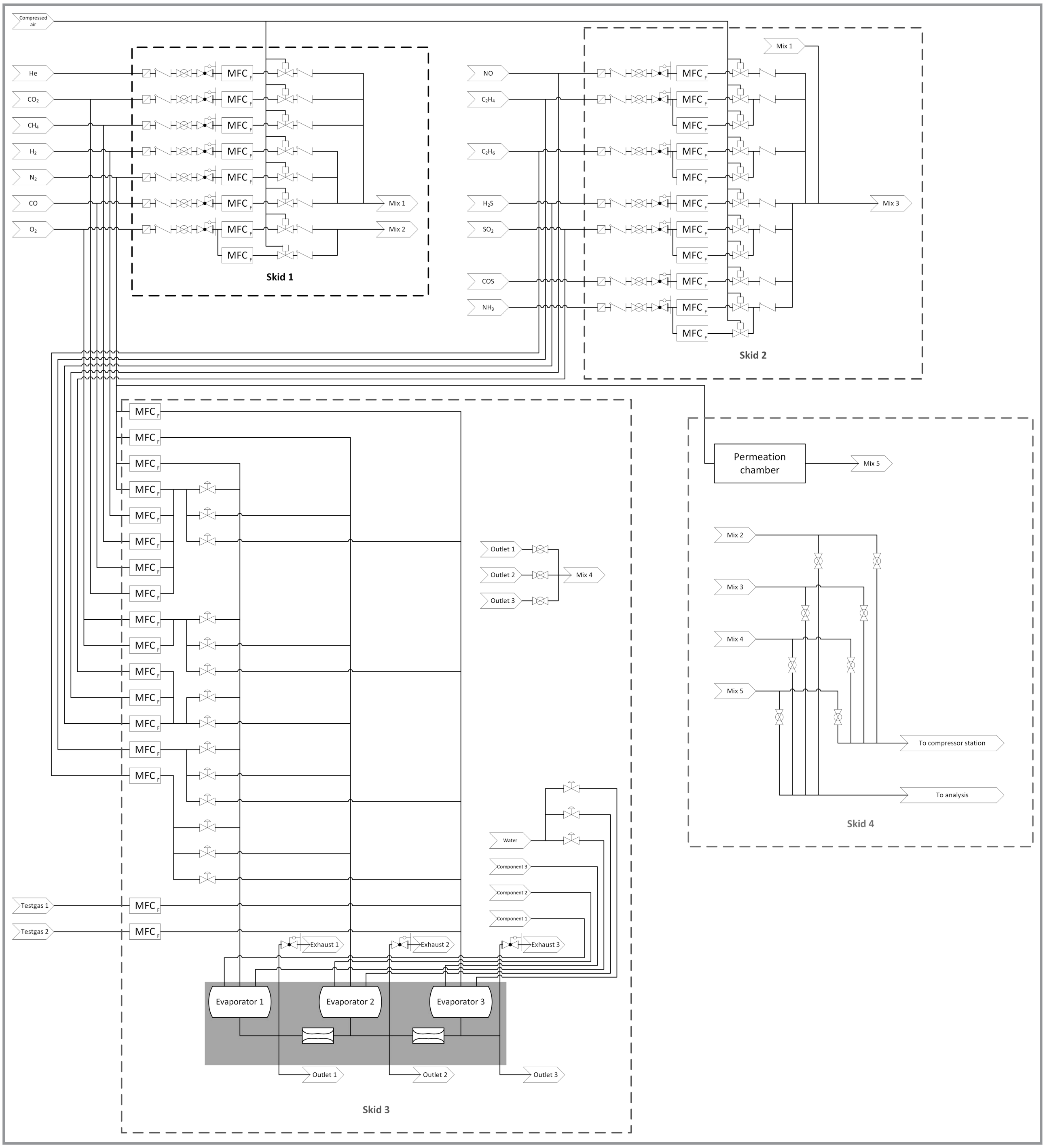

Figure 2. Flow diagram of the test gas generating system.

laboratory located at the facilities of the Fraunhofer Institute UMSICHT in Oberhausen, Germany.

The working pressure of the system is 1 bar, but by an additional two-stage compression unit the mixed gas can be provided with a pressure of up to 60 bar to subsequent units, such as purification units and catalytic reactor setups. The whole system comprises 37 mass flow controllers (MFC) from Bronkhorst Deutschland GmbH. For some components, e.g., oxygen, two different MFCs are needed in order to cover a wider range of concentrations. All pneumatic valves are actuated using compressed air. Additional check valves ensure cross contamination between the components is avoided. Special coated piping (SilcoTek® 2000) was used to prevent adsorption of compounds, e.g., sulfur

Figure 3. External view of the test gas generating system at the Carbon2Chem® Laboratory. From left to right: skid 1, 2, 3, and 4.

and ammonia [53] on metallic surfaces within the pipes. Hence, the use of coated piping is preventing false concentrations due to memory effects in transfer piping as well as minimizing unwanted decomposition reactions at metal surfaces, especially in the presence of humidity [54], which results in the production of corrosive compounds. This is important especially for the simulation of short-term pulses of fluctuating concentrations.

Since not all components can easy be mixed directly and to avoid backflowing especially for the trace components the system was built in a modular way with certain mixing points for main, minor and trace components. This also results in a high level of flexibility for cases where simultaneously reactor setups, purification systems and the analytical instruments have to be fed with different gas matrices enabling several points of withdrawal. Furthermore, a modular concept allows easily temporal or permanent changes and adjustments if further additions are required. Therefore, it was built in four skids. Shortly, in skid 1, the main components are premixed and this mixture can be subsequently mixed with the minor components in skid 2. The focus of skid 3 is on the injection of liquid components into the gas stream, while skid 4 is equipped with a permeation unit for the introduction of components solid at ambient conditions as well as contains the chasing for the distribution of the generated gas streams. For example, if VOCs are not needed for investigations of the catalytic reactions or purification processes, main and minor components are mixed in skid 1 and skid 2 and provided for these via the compression unit while in parallel method development with VOCs from skid 3 and skid 4 with a PTR-TOF-MS can be performed.

The operation of the setup is controlled by a PC that sends the set-points to the peripheral components and receives the measured data via TCP/IP (Transmission Control Protocol/Internet Protocol), which guarantees fast and correct synchronization between entered settings and measured data. The control system was built in 19″ racks located at the bottom of the 4 skids.

The control software is based on a LabVIEW® Library (National Instruments). The software allows the control of all necessary parameters, such as gas lines and evaporator temperatures, gas flows, valve switching, humidity level, injection rates and set concentrations. Because of reciprocal dependencies on concentrations, humidity, nitrogen content and total flow, the software informs about out-of-range values, since the allowed ranges are variable. Single-run experiments or sequences can be programmed, in order to execute experiments with changing conditions or repetitions. All flows and concentrations entered are related to standard conditions (0 °C and 1013 hPa). Some parameters are fixed for safety reasons, such the min and max flow levels, the temperature of the capillaries connecting the vaporizers. Special care has been given for oxygen, which cannot exceed an explosion limit. The Set points of all parameters like flows, temperatures, concentrations, etc. can be displayed and saved as a text file. Additionally, pre-settings can be saved and uploaded.

Finally, the generated gases are analyzed applying a gas chromatograph (Agilent 7890B Series) for the analysis of the main components as well as minor components with higher concentrations, while for the analysis of the trace components the system is equipped with a proton transfer reaction-time-of-flight-mass spectrometer (PTR-TOF-MS; IONICON PTR-TOF1000). Thanks to its short response time (< 1 s) and low detection limits (pptv), PTR-TOF-MS has proven successful for complete and real-time monitoring of highly resolved mass spectra of volatiles organic compounds (VOCs) without the need to use any pre-separation techniques such as gas chromatography. It also allows unambiguous identification of isobaric compounds via sum formula information [28, 55]. The key advantages of PTR-TOF-MS are: no sample preparation, soft chemical ionization, which reduces fragmentation and spectral complexity, a much higher mass range compared to conventional mass spectrometers, a complete mass spectrum in a split second and the higher mass resolution and sensitivity, which multiply the analytical information contained in the spectra [56]. However, the main obstacle for its use in this contemporary work, analyzing VOCs emanating from steelmaking industry, is the size and complexity of the data sets generated and the lack of clear receipts for data analysis. Basically, there is no extensive, searchable database to compare the spectrum with. Therefore, to make sure that the information obtained from PTR-TOF-MS is indeed reliable, calibration of measurement instruments and validation of analytical procedures are required.

A preferred approach is to use standard gas mixtures (SGM) or reference material (RM). According to the ISO/-IEC Guide 30 [37], a reference material is a material or substance whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method or the assignment of values to materials. There are some basic characteristics that SGM / RM must fulfill in order to be useful as follows:

- Homogeneity and stability,
- Similarity to real samples.

The use of SGM with matrix compositions and analyte concentrations similar to those found in steel mill flue gases allows to obtain very reliable result.

4 Results and Discussion

While mixing pure gases is a standard application, the introduction of low levels of impurities into a mixture is, depending on the required substances, the most difficult task to provide the desired complex gas mixtures. Therefore, the focus for the first validation was set on the feeding of trace components under dry and humid conditions. Toluene was chosen as benchmark due to its non-polar character and its proton affinity (784 kJ mol^{-1} [57]), which lies in between the proton affinities of H_3O^+ (691 kJ mol^{-1}) and the first water cluster, $[H_2O]H_3O^+$ (808 kJ mol^{-1}) [58]. It means, it can undergo protonation from the H_3O^+ ion but not from the $[H_2O]H_3O^+$ ion.

Due to the highly demanding requirements of the chosen online analytics and the catalyst systems, which can deactivate in short time with specific substances at ppb level, the gas generating system was checked for intrinsic contaminations under dry and humid conditions using online monitoring with two PTR-TOF-MS instruments. The first one, a PTR-TOF1000 from IONICON, Innsbruck, Austria has a resolution of about 1000 $m/\Delta m$ and the second one, a proton transfer reaction quadrupole interface time-of-flight mass spectrometer (PTR-QiTOF) [27] also from IONICON exhibits a mass resolution of about 6000 $m/\Delta m$. This high resolution enables the identification of unknown compounds by formula and the separation of isobaric compounds. Measurements were conducted using H_3O^+ as primary ion. H_3O^+ ions are generated in the hollow cathode ion source using a water vapor flow of 7 mL min^{-1}. The drift tube parameters were set to 900 V, 3.50 mbar and 60 °C for the PTR-QiTOF and 600 V, 2.5 mbar and 60 °C for the PTR-TOF1000, both resulting in an E/N of about 131 Td (Townsend, $1\,\mathrm{Td} = 10^{-17}\,\mathrm{V\,cm^2}$). A E/N range between 120–140 Td has been established as a standard value, since it is a good compromise between excessive water cluster formation and product ion fragmentation [51, 59]. In the detection region, orthogonal acceleration in the V-mode was used. The cycle time was set to 1 s. The spectra were acquired at a frequency of 20 kHz. The collected signals are corrected for the instrumental transmission and before quantification normalized to the primary ion. Mass calibration was carried out using the masses of the internal standard equipped in the PTR-QiTOF, the so-called PerMaSCal® (1,3-Diiodobenzene) at *m/z* 203.94305 ($C_6H_5I^+$) and at *m/z* 330.84752 ($[C_6H_4I_2]H^+$) and the masses of NO^+ (*m/z* 29.99744) and the second isotope of H_3O^+ ($H_3{}^{18}O^+$, *m/z* 21.02209).

A comparison of the background measurements of nitrogen 5.0 (99.999 % quality) under dry and humid conditions is shown in Fig. 4. A time series of the mass spectra was recorded for a humidity variation from 80, 60, 50, 40, 20, 10, and 0 % RH as well as the increasing trend 0, 10, 20, 40, 50, 60 and 80 % RH using the first water cluster ($[H_2O]H_3O^+$) formed inside the drift tube of both instruments as a proxy of the humidity level [60]. Due to high sensitivity of this kind of instruments, small changes in humidity are registered as significant fluctuations. The different humidity steps are reproducible, although the ion distribution in both instruments appears to be quite different. Such difference has been reported before [33]. In general, the response time after changing to a new set value is short. At 10 % RH some signal distortion was observed. This could indicate that the smallest variations due to an unestablished equilibrium at the surface of the tubing causes a signal distortion, only when the surfaces have been saturated with water molecules, signals appear more stable. A knowledge of the humidity level is very important because raw industrial gases are normally saturated with water, whereas purified gases tend to have a very low water content. Therefore, for analysis of traces before and after a purification process, it is important to know the effect of humidity on the background signal. The sensitivity dependency to humidity of conventional VOCs can be negative [34] or positive [61].

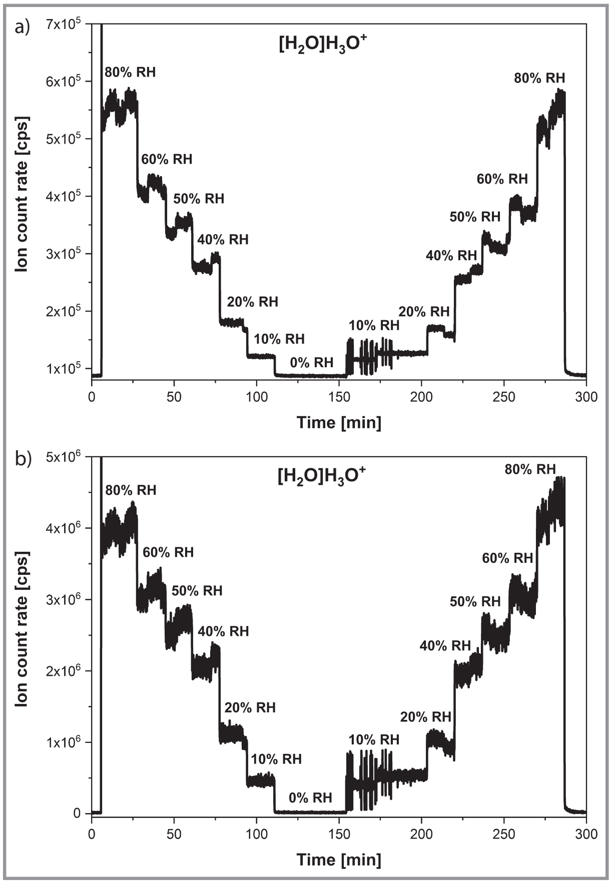

Figure 4. Time series of the signal of the first water cluster formed in both PTR instruments, a) PTR-TOF1000 and b) PTR-QiTOF.

Fig. 5 shows the time series of the recorded spectra of the first water cluster $[H_2O]H_3O^+$ and toluene under dry and humid conditions. In contrast to previous results [34], the

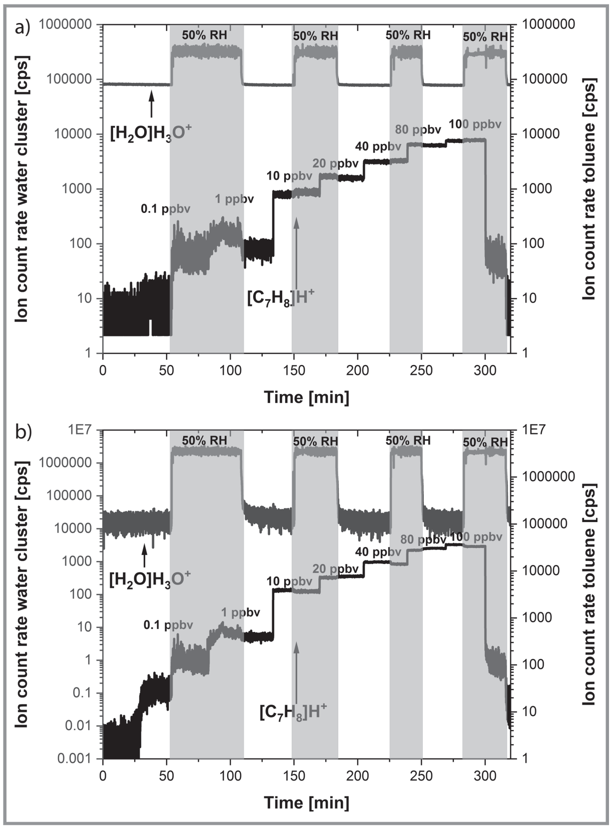

Figure 5. Time series of the signal of the first water cluster and toluene in both PTR instruments, a) PTR-TOF1000 and b) PTR-QiTOF.

signal of toluene at low concentrations approaching the detection limit, does not exhibit a clear humidity dependency. At higher concentrations, the humidity dependency becomes negligible. The apparent increase in sensitivity under humid conditions is ascribed to the longer reaction times in the drift tube and for less fragmenting molecules due to the lower collision energy caused by the presence of water clusters. However, depending on the conditions in the drift tube and the humidity levels a negative effect can be observed as a result of the consumption of H_3O^+ ions in the formation of the water cluster ions or due to the subsequent brake up of the water clusters in the transfer region, which leads to apparent more H_3O^+ ions and thus, results in an underestimation of the VOCs [58]. The calibration steps shown give crucial information about the humidity dependency of toluene when changing from a dry to a humid regime. For the measurement of real samples, it is of paramount importance to know if such dependency plays a significant role on sensitivity. The profiles of toluene in both instruments are very similar, they only differ on the higher intensities of the PTR-QiTOF, ascribed to its higher sensitivity [27] but instrument dependencies are not observed. After switching off the toluene injection, a quick signal drop of about two orders of magnitude is observed, showing that the memory effect for toluene is low and after about 25 minutes a near background signal is achieved again.

The experiments with toluene in a broad concentration range validates the performance of the designed gas generating system in a first step. However, further investigations will follow to extend these findings on additional components considered during the dimensioning of the set-up. As conclusion, the novel gas generating system introduced here will allow to provide complex gas mixtures mimicking steel mill gases for investigations on their possible application as feedstock for the chemical industry. Furthermore, the gas generating system will help to create a spectral database in order to understand the fragmentation patterns of selected molecules under controlled conditions (changing humidity, different gas matrices) in PTR instruments. Furthermore, by the calculated sensitivity, the k-rates for the protonation process can be derived.

5 Conclusions

The introduced gas generating system will play a crucial role within the Carbon2Chem® project dealing with concept development and feasibility studies for the application of steel mill exhaust gases as feedstock for chemical industry. The automated system enables mimicking the gases of interest with defined concentrations of all main, minor and trace components and the mixed gases are provided for the main tasks within the project. Here, chosen gas purification methods can be verified as well as upcoming issues during gas purification can be addressed to understand their background and adjust the overall concept with respect to these issues. An additional task will be providing mixed gases according to the developed process concepts for subsequent catalytic processes such as methanol synthesis to prove their feasibility for application using the pre-treated steel mill gases. This includes also more detailed deactivation studies including matrix effect for poisoning when several trace components are present in the feed gas. Furthermore, the gas generating system combines the mixing of gases, the evaporation of analytes and water, the dilution of premixed gases to produce dry or humid multi-component test gases with defined VOC concentrations enabling the calibration of analytical instruments under real conditions. This will help to understand the matrix effect and the fragmentation patterns in PTR-TOF-MS instruments, which are applied for the trace analysis of the steel mill gases on site before and after a purification. Based on this, a spectral database can be built with PTR spectra under defined conditions. Due to its modular concept, the gas generating system can supply test gases in parallel to various facilities with dry/humid gases enriched with VOCs or without. Additionally, it offers the confection of complex gas mixtures with toxic and corrosive gases in a concentration range of about four orders of magnitude. Therefore, this unique and versatile setup enables a variety of studies in catalytic reactions, gas purification methods and calibration as well as method development of analytical instruments allowing novel investigations on these topics.

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Symbols used

d	[mm]	thickness of the tubes wall
E	[kJ mol^{-1}]	apparent activation energy
H_3O^+	[cps]	primary ion signal
k_i	[cm^{3}s^{-1}]	reaction rate constant
L	[mm]	length of permeation tube
m/z	[–]	mass-to-charge ratio
P	[–]	permeability
P_d	[mbar]	drift tube pressure
P_i	[mbar]	pressure of desired analyte inside the tube
P_0	[mbar]	pressure of desired analyte outside the tube
R	[mm]	radius of permeation tube
q_s	[ng min^{-1}]	sample emission rate
Td	[V cm^2]	Townsend
T_d	[°C]	drift tube temperature
Tr_{H3O+}	[–]	transmission factor for mass of primary ion H_3O^+
$Tr_{[VOC]H+}$	[–]	transmission factor of mass of product ion $[VOC]H^+$
U	[V]	drift tube voltage
$[VOC]H^+$	[cps]	product ion signal of protonated molecule

Greek symbols

Δ	[–]	delta
θ	[°C]	temperature
π	[–]	Pi

Abbreviations

BFG	blast furnace gas
BMBF	Bundesministerium für Bildung und Forschung
BOFG	basic oxygen furnace gas
BSF	benzene soluble fraction
BTEX	benzene, toluene, ethylbenzene, xylene
COG	coke oven gas
COS	carbonyl sulfide
cps	counts per second
E/N	reduced electric field
GC	gas chromatograph
GHG	greenhouse gas
ISO/IEC	International Organization for Standardization/International Electrotechnical Commission
LOD	limit of detection
LOQ	limit of quantification
MFC	mass flow controller
MPI-CEC	Max Planck Institute for Chemical Energy Conversion
OSH	occupational safety and health
PAHs	polycyclic aromatic compounds
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
RH%	relative humidity
RM	reference material
SGM	standard gas mixtures
STP	standard conditions for temperature and pressure
TOF	time-of-flight
TCP/IP	transmission control protocol/internet protocol
VOCs	volatile organic compounds

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