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Qualification of a Gas Mixing Apparatus for Complex Trace Gas Mixtures

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Introduction

The detection of gases, especially Volatile Organic Compounds (VOCs), is important for many areas of daily life, such as Indoor Air Quality (IAQ) [1]. VOCs in particular can negatively affect cognitive performance or even cause health impairments in higher concentrations or long-term exposure [2]. However, the current gold standard to detect these VOCs, gas chromatography with mass spectrometry (GC-MS), is not suitable for these everyday situations due to cost and real-time constraints. A cost-effective alternative for IAQ monitoring is offered by metal oxide semiconductor (MOS) gas sensors, which offer, however, very poor selectivity. Temperature cycled operation (TCO) [3] can be used to boost the sensitivity as well as increase the selectivity together with advanced signal processing, but requires a complex lab calibration [4]. For this calibration, a gas mixing apparatus (GMA) is used to provide the required gas mixtures. Due to the large number of VOCs found in indoor air, it is not possible to include all occurring VOCs in the calibration. In a previous work we could show that it is sufficient to use only a few representatives per substance group, due to the fact that the reaction of MOS sensors depend mostly on the functional group of the VOC [5]. This reduces the number of relevant target gases to 12 [6], but interfering gases (at least CO, H_2, RH) also have to be included in the calibration. Thus, a new GMA, Fig. 1, was designed and constructed for calibrating MOS gas sensors with a realistic setting for applications like IAQ [7]. In this study, qualification measurements of the GMA are carried out and discussed which are the basis for sensor calibration.

Modular design and functionality

The GMA is designed on a modular basis, Fig. 2. Desired gases are injected into the so-called measurement line with zero air as carrier gas provided by a zero air generator (GT Plus 30000 Ultra-Zero Air Generator, Labor + Service GmbH & Co. KG, Dettingen, Germany). Zero air is dry and highly purified air with low concentrations of other trace gases. It is controlled by the carrier flow module with a mass flow controller (MFC). The total flow in the measurement line is kept constant during the measurement with typical values between 500 and 1000 ml/min. MFCs precisely control the flow given a sufficient pressure difference between inlet and outlet. The concentration

Figure 1 Picture of the assembled and ready-to-operate system from the operator's site

of added gases is given by the dilution factor defined by the ratio of the injection flow of the gas to the total flow. Humidity is set by a dedicated module (marked blue in Fig. 2) bubbling a flow of the zero air through water (HPLC grade) in a temperature controlled wash bottle (typically 20 °C). By this procedure the zero air is humidified to saturation vapor pressure (100 % relative humidity at the controlled temperature). To filter out large water particles and aerosols, a second wash bottle filled with analytical grade glass wool is used downstream. This prevents water droplets in the GMA which could corrupt the measurement due to an incorrect RH or even damage MFCs or sensors.
The desired gases are usually provided in gas cylinders. The test gas from these cylinders can be injected into the measurement line through different modules. The most basic is the so-called normal line (marked yellow in Fig. 2). It consists of only one MFC, the Injection MFC (typically max. 20 ml/min), which injects a flow of gas into the measurement line achieving a one stage dilution.
Another module is the predilution module (marked green in Fig. 2) featuring two dilution stages. The gas from the cylinder is diluted with zero air prior to injection into the measurement line by the Injection MFC. The MFC connected to the gas cylinder ("Gas MFC")

typically provides 20 ml/min, while the Dilution MFC provides zero air with up to 500 ml/min. This predilution is required for very small concentrations. Even gas cylinders with a purity class of e.g. 5.0 (purity of 99.999 %) include up to 10 ppm of impurities. To ensure that the target gas dominates over any impurities cylinder concentrations below 100 ppm have to be avoided. The predilution lines dilute not only the target gas, but also the impurities. Thus, the GMA can provide very low concentrations of a target gas down to 1 ppb without impurities becoming dominant.
For predilution modules, a distinction is made between two operation modes. Dilution mode with two stage dilution and No-Dilution mode with just one. If higher concentrations are required, predilution is not necessary, so No-Dilution is chosen. A fully equipped predilution module allows switching smoothly between the two modes offering a very large dynamic concentration range that can be set purely via MFC settings. With known gas cylinder concentrations and flow rates of each MFC, the correct set-points for a desired gas concentration at the outlet can be calculated automatically by a software.

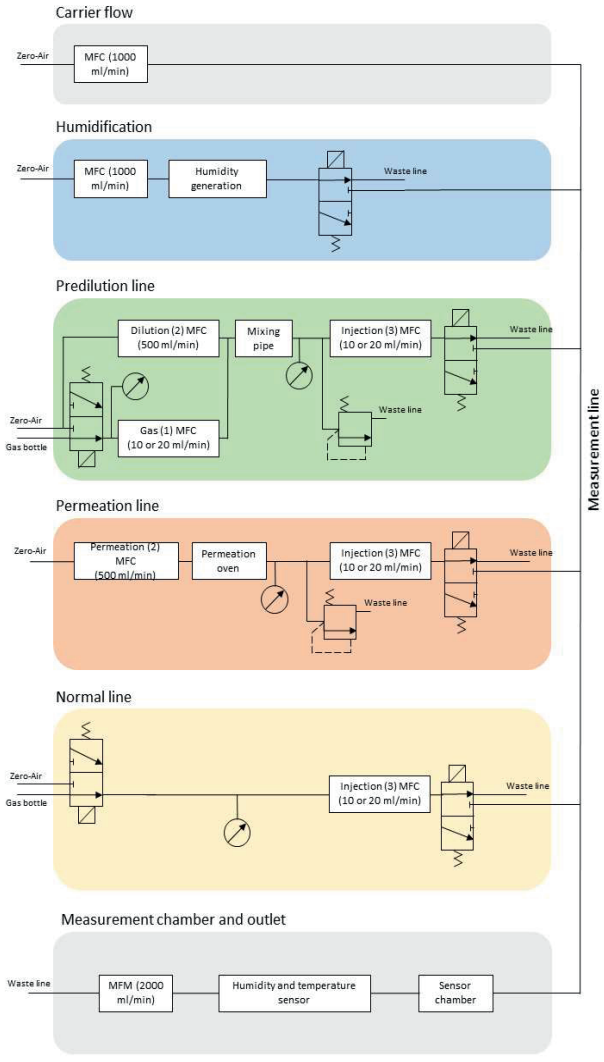

Figure 2 Overall schematic of the GMA based on [7]

Each MFC is identified by two numbers in addition to the letter M. The number before the M denotes the module in which the MFC is installed and the number after the M the position in the module. The Injection MFC always has number 3. Therefore, the Injection MFC in the fifth module of the GMA is called 5M3.
It is also possible to provide gases via permeation modules consisting of a so called Permeation MFCs (typically max. 500 ml/min), which control the flow through an oven kept precisely at a constant temperature. Based on the permeation rate of the gas and the tube used, a certain amount of the substance in the tube permeates into the zero air flow. To allow variable concentrations a pressure regulator and an Injection MFC are installed after the oven. Note that this module is not yet realized and is therefore not part of the measurements carried out in this study.
In addition to the MFCs, 3/2-way valves have been installed, with which the gas flow can be switched on and off selectively in order to provide additional functions, which are described in detail below. Finally, pressure sensors have been installed for self-monitoring of the system in the gas lines (downstream of the pressure regular at the gas cylinder) and, for predilution modules, also the pressure in the modules themselves.

Basic functional investigation

At the beginning of the qualification of the system, basic checks were carried out. On the one hand, this includes the electrical side, which was carried out via an industry-typical commissioning. In addition to a classic visual inspection, the resistance of the protective conductor in the AC part of the electrical system and the shutdown devices were checked. On the other hand, the important fluidic side was also checked. Here, the control values of all components such as pressure regulators are adjusted and tested, as are the MFCs themselves.
The offset calibration of the MFCs is particularly important for the correct concentration setpoint. These were recalibrated on site for the first time when the system was assembled on 12 February 2021. The second recalibration took place as a check on 12.05.2022. The documented offsets before the second recalibration are shown in Table 1. The offset depends on the maximum flow rate of the MFCs. For reliable operation the manufacturer recommends a monthly recalibration in the data sheet [8].

Table 1 Measured offset values of the MFC before and after recalibration

MFC & max. flow in ml/min	Feedback before cal. in ml/min	Feedback after cal. in ml/min	Delta in ml/min
4M1 (20)	0.781	-0.001	0.780
10M2 (500)	2.735	-0.081	2.654
5M1 (10)	0.249	-0.001	0.248

If a common setting in dilution mode for module 4, chosen at random, is considered, a large difference in the set concentrations with and without offset errors can be observed. One example is shown in Table 2, where the first line describes the set state and the second line the real set values due to the offset error.

Table 2 Comparison of resulting concentration for settings with and without offset errors, calculated for a total flow of 500 ml/min and a gas cylinder concentration of 100 ppm

4M1 in ml/min	4M2 in ml/min	4M3 in ml/min	Concentration in ppb
2	25	18	266.67
1.219	25.881	18.024	177.82

It becomes apparent that recalibration should be carried out regularly on a monthly basis in order to avoid such major errors. However, recalibration is time-consuming (approx. 2 hours) and requires all MFCs to be in a completely depressurised state during the recalibration phase.

Another very important aspect are impurities in the system, i.e. residual compounds in the system, e.g. from cleaning etc., which uncontrollably change the gas mixture that is offered to the sensor. To rule this out, the system was flushed with zero air for four days. For this purpose, all inputs were switched to zero air and all MFCs were set to maximum flow. The total flow rate of the system was 630 ml/min. In order to detect any remaining impurities, samples were taken with thermal desorption tubes (Tenax and Sulficarb) and analysed by a certified laboratory using GC-MS (eco-INSTITUT [9]). Due to uncertainties regarding the suitability of the tubes under humid air, the humidity module was not tested for the time being. A sample volume of 10 l was taken at a flow rate of 100 ml/min. The high sampling volume (normally 3 l samples are used) was chosen because only minimal contaminations were expected. Since a new zero air generator was purchased for the GMA, the measurement was carried out twice, once with the older zero air generator connected and once with the new generator. The results are shown in Table 3. For reference, the values were compared with a background air measurement in a standard office room.

Table 3 VOCs found when flushing the entire apparatus with a newly acquired zero air generator (ZAG) compared to the old ZAG. A background air measurement taken in an office room serves as a reference.

Gas	New ZAG in ppb	Old ZAG in ppb	Reference in ppb
Toluene	0.39	0.39	0.79
Ethanol	4.18	3.13	10.97
Acetone	1.24	2.07	/
2-Propanol	0.80	0.80	26.42
Acetic acid	0.4	0.20	3.61

Many other VOCs were below the detection limit. It should be noted that errors of up to 23.9 % are given by the laboratory for toluene. The remaining VOC concentrations are therefore considered negligible, also with regard to the accuracy of MOS sensors. The system is therefore clean, as far as can be reasonably verified.

Optimization of GMA time constant

The possibility to generate identical concentrations by different MFC settings also provides the possibility to optimize these parameters with respect to different target values. More important, unfavourable, slow, or error-prone combinations should be avoided. Since calibration measurements take a long time, it makes sense to optimize the gas adjustment time considering the GMA utilization. In order to find a sensible optimum, investigations in this respect were already carried out on existing GMAs during the design phase of the GMA [7]. In order to verify the obtained results on the new apparatus and, if necessary, to optimize them further, additional measurements were carried out. These measurements investigate the influence of the three MFCs in the pre-dilution modules on the time constant for gas adjustment times. For this purpose, one MFC was varied in each case, while the other two were kept at a constant level. A total flow of 500 ml/min at 40 % relative humidity was used throughout. A commercially available MOS sensor, i.e. layer 1 of SGP30 (Sensirion, Stäfa, Switzerland), was used for evaluation. The sensor response (i.e. signal in gas normalized to signal under zero air), was used for evaluation. The results for all three variations are shown in Fig. 3.

The results correspond to the previous tests. Accordingly, the influence of the Injection MFC is particularly relevant, while the Dilution MFC can be neglected. This is explained by the fact that the section upstream of the Injection MFC has a large volume due to its structure, which is flushed only by the relatively small flow of the Injection MFC. The greater the flow, the faster this relevant section is flushed. This volume is marked blue in Fig. 4. The Dilution MFC, on the other hand, flushes a smaller part of the module with a larger flow. The Gas MFC also has an influence which is, however, smaller than that of the Injection MFC. The influence here is assumed to be that the line was purged with zero air from the Dilution MFC in preparation for the measurement. The part of the module behind the Gas MFC (marked green in Fig. 4), which is filled with the full cylinder concentration is thus also purged. This reduces the concentration of the gas in this section, which must be increased again by the small Gas MFC flow for the next gas supply. Furthermore, this has the disadvantage of greater gas consumption while being opened wider. For the system, the settings are therefore optimized by first maximising the flow of the Injection MFC before increasing the flow of the Gas MFC. Further adjustments should

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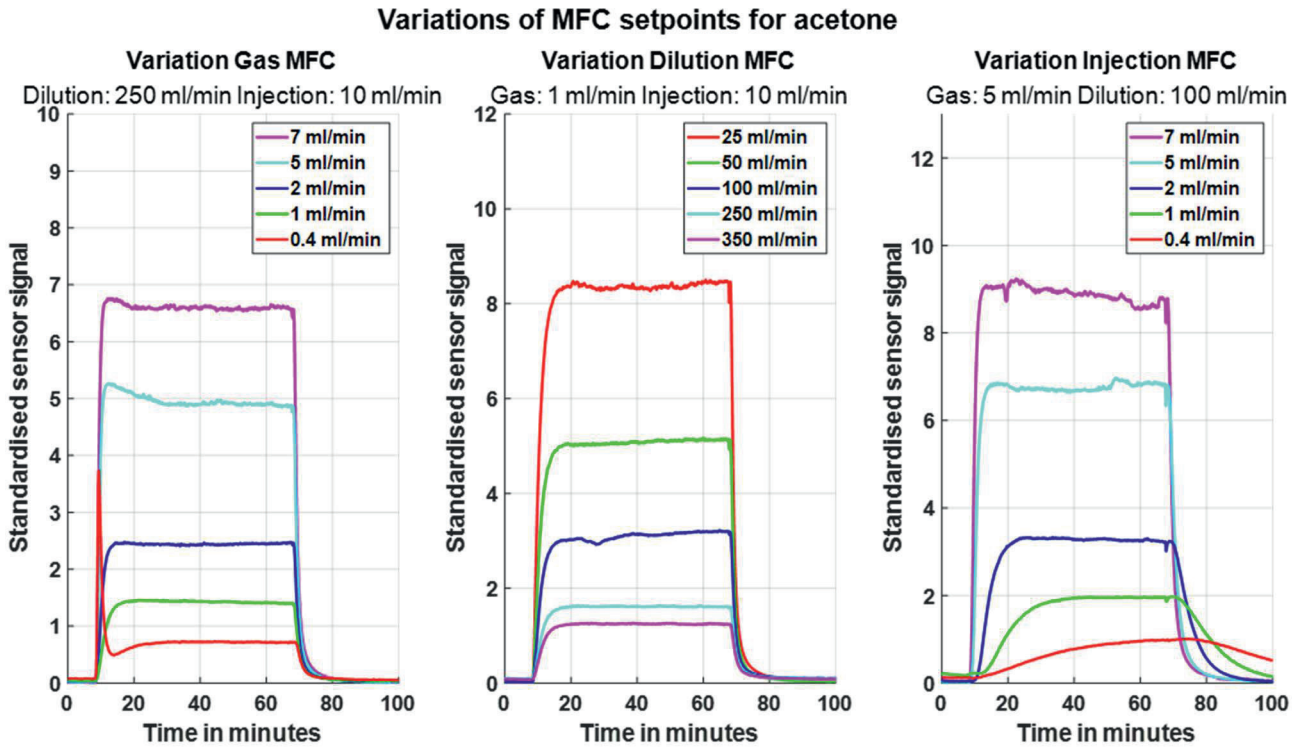

Figure 3 Sensor signals for different variations of MFCs for constant values of the other two MFCs

always be made by the Dilution MFC, as this shows no relevant influence on the adjustment speed. Similarly, the reduction of all dead volumes, especially the part before the Injection MFC, is beneficial.

The automatic control software of the GMA was also adapted. In order to further optimise the setting time, a new so-called flush state was integrated into the software. The 3/2-way valve behind the Injection MFC is used for this purpose. For six minutes, the Gas and Dilution MFCs are set to their respective target values. The Injection MFC on the other hand is set to its maximum value in order to flush the relevant volume as quickly as possible, while the valve is set to exhaust. After this flush period, the Injection MFC is set to its target value and the injection valve is switched to the measurement line. The flush duration was determined by tests with different VOCs (acetone and ethanol) and represents a compromise between time and signal quality. By using all these optimisations, it is possible to produce the desired concentrations stably and reproducibly with the GMA. Fig. 5 shows a measurement in which all optimisations were integrated. For this purpose, layer 0 of an SGP 40 (Sensirion, Stäfa, Switzerland) was evaluated. The data were recorded in TCO, with the quasi-static signal at 400 °C shown. Standard flow was 1000 ml/min at 50 % RH, changed flow at 200 ml/min and humidity at 25/75 % RH are indicated. It is noticeable that almost all gas sequences show stable plateaus without large transient effects, which is required for the calibration of MOS sensors. Exceptions are the first ethanol signal around 20 hours, which can be explained by the slow recovery after the acetaldehyde exposure, which could be caused by adsorption effects in the GMA. The overshoot for the first gas sequence of ethyl acetate can be explained by the simultaneous change of the concentration and the total flow. Furthermore, it can be seen from the mean

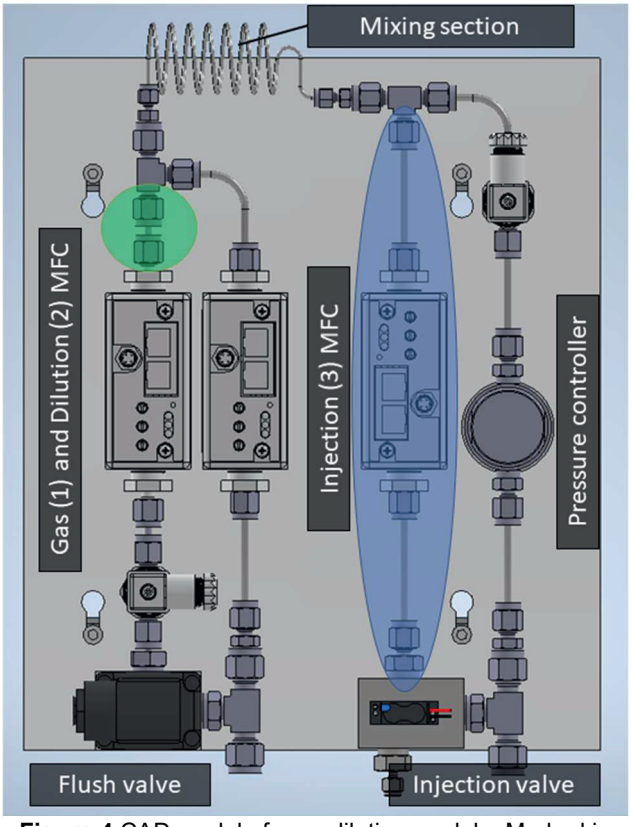

Figure 4 CAD model of a predilution module. Marked in green is the volume behind the Gas MFC. The section in blue is only influenced by the flow of the Injection MFC.

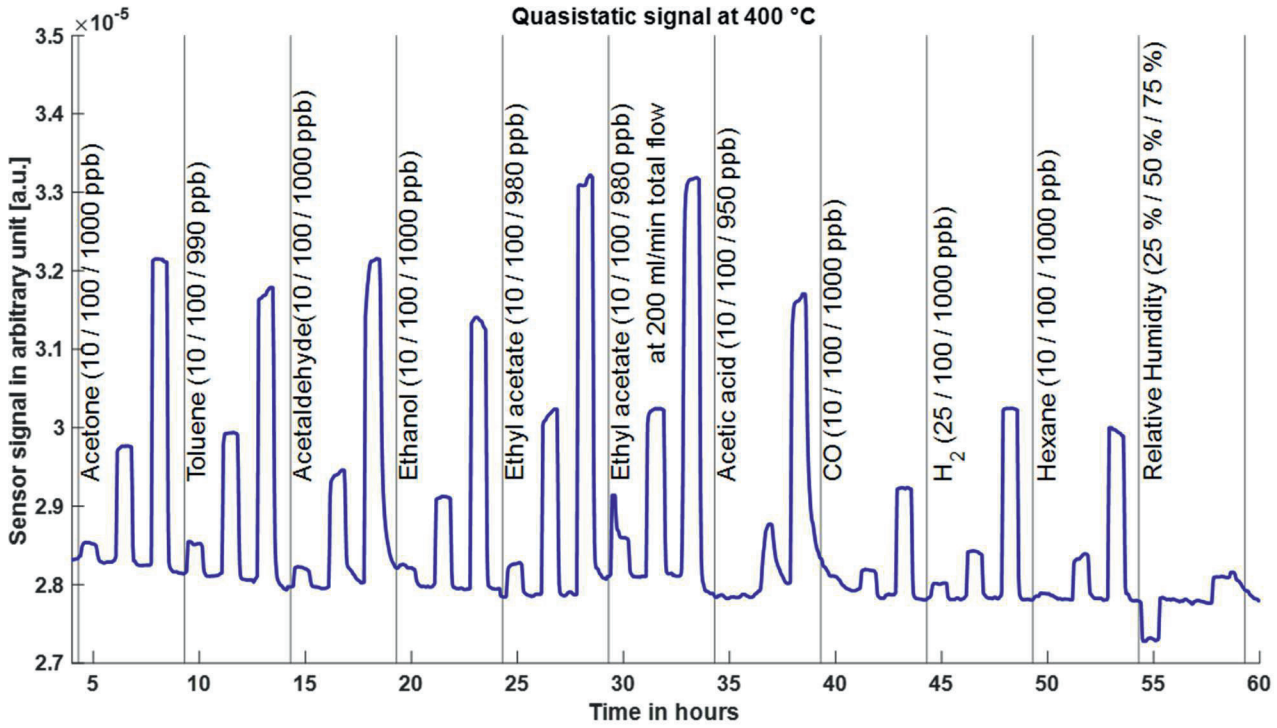

Figure 5 Multiple sequential gas peaks with different concentrations at 1000 ml/min total flow and 50 % humidity

values during the ethyl acetate exposures that the total flow of the system has little influence on the MOS sensor signal, although a baseline shift can be observed. In particular, this shows the reproducibility of the concentration sequences, since other MFC setpoints are also changed to adjust to the reduced total flow. The sequences with acetic acid exposures do not show the expected stable plateaus. This is attributed to adsorption effects of the gas. Finally, the change in relative humidity is also easy to see as well as the good reproducibility of 50 % RH after reduction to 25 %.

In summary, both the hardware improvements (dead volumes) and the software improvements (MFC settings and flush state) are useful for generating stable gas supplies as quickly as possible. Taking ethanol (bottle concentration of 200 ppm) at a total flow of 500 ml/min as an example, it is possible to set any concentration in the range from 4 ppm down to 16 ppt (dilution ratio of 50 to 1.563.750, dynamic range 31.275) within about 10 minutes with the GMA.

Reference analytics

Just as important as the time constant for the GMA is the accuracy of the GMA in setting desired concentration values. To test this, various analytical reference instruments were used. Again, as for the detection of impurities, samples were taken with thermal desorption tubes and evaluated by the eco-INSTITUT. A concentration of 150 ppb was set in the GMA at 500 ml/min total flow and 50 % RH. All optimisations described above were used and an additional 9 min delay after the flush state was selected before starting the sampling to ensure that the set concentration is correctly present at the tube. This was additionally monitored and verified with MOS sensors. Two gases, toluene and ethanol, were tested. The tubes were filled with 3 l at 100 ml/min. Sampling material for Toluene was again Tenax while Carboxen were used for ethanol. The results were 109,5 ppb for Toluene (Δ -40,5 ppb) and 87,6 ppb for Ethanol (-62,4 ppb).

The determined concentrations show a large offset of more than 40 % from the nominal value. However, the determined concentrations are heavily influenced by several factors. On the one hand, by the sampling method itself, which is usually optimized for measurement without a constant flow as generated by the GMA. On the other hand, the evaluation by means of Tenax thermodesorption tubes, which has an uncertainty of 23.9 % for toluene as described above, corresponding to ± 35.85 ppb at 150 ppb. Since both sources of error show a great influence and no other validation is available, the results are satisfactory for the time being. More important is the excellent reproducibility, which was observed for multiple measurement points at the same concentration but with gas changes in between.

During similar measurements with other gases even lower concentrations were recorded. Here, a decay of the gases in the gas cylinder itself was suspected. To test this hypothesis, glass vials were filled with the maximum cylinder concentration, sealed airtight with a septum and then analysed qualitatively by GC-MS (Thermo Fischer scientific, Trace 13000 Gas Chromatograph, ISQ 7000 Single Quadrupole Mass

Spectrometer) in the range of 15-200 u. The evaluation was carried out using the usual NIST sources (mainlib and replib). In addition to the expected gases (N_2, O_2, CO_2, water, and ethyl acetate), acetaldehyde, ethanol, and ethyl ether were also identified in the sample. These gases could be the result of a decomposition of ethyl acetate molecules and, thus, support the above theory. A control measurement with ammonia and toluene samples showed no additional gases, so this method can help to identify impurities or decay in gas cylinders.
In conclusion, GC-MS analysis can primarily be used to qualitatively evaluate the GMA mixture to back up all measurements, but not to quantify the concentration set-points. Quantitative validation of the GMA has proven to be difficult, due to the inherent high uncertainty of even the best analytical methods. However, for the calibration of not only MOS sensors reproducibility of the concentrations is more important than the absolute value. High reproducibility was shown with repeated analytical measurements and is also supported by the MOS sensor data themselves showing excellent quantification of unknown mixtures.

Conclusion and Discussion

This paper describes several measurements and verification possibilities that can and should be carried out on any GMA. First, impurities in the GMA, which could distort any measurement result or impair the long-term reproducibility, were shown to be negligible. Second, existing operating parameters such as the set-points of the MFCs, especially for the predilution modules which allow different set-point combinations for a given target concentration, were further optimised. In the process, a new flush state was integrated, which further improves the time constant and thus the efficiency of the system. Finally, several possibilities for quantitative validation of the system were tested. Analytical reference methods often showed large deviations, which can be attributed either to the high inherent uncertainty of the method or problems in sampling. Using other methods, the importance of monitoring all relevant GMA components, not least of all the test gas cylinders themselves, but also the MFCs by periodic calibration, was also demonstrated. All findings should also be applied also to any existing GMAs. Especially the set point parameters and the flush state can achieve a significant improvement with minimal software input.
The lack of quantification remains a challenge. In order to achieve reliable quantification, the sampling method for all applied methods, e.g. thermal desorption tubes, must be improved. However, doing this empirically is expensive and requires a calibrated GC-MS which is not available in our laboratory. More important than the absolute concentration for sensor system calibration are reproducibility and correct scaling, since an offset can easily be added later.
Finally, the new highly complex GMA is now fully functional for our research priorities and suitable for upcoming tasks. These will include not only the calibration of MOS sensor systems for complex gas mixtures in indoor air, but also development and optimization of gas measurement systems for challenging applications in medicine [10].

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