

Preparation of SI-traceable calibration gas mixtures by using permeation units

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Abstract

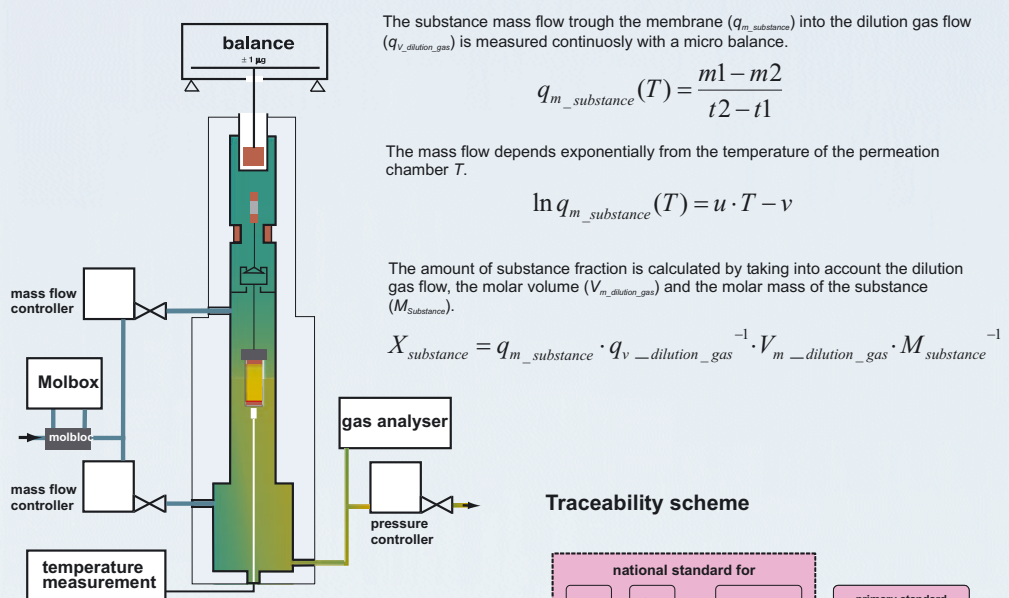
The dynamic method for preparing standard gas mixtures by means of permeation devices is an accurate method for reactive compounds like nitrogen dioxide and ammonia at very low concentrations. Characterisation of commercially available permeation devices and of the complementary gases is fundamental for the determination of the uncertainty of the gas mixture. Results from studies of the stabilisation time, the stability of permeation devices, the purity of the analyte and of the complementary gases are presented.

Introduction

The dynamic preparation is complementary to the conventional gravimetric preparation of standard gas mixtures in pressurized bottles. The ISO standards 6145-1 to 6145-11 describe various dynamic volumetric methods for the preparation of calibration gas mixtures. The Gas Analysis Laboratory of the Federal Office of Metrology METAS combines the permeation method with dilution units like critical orifices or thermal mass flow controllers for the preparation of standard gas mixtures with amount of substance fraction in the nmol·mol⁻¹ (ppb) range. With a single measurement set-up the amount of substance fraction can be varied within a factor of about 20. The required infrastructure is moderate, all the more a complete validation and characterisation of all components is necessary to assure the high reliability and accuracy of the reference values of the gas mixtures.

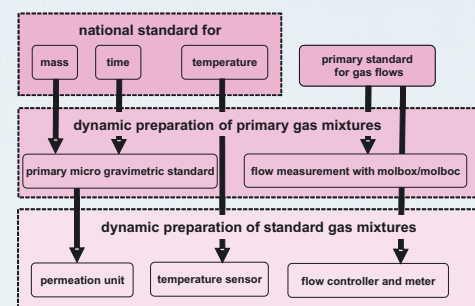
A. Characterisation of permeation devices

Experimental setup



The central part of the micro gravimetric standard consists of a magnetic suspension balance from Rubotherm with a mass range of 0 g to 30 g and a resolution of 1 µg. It measures the mass change of the permeation process. The permeation unit is linked contactlessly to the micro balance by means of a magnetic system. The temperature controlled permeation chamber is entirely made out of glass. The two volume flows of the dilution gas are regulated by thermal mass flow controllers. The gas pressure in the permeation chamber is kept constant at 1013 hPa with a pressure regulator. If the produced gas mixture is directly used for calibrating gas analysers the total dilution gas volume flow is measured by a molbox/molbloc system from DH Instruments.

Traceability scheme



Results

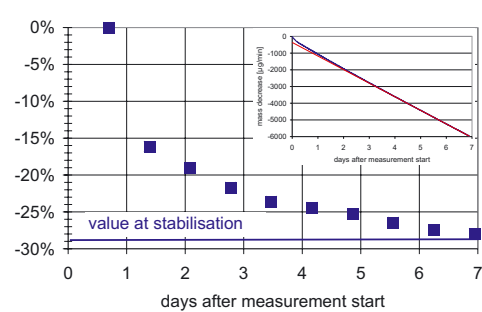


Fig. 1: Stabilisation time for a NH₃ permeation unit. Mass flow after stabilisation (553 ± 4) ng·min⁻¹

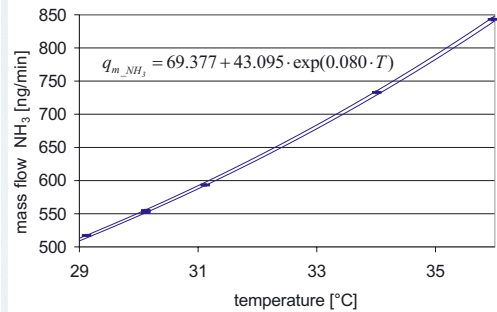


Fig. 2: Dependence of NH₃ mass flow through the membrane from the temperature in the permeation chamber. The graph shows the 95% confidence interval of the calibration function. The mass flows are after the stabilisation time period.

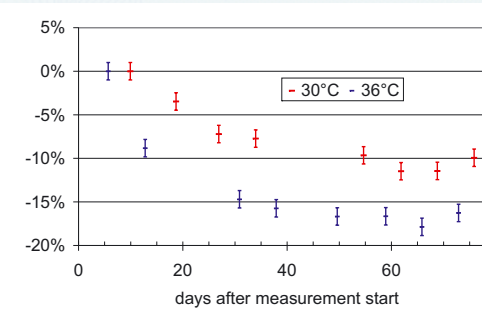


Fig. 3: Stabilisation time for a m-xylene permeation unit after installation of the permeation unit into the permeation chamber of the micro gravimetric standard. Alternate measurements between 30 and 36°C. Each single point is a measurement over at least 2½ days. Mass flow at stabilisation at 30°C is (62 ± 1) ng·min⁻¹, at 36°C (113 ± 2) ng·min⁻¹.

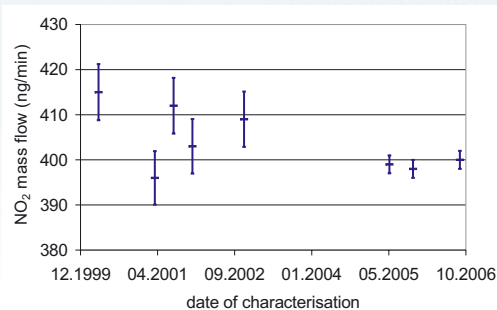


Fig. 4: Stability of the mass flow of a NO₂ permeation unit over 7 years. Between measurements the unit was stored in a box with desiccation- and adsorption agents at 5 to 10 °C. The mass flows are at (30.00 ± 0.05)°C

Uncertainty budget

As example the uncertainty budget for a NH₃ permeation unit at a defined temperature is represented. The combined uncertainty is for a mean NH₃ mass flow of 558 ng/min. The budget has been established using the GUM Workbench Pro software. A simplified model for the mass measurements is used. In fact the mass flow is calculated using at least 1000 single measurements. The corrections of the drifts of the zero points and spans of the balance are also considered. The major contributions are from the standard deviation of the slope of the linear regression of the mass flow (lin), from the resolution of the balance (m, zp, ci) and from the purity of the permeated NH₃ (p_{NH3}).

$$q_{m_NH3} = ((m \cdot cal_{ci} + zp) \cdot (m_2 \cdot cal_{ci} + zp)) / (t_2 - t_1) \cdot lin \cdot p_{NH3}$$

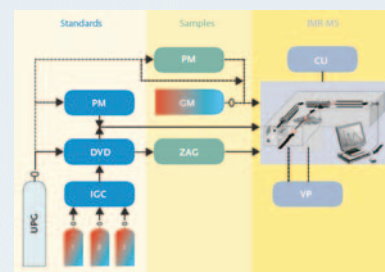
$$cal = cal_{high} - cal_{low}$$

q_{m_NH3} : NH₃ mass flow
 p_{NH3} : purity of permeated NH₃
 m : mass at time t
 c : span correction of balance at t
 lin : linearity of the mass flow
 t : time
 zp : zero correction of balance at t
 cal_{high} and cal_{low} : reference values of calibration weights

Uncertainty source	Value	Standard uncertainty	Sensitivity coefficient	Contribution to standard uncertainty
p_{NH3}	0.9995	$289 \cdot 10^{-9}$	$560 \cdot 10^9$	$160 \cdot 10^{-12}$ g/min
t_1	3002.970 min	0.025 min	$590 \cdot 10^{-12}$	$15 \cdot 10^{-12}$ g/min
t_2	3950.370 min	0.025 min	$-590 \cdot 10^{-12}$	$-15 \cdot 10^{-12}$ g/min
m_1	23.154819745 g	$289 \cdot 10^{-9}$ g	$1.1 \cdot 10^3$	$300 \cdot 10^{-12}$ g/min
m_2	23.154290627 g	$289 \cdot 10^{-9}$ g	$-1.1 \cdot 10^3$	$-300 \cdot 10^{-12}$ g/min
lin	1	$1.2 \cdot 10^{-3}$	$560 \cdot 10^9$	$670 \cdot 10^{-12}$ g/min
zp_1	0 g	$289 \cdot 10^{-9}$ g	$1.1 \cdot 10^3$	$300 \cdot 10^{-12}$ g/min
zp_2	0 g	$289 \cdot 10^{-9}$ g	$-1.1 \cdot 10^3$	$-300 \cdot 10^{-12}$ g/min
c_1	24.0234312 g	$289 \cdot 10^{-9}$ g	$1.0 \cdot 10^3$	$-290 \cdot 10^{-12}$ g/min
c_2	24.0234312 g	$289 \cdot 10^{-9}$ g	$-1.0 \cdot 10^3$	$290 \cdot 10^{-12}$ g/min
cal_{high}	54.0653340 g	$30 \cdot 10^{-6}$ g	$23 \cdot 10^9$	$700 \cdot 10^{-12}$ g/min
cal_{low}	30.0419028 g	$30 \cdot 10^{-6}$ g	$-23 \cdot 10^9$	$-700 \cdot 10^{-12}$ g/min
Combined standard uncertainty 1.01 ng/min				

B. Purity analysis

Experimental setup



Ion-Molecule Reaction Mass Spectrometer (IMR-MS)

The method is based on a commercial quadrupole mass spectrometer (QMS) with ion-molecule reaction ionization (IMR). The instrument and its modifications have been described previously. The three ionising gases are Hg⁺ (10.4 eV), Xe (12.13 eV) and Kr⁺ (14 eV). The implemented computer-controlled gas selection unit in combination with measurement procedures based on LabView and TestStand sequences (both National Instruments) allow the fully automated operation of the MS and all peripherals. The reproducibility of results has largely improved by a rigorous control of the measurement parameters, using longer sampling times and external data analysis. For the external calibration either a gas dilution system or the permeation method are used for setting the amount of substance fractions of the various standard gas mixtures.

Schematic of the IMR-MS setup with the standards and the various samples

UPG: Ultra pure matrix gas
PM: Permeation method
DVD: Dynamic volumetric dilution

IGC: Intergrated gas controller
1, 2, 3: Standard gas mixtures
GM: Gas mixture

ZAG: Zero air generator
CU: Control unit
VP: Vacuum pumps

Analyte

In order to identify and quantify possible impurities of the NH₃ permeator, the measurement set-up and MS parameters were optimized for maximum signal and minimal drift for NH₃. The mass-scale and mass resolution of the QMS were set with the signal of ¹⁵NH₃ (m/z=17.027) and least contribution from the ubiquitous neighboring H₂¹⁸O (m/z=18.011). The response time of the NH₃ signal T_{90%} was typically 27 min. and much longer than for e.g. NO₂ and all the other analytes measured so far.

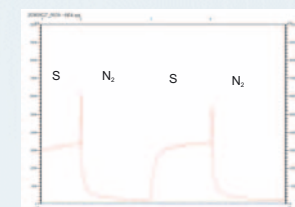


Fig. 5: Mass chromatograms for masses 17 and 18 of 2 sample cycles each: standard (S) with 438 nmol/mol NH₃ in N₂ and N₂. The response times for NH₃ were optimized by using thinner SiO₂-coated SST tubings instead of PFA and by controlling the gas flow through the MS. From the last 62 datapoints of the last two cycles a limit of detection for NH₃ of 1.7 ± 0.9 ppb was calculated.

Zerogases

MS survey spectra with the three ionizing gases were recorded for three qualities of N₂. More detailed analysis with the potential to quantify traces were made with mass chromatograms for NH₃ (mass 17), H₂O (mass 18) and O₂ (mass 32).

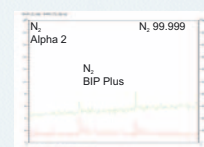


Fig. 7: Mass chromatograms of three N₂ qualities with the masses 17 (red) and 18 (green). The sensitivity is optimized for NH₃. For all three nitrogen qualities the x_{NH3} is below the detection limit.

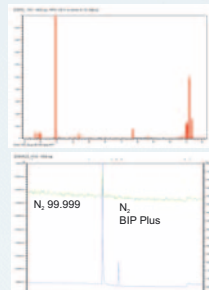


Fig. 8: Stick plot mass spectrum of the NH₃ standard with Kr⁺ ionisation. All three N₂ qualities show signals at masses 110, 111, 112 and 114 with less intensities for the better qualities. The substances have not been identified so far. The masses 112 and 114 are indicative for chlorobenzene.

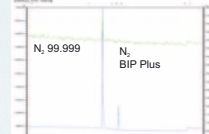


Fig. 8: Mass chromatograms with the masses 17, 18 and 32. The sensitivity is optimised for O₂ (blue trace). x_{O2} in BIP Plus nitrogen is specified < 10 ppb and is slightly lower than in N₂ (99.999 %).

C. Conclusions

For the purity analysis the long response times for NH₃ have to be considered. MS survey spectra and mass chromatograms of the permeate have not revealed detectable impurities so far. The amount of ammonia in the three N₂ qualities measured is below 1.7 ppb. The better the N₂ quality the less O₂ and yet unidentified substances in the mass range 110 to 114 amu. Their contribution to the uncertainty and possible influence on the NH₃ measurement remain to be analysed.

After installation of a permeation unit in the temperature controlled permeation chamber of the micro gravimetric standard a stable mass flow is reached after 7 to 10 days. This effect has been observed for permeation units containing NH₃ (Fig. 1) or NO₂. For certain substances, as the reported example for m-xylene shows (Fig. 3), an other behaviour manifests. In these cases the stabilisation time can rise up to 1 month. The possible reasons have not been studied yet. Fig. 4 shows the good long term stability of the NO₂ mass flow of a permeation unit. The excellent reproducibility of the results for the last two years is very likely due to the accurate maintenance of the stabilisation time.

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