Reduction of the Measuring Gas Dew Point

Concentration Changes and Washing Out of Noxious Gases and Odorous Compounds

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Gas cooling devices are used as a means of conditioning humid measuring gas flows. In these devices, the dew point is lowered. This causes the surplus quantity of water to condense. Two resulting effects influence the concentration of noxious gases and odorous compounds. The condensation part of the humidity reduces the total gas flow. Therefore, the concentrations of the other gas components rise. Water-soluble components, however, cause additional washing-out due to absorption in the condensate. The concentration of these components diminishes. Both effects are influenced by the degree of dew point reduction and the temperature in the cooler. At low temperatures, gas solubility and the quantity of condensing water increase. Therefore, the largest washing out effect occurs here.

In the case of odorous compounds, the washing-out effect must be taken into special consideration. In order to pass the mucous membrane which covers the olfactory receptors in the nose, odorous molecules must be water-soluble. Depending upon the degree of water solubility, different concentration shifts occur. The resulting odour impression may therefore alter significantly due to the change in relative composition. The alternative dilution of the measuring gas with dry air for dew point reduction results in a considerable reduction of the concentrations.

In this contribution, the fundamental procedures and methods for the calculation of these effects are presented.

Keywords
Ammonia, gas cooler, washing out, dew point, odour, electronic nose

Introduction

The water content in the measuring gas must always be taken into account, especially when measuring biological sources. The formation and release of substances always take place in a humid medium. In addition, the temperature level is higher due to the biological conversion processes. When samples from emitting composting facilities or biofilters are taken, temperatures may reach approximately 60°C. The measuring gas flows are saturated with water, and the dew points are accordingly high. Heated measuring gas pipes allow the gas to be conveyed without condensation. When measuring concentration, a problem always occurs when, due to the design or the measuring principle, the gas analyser is operated at a temperature below the dew point. In this case, a reduction of gas humidity is unavoidable and must be carried out under controlled conditions. The standard method is the use of a measuring gas cooler (cf. **figure 1**), which guarantees a controlled reduction of the dew point when the measuring gas enters into intensive contact with the cooled wall surfaces. The condensate is continuously drained with the aid of a condensate pump [1].

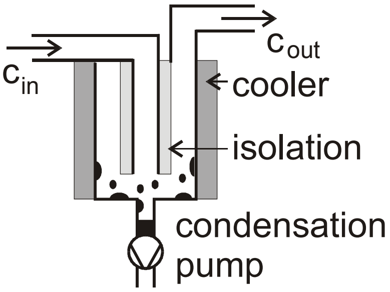

Figure 1: Principle diagram of a measuring gas cooler for dew point reduction

Reduction of the Gas Dew Point

Measuring gas coolers are often run at a temperature of 5°C, which guarantees the condensation of the largest part of the water content. **Table 1** shows the relative percentage of water at different dew points. At 5°C, the water content accounts for only 0.54% of the entire air mass (including the water) as compared with 21.74% at 70°C. The difference, i.e. approximately 21%, is abstracted from the measuring gas flow through condensation. The difference in the volume of the water and dry air components is even more significant. At 5°C, 0.87 vol.% of the gas consists of water, while at 70°C water already accounts for 44.52% of the total volume. The above mentioned abstraction of 21% of the total mass thus even means the abstraction of about 44% of the gas volume. This is caused by the difference in the molar mass between light water (18 g/mol) and heavier air (28.94 g/mol), which, according to the ideal gas law, leads to a corresponding volume relation. Since all concentrations of noxious gases or odorous compounds relate to the total gas volume, the volume effect therefore causes a significant increase in these concentrations if the dew point goes down substantially.

The values in the table are calculated using the following relation [2]:

$$x = \frac{M_W}{M_{air}} \cdot \frac{p_d}{p_{tot} - p_d} \qquad (1)$$

with M_W = 18.016 [kg/kmol] and M_{air} = 28.96 [kg/kmol] (average molecular weight). The partial pressure of the water p_d is calculated using the saturation vapour pressure p_s and relative humidity RH:

$$p_d = RH \cdot p_s \qquad (2)$$

According to the equation from [3], the saturation vapour pressure of water is calculated as follows:

$$p_s = 0.001 \cdot 10^{8.3246 - \frac{1799.73}{(\vartheta + 238.734)}} \cdot [\text{bar}] \qquad (3)$$

Table 1: Percentage of water at different dew points, related to the percentage of dry air and the entire gas

T	[°C]	5	10	20	30	40	50	60	70
x	[kg $_{W}$/kg $_{da.}$]	0.54%	0.76%	1.47%	2.72%	4.89%	8.63%	15.26%	27.79%
x'	[kg $_{W}$/kg $_{tot}$]	0.54%	0.76%	1.45%	2.65%	4.66%	7.95%	13.24%	21.74%
n_W/n_A	[mol $_{W}$/mol $_{da.}$]	0.87%	1.23%	2.36%	4.37%	7.85%	13.88%	24.53%	44.66%

The mole and volume relation is calculated with the aid of the following equation:

$$\frac{n_W}{n_{air}} = x \cdot \frac{M_{air}}{M_W} \qquad (4)$$

Washing Out of Gas Components

Gas components can dissolve in the condensate that is formed due to the lowering of the dew point. Under physical and chemical view point, the washing out process is the absorption of the gases in the condensate [4].

The absorption of gases is described using Henry´s law, which assumes a linear relation between the concentration of a gas component above the absorber and the resulting equilibrium concentration:

$$c_{diss.gas} = \lambda(\vartheta) \cdot p_{gas} \qquad (5)$$

The Henry's absorption coefficient λ is dependent on the temperature ϑ. An exponential set-up for λ reads:

$$\lambda(\vartheta) = e^{\left(\mathrm{A} + \frac{\mathrm{B}}{(\vartheta + 273.15)}\right)} \left[\frac{\text{mol}}{\text{kg bar}}\right] \qquad (6)$$

The coefficients A and B are often not listed in tables; instead, a reference value for $\lambda_{25°C}$ at 25°C is given along with a coefficient C = d(ln(λ))/d(1/T) which describes the course of the Henry's coefficient with the temperature [5].

For the conversion of $\lambda_{25°C}$ and C into the coefficients of the exponential form, the following equations are employed:

$$B = C \qquad (7)$$

$$A = \ln(\lambda_{25°C}) - \frac{C}{298.15} \qquad (8)$$

For calculations in connection with gas concentration measurements, it makes sense to use a modified form of Henry´s law [6]:

$$c_{gasdiss.} = \Lambda(\vartheta) \cdot c'_{gas} \qquad (9)$$

Gas concentration is put into this equation as mole relation. (According to the ideal gas law, the mole relation corresponds to the volume relation and, hence, the usual concentration unit ppm_v, divided by 10^6).

The two Henry coefficients are converted using the following equation:

$$\Lambda = \lambda \cdot p_{tot} \qquad (10)$$

Condensation and Washing Out

The relation between condensation and washing out processes leads to concentration changes during the use of measuring gas coolers. **Figure 2** represents the processes for two different strong dew point reductions. On the left hand side, only a little condensate is produced due to the slight dew point reduction, and at a higher temperature only little gas is dissolved in the condensate. On the right hand side, the temperature is lower, and the condensate quantity as well as the amount of washed-out gas increase. The percentage of dry air remains constant. The concentration changes are caused by the reduction of the total gas quantity after condensation.

The concentration change of a soluble gas after dew point reduction is given by the following relation (detailed deduction in [6]):

$$c_{\text{out}} = \left[(p_{\text{sdew}} - p_{\text{sK}}) \cdot M_{\text{W}} \cdot \Lambda_K + p_{\text{tot}} - p_{\text{sdew}}\right]^{-1} \cdot (p_{\text{tot}} - p_{\text{sK}}) \cdot c_{\text{in}} \qquad (11)$$

with ϑ_{dew} as the dew point of the measuring gas and ϑ_{K} as the temperature of the cooler and the reduced dew point temperature as well.

For a certain value of Λ, the input and output concentrations are identical because the effects of condensation and washing out exactly compensate each other. The value of Λ is calculated as follows:

$$\Lambda(\vartheta_{\text{K}}) = \frac{1}{M_{water}} \qquad (12)$$

Figure 3 shows the solubility coefficient Λ for different gases. The horizontal line represents the reciprocal value of the molar mass of water. Gases with solubilities which intersect with this line have a temperature value at the intersecting point which, for arbitrary input dew points, results in an unchanged concentration at the exit of the measuring gas cooler.

Washing Out of Ammonia

The solubility curve of ammonia intersects with the reciprocal value of the molar mass of water at 26.34°C. **Figure 4** shows the concentration changes and the alteration of the measuring gas cooler temperature for four different input dew points (plotted towards the right). Above the neutral temperature, concentrations increase, while they diminish below this temperature. The percentage of ammonia washed out with the condensate is plotted towards the left. At a high input dew point and a low cooler temperature, large percentages of ammonia (e.g. 55% at an input dew point of 70°C and a cooler temperature of 5°C) are washed out with the condensate.

In insoluble gases, the reduction of the total gas quantity as a result of water condensation always causes an increase in gas concentration which is all the higher the more water condenses due to dew point reduction. In **figure 5**, the upper family of curves stands for the insoluble gases. For comparison, the curves for soluble ammonia are plotted as well.

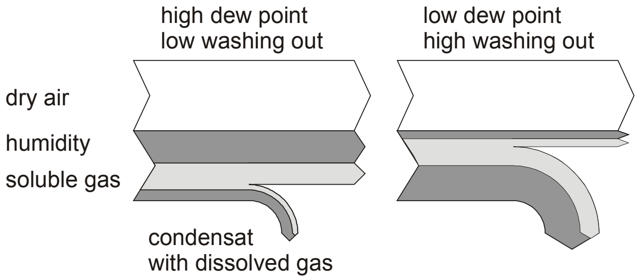

Figure 2: Diagram of condensation and absorption caused by dew point reduction

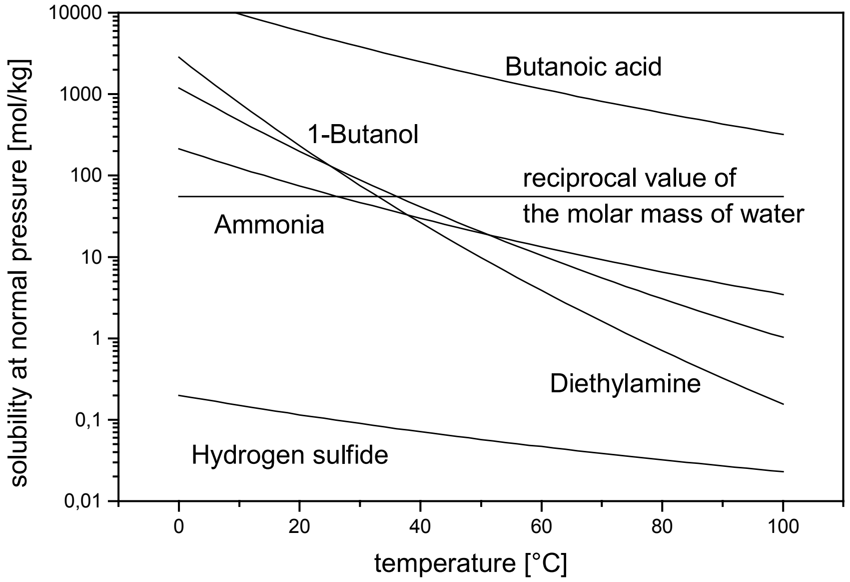

Figure 3: Henry's coefficient of solubility Λ for different gases

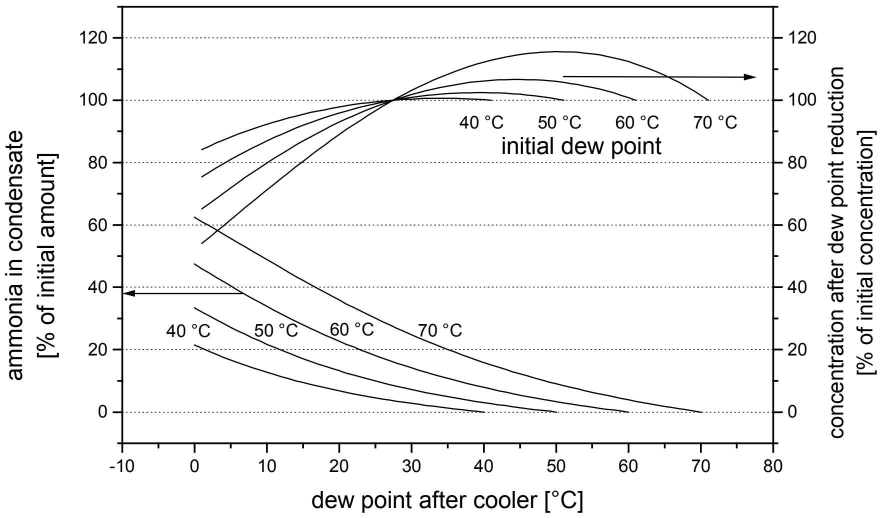

Figure 4: Concentration shift and washing out of ammonia

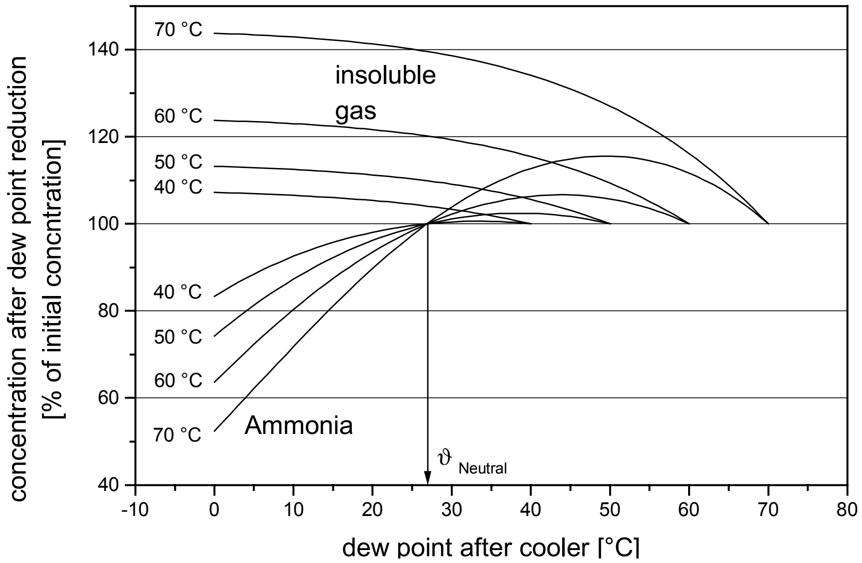

Figure 5: Comparison of the concentration changes of insoluble gases with ammonia

Washing Out of Odorous Compounds

The use of micro-sensorial odour measuring technology ("electronic noses"), which is to be expected in the future, generally requires the conditioning of the measuring gas flows. The measuring gases cannot be directly admitted to the sensors because humidity acts as a disrupting component. If, however, odour mixtures are to be identified by an odour sensor system, the changing influence of gas conditioning, such as washing out, must be known.

Odorous compounds must have a certain water-solubility because absorption by the mucous membrane of the nose is the prerequisite for their binding at the receptors of the olfactory cells. Of course, this water solubility may also lead to washing out if the degree of solubility is high. **Table 2** lists data for some selected odorous compounds, along with the calculation of the coefficients of the Henry equation, as defined in equation 6, 7, and 8. The last line gives the calculated neutral temperatures, the intersecting points of the solubilities with the reciprocal value of the molar mass of water.

The solubility data of Table 2 result in concentration changes, as shown in **figure 6** using an input dew point of 50°C as an example. Especially butyric acid, but also n-butanol are washed out to a very large extent. Three of the odorous compounds discussed here, namely ammonia, which has already been presented, n-butanol, and diethylamine, have a neutral temperature. The intersecting points with the reciprocal value of the molar mass of water at ϑ = 26.3°C (ammonia), ϑ = 36.3°C (n-butanol), and ϑ = 33.0°C (diethylamine) have already been given in Figure 2.

The calculated concentration changes lead to alterations of the composition of a mixture of odorous compounds. For the selected odorous compounds, **figure 7** shows the alterations using a radar plot for differently large dew point reductions as an example. The original mixture of odorous compounds always has an initial concentration of 100%. The lowering of the dew point has different effects. The highly soluble gases show significantly reduced concentrations. The concentrations of those gases, however, which are less soluble or largely insoluble even exhibit an increase.

Table 2: Coefficients of the Henry equation (data from [5])

Coefficients of the Henry equation	Butanoic acid	1-Butanol	Ammonia	Diethylamine	Hydrogen sulfide
B and C	4000*	7200	4200	10000	2200
$\lambda_{25°C}$	4700	130	58	130	0.1
A	-4.96	-19.28	-10.03	-28.76	-9.68
$\vartheta_{neutral}$	-	36.2	26.3	33.0	-
* no value available, assumption					

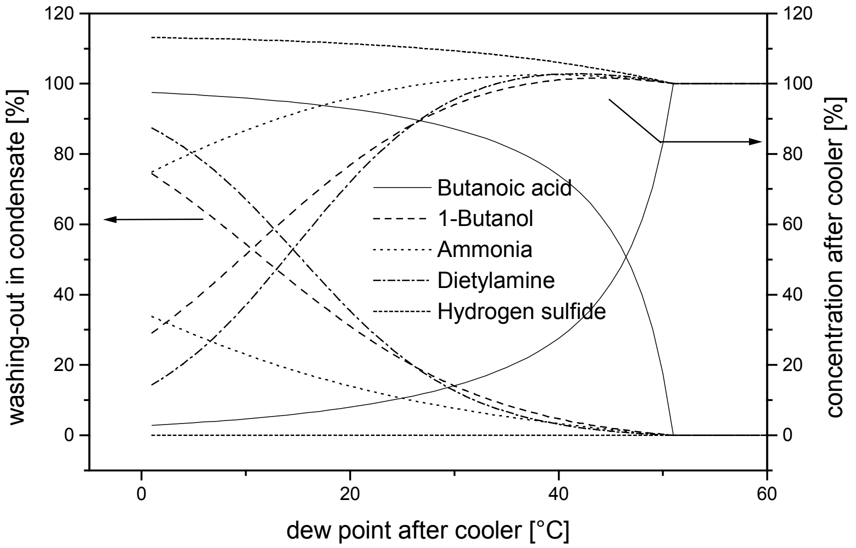

Figure 6: Alterations of the concentration of odorous compounds

Lowering Dew Point by Means of Dry Air Mixture

When taking samples of odour polluted air flows, dry air is mixed instead of condensing the water component in order to avoid the washing out problem. Diluting samples for olfactometric measurement is unproblematic because in the olfactometer they need to be diluted to the odour threshold in any case. For the on-line measurement of odorous compounds, however, dilution is a problem because the typical low concentrations are diluted further. For the calculation of the dilution effect, the water content x defined in equation 1 can be employed. The percentage of dry air sets the high input humidity x_{in} apart from the final humidity x_{fin} after the mixture of dry air.

Simply, by balancing the equations:

$$c'_{in} = \frac{m_G}{m_{tot,in}} = \frac{m_G}{m_{da.in} + m_W} = \frac{m_G}{m_{da.in}\left(1 + x_{in}\right)} \qquad (13)$$

$$c'_{fin} = \frac{m_G}{m_{tot,fin}} = \frac{m_G}{m_{da.fin} + m_W} = \frac{m_G}{m_{da.fin}\left(1 + x_{fin}\right)} \qquad (14)$$

$$m_{da.fin} \cdot x_{fin} = m_{da.in} \cdot x_{in} \qquad (15)$$

leads to the relation:

$$c'_{fin} = c'_{in} \frac{\dfrac{1}{x_{in}} + 1}{\dfrac{1}{x_{fin}} + 1} \qquad (16)$$

Figure 8 shows three final dew points after the mixture of dry air which have been calculated using equation 16. It is demonstrated that, given an input humidity with a dew point of 60°C and a final target humidity with a dew point of 20°C, concentration drops to only 11%. For on-line measurements, the method of gas dilution is therefore problematical even if the mixture of odorous compounds remains constant when diluted.

Correction Calculations for Gas Measurements

The presented calculation methods for concentration changes allow the actual emissions of biological emitters to be calculated. Without the calculation of the concentration effects, considerable under and overestimations occur.

Figure 9 shows the measuring chain for the examination of a warm biological emitter with forced ventilation. This case corresponds to the sampling of a biofilter or a housed composting facility, for example. The goal is the measurement of the emission mass flow which leaves the emitter. The warm, humid measuring gas is dehumidified by a cooler. After the cooler, the gas analyser measures an altered concentration c_{out}, which has been changed due to condensation and washing out.

The actual concentration c_{in} before the cooler is calculated back as follows:

$$c_{in} = \left[\left(p_{sdew} - p_{sK}\right) \cdot M_W \cdot \Lambda_K + p_{ges} - p_{sdew}\right] \cdot \left(p_{tot} - p_{sK}\right)^{-1} \cdot c_{out} \qquad (17)$$

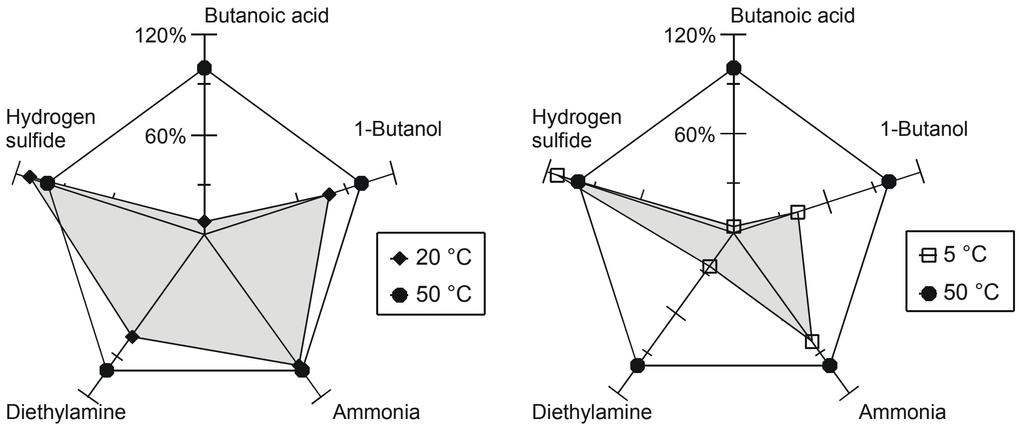

Figure 7: Alteration of the odour pattern due to the lowering of the dew point from 50°C to 20°C and 5°C

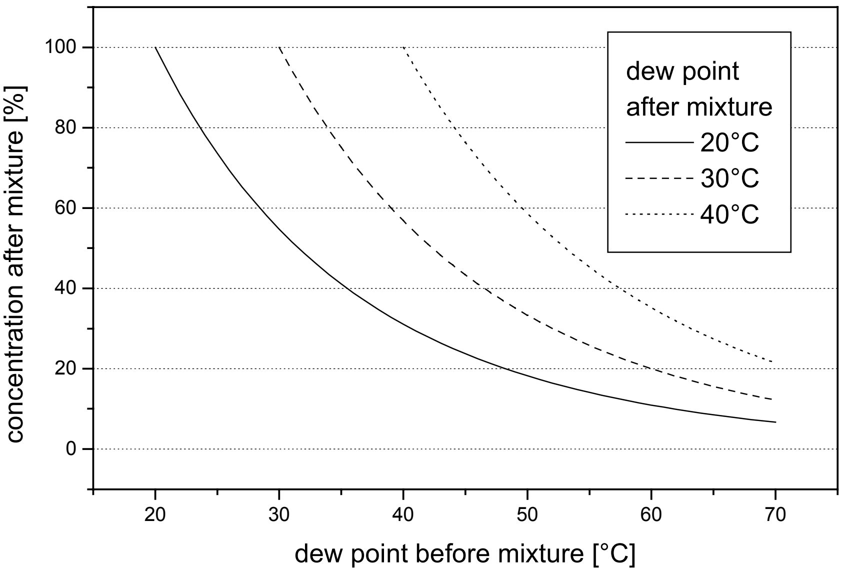

Figure 8: Concentration dilution at lowered dew points due to the mixture of dry gas

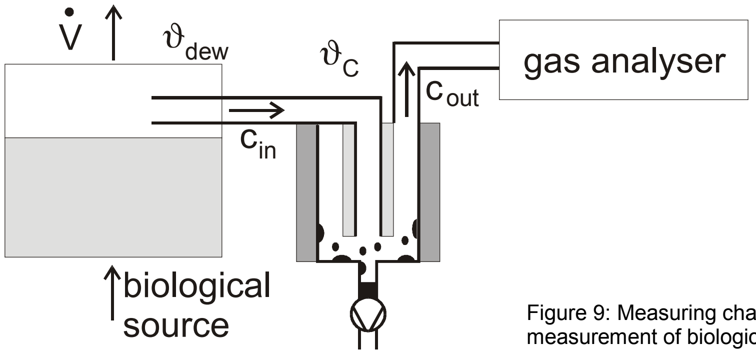

Figure 9: Measuring chain for the measurement of biological emissions

If the volumetric flow $\dot V_{air}$ which leaves the emitter is known, the emission mass flow is given by the following equation:

$$\dot m = \frac{c_{in} \cdot \dot V_{air} \cdot M_{gas} \cdot T_{stand}}{v_{molar} \cdot T_{meas}} \tag{18}$$

The temperature correction T_{stand}/T_{meas} is necessary for the conversion of the volumetric flow $\dot V_{air}$ measured at T_{meas} to standard conditions.

Summary

When measuring gas concentrations after gas coolers alterations of the gas concentrations due to condensation and washing out have to be taken into account. If the concentration shifts are not compensated, this leads to significant errors when measuring the concentration of both water soluble and insoluble gases.

Odorous compounds exhibit an additional effect. Due to different solubilities, the composition of the mixture and the odour impression changes. For olfactometric sampling, the use of measuring gas coolers is therefore problematical. Conversely, concentration drops drastically when sample gases are diluted, which makes measurements more difficult.

In this contribution, the necessary calculation relations are given, and the back calculation, as well as the determination of the emission mass flow are carried out using an example.

Symbols Used

p_{tot}	[bar]	Total pressure
$p_s(\vartheta)$	[bar]	Saturation pressure of water at the temperature ϑ
p_{sK}	[bar]	Saturation pressure of water at the temperature ϑ_K
p_{sdew}	[bar]	Saturation pressure of water at the temperature ϑ_{dew}
p_d	[bar]	Partial pressure of water
p_{gas}	[bar]	Partial pressure of the gas
RH	[%]	Relative humidity
n_i	[mol]	Number of moles of a component i
x	[kg/kg$_{da}$]	Humidity load related to the amount of dry air
x'	[kg/kg$_{tot}$]	Humidity load related to the entire air
M_W	[kg/kmol]	Molar weight of water (18.016)
M_{air}	[kg/kmol]	Molar weight of air (mean value: 28.96)
M_{gas}	[kg/kmol]	Molar weight of the gas
$C_{diss.gas}$	[mol/kg]	Equilibrium concentration in water
c_{in}	[m$^3_{gas}$/m$^3_{air}$]	Concentration of the measuring gas
c_{out}	[m$^3_{gas}$/m$^3_{air}$]	Concentration after the cooler
c_{fin}	[m$^3_{gas}$/m$^3_{air}$]	Concentration of the measuring gas after mixing
c'	[kg$_{gas}$/kg$_{air}$]	Mass related concentration
m_I	[kg]	Mass percentage of I: gas, water, and dry air
$\lambda(\vartheta)$	[mol/kg bar]	Absorption coefficient
$\Lambda(\vartheta)$	[mol/kg]	Absorption coefficient
Λ_K	[mol/kg]	Absorption coefficient at temperature ϑ_K
ϑ_K	[°C]	Temperature of the cooler
ϑ_{dew}	[°C]	Dew point of the measuring gas
$\vartheta_{\mathrm{neutral}}$	[°C]	Neutral temperature (no concentration change)
T_{stand}	[K]	Standard temperature (273.15 K)
T_{meas}	[K]	Temperature under measuring conditions
$\dot V\ (T_{meas})$	[m^3/s]	Volumetric flow of the source at T_{meas}
v_{molar}	[m^3/mol]	Molar volume at T_{stand} (22.4 10^{-3} m^3/mol)
$\dot m$	[kg/s]	Emission mass flow

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