

## Method sheets

The selected methods were evaluated a second time in more detail, paying special attention to the method validation data. If the required data are available, the overall uncertainty according to EN 482 (1994) and the expanded uncertainty according to prEN 482 were calculated.

Most other requirements were the same as used for the indicative rating. The additional requirements for final rating of a method were mainly the results of the uncertainty calculations and the working range of the method.

### Structure of a method sheet

The method sheet in its first part gives an extended description of the individual sampling and analytical conditions. Furthermore the European IOE-LV and the range of limit values from the lowest limit value (LLV) to the highest limit value (HLV) in other European countries is given for long term and short term measurements.

In the section method evaluation data and in the subsequent sections, all available data for evaluation are given. The working group tried to identify all components of measurement uncertainty. For several of the components the numerical value was unknown and as a consequence had to be agreed upon in form of a consensus.

### Overall uncertainty (EN 482)

For calculation of the overall uncertainty (OU) the formula

$$OU = \frac{|\bar{x} - x_{ref}| + 2s}{x_{ref}} \times 100$$

was used.

$\bar{x}$  mean value of results of a number n of repeated measurements

$x_{ref}$  true or accepted value of the concentration

$s$  standard deviation of measurements

In most methods the analytical or method bias ( $|\bar{x} - x_{ref}|$ ) is stated, for gases and vapours this value can be used for calculation of the overall uncertainty.

For aerosols the formulas according to EN 13890 are used.

For all *inhalable dust samplers* this formula relies on the assumption that the sampling bias is < 5 % and the sampling precision is < 5,3 %:

$$OU = \left( \left( 0,95 \times bias_{analytical} \right) + 0,05 \right) + 2 \times \sqrt{0,00278 + RSD_{analytical}^2} \times 100$$

For all *respirable samplers* this formula relies on the assumption that the sampling bias is < 10 % and the sampling precision is < 7 %:

$$OU = \left( \left( 0,9 \times bias_{analytical} \right) + 0,1 \right) + 2 \times \sqrt{0,00518 + RSD_{analytical}^2} \times 100$$

## Sampled air volume

For the sampled air volume the data given in prEN 482 – Annex C chapter 2.1 were used.

- Pump flow measurements  
Table C1 uncertainty data for flow meters were used
- Pump flow stability  
EN 1232 and EN 12919 require that the flow rate is maintained to within  $\pm 5$  % of the set value throughout the sampling period. Assuming a rectangular probability distribution, the non-random uncertainty component of the pump flow stability is  $u_{pumpflow} = 5 / \sqrt{3}$  %.
- Sampling time  
In case of long term measurements this uncertainty component is very small and can be disregarded.  
For short term measurements, if the time is recorded to the nearest minute, the relative standard deviation is, for example, 3,8 % for a sampling time of 15 min.
- Uptake rate for diffusive sampling  
The uncertainty of the uptake rate is normally given in the method or by manufacturer as relative standard deviation in percent.

## Sampling efficiency

- In case of vapours the assumption is a sampling efficiency of 100 %.
- For diffusive samplers the back diffusion has to be taken into account. If information is given in the method this value was used. If no value was given, a default value of 10 % was fixed. Assuming a rectangular probability distribution, the non-random uncertainty component of the back diffusion is then given by  $(u_{backdiffusion} = 10 / \sqrt{3} \text{ %})$ .

For sampling inhalable aerosols several sampler types are used. The most commonly used samplers that fulfil the requirement of EN 481 are GSP, IOM and the multi orifice sampler. In Europe these aerosol samplers are widely used. For all uncertainty calculation methods involving an aerosol sampling a rough estimation as consensus value for these samplers was used:

- Calibration of the sampler test system  
Uncertainty value: 0,5 %
- Experimental imperfection  
Uncertainty value: 4,0 %
- Deviation from sampling convention  
Uncertainty value: 7,5 %

NOTE: When using another sampler the user has to consider that the uncertainty value for sampling can be much larger.

### Sample storage and transportation

Data given in the method when available

In many methods information similar to “The sample can be stored at room temperature for about two weeks” or “There is a risk of sample loss from the filter if it is not handled carefully during transportation, especially for higher sample loadings, but once in the laboratory samples are stable indefinitely” is given. This is a sufficient information.

NOTE: For critical substances: If no information was given downgrade the method to B. For uncertainty calculation use a value of 10 % ( $u_{stor/trans} = 10/\sqrt{3}$  %).

NOTE: For aerosol measurements sample stability is normally a negligible problem.

### Method recovery

- If a method prescribes a correction for bias the random uncertainty component of the method bias is to be taken into account.
- If no correction is required, the non-random uncertainty was taken into account.

### Test gas atmosphere

Test gas atmospheres have a random uncertainty component. A typical value of experience is  $\pm 3$  % stability of test gas atmosphere. For uncertainty calculations a numeric value of 3 % ( $u_{testgas} = 3/\sqrt{3}$  %) was therefore used.

### Sample spiking

Uncertainty components for the purity of chemical standards, compound weighing and the uncertainty of syringes/micropipettes were taken into account.

- Mostly the chemical standards have a purity  $> 99$  %, in which case the uncertainty component is very small. For chemicals with purity  $> 99,9$  % this value can be disregarded.  
For uncertainty calculations the value of purity reported in the method was used, if no information is given an uncertainty value of 1 % was used.
- For compound weighing an uncertainty value of  $\pm 0,5$  % was used.

- For syringes/micropipettes an uncertainty value of  $\pm 3\%$  was used.

### **Humidity**

For several methods, and especially in case of gas and vapour methods, humidity can cause a strong influence on method uncertainty.

- If the humidity was taken into account during method validation (recovery developed at high and low humidity) humidity influence is included in the method precision.
- When the method validation was carried out at medium humidity (e.g. laboratory air) an additional uncertainty value of  $\pm 3\%$  for uncertainty calculations ( $u_{\text{humidity-medium}} = 3/\sqrt{3}\%$ ) is used.
- When no information about humidity was available or experiments were carried out with dry air an uncertainty value of  $\pm 5\%$  for uncertainty calculation ( $u_{\text{humidity}} = 5/\sqrt{3}\%$ ) is used.

### **Lack of fit of the calibration curve**

A value of  $2\%$  was used as an estimation for the uncertainty associated with the lack of fit of the calibration curve.

### **Instrumental drift**

A value of  $\pm 5\%$  ( $u_{\text{instrumental drift}} = 5/\sqrt{3}\%$ ) was used as a default value for instrumental drift when no information was available in the method.

### **Dilution of standard solution/Preparation of standard solutions**

The uncertainty is normally included in the analytical uncertainty.