



Update on the revised EN 13725:2021

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On the 20th of November 2012 the first meeting took place of Working Group 2, tasked by CEN/TC274 "Air Quality" to revise EN 13725:2003 'Air Quality - Determination of odour concentration by dynamic olfactometry'. After 8 years of work and 17 meetings, the work is finally completed and submitted for formal vote in the CEN Technical Committee 264 "Air Quality" in 2021. This paper describes some of the important changes that will affect the practice of olfactometry in Europe, once this standard is published as EN 13725:2021.

1. Introduction

EN 13725 was initially published as EN 13725:2003, after the draft was completed by working group 2 'Dynamic Olfactometry' of the Technical Committee 264 'Air Quality' of the European Committee for Standardization (CEN). In the 17 years since the standard was introduced a lot of experience was built up while working with this standard, often under ISO17025 accreditation. The standard has been widely adopted in Europe. Outside Europe various countries introduced national standards based on EN 13725 (Australia, Chile and Colombia).

According to the internal regulations of CEN a standard is reviewed every 5 year to determine if revision is needed or if the standard continues to be fit for purpose until the next review. There were two reasons for the revision of standard identified at the start of this project in 2012:

- the outcome of the systematic review of EN 13725 indicated the need for a revision;
- a lot of things have changed in the practice of odour measurements.

Since this standard is very important for the enforcement of odour policy and compliance with environmental licenses in Europe, key topics are widely discussed by those actively using the method. The revision took 8 years of work and 17 meetings before a final draft for formal vote could be submitted to CEN before the deadline of 24th of March 2021. The formal vote by TC264 "Air Quality" is expected within 8 weeks after the deadline.

Upon a positive voting outcome, the standard will undergo editorial checks, and will then be translated into German and French before publication.

A great amount of work has been done by the members of WG2, which led to an increase of the number of pages from 74 to 125. To get the job done effectively, the work was divided over several task groups. The main task of a task group is:

- to collect information;
- to derive key issues from that information;
- to give a summary of that information.

The recommendations of the task groups are then discussed in the plenary meeting of the Working Group to find a consensus on the content and the final text of the standard.

The aim of this paper is to summarize some of the key changes which will affect the practice of olfactometry in Europe, once this standard is published in 2021. This paper has been structured into 9 sections corresponding with each of the task groups created.

2. Task Group 1. Sample storage and materials for olfactometry

This group addressed questions raised on recovery of odorants in dilution systems and sample containers, on the basis of studies using real-time PTR-MS techniques or GC-MS (Kasper et al., 2017; Sironi et al., 2014; Eusebio et al., 2017). The task group reviewed the new experimental data on recovery of odorants and reviewed the recommendations for the use of materials.

Polytetrafluoroethylene (PTFE), tetrafluoroethylene hexafluoropropylene copolymer (FEP), polyethyleneterephthalate (PET or Nalophan), titanium, passivated stainless steel and aluminium were considered appropriate material as sample equipment.

The requirement for treating stainless steel and only using passivated stainless steel for surfaces in contact with the odorant sample, is a significant modification of the standard's requirements. In addition to listing materials the revised standard contains a minimum requirement for the recovery achieved by the dilution apparatus. This is a new requirement which will require additional type testing by olfactometer manufacturers.

Inappropriate materials, not allowed to get into contact with the sample, are for example silicone or natural rubber. Sampling probes and tubes that are exposed to odorous gas sample during a sampling session, shall not be re-used unless they are effectively cleaned and odourless before re-use.

Fluorine polymers such (FEP), polyvinylfluoride (PVF, Tedlar™), polyvinylidene fluoride (PVDF), polyethyleneterephthalate (PET, Nalophan™) are considered appropriate for making sample containers. Alternative materials can become available after testing. To test new materials for suitability, they shall be assessed for being odourless and shall be assessed to confirm that they can hold odorants with a recovery that is equal or better than that of appropriate materials. Some small molecules have been observed to readily diffuse/absorb through specific materials (e.g. DMS and H₂S through Flexfoil™; H₂O and polar compounds, H₂S, acid etc through PVF (Tedlar™), NH₃, H₂S and H₂O through PET (Nalophan™). For this reason, storage time shall be minimized. The maximum storage time of 30 hours that was stated in the first edition was maintained after review.

3. Task Group 2. Reference material for panel selection and panel management procedures

The introduction in the first edition of EN 13725 of a reference odorant, n-butanol, with a conventional quantity value for its detection limit, defined as the European Reference Odour Mass (EROM), allowed for rigorous selection of panel members, to achieve a group of human 'sensors' with very similar olfactory sensitivity.

The fact that the selection was done with one reference odorant, with a necessary assumption of transferability of the panel selection effectiveness to other odorants, caused widespread discussion and reservations among practitioners.

The need for additional reference odorants, both single compound and defined multi-odorant mixtures became evident.

The revision addressed this issue by introducing an experimental procedure for establishing a Secondary Reference Odour Mass (SROM) for single odorants and defined mixtures of odorants. Once an SROM value

has been established, with its associated uncertainty, a laboratory can choose to use multiple reference odorants and also choose these odorants to be more relevant to their area of application. The use of n-butanol as a reference material for QA/QC was maintained, to provide continuity.

Establishing a procedure for determining SROM values that are traceable to the EROM allows the use of a wider range of reference materials and reducing the concerns about the transferability of panel selection procedures. It also allows the determination of laboratory bias on multiple reference odorants, which benefits the perspective on the uncertainty of the measurement results of a laboratory.

4. Task Group 3. Sampling of passive area sources

By definition, a passive area source does not have a controlled or controllable outward flow and can represent a large surface (from few to thousands of square meter). It is typically the case for areas like waste landfills, lagoons (wastewater or sludge), fields after manure spreading and unaerated compost piles. In order to characterize a source-specific odour emission rate for passive area, approaches are based on covering a small part of source with a sampling device and then flush the covered area with an odourless gas and collect a sample (Capelli et al., 2018). Two main types of devices are used worldwide: flux chambers with a very low flow and wind tunnel that can be used with a larger range of internal flow. Experiments showed that the difference between different devices can produce differences in the sampled odour concentration up to a factor 100 (Guillot et al., 2014).

Indeed, the odorant emission or transfer rate depends on several factors such as, concentration in liquid phase (boundary layer), concentration in gas phase (boundary layer), temperature (both of the liquid and the atmosphere), relative humidity in the atmosphere, characteristics of the flow of air over the surface (sweep velocity, turbulence), turbulence in the liquid boundary layer, the Henry constant for the odorant being transferred. All the combinations of these non-exhaustive factors can sometimes lead to overestimating emissions and sometimes to underestimating emissions. Models of emission for a pure compound have been developed for controlled conditions (in a laboratory) (Lucernoni et al., 2017, Invernizzi et al., 2019). However, real-world open-air situations and complex mixtures can produce different results. The case of solid sources is even more complex than for liquids because of the limitation of compound diffusion into the solid itself (Lucernoni et al., 2018).

Wind tunnel sampling devices are often used in situations where the volatilization of odorants from the source to the atmosphere is mainly driven by forced convection, i.e. the mass transfer due to the action of the wind flow over the surface like for wastewater treatment tanks.

Since all the above-mentioned aspects linked to sampling conditions affect the relative transfer, it is important to specify all parameters. If a protocol from an existing guideline is used to collect the odorous sample this also affects the outcome. Therefore, two samples collected with different devices (or different protocols) cannot be compared.

The revised standard does not require the adoption of a specific device. The Task group considered setting a criterion for suitable devices based on a specific mass transfer rate of a test compound under standardised conditions. However, despite a lot of experimental efforts, no standard meteorological or operational conditions for odour emission measurement for passive area sources could be defined to pursue this approach.

Regrettably, the sampling of passive area sources is not addressed in the revised normative text. For now, the subject remains outside the scope of EN 13725:2021. The standard will contain an informative Annex M which provides relevant information and examples of devices which may provide a starting point for a future revision.

5. Task Group 4. Sampling of active area sources

The chapter on active area sources is new compared to the previous edition of the standard. The task group reviewed national standards which have addressed this topic, such as the German VDI3880 guideline.

The new normative clause describes a procedure for sampling odour emissions from active area sources, which are defined by having an exit velocity > 0,008 m/s. Depending on the size and character of the surface the sampling can be performed by sheet covering of the total area or by collecting samples on using sheet covers on selected partial areas which each have been shown to have a homogeneous flow in a preliminary flow rate survey of the entire area source. Sampling by covering the whole area is preferred if possible, because the most representative sample is obtained in this way.

Sampling on selected part areas can also be performed by means of a sample hood with at least 1 m² area.

The volume flow is measured in the chimney on the hood according to EN-ISO 16911-1. The odorant gas samples are drawn at the same point.

6. Task Group 5. Dynamic dilution during stack sampling

The first edition of the EN 13725 standard described static and dynamic pre-dilution during sampling. It required the dilution apparatus to be calibrated in a similar way the olfactometer is calibrated.

This approach did not provide a direct measurement in the collected samples of the dilution factor applied during sampling. Such a direct check is desirable to compensate for the fact that differences in pressure (and temperature) in the stack may cause the diluting probe to produce different dilution factors from those under laboratory conditions.

For this reason, the revised EN 13725 requires measurement of indicator compounds in the undiluted gas and in the diluted sample. Often this can be achieved measuring oxygen, which naturally occurs in ambient air, when oxygen free nitrogen is used as neutral gas for dilution. Other compounds can be used for this purpose, depending on the sampling conditions. This requirement applies equally to static dilution.

In special cases, where it can be ascertained that the influence of pressure and temperature on the dilution factor is negligible, measurements of flow rate of sample and dilution gas can be applied as an alternative method for determining the dilution factor.

7. Task Group 6. Implications of EN 15259 Air quality - measurement of stationary source emissions and other relevant sampling standards

The sampling part of the standard, which was previously poorly developed, has been improved significantly, aligning with the requirements of framework standards relating to measurement of emissions from stationary sources such as EN 15259. This includes the definition of measurement objectives and the design of a measurement plan. EN 15259 defines requirements for measurement sections and sites at waste gas ducts of industrial plants and for measurement objective, plan and report.

The revised EN 13725 requires that the measurement plan shall be drafted, prior to the measurement, describing a sampling strategy. The plan shall be based on a preliminary investigation and shall be compliant with EN 15259 as far as possible, considering the constraints of odour sampling. The resulting sampling strategy shall fix for example the location of the sampling points, the duration of sampling, the number of samples.

The EN13725 standard specifies aspects for the methods used for the sampling of odorous emissions from:

- a) point sources (conveyed or ducted emissions);
- b) active area sources (e.g. biofilters);

The enforcement of legislation often requires the determination of the odour emission rate from the stationary sources. For point sources and active area sources (using sampling hood), it requires an accurate measurement of the volume flow rate of the waste gas. The measurement section and measurement site shall comply with EN 15259. The volume flow rate shall be measured according to EN-ISO 16911-1. The introduction of EN 15259 also required an in-depth review of the terminology used in EN 13725 to align it with EN 15259

8. Task Group 7. Calculation of uncertainty

In the first edition, EN 13725:2003 introduced a framework for quality assessment based on ISO 5725, and the use of n-butanol as a reference odorant with a known European Reference Odour Mass, providing an anchor for metrological traceability. The estimation of uncertainty was made possible by odour measurements on reference materials of the reference odorant under reproducibility or repeatability conditions.

Critical views were noted on this approach, asserting that it rested on the assumption of transferability of the results obtained for the primary reference odorant gas n-butanol to samples of different composition.

Also, the issue of sources of additional uncertainty were raised, which were not included in the quality assessment framework. This included, for example, the composition of the panel in each panel session, which varies in normal operations in a laboratory, but not always in proficiency testing.

To address these concerns the task group developed a more inclusive approach to uncertainty assessment which includes the uncertainty introduced by using different panel composition. The task group also devised an approach which allows the determination of uncertainty using duplicate samples of environmental odours. In a

further move to enrich the uncertainty assessment possibilities the use of secondary reference odorant gas was included in the approach, allowing both single odorant and multi-odorant reference materials to be developed. A specific method was introduced to determine the relation of the Secondary Reference Odour Mass (SROM) with the EROM value for the primary reference n-butanol in an olfactometric procedure. This allows laboratories to introduce a wider range of reference materials to assess uncertainty with more relevant reference odorants and with environmental odour samples. The approach to determining uncertainty is closely following methods included in EN20988:2007

The efforts of the task group have resulted in a far more comprehensive approach to uncertainty assessment for dynamic olfactometry which will hopefully address some of the issues raised on the transferability of n-butanol based uncertainty estimates to the actual results of a laboratory used for odour regulation compliance testing.

9. Task Group 8. Compatibility of Yes/No and Forced Choice methods

The responses of the panel members can be gathered in two ways: Firstly, in a “yes/no” inquiry in which the panel members must choose between “Yes, there is an odour” and “No, there is no odour” for each presentation of the diluted odorous gas sample. The alternative procedure is a forced choice inquiry. Here, the panel member must indicate in which of the presented sample ports they detect the diluted odorant gas. Typically, this is two alternative or three alternative forced-choice. Even if panel members are unable to detect a difference, they must indicate their choice. Subsequently they indicate how convinced they are of their choice: “certain”, “inkling” or “guess”. The results are then evaluated as described in EN 13725, through an evaluation of the “certain” responses.

Since only the “certain” and “yes” responses are used in the calculation of the results, both methods yield comparable results and are accorded equal status in EN 13725.

Questions were raised if the assumption of equivalence of the results can be maintained as valid. The task group looked at the available published investigations and concluded that the equivalence of the two response modalities is supported by the results of several round robin tests (van Harreveld et al., 2009, Maxeiner, 2015).

10. Task Group 9. Health and safety issues

The inclusion of sampling in the standard required a review of the Health and Safety precautions. Also, the risk assessment for assessors and panel members and laboratory staff was a matter that needed more specific guidance. After all, dynamic olfactometry is a biometric test procedure involving exposure of human subjects to samples of odorant chemicals, some of which are known to be associated with a potential risk.

The task group considered the Health and Safety precaution guidance for all personnel involved in measurement of odour emissions. Their advice led to the following revisions of the standard. Risk assessments shall be carried out for all stages of the measurements. The sampling team can be at risk from toxic compounds within the odorous gas being sampled, there are risks when transporting samples and risks to the olfactometry operator and the panel members. The text in particular points out the hazards of hydrogen sulfide and carbon monoxide, both relevant to the processes sampled for implementing odour regulations.

The sampling team is often exposed to hazardous working conditions therefore preliminary safety assessments shall be carried out prior to sampling to ensure, for example safe access to the sampling location, provision of protective equipment and clothing, protection from heat, dust, bio-aerosols, confined spaces, hazardous weather condition, etc. These aspects are also addressed in framework standards such as EN 15259.

Panel members have no opportunity to make their own risk assessment and depend on the sampling team and the olfactometry operator to protect them. The revised standard provides detailed guidance on when to conduct a specific risk analysis and provides a general approach.

The olfactometry operator is at particular risk in handling the samples when they contain high concentrations of toxic compounds from industrial processes, and they shall be informed about any potential toxicity on the chain of custody form prepared by the sampling team.

11. Conclusions

The revision of the first edition of EN 13725:2003 seeks to address the issues where practitioners, but also users of the results of these measurements, felt the method fell short of expectations. The review, while part of the regular review cycle all CEN standards are subject to, has led to substantial new content. The clauses on sampling, poorly developed in the first edition, now aspire to provide clear guidance to practitioners, while aligning the practice to framework standards such as EN 15259. The revised approach to uncertainty assessment has addressed fundamental perceived flaws in the first edition. The use of a wider range of reference odorant gases and paired environmental samples significantly improves the estimate of measurement uncertainty of olfactometry. One main topic eluded the working group charged with the revision. The sampling of passive area sources remains outside the scope of the standard. This relevant issue will need to be revisited in the next round of revision.

If the vote of TC264 "Air Quality" is favourable for the revised draft standard delivered by Working Group 2 "Dynamic Olfactometry" the olfactometry practitioners will have a challenge ahead to adapt their practice to a thoroughly revised and improved EN 13725:2021.

References

- Capelli L., Sironi S., Del Rosso R., 2013, Odor Sampling: Techniques and Strategies for the Estimation of Odor Emission Rates from Different Source Types, *Sensors* 13, 938-955.
- CEN, EN 12619:2013, Stationary source emissions - Determination of the mass concentration of total gaseous organic carbon - Continuous flame ionisation detector method, Committee Européen de Normalisation, 2013
- CEN, EN 13725:2003, Air quality. Determination of odour concentration by dynamic olfactometry (European Standard EN 13725:2003). European Committee for Standardization, 2003.
- CEN, EN 15259:2007 Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report, 2007.
- CEN, EN ISO 16911-1:2013, Stationary source emissions - Manual and automatic determination of velocity and volume flow rate in ducts - Part 1: Manual reference method (ISO 16911-1:2013)
- CEN, EN ISO 20988:2007, Air quality — Guidelines for estimating measurement uncertainty
- Eusebio L., Capelli L., Sironi S., 2017, H2S Loss through Nalophan™ Bags: Contributions of Adsorption and Diffusion, *The Scientific World Journal* 2017, 1-15.
- Guillot J., Clincke A., Guilleman M., 2014, Odour Emission from Liquid and Solid Area Sources: a Large Intercomparison of Sampling Devices, *Chemical Engineering Transactions* 40, 151-156.
- van Harreveld A. P., Mannebeck D., Maxeiner B., 2009, Proficiency testing as the key element in implementing EN13275 olfactometry, *Water Science & Technology* 59,1649-1655.
- Invernizzi M., Bellini A., Miola R., Capelli L., Busini V., Sironi S., 2019, Assessment of the chemical-physical variables affecting the evaporation of organic compounds from aqueous solutions in a sampling wind tunnel, *Chemosphere* 220, 353-361.
- Kasper P.L., Mannebeck D., Oxbøl A., Nygaard J.V., Hansen M.J., Feilberg A., 2017, Effects of Dilution Systems in Olfactometry on the Recovery of Typical Livestock Odorants Determined by PTR-MS, *Sensors* 17, 1859.
- Lucernoni F., Capelli L., Busini V., Del Rosso R., Prata Jr. A.A., Stuetz R.M., Sironi S., 2018, Investigation of mass transfer phenomena affecting emission rate of gaseous compounds from porous solids, *Process Safety and Environmental Protection* 116, 516-526.
- Lucernoni F., Capelli L., Busini V., Sironi S., 2017, A model to relate wind tunnel measurements to open field odorant emissions from liquid area sources, *Atmospheric Environment* 157, 10-17.
- Maxeiner, Björn, Proficiency test for dynamic olfactometry with real odour, 6th IWA Conference on Odours & Air Emissions, Paris, 2015
- Sironi S., Eusebio L., Capelli L., Boiardi E., Del Rosso R., 2014, Ammonia Diffusion through Nalophan Double Bags: Effect of Concentration Gradient Reduction, *The Scientific World Journal* 2014, 1-8.
- VDI 3880:2011-10, Olfaktometrie – Statische Probenahme (Olfactometry; Static sampling), Berlin, Beuth Verlag.