Preliminary Remarks

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Evaluation of methods for air analysis without experimental examination

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1 Introduction

In Germany the "Air Analysis" Working Subgroup of the Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area of the Deutsche Forschungsgemeinschaft (DFG) and the Analytical Subcommittee of the Chemistry Board of Experts of the German Social Accident Insurance (DGUV)[1] are the two major groups involved in the development, checking and publication of analytical methods to determine the concentration of hazardous substances in the air of working areas. Whereas the methods issued by the DFG working subgroup have been experimentally checked up to date, a board of experts examines the suitability of methods in the Analytical Subcommittee of the DGUV. It has become increasingly difficult in recent years to find examiners of the methods for the "Air Analysis" Working Subgroup who have the necessary means and personnel resources to carry out an experimental test. Shortfalls have frequently occurred when analytical methods were to be examined, with the consequence that it was not possible to publish important methods that should have been checked with respect to newly issued occupational exposure limits. Therefore, a concept was devised for an equivalent examination carried out by experts to ensure a more rapid implementation of methods. The principle of such plausibility checks is to comprehend all the required performance data of the method to be tested. Experimental testing will still be the preferred procedure of the "Air Analysis" Working Subgroup in the future.

1 Formerly: of the Federation of the Employment Accidents Insurance Institutions of Germany (HVBG).

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2 Prerequisites and important contents of the check

The author must have the necessary expertise to develop methods for the measurement of hazardous substances in workplace air and to assess occupational exposure. These requirements are listed in the LASI (Länderausschuss für Arbeitsschutz und Sicherheitstechnik) publication LV 2.2 [1].
The test protocol must comply with the requirements of EN 482 [2] and also with EN 481 [3] in the case of particulate hazardous substances. In addition, the method description must meet the requirements of ISO 78/2 (1999) [4].
Complete basic information on the method must be given, and it must be stated in particular whether the method is new or was experimentally developed on information for workplace measurements given in the literature. As a rule, a plausibility check is impossible in the case of newly developed analytical methods.
The following fundamental criteria must be taken into consideration for a preliminary decision on whether to use experimental testing or a plausibility check:

- the substance or substance group to be determined
- the sampling procedure to be used
- the analytical determination method

The substance to be analysed (analyte) is the first decisive parameter to be considered. If a known analytical method is to be applied to analyse a new substance or a new substance group with physical and chemical properties comparable to those of the substances for which it has been previously used, a plausibility check would seem to be possible without any reservations. However, experimental testing is necessary as a rule if a determination is to be carried out on a new substance or a new substance group that is chemically unrelated to the previous analytes, especially if the physical properties differ from those of former analytes.
The initial prerequisite in favour of a positive decision for a plausibility check is fulfilled if the sampling and analytical determination procedures used for comparable substances have already been established and are generally accessible.
However, an experimental testing is required as a rule if the sampling and/or determination procedure is novel. As an exception it is still possible to conduct a plausibility check, e. g. if a completely documented validation exist.

Content and procedure of the check

Before beginning the expert examination it is necessary to check with the scientific secretariat of the “Air Analysis” Working Subgroup whether the submitted documentation is complete. If important documents are missing, the author of the method must provide subsequently the relevant information, otherwise the analytical method will be refused.
The author presents the method to the “Air Analysis” Working Subgroup, which than decides whether an experimental test or a plausibility check is to be carried out and designates a suitable examiner.

Fundamental points to be decided

First it must be ascertained, without checking the details, whether the method is basically suitable for a measurement of hazardous substances in workplace air. The following questions must be clarified from the basic performance characteristics:

- Does the substance have an occupational exposure limit value?
- Can the occupational exposure limit value be monitored using the analytical method?
- Are the requirements of EN 482 with regard to the minimum measuring range met?
- In the case of particulate matter is there compliance with the requirements of EN 481?
- Has the range of application of the method been described?
- Is the analytical method based on a method already described in the literature? The sources in Table 1 can be regarded as suitable.
- Was a test gas atmosphere used in the validation in the case of vaporous or gaseous hazardous substances?

Table 1. Selection of suitable sources for analytical methods for hazardous substances

ISO TC 146 "Workplace Atmosphere" method, available from: International Organization for Standardization (ISO), 1, Rue de Varembé, Case Postale 56, CH-1211 Geneva 20, Switzerland, http://www.iso.org
Analytische Methoden zur Prüfung gesundheitsschädlicher Arbeitsstoffe – Luftanalysen, editor: H. Greim, WILEY-VCH Verlag, Weinheim, Deutsche Forschungsgemeinschaft (DFG).
Von den Berufsgenossenschaften anerkannte Analysenverfahren zur Feststellung der Konzentration krebserzeugender Arbeitsstoffe in der Luft in Arbeitsbereichen (BGI 505-Verfahren), Carl Heymanns, Cologne, issued by: Hauptverband der gewerblichen Berufsgenossenschaften (HVBG), Fachausschuss "Chemie", www.hvbg.de/d/pages/praev/vorschr/bgvr/bgvr1.html
BGIA-Arbeitsmappe, Messung von Gefahrstoffen, Sankt Augustin, Erich Schmidt Verlag, Berlin, www.bia-arbeitsmappedigital.de/
Methods for the Determination of Hazardous Substances (MDHS), Health and Safety Laboratory (HSL), Harpur Hill, Buxton, Derbyshire SK17 9JN, UK, http://www.hse.gov.uk/pubns/mdhs/
MétroPol – Métrologie des polluants (Recueil des méthodes de prélèvement et d'analyse de l'air pour l'évaluation de l'exposition professionnelle aux agents chimiques) – Institut National de Recherche et de Sécurité (INRS), Paris, http://www.inrs.fr/metropol/
Instituto Nacional de Seguridad e Higiene en el Trabajo (INHST): Métodos de Toma de Muestra y Análisis (MTA), http://www.mtas.es/insht/en/information/mtm_en.htm
NIOSH Manual of Analytical Methods (NMAM), DHHS (NIOSH) Publication 94–113 (August, 1994), 1st Supplement Publication 96–135, 2nd Supplement Publication 98–119, 3rd Supplement 2003–154, http://www.cdc.gov/niosh/nmam/
OSHA Sampling and Analytical Methods, Occupational Safety and Health Administration (OSHA), Salt Lake City, http://www.osha.gov/dts/sltc/methods/

Detailed check

The detailed check serves to ascertain whether the described analytical method is suitable and complies with the requirements. For this purpose the examiner designated by the "Air Analysis" Working Subgroup must check the entire author's data.

- Is the list of chemicals, solutions and equipment complete?
- Are the procedures for the preparation of solutions described?
- Is the sampling system suitable and are the sampling conditions precisely specified?
- Are sample preparation and analytical determination adequately described?
- Is the calculation presented in a comprehensible manner?

Performance characteristics of the method

This check is performed to ascertain whether the described method meets the requirements of EN 482. The examiner must evaluate the performance characteristics provided by the author, in particular with regard to the requirements for the minimum measuring range and the maximum permissible uncertainty of the measurement. The entire method, including sampling, must be taken into account in this check.
The following performance characteristics must be given in detail in a comprehensible manner:

- Measuring range, calibration function
- Precision and expanded uncertainty
- Recovery
- Limit of quantification (LOQ), if necessary, limit of detection (LOD)
- Storage stability
- If possible or necessary: sources of interference, robustness and blank value

Evaluation of the method

Finally, the examiner must ascertain whether the method complies with all the requirements of EN 482 and meets all the other requirements. The examiner can make the following recommendations to the working subgroup on the basis of the data available to him:

- The method is suitable and inclusion into the "Luftanalysen" (air monitoring) collection is recommended without further experimental testing.
- The decision as to whether the method is suitable cannot be finally taken on the basis of the available data. An experimental testing is recommended.

The result of the check is discussed comprehensively in the "Air Analysis" Working Subgroup. When the analytical method is published, it must be stated whether it was checked by experiment or for plausibility.

3 Performance of the check

The check for plausibility is carried out using the checklist in Annex and questioning the parameters given in the method.
Computerised supported aids can be used for this purpose. It is advisable to make the raw data electronically available to the examiner.
The checklist for checking methods for the determination of hazardous substances in workplace air is based on the agreements between the "Air Analysis" Working Subgroup of the DFG and the Analytical Subcommittee of the Chemistry Board of Experts of the DGUV.

4 Assessment and release of the check by the working subgroup

On completion of the check the author and examiner should discuss the test report together. The meeting should take place at the author's premises. Any missing data can be checked on the spot and/or information to be subsequently provided can be defined.
Then the examiner submits his test report with his recommendations to the "Air Analysis" Working Subgroup, which decides on further actions.

5 References

[1] Länderausschuss für Arbeitsschutz und Sicherheitstechnik (LASI) (2005) LASI-Veröffentlichung LV 2.2 – Handlungsanleitung „Grundsätzliche Anforderungen an akkreditierte Messstellen zum Vollzug des Gefahrstoffrechts", http://lasi.osha.de/docs/lv2_2.pdf.
[2] EN 482, Workplace atmospheres – General requirements for the performance of procedures for the measurement of chemical agents, European Standard, Issue: October 2006.
[3] EN 481, Workplace atmospheres – Size fraction definitions for measurement of airborne particles, European Standard, Issue: September 1993.
[4] ISO 78–2, Chemistry – Layouts for standards – Part 2: Methods of chemical analysis. Geneva 1999.

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6 Annex

Checklist to check an analytical method for plausibility

Test item	Decision criterion	Performance data/ remarks	Test item complies with requirements
Fundamental decisions to be taken by the scientific secretariat			
Are the documents complete? A template for the method description can be obtained from the working subgroup's scientific secretariate (see Annex B of EN 482)			☐ **Yes** ☐ **No**
Decisions to be taken by the "Air Analysis" Working Subgroup			
Does the author have the necessary expertise?			☐ **Yes** ☐ **No**
Is the method based on a method that has already been described?			☐ **Yes** ☐ **No**
Is the method new?			☐ **Yes** ☐ **No**
Does the method seem suitable?			☐ **Yes** ☐ **No**
Has the method been successfully used (for comparable substances)?			☐ **Yes** ☐ **No**
A check is to be carried out	☐ **experimentally** ☐ **for plausibility**		
Designated examiner	**……**		

Results of the detailed check by the examiner (1)

Test item	Decision criterion	Performance data/ remarks	Test item complies with requirements
Have the specifications for standardisation been taken into account, in particular EN 481 and 482?	☐ **EN 481** ☐ **EN 482**		☐ **Yes** ☐ **No**
Are the documents complete? Method description (calibration, precision, recovery, influence of air humidity, storage experiments, limit of quantification, expanded uncertainty, literature)			☐ **Yes** ☐ **No**
Is there an occupational exposure limit value?	☐ **Yes** ☐ **No**	**State the limit value:** **……**	
Is it possible to monitor the 8 h occupational exposure limit value with the method?			☐ **Yes** ☐ **No**
Is it possible to monitor the short-term occupational exposure limit value with the method?			☐ **Yes** ☐ **No**
Is the range of application described?			☐ **Yes** ☐ **No**
Are exceptions for the use of the method described?	☐ **Yes** ☐ **No**		☐ **Yes** ☐ **No**
Are references given?			☐ **Yes** ☐ **No**
Is the minimum measuring range according to EN 482 (from 0.1 times to 2 times the 8 h occupational exposure limit value) covered?	☐ **Yes** ☐ **No**		☐ **Yes** ☐ **No**

Results of the detailed check by the examiner (2)

Test item	Decision criterion	Performance data/ remarks	Test item complies with requirements
Is the sampling procedure (gaseous, particulate or aerosol) applicable?			☐ **Yes** ☐ **No**
Was a test gas atmosphere used for the method validation?	☐ **Yes** ☐ **No**		☐ **Yes** ☐ **No**
Is the list of chemicals, solutions and equipment complete?			☐ **Yes** ☐ **No**
Has the preparation of the solutions to be used been sufficiently described?	☐ **Yes** ☐ **No**		☐ **Yes** ☐ **No**
Is the sampling system suitable?			☐ **Yes** ☐ **No**
Is the sampling system commercially available?	☐ **Yes** ☐ **No**		☐ **Yes** ☐ **No**
Have the sampling conditions been precisely stipulated?			☐ **Yes** ☐ **No**
Can the sampling conditions be reproduced?			☐ **Yes** ☐ **No**
Is sample preparation sufficiently described?			☐ **Yes** ☐ **No**
Is analytical evaluation sufficiently described?			☐ **Yes** ☐ **No**
Is the calculation comprehensible?			☐ **Yes** ☐ **No**

Results of the detailed check by the examiner (3)

Test item	Decision criterion	Performance data/ remarks	Test item complies with requirements
Have sampling experiments been carried out?	☐ **Yes** ☐ **No**		☐ **Yes** ☐ **No**
If not, for what reason, and is this comprehensible?	☐ **Yes** ☐ **No**		☐ **Yes** ☐ **No**
Performance data of the method	**Specification**	**Value of the method**	**Test item complies with requirements**
Measuring range	**0.1 to 2 times the occupational exposure limit value**	**State the limit values:** **……**	☐ **Yes** ☐ **No**
Precision		**State the value:** **……**	☐ **Yes** ☐ **No**
Uncertainty of the measurement (according to EN 482) $u_{c_r} = \sqrt{u_{s_r}^2 + u_{a_r}^2}$ $u_{c_{nr}} = \sqrt{u_{s_{nr}}^2 + u_{a_{nr}}^2}$ $u_c = \sqrt{u_{c_{nr}}^2 + u_{c_r}^2}$ $U = 2 \times u_c$	**Short-term occupational exposure limit value (e.g. 15 min)** **0.5 to 2 times the occupational exposure limit value ≤ 50 %** **8 h occupational exposure limit value** **0.1 to 0.5 times occupational exposure limit value ≤ 50 %** **0.5 to 2 times the occupational exposure limit value ≤ 30 %**	**State the value:** **……**	☐ **Yes** ☐ **No** ☐ **Yes** ☐ **No** ☐ **Yes** ☐ **No**
Has the recovery been given and taken into account?		**State the value**: **……**	☐ **Yes** ☐ **No**

Results of the detailed check by the examiner (4)

Test item	Decision criterion	Performance data/ remarks	Test item complies with requirements
Is the limit of quantification given?		**State the value: ……**	☐ **Yes** ☐ **No**
Is the procedure for determining the limit of quantification comprehensibly described?			☐ **Yes** ☐ **No**
For which storage duration has the storage stability been established?		**State the value: ……**	☐ **Yes** ☐ **No**
Is any interference known?	☐ **Yes** ☐ **No**		☐ **Yes** ☐ **No**
Do blank values have to be taken into account?	☐ **Yes** ☐ **No**		☐ **Yes** ☐ **No**

Remarks of the examiner:

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Recommendation of the examiner to the "Air Analysis" Working Subgroup

☐ Publication of the method is recommended.
☐ The method cannot be finally evaluated.
An experimental test is necessary.
☐ Publication of the method is not recommended.

. . . . . .
Date

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Signature of the examiner