

COLLECTIVE EXPERT APPRAISAL: SUMMARY AND CONCLUSIONS

Regarding the "expert appraisal for recommending occupational exposure limits for chemical agents"

concerning the assessment of measurement methods for 27 substances listed in the annex of the European Directive 2017/164/EU

This document summarises the work of the Expert Committee on "health reference values", on "expert appraisal for recommending occupational exposure limits for chemical agents" (OEL Committee) and the Working group on metrology.

Presentation of the issue

Prior to the transposition of indicative European occupational exposure limits into French law, ANSES is mandated by the Ministry of Labour to conduct an assessment of the methods available for measuring the substances listed in the European Directives.

Since 2015, ANSES has thus included in its work programme the expert metrological appraisal of substances listed in Directive 2017/164/EU.

Scientific and legal background

The European Commission establishes indicative European occupational exposure limits. To carry out this task, it is assisted by a European expert committee, the SCOEL¹.

The indicative European occupational exposure limits are set on the basis of scientific recommendations issued by the European expert committee. They indicate the exposure thresholds below which, in general, the substances concerned should have no harmful effects after short-term exposure (for the short-term limit value), or daily exposure over a working lifetime (for the 8-hour limit value).

For all indicative European limit values, the Member States are required to establish a national occupational exposure limit value based on the EU limit value, but may determine its nature in accordance with national legislation and practices².

¹ European Scientific Committee on Occupational Exposure Limits

² Commission Directive 2017/164/EU of 31 January 2017 establishing a fourth list of indicative occupational exposure limit values pursuant to Council Directive 98/24/EC, and amending Commission Directives 91/322/EEC, 2000/39/EC and 2009/161/EU.

Since the SCOEL recommendations are available for all the substances covered by the Directive, a reassessment of the health effects of these substances is not conducted by ANSES when European directives establishing OELs are published.

Since the SCOEL made no in-depth assessments of the available measurement methods, ANSES is requested to carry out these assessments in order to provide the Ministry of Labour with all the necessary information to determine the binding or indicative nature of the limit values in national law.

The quality of these methods and their applicability to the measurement of exposure levels for comparison with an OEL are assessed, particularly with regard to their compliance with the performance requirements in the EN 482 standard and their level of validation.

Commission Directive (EU) 2017/164 of 31 January 2017 established a fourth list of indicative occupational exposure limits for 31 substances.

Among these 31 substances, four had been the subject of a previous appraisal by ANSES to establish OELs and recommend measurement methods associated with these recommended OELs. These were acetic acid (ANSES, 2014), methylene chloride (AFSSET, 2009), tetrachloroethylene (ANSES, 2010) and carbon monoxide (ANSES, 2011). The methods for measuring these substances were therefore not re-assessed in this expert appraisal, as they were already available.

Of the 27 other substances listed in the Directive, most have French OELs, either binding regulatory values laid down by decree, indicative regulatory values laid down by ministerial order, or indicative non-regulatory values published by circular. Where these French OELs were lower than the values set out in the Directive, or of a different nature (8h-OELs instead of 15min-STEELs, or vice versa), the Ministry of Labour was called on to rule on the choice of OELs to be used, so as to be able to assess the measurement methods.

Organisation of the expert appraisal

ANSES entrusted examination of this request to the Expert Committee on expert appraisal for recommending occupational exposure limits for chemical agents (OEL Committee). The Agency also mandated the working group on metrology.

The methodological and scientific aspects of the work of this group were regularly submitted to the Expert Committee.

This report has been prepared from metrology reports developed individually for each substance by the Working Group on Metrology. The Working Group report takes into account the additional observations and information provided by the members of the OEL Committee. Considering the wording of the question, the OEL Committee did not examine the relevance of the values laid down by the Directive.

This expert appraisal was therefore conducted by a group of experts with complementary skills. It was carried out in accordance with the French Standard NF X 50-110 "Quality in Expertise Activities".

Preventing risks of conflicts of interest

ANSES analyses interests declared by the experts before they are appointed and throughout their work in order to prevent potential conflicts of interest in relation to the points addressed in expert appraisals.

The experts' declarations of interests are made public on ANSES's website (www.anses.fr).

Description of the method

An assessment report of the measurement methods was prepared by the working group on metrology and submitted to the OEL Committee, which added its own comments.

Each assessment report presents the various protocols for measuring the respective substance in workplace atmospheres grouped together based on the methods they use. These methods were then assessed and classified based on the performance requirements set out particularly in the French Standard NF EN 482: "Workplace atmospheres - General requirements for the performance of procedures for the measurement of chemical agents" and the decision-making criteria listed in the methodology report (ANSES, 2016).

A list of the main sources consulted is detailed in the methodology report (ANSES, 2017).

These methods were classified as follows:

- Category 1A: the method has been recognized and validated (all of the performance criteria in the NF-EN 482 Standard are met);
- Category 1B: the method has been partially validated (the essential performance criteria in the NF-EN 482 Standard are met);
- Category 2: the method is indicative (essential criteria for validation are not clear enough);
- Category 3: the method is not recommended (essential criteria for validation are lacking or inappropriate).

A detailed comparative study of the methods in Categories 1A, 1B and 2 was conducted with respect to their various validation data and technical feasibility, in order to recommend the most suitable method(s) for measuring concentrations for comparison with OELs.

This overall report was prepared from metrology reports developed individually for each substance. The details concerning the adoption of each measurement method assessment report are given in the following table.

Table 1: Adoption dates of the reports on assessment of measurement methods for each substance

Substance		Adoption date	
Name	CAS number	By the WG	By the OEL Committee
Vinylidene chloride	75-35-4	08/09/2015	12/10/2015
Sulphur dioxide	7446-09-5	05/11/2015	14/12/2015
Manganese and inorganic compounds	7439-96-5	12/04/2016	10/05/2016
Acrolein	107-02-8	11/04/2016	05/07/2016
Amitrole	61-82-5	11/04/2016	05/07/2016
Nitroethane	79-24-3	07/06/2016	05/07/2016
Tetraethyl orthosilicate	78-10-4	07/06/2016	11/10/2016
Diphenyl ether	101-84-8	11/04/2016	11/10/2016
Lithium hydride	7580-67-8	12/09/2016 and 08/11/2016	11/10/2016
Nitroglycerin	55-63-0	12/09/2016	01/10/2016
Calcium oxide and calcium hydroxide (CaO and Ca(OH) ₂)	1305-78-8; 1305-62-0	01/12/2016	13/12/2016
1,4-butyne diol	110-65-6	01/12/2016	13/12/2016
Carbon tetrachloride	56-23-5	01/12/2016	12/12/2016
Methyl formate	107-31-3	01/12/2016	12/12/2016
Ethyl acetate	141-78-6	08/11/2016	12/12/2016
2-ethylhexan-1-ol	104-76-7	17/01/2017	13/03/2017
Bisphenol A	80-05-7	17/01/2017	13/03/2017
Diacetyl	431-03-8	01/12/2016	13/03/2017
Hydrogenated terphenyls	61788-32-7	09/03/2017	16/05/2017
1,4-dichlorobenzene	106-46-7	25/04/2017	16/05/2017
Acrylic acid	79-10-7	16/06/2017	03/07/2017
Nitric oxide	10102-43-9	16/06/2017	03/07/2017
Nitrogen dioxide	10102-44-0	16/06/2017	03/07/2017
Cyanides: HCN, KCN, NaCN	74-90-8, 151-50-8, 143-33-9	16/06/2017	03/07/2017

The report, as well as the summary and conclusions of the collective expert appraisal, were adopted by the Expert Committee on expert appraisal for recommending occupational exposure limits for chemical agents on 03/07/2017.

This collective expert appraisal work and the summary report were submitted to public consultation from 10/11/2017 to 10/01/2018. The people or organizations that contributed to the public consultation are listed in appendix 3 of the report (only available in French). The comments received were reviewed by the Committee on Health Reference Values (term of office 2017-2020) who finally adopted this version on the 09/03 2018.

Conclusions of the collective expert appraisal

The assessment of the reference methods for measuring workplace exposure levels for the 27 substances for assessment listed in Directive 2017/164/EU when compared with the values established by the Directive³ found that:

- no substance has a measurement method classified in Category 1A;
- thirteen substances have a measurement method classified in Category 1B, at least for one type of OEL; these are vinylidene chloride, tetraethyl orthosilicate, nitroglycerin, carbon tetrachloride, 1,4-dichlorobenzene, ethyl acetate, sulphur dioxide, manganese, acrylic acid, diacetyl, nitroethane, bisphenol A, hydrogen cyanide;
- six substances have a measurement method classified in Category 2, at least for one type of OEL; these are 2-ethylhexan-1-ol, lithium hydride, nitric oxide, nitrogen dioxide, calcium oxide and calcium hydroxide;
- eight substances do not have either a validated or an indicative measurement method for monitoring OELs, or the available data were insufficient to evaluate the measurement methods; these are acrolein, amitrole⁴, diphenyl ether, methyl formate⁵, hydrogenated terphenyls, 1,4-butyne-1,3-diol, potassium cyanide and sodium cyanide.

Three summary tables in the annex show the measurement methods recommended for all 27 substances, according to their classification.

Recommendations

After assessing the available measurement methods, the Committee issued recommendations for the following groups of substances:

- **Those for which there is no suitable method for monitoring OELs listed in the fourth Directive: acrolein, amitrole, methyl formate, diphenyl ether, hydrogenated terphenyls, 1,4-butyne-1,3-diol, potassium cyanide and sodium cyanide**

As there are no suitable measurement methods for monitoring 8h-OELs and 15min-STELs for these eight substances, the Committee recommends developing and validating a measurement method.

For acrolein, alternative methods are described in the literature that would be worth investigating in order to acquire all the validation data required.

For diphenyl ether, the methods identified only concern measurements for the gaseous phase of the pollutant and leave gaps in their validation data that led to a classification in Category 3 with regard to the assessment of the risk of exposure to diphenyl ether vapours alone. However, in view of the vapour pressure of diphenyl ether, a measurement method should be validated that is capable of monitoring both the particulate and gaseous phases of the substance, in accordance with the requirements of the EN 13936 standard.

³ Or possibly in the light of the current French OELs, if the values are lower or of a different nature

⁴ Insufficient data to perform the assessment

⁵ Insufficient data to perform the assessment

For potassium cyanide and sodium cyanide, only one method has validation data for the measurement of cyanide salts, but the conventional fraction collected by the sampling device is not known. Two other methods, developed for the measurement of hydrogen cyanide, specify that it is possible to analyse particulate cyanides by analysing the quartz fibre filter contained in the sampler but they have not been validated. A method for the collection and analysis of particulate cyanides should be developed and validated.

For hydrogenated terphenyls and 1,4-butyne-1,3-diol, no measurement method was identified.

- **Those for which there is no appropriate method for measuring the mixed phase: nitroglycerin, 2-ethylhexan-1-ol and diphenyl ether**

In order to choose the most suitable method, it is first necessary to find out whether the compound consists of a particulate phase, a gaseous phase or a mixture of particulate and gaseous phases (mixed phase). The EN 13936 standard on the measurement of mixtures of particles in suspension and gases sets the requirements and the testing methods to be followed to assess these measurement methods. It specifies whether to choose a single or a combined device depending on the vapour pressure, and a test to find the distribution of the sample between the two phases.

In the absence of distribution data, and for vapour pressure less than 100 Pa, the standard stipulates that *a priori* a serial system should be used in order to take the mixed phase into account.

The three substances listed have a vapour pressure of less than 100 Pa. A measurement method should therefore be developed that is capable of sampling both the particulate and gaseous phases of these substances, in accordance with the requirements of the EN 13936 standard.

- **Those for which there is no appropriate method for monitoring the 1min-STEEL recommended by Directive 2017/164: acrylic acid**

The Committee recommends developing and validating a method for the continuous measurement of the concentration of acrylic acid.

Bibliographic references

Afnor NF EN 482 + A1: November 2015 – Workplace atmospheres – General requirements for the performance of procedures for the measurement of chemical agents.

AFSSET (2009) *Valeurs limites d'exposition en milieu professionnel – Évaluation des effets sur la santé et des méthodes de mesure des niveaux d'exposition sur le lieu de travail pour le dichlorométhane* (Occupational exposure limits – assessment of the effects on health and techniques for the measurement of exposure levels in the workplace for dichloromethane) – AFSSET Opinion and Report on the collective expert appraisal – French Agency for Food, Environmental and Occupational Health Safety, Maisons-Alfort, France.

ANSES (2010) *Valeurs limites d'exposition en milieu professionnel – Le perchloroéthylène* (Occupational exposure limits: perchloroethylene. ANSES Opinion and Report on the collective expert appraisal. French Agency for Food, Environmental and Occupational Health & Safety, Maisons-Alfort, France

ANSES (2011) *Valeurs limites d'exposition en milieu professionnel – Le monoxyde de carbone* (Occupational exposure limits: carbon monoxide). ANSES Opinion and Report on the collective expert appraisal. French Agency for Food, Environmental and Occupational Health & Safety, Maisons-Alfort, France

ANSES (2014) *Expertise en vue de la fixation de valeurs limites d'exposition à des agents chimiques en milieu professionnel - Évaluation des effets sur la santé et des méthodes de mesure des niveaux d'exposition sur le lieu de travail pour l'acide acétique* (Collective expert

appraisal for setting occupational exposure limits for chemical agents – Assessment of the health effects and methods for measuring workplace exposure for acetic acid) (CAS no. 64-19-7) French Agency for Food, Environmental and Occupational Health & Safety, Maisons-Alfort, France. Report submitted for public consultation from 30/06/2014 to 02/09/2014 (www.anses.fr).

ANSES (2017) *Document de référence pour l'élaboration de valeurs limites d'exposition à des agents chimiques en milieu professionnel (VLEP)* (Reference Document for the recommendation of exposure limit for chemicals agents in the workplace (OELs). French Agency for Food, Environmental and Occupational Health & Safety, Maisons-Alfort, France.

Commission Directive 2017/167 of 31 January 2017 establishing a fourth list of indicative occupational exposure limits in implementation of Council Directive 98/24/EC and amending Commission Directives 91/322/EEC, 2000/39/EC and 2009/161/EU.

Annex: Summary of recommended measurement methods

Of the 27 substances studied, most have French OELs, either binding regulatory values laid down by decree, indicative regulatory values laid down by ministerial order, or indicative non-regulatory values published by circular. Where these French OELs were lower than the values set out in the Directive, or were of a different nature (8h-OELs instead of 15min-STEELs, or vice versa), the Ministry of Labour was called on to rule on the choice of OELs to be used, so as to be able to assess the measurement methods. When measurement methods were assessed in the light of current French OELs rather than in the light of the OELs established by Directive 2017/164, the OEL or OELs used as references are given in the following tables.

The three following tables show the measurement methods recommended, according to their classification.

Table 2: Substances with a measurement method classified in Category 1B for at least one OEL

Identification of the substance		Principle of the method recommended	Usage protocols (Reference)	Category		
Substance	CAS number			Regulatory technical control		Monitoring short-term exposure
				8h-OEL	15min-STEEL	
Manganese	7439-96-5	Active sampling of the inhalable or respirable fraction – mineralisation in an acid medium – Analysis by atomic emission spectrometry with inductively coupled plasma (ICP–AES)	NF ISO 15202-1 NF ISO 15202-2 NF ISO 15202-3 NIOSH 7300 NIOSH 7301 NIOSH 7302 NIOSH 7303 NIOSH 7304 NIOSH 7306 INRS Metropol 003 OSHA ID125 G	1B (inhalable) 1B (respirable)	NA	NA
		Active sampling of the inhalable or respirable fraction – mineralisation in an acid medium – Analysis by mass spectrometry with inductively coupled plasma (ICP–MS)	NF ISO 30011 IRSST MA 362	1B (inhalable) 1B (respirable)	NA	NA
Nitroglycerin	55-63-0	Sampling on adsorbent medium Solvent desorption + ultrasound HPLC–UV analysis	DFG Method 1 IFA 7560 OSHA 43	1B <u>only for measuring the gaseous phase (Cat. 3 for measuring the mixed phase – not recommended)</u>	1B <u>only for measuring the gaseous phase (Cat. 3 for measuring the mixed phase – not recommended)</u>	1B <u>only for measuring the gaseous phase (Cat. 3 for measuring the mixed phase – not recommended)</u>

Identification of the substance		Principle of the method recommended	Usage protocols (Reference)	Category		
Substance	CAS number			Regulatory technical control		Monitoring short-term exposure
				8h-OEL	15min-STEEL	
		Sampling with a tube containing an adsorbent medium Solvent desorption GC-ECD	NIOSH 2507	1B <i>only for measuring the gaseous phase</i>	3 <i>(not recommended)</i>	3 <i>(not recommended)</i>
Carbon tetrachloride	56-23-5	Active sampling on activated charcoal tube CS ₂ desorption Analysis using GC/FID	INSHT MTA/MA-042/A99 NIOSH 1003 OSHA 07	1B	3 <i>(not recommended)</i>	1B
HCN KCN NaCN	74-90-8	Active sampling on soda-lime medium Water desorption Analysis using spectrophotometry	NIOSH 6010	1B for HCN	3 for HCN <i>(not recommended)</i>	1B for HCN
	151-50-8			Category 3* for KCN and NaCN <i>(not recommended)</i>		
	143-33-9	Active sampling on soda-lime medium Water desorption Analysis using ion chromatography	NIOSH 6017	1B for HCN	3 for HCN <i>(not recommended)</i>	1B for HCN
				Category 3* for KCN and NaCN <i>(not recommended)</i>		
Vinylidene chloride	75-35-4	Active sampling on an adsorbent tube Solvent desorption Gas chromatography analysis, and flame ionisation detection (GC/FID)	OSHA 19	1B	1B	1A
Tetraethyl orthosilicate	78-10-4	Sampling on medium containing a solid adsorbent Solvent desorption Gas chromatography analysis, and flame ionisation detection (GC/FID)	NIOSH S264 Métropol M208	1B	NA	NA
Acrylic acid	79-10-7	Active sampling with Amberlite XAD-8 resin Determination by liquid chromatography using a UV/visible detector	OSHA 28	1B (French 8h-OEL and EU 8h-OEL)	1B French 15min-STEEL	1B French 15min-STEEL

Identification of the substance		Principle of the method recommended	Usage protocols (Reference)	Category		
Substance	CAS number			Regulatory technical control		Monitoring short-term exposure
				8h-OEL	15min-STEEL	
Nitroethane	79-24-3	Active sampling with XAD-2 tube Ethyl acetate desorption Analysis using GC/FID	NIOSH 2526	1B	3 <i>(not recommended)</i>	1B
Bisphenol A	80-05-7	Active sampling on a GF filter Solvent extraction Analysis by HPLC/UV/VIS or PAD	BGI 505-75-01 OSHA 1018	1B	NA	NA
1,4-dichlorobenzene	106-46-7	Active sampling in an activated charcoal tube – CS ₂ desorption – GC/FID analysis	NIOSH 1003	1B (French 8h-OEL)	1B (EU 15min-STEEL)	1B (EU 15min-STEEL)
		Active sampling in a Tenax tube – Thermal desorption – GC/FID analysis	DFG method 1 (2010) NF ISO 16017-1	1B (French 8h-OEL)	1B (EU 15min-STEEL)	1B (EU 15min-STEEL)
Ethyl acetate	141-78-6	Active sampling on activated charcoal tube CS ₂ desorption Analysis using GC/FID	NIOSH 1457, DFG2, MTA/MA-023/A92, BGIA 7322 and protocols using similar trapping devices	1B	1B	1B
		Active sampling on activated charcoal tube Solvent desorption Analysis using headspace GC/FID	DFG solvent Mixtures Method 4	1B	1B	1B
		Passive sampling on adsorbent media (activated charcoal) – CS ₂ desorption – GC/FID analysis	MétoPol 021+C, MDHS 88, ISO 16002-2	1B	3 <i>(not recommended)</i>	3 <i>(not recommended)</i>
Diacetyl	431-03-8	Active sampling on an adsorbent tube Solvent desorption + derivatisation Analysis using GC/ECD	OSHA 1012	1B	1B	1B

Identification of the substance		Principle of the method recommended	Usage protocols (Reference)	Category		
Substance	CAS number			Regulatory technical control		Monitoring short-term exposure
				8h-OEL	15min-STEL	
Sulphur dioxide	05/09/74 46	Active sampling with a glass tube containing (in series) a glass-fibre filter (non-impregnated), a filter impregnated with a solution of Na ₂ CO ₃ and two layers of silica gel impregnated with silver nitrate – desorption solution of Na ₂ CO ₃ / NaHCO ₃ + H ₂ O ₂ Analysis using ion chromatography with a suppressor column	OSHA 1011	1B	1B	1B
NA: Not applicable – Directive 2017/164/EU does not establish a limit value (*) Insufficient data to perform the assessment						

Table 3: Substances with a measurement method classified in Category 2 for at least one OEL

Identification of the substance		Principle of the method recommended	Usage protocols (Reference)	Category		
Substance	CAS number			Regulatory technical control		Monitoring short-term exposure
				8h-OEL	15min-STEL	
2-ethylhexan-1-ol	104-76-7	Active sampling on activated charcoal tube CS ₂ desorption Analysis using GC/FID	MétoPol M 88 OSHA PV 2033	2 <i>Only for measuring the gaseous phase</i> (Cat. 3 for measuring the mixed-phase (not recommended))	NA	NA
Calcium oxide Calcium hydroxide	1305-78-8 1305-62-0	Active sampling of the respirable fraction on an MCE filter - Solvent desorption - Analysis by flame atomic absorption spectrometry (FAAS)	OSHA ID 121 IRSST-1 NIOSH 7020	2	2	2
		Active sampling of the respirable fraction - Mineralisation in an acid medium - Analysis by atomic emission spectrometry with inductively coupled plasma (ICP-AES)	NF ISO 15202 (parts 1 to 3) NIOSH 7300, 7301, 7302, 7303, 7304, 7306 INRS M122	2	2	2
		Active sampling of the respirable fraction on a quartz filter - Water and diluted acid desorption - Analysis by ion chromatography / Conductometric detection (IC-CD)	DFG-1 BIA 7695 BGIA 7638 NF ISO 17091	2	3 <i>(not recommended)</i>	2

Identification of the substance		Principle of the method recommended	Usage protocols (Reference)	Category		
				Regulatory technical control		Monitoring short-term exposure
Substance	CAS number			8h-OEL	15min-STEL	
Lithium hydride	7580-67-8	Active sampling of the inhalable fraction – Mineralisation in an acid medium – Analysis by atomic emission spectrometry with inductively coupled plasma (ICP-AES)	NF ISO 15202-1 NF ISO 15202-2 NF ISO 15202-3 NIOSH 7300 NIOSH 7301 NIOSH 7302 NIOSH 7303 NIOSH 7304 NIOSH 7306	NA	2	2
Nitric oxide	10102-43-9	Active sampling in a tube impregnated with TEA – Solvent desorption – Analysis by visible spectrometry	NIOSH 6014	2	NA	NA
		Active sampling in a tube impregnated with TEA – Solvent desorption – Analysis by ion chromatography	OSHA ID 190	2	NA	NA
Nitrogen dioxide	10102-44-0	Active sampling in a tube impregnated with Triethanolamine (TEA) – Solvent desorption – Visible spectrometry analysis	NIOSH 6014	2	3 <i>(not recommended)</i>	2
		Active sampling in a tube impregnated with TEA – Solvent desorption – Analysis by ion chromatography	OSHA ID 182	2	3 <i>(not recommended)</i>	2
NA: Not applicable - Directive 2017/164/EU does not establish a limit value						

Table 4: Substances with no validated or indicative measurement method for any OEL

Identification of the substance		Note
Substance	CAS number	
Amitrole	61-82-5	There is currently no validated or indicative measurement technique for any OEL established by Directive 2017/164.
Diphenyl ether	101-84-8	
Acrolein	107-02-8	
Methyl formate	107-31-3	
1,4-butyndiol	110-65-6	
Hydrogenated terphenyls	61788-32-7	
KCN, NaCN	151-50-8 143-33-9	There is currently no validated or indicative measurement technique for any OEL established by Directive 2017/164 (an unvalidated method and insufficient data available to assess alternative methods)
Acrylic acid	79-10-7	There is currently no validated or indicative measurement technique for monitoring 1min-STEELs, as recommended by Directive 2017/164.