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**HEALTH & SAFETY
LABORATORY**

Draft 2nd Indicative Occupational Exposure Limit Value (IOELV) List : Workplace Measurement Method Summaries

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EXECUTIVE SUMMARY

OBJECTIVES

1. To draft summaries of analytical methods (in air) for substances that are definitely included in the 2nd IOELV directive, or likely to be added.
2. The summaries to be of style and length similar to the most recent *measurement* sections in the EH64 series.
3. To anticipate problems in measurement that may prevent practicable compliance with a proposed IOELV.
4. To assess published methods against any relevant European or international performance standards.

Specific activities

Substances in original proposal for 2nd IOELV directive		**Draft/proposed IOELVs**			
		8h-TWA		15 min-STEL	
		mg/m^3	ppm	mg/m^3	ppm
1	2-Aminoethanol	2.5	1	-	
2	Chlorine	-	-	1.5	0.5
3	Chloroethane	268	100	-	-
4	Chromium metal & inorganic Cr(II) and Cr(III) salts	2	-	-	-
5	n-Hexane	72	20	-	-
6	Morpholine	36	10	72	20
7	Nitric acid	-	-	1.3	0.5
8	Pentanes (n-, iso-, neo-)	3,000	1,000	-	-
9	Phosphine	0.14	0.1	0.28	0.2
10	Sulphur dioxide	1.3	0.5	2.7	1
11	Toluene	192	50	306	80
Substances from 91/332/EEC proposed for retention in 2nd IOELV directive					
12	Acetonitrile	70	40	-	-
13	Barium, soluble compounds	0.5	-	-	-
14	Bromine	0.7	1	-	-
Substances from 91/332/EEC proposed for retention in 2nd IOELV directive (cont.)					
15	Carbon dioxide	9,000	5,000	-	-

16	Formic acid	9	5	-	-
17	Methanol	260	200	-	-
18	Nicotine	0.5	-	-	-
19	Oxalic acid	1	-	-	-
20	Phosphorus pentachloride	1	-	-	-
21	Phosphorus pentasulphide	1	-	-	-
22	Phosphorus pentoxide	1	-	-	-
23	Resorcinol	46	10	-	-
24	Silver, soluble compounds	0.01	-	-	-

Substances (91/322/EEC) proposed after consideration by SCOEL					
25	Acetic acid	In progress			
26	Cresols	In progress			
27	Cyanamide	Health-based OELV unlikely			
28	Diethylamine	In progress			
29	Naphthalene	No health-based OELV			
30	Nitrobenzene	5	1	-	-
31	Nitrogen monoxide	In progress			
32	Picric acid	In progress			
33	Pyrethrum	In progress			
34	Pyridine	In progress			
35	Tin, organic compounds	In progress			
Substances likely to be added to proposal for 2nd IOELV directive					
36	Cyclohexane	In progress			
37	2(2-Butoxyethoxy)ethanol	-	10	-	15
38	Mercury and inorganic divalent compounds	0.02	-	-	-
39	2(2-Methoxyethoxy)ethanol	-	10	-	-
40	Sulphuric acid mist	In progress			
Substances with potential for inclusion in an IOELV directive					
41	Carbon disulphide	in progress			
42	Ethyl acetate	in progress			
43	Tetraethyl silicate	in progress			

Substances added to current draft of 2nd IOELV directive		**Draft/proposed IOELVs**			
		8h-TWA		15 min-STEL	
		mg/m^3	ppm	mg/m^3	ppm
44	Monochlorobenzene	23	5	70	15
45	Calcium dihydroxide	5	-	-	-
46	Lithium hydride	0.025	-	-	-
47	Platinum (metallic)	1	-	-	-

MAIN FINDINGS

The table summarises the status of TWA air sampling methods available for each substance and availability of a direct-reading method . It is difficult to answer the question - *Will existing air monitoring methods be acceptable at or around any proposed/actual IOELV ?* with a single Yes/No answer. There are degrees of acceptability or compliance with standards. No single European standard describes exact criteria for degrees of compliance in this way. The closest approach is by EN 838 which designates three categories, paraphrased here in the following terms:

- A: Full compliance, all <u>relevant</u> environmental factors tested;
- B: Partial compliance, tests over a more limited range than specified in A;
- C: Compliance inferred from close analogues that do comply with A or B.

For categories A-C it is more likely than not that the uncertainty of measurement is less than ±50% from the “true” value over the range 0.1-2 LV. A-C correspond to a *Yes* (or qualified Yes) answer. To these three we add a fourth category:

- D: Although methods exist, there is no documented evidence of compliance with part(s) of any European performance standard <u>and</u> it is more likely than not that the uncertainty of measurements is greater than ±50% from the “true” value over the range 0.1-2 LV.

D corresponds to a *No* answer (shaded cells in the following table), although absence of evidence alone does not necessarily fail a method. A judgement is needed based on similar substances and methods. Substances in this category are the pentachloride, pentasulphide and pentoxide of phosphorus, cyanamide, nitrogen monoxide and carbon disulphide.

	Validation category				
Substances in original proposal for 2nd IOELV directive	**A**	**B**	**C**	**D**	Direct Read.
2-Aminoethanol			✓		✓
Chlorine		✓			✓
Chloroethane		✓			✓
Chromium metal & inorganic Cr(II) and Cr(III) salts	✓				
n-Hexane	✓				✓
Morpholine			✓		✓
Nitric acid		✓			✓
Pentanes (n-, iso-, neo-)	✓				✓
Phosphine		✓			✓
Sulphur dioxide		✓			✓
Toluene	✓				✓

Substances from 91/332/EEC proposed for retention in 2nd IOELV directive	**A**	**B**	**C**	**D**	Direct read.
Acetonitrile		✓			✓
Barium, soluble compounds	✓				
Bromine		✓			✓
Carbon dioxide	✓				✓
Formic acid		✓			✓
Methanol	✓				✓
Nicotine		✓			
Oxalic acid			✓		
Phosphorus pentachloride				✓	
Phosphorus pentasulphide				✓	
Phosphorus pentoxide				✓	
Resorcinol		✓			
Silver, soluble compounds		✓			

Substances (91/322/EEC) proposed after consideration by SCOEL					
Acetic acid		✓			✓
Cresols		✓			✓
Cyanamide				✓	
Diethylamine					✓
Naphthalene		✓			✓
Nitrobenzene		✓			✓
Nitrogen monoxide				✓	
Picric acid		✓			
Pyrethrum			✓		
Pyridine			✓		
Tin, organic compounds		✓			

Substances likely to be added to proposal for 2nd IOELV directive	**A**	**B**	**C**	**D**	Direct Read.
Cyclohexane	✓				✓
2(2-Butoxyethoxy)ethanol			✓		✓
Mercury and inorganic divalent compounds	✓				
2(2-Methoxyethoxy)ethanol			✓		✓
Sulphuric acid mist			✓		✓

Substances with potential for inclusion in an IOELV directive					
Carbon disulphide				✓	✓
Ethyl acetate		✓			✓
Tetraethyl silicate			✓		✓

Substances added to current draft of 2nd IOELV Directive					
Monochlorobenzene		✓			
Calcium dihydroxide		✓			
Lithium hydride		✓			
Platinum (metallic)	✓				

INTRODUCTION

The objective of Council Directives in relation to chemical agents, using 98/24/EEC as an example, is to establish minimum requirements for the protection of workers from risks arising from chemical agents, either within the workplace or as a result of workplace activities. The key requirements are for employers to:

- assess the risk from hazardous chemical agents (Article 4);
- prevent or reduce such risks to a minimum (Articles 5 and 6);
- monitor personal exposure where appropriate (Article 6);
- establish procedures for accidents, incidents and emergencies (Article 7);
- provide information and training (Article 8);
- carry out appropriate health surveillance (Article 10);

Where employers cannot clearly demonstrate that risks are properly controlled, for example, by design of engineering processes or substitution, Article 6 (4) requires that measurements be carried out, particularly in relation to the occupational exposure limit values. Article 3 (10) establishes the need for standardised methods for this purpose.

Methods for assessing occupational exposure to chemical agents have been developed semi-independently by a number of standards organisations and regulatory authorities in Europe and the USA. Few of these have been systematically reviewed against Comité Europeén de Normalisation (CEN) criteria for accuracy and reliability.

For each substance, the review text in this report lists any relevant direct-reading measurement methods, including colour stain-length tubes. Performance requirements exist for direct-reading instruments (electrical apparatus) in the form of EN 45544:1999 Parts 1-4: *(1) general requirements and test methods; (2) measuring concentrations around the LV; (3) measuring concentrations well above the LV; (4) guide for selection installation, use and maintenance*. It is not mandatory for direct-reading instrument manufacturers to test to EN 45544 and, with the possible exception of carbon monoxide, growth in the use of this standard may be slow.

The review then makes some assessment of how well the procedure(s) for time-weighted average measurements (TWA) comply with European or International performance standards for the measurement of chemical agents in air at or around the IOELV (that is if a proposed or actual numerical IOELV exists, otherwise the OES or MEL is used). The primary published standard, developed by CEN/TC137, is EN 482:1994 (general requirements for the performance of procedures) in which requirements for selectivity and overall uncertainty[1] are described. For measurement in comparison with limit values (LV) the overall uncertainty is to be ≤30% at 0.5-2 LV and ≤50% at 0.1-0.5 LV averaged over the reference period. In practice, particularly for older work, the information is not always available in the validation documents to make a clear Yes/No statement. A judgement must be made on the balance of probability. Sometimes a method is acceptable for monitoring compliance with the 8h -TWA but not the 15 min STEL or possibly the range of concentrations studied is more limited than strictly required by EN 482.

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[1] A pragmatic definition of *overall uncertainty* in EN 482 has been defined more formally in subsequent ISO and CEN documents, but this has little effect on compliance in practice.

EN 482 does not detail the sampling/analysis equipment requirements of methods. These are laid down in standards for particulates, such as EN 481:1993 *(target specification for size fraction definitions),* and for gases and vapours - EN 1076:1997 *(pumped sorbent tubes)* and EN 838:1996 *(diffusive samplers).* Also for some metals there are specific ISO standards for analysis either published or in preparation. They all detail a series of environmental factors to be tested. However, each method may have its own features that demand different levels of importance be attached to these tests. The standards allow for flexibility. Therefore to say a method is in full compliance with EN 482, EN 1076, EN 838 or an ISO standard is not necessarily to imply that every single listed test has been performed and documented, but only the important tests, in the opinion of the authors of this report.

Literature sources for this review include mainly agency references to published NIOSH, OSHA and HSE (MDHS series) air sampling methods. Other European agency publications, such as those of *Institut National de Recherche et de Sécurité* (INRS – *Métrologie des Pollutants*), *Deutsche Forschungsgemeinschaft* (DFG), *Bundesanstalt fürArbeitsschultz und Arbeitsmedizin* (BAuA - *Empfohlene Analysenverfahren für Arbetsplatzmessungen*) and *Berufsgenossenschaftliches Institut für Arbeitssicherheit* (BIA), were also consulted. Normally the methods are closely equivalent. Citations to these are given in a few cases where either recommendations from NIOSH/OSHA/HSE are lacking or there are significant differences. All recent MDHS methods are assessed to EN 482 standards in the document. NIOSH and OSHA classify their own published methods in various ways, for example, fully validated, partially validated, stop-gap, provisional, in-house file etc. We have been informed by their opinion, but have looked at the actual raw data provided in order to assign a validation level. Usually there was agreement. If there are discrepancies they may be due to the age of the validation or our observation on the robustness of the method.

A bibliography of non-agency peer-reviewed citations will also exist for each substance. The only citations included of this type are those concerned primarily with validation of the analytical methods themselves, since no conclusions can be drawn from papers where methods are cited with little or no comment. In order that each substance review can stand alone, many citations are repeated and there is no final compilation of references.

Limits of detection and quantification in measurement procedures

Terminology recommended by the International Union of Pure and Applied Chemistry (IUPAC) is given in the *IUPAC Compendium of Analytical Nomenclature – Definitive rules, 1997*. A summary is presented here, but a detailed treatment is outside the scope of this report.

Limit of Detection (L_D): the minimum detectable (true) level of the measurand, generally taken to be three times the standard deviation of the signal that represents the quantity of true value = 0.
Limit of quantification (L_Q): The estimate of the measurand having a relative standard deviation at a defined level, commonly 10%, generally taken to be ten times the standard deviation of the signal that represents the quantity of true value = 0.

In some literature L_Q is also known as the *Limit of Determination*.

In this report we have tried to estimate performance limits, where known, in terms of L_Q and not $L_{D,}$ because the uncertainty inherent in L_D is easily underestimated. The rules are not necessarily applied consistently in validation. Unexpected variance in the signal blank has a large effect in practice.

MEASUREMENT METHOD SUMMARIES

2-AMINOETHANOL

CAS	141-43-5
OES	3 ppm (7.6 mg m-3) 8h-TWA; 6 ppm (15 mg m^{-3}), STEL
IOELV	1 ppm (2.5 mg m-3) 8h-TWA; 3 ppm (7.6 mg m^{-3}), STEL

Self-indicating colourimetric tubes specifically calibrated for 2-aminoethanol are not available. Direct-reading instruments based on infra-red spectrophotometry may be suitable, depending on interferences from similar compounds. The detection limit with a portable infra-red spectrometer is reported as 3 ppm at a wavelength of 13 µm. Personal exposure to ethanolamine in air may be measured by pumped sampling at up to 0.2 L min^{-1} on silica-gel tubes and desorbing with 80/20 methanol/water containing 0.12 N HCl (NIOSH method 2007 [1]). If analysis is to be delayed more than a few days the sample tubes can be stabilised by addition of 20 µL of strong HCl just after sampling. To analyse the samples the extract must be made alkaline. 2-Aminoethanol is determined by gas chromatography as the free form or as the benzaldehyde derivative. The validation of NIOSH 2007 is based on earlier NIOSH reports (P&CAM 270 [2], S140 [3]) and does not address all the concerns of the later performance standards EN 482 [4] and EN 1076 [5]. Desorption efficiency was 0.97 at a concentration of 30 mg m^{-3} (24 L air sample). A limit of quantification (L_Q) equivalent to about 0.5 mg m^{-3} is stated, however, this is an estimate not based on actual tests at this concentration. The method as described does not have enough sensitivity for a proposed limit value of 2.5 mg m^{-3}, 8h-TWA, 7.6 mg m^{-3} STEL. Selective gas chromatography detectors such as the N/P detector may improve sensitivity, but it remains for the user to confirm that the desorption efficiency is greater than 75% at or below 2.5 mg m^{-3}, as required by EN 1076. NIOSH have also reported a liquid impinger method based on ion chromatography as NIOSH 3509.[8,9] This method has been partially validated for 2-aminoethanol and is potentially more sensitive than NIOSH 2007, however, it is not very suitable for personal monitoring. Serbin and Berkholz reported a variation of the silica gel sampling procedure of NIOSH 2007 in which they derivatised 2-aminoethanol with 9-fluorenyl methyl chloroformate and analysed by LC with fluorescence detection.[10] The sensitivity achieved was about 10x better than that by GC-FID. Desorption efficiency of 2-aminoethanol from silica gel was acceptable down to 0.5 mg m^{-3} for a 24 L air sample. An alternative OSHA method is to sample at up to 0.1 L min^{-1} on XAD-2 sorbent tubes coated with 10% naphthylisothiocyanate (NITC) reagent.[6] NITC-coated tubes are commercially available. They are desorbed with dimethylformamide, followed by analysis with liquid chromatography (LC) with UV detection. OSHA have not reported validation details specifically for 2-aminoethanol, however, OSHA have published the same NITC method for diethanolamine (PV2018 [7]). PV2018 complies with EN 1076 with respect to 2-week storage and desorption efficiency at low concentrations. The performance of PV2018 for 2-aminoethanol and diethanolamine is expected to be similar. The detection limit is < 0.2 mg m^{-3} for a 10 L sample and is the preferred method for the proposed 8h-TWA and STEL limit values.

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CHLORINE

CAS	7782-50-5
OES	0.5 ppm (1.5 mg m^{-3}), 8h-TWA; 1 ppm (2.9 mg m^{-3}), STEL
IOELV	0.5 ppm, STEL

Self-indicating colourimetric tubes calibrated for chlorine in air are available from Dräger, Gastec and Kitagawa. Their limit of detection is in the range 0.1-0.3 ppm. Tubes may indicate chlorine dioxide with twice the sensitivity of chlorine. Bromine and nitrogen dioxide may also interfere, but with a different colouration. Direct-reading instruments are available based predominantly on electrochemical sensors, which can be used in portable instruments**.** Their limit of detection is typically around 0.5 ppm. Potential interferents vary depending on the technology but may include nitrogen dioxide. Other measurement techniques used include colourimetry (eg tubes, paper tapes) and UV photometry. Personal exposure to chlorine in air may be measured by pumped sampling up to 90 L at 0.3-1 L min^{-1} through a silver membrane filter and eluting as bromide with 0.25 mM sodium bicarbonate/ 4 mM sodium carbonate solution, followed by ion chromatography (IC) with conductometric detection, as described in NIOSH method 6011.[1] NIOSH 6011 complies with the performance standard EN 482 [2] with respect to overall uncertainty over the range 0.05-1 ppm for a 15 L air sample. It is suitable for short-term monitoring. The limit of quantitation is <0.01 ppm for a 90 L air sample. A liquid impinger method is also available, using an absorption solution of 0.1% sulfamic acid, as described in OSHA ID-101.[3] After sampling, aliquots of sulfamic acid solution are added to buffered potassium iodide. The liberated iodine is determined with a residual chlorine specific electrode. ID-101 complies with the performance standard EN 482 with respect to overall uncertainty over the limited range of 0.05-0.2 ppm for a 30 L sample at 0.5 L min^{-1} and a working range of 0.015-0.3 ppm is stated. However, where larger volumes in excess of 100 L are required to measure concentrations below the IOELV, liquid impinger methods are unlikely to comply with EN 482 in practice. Strong oxidising agents, such as iodate and bromine, will interfere. Alternatively, a long-term self-indicating colourimetric tube is available from Dräger. The limit of detection is 0.1 ppm over 8 hours, or 1 ppm for 1 hour, when used with a dedicated pump. A colourimetric diffusion tube is available from SKC Inc. The performance characteristics of diffusion or long-term pumped colourimetric tubes are not available and their compliance with the performance standard EN 838 [4] is unknown. They are unsuitable for short-term monitoring below the IOELV.

References

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CHLOROETHANE

CAS	75-00-3
OES	1000 ppm (2700 mg m^{-3}) 8h-TWA; 1250 ppm (3380 mg m^{-3}), STEL (OES withdrawn)
IOELV	100 ppm, 8h-TWA

Self-indicating colourimetric tubes calibrated for chloroethane in air are available from at least one manufacturer (MSA). Alternatively, manufacturers may recommend a trichloroethane tube. The lower end of the calibrated range of commercial tubes is 50-250 ppm, therefore they are less suitable for estimating personal exposure around the proposed IOELV of 100 ppm. Direct-reading instruments are available, based on infra-red spectrophotometry (IR). The IR detection limit for chloroethane is about 1 ppm at a wavelength of 10.6 µm. Personal exposure to chloroethane in air may be measured by pumped sampling on activated charcoal sorption tubes at 0.02-0.05 L min^{-1}, desorbing with carbon disulphide and analysing by gas chromatography with flame ionisation (FID) or mass spectrometry detection (MS) as described in NIOSH method 2519.[1] This method is based on an early validation [2] which did not address all the concerns of newer performance standards and was not evaluated below 130 ppm. However, NIOSH 2519 is likely to comply fully with EN 482 [3] with respect to overall uncertainty and with EN 1076 [4] with respect to desorption efficiency, storage and environmental factors, over the range 10-200 ppm. The limit of quantitation (L_Q) is about 2 ppm for a 3 L air sample (with FID detection). A maximum safe sampling volume of 3 L on two 400/200 mg tubes in series is recommended. Migration of chloroethane though the charcoal bed can occur in storage. After sampling the tubes are separated and sealed in order that any breakthrough onto the second tube during the sampling period is clearly distinguished from migration in storage.

References

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CHROMIUM METAL & INORGANIC CR(II) AND CR(III) SALTS

CAS	7440-47-3 (Cr, metallic)
OES	0.5 mg m^{-3}, 8h-TWA (as Cr)
IOELV	2 mg m^{-3}, 8h-TWA (as Cr)

Self-indicating colourimetric tubes and direct-reading instruments are not appropriate for the measurement of metals and metal compounds. Personal exposure to chromium and chromium compounds may be measured by sampling air at 2.0 L min^{-1} through a filter mounted in an inhalable dust sampler operated according to MDHS 14/3.[1] Mixed cellulose ester 0.8 µm filters are suitable. Filters are digested using one of the dissolution procedures given in the method MDHS 12/2. [2] Choice of dissolution procedure depends on whether the chromium compounds are readily soluble in acid and on whether chromium metal is present.[3] The resultant solution is analysed by aspiration into the nitrous oxide/acetylene flame of an atomic absorption spectrometer (AAS) measuring at 357.9 nm. The limit of quantification with the hydrochloric/nitric acid dissolution procedure is 0.03 mg m^{-3} for a 30 L air sample. MDHS 12/2 complies with the performance standard EN 482 with respect to overall uncertainty [3,4] and is suitable for short-term monitoring, with the exception of the sodium peroxide fusion procedure which is unsuitable for sampling times less than 2 hours. Methods NIOSH 7024 [5] and OSHA ID-121 [6] describe AAS procedures that are broadly similar to MDHS 12/2. Alternative methods include inductively coupled plasma-atomic emission spectrometry (ICP-AES), X-ray fluorescence spectrometry (XRFS) and inductively coupled plasma-mass spectrometry (ICP-MS). The performance of dissolution procedures for ICP-AES has been assessed in an interlaboratory trial.[7] NIOSH 7300 [8] and OSHA ID-125G [9] are two published versions of the ICP-AES method. The XRFS method is non-destructive and gives adequate sensitivity for a 60 L air sample. A generic method for metals analysed by the XRFS procedure is given in MDHS 91.[10] Chromium by XRFS complies with EN 482 with respect to overall uncertainty, but validation is subject to certain limitations of particle size, matrix effects and sample load. ICP-MS is very sensitive and selective. Generic published standard methods for elements by ICP-MS are in preparation.

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N-HEXANE

CAS	110-54-3
OES	20 ppm (72 mg m^{-3}), 8h-TWA
IOELV	20 ppm (72 mg m^{-3}), 8h-TWA

Self-indicating colourimetric tubes calibrated for hexane isomers in air are available from Dräger, Gastec and Kitagawa. The lower end of the calibrated range of commercial tubes is 50-100 ppm, therefore these tubes are less suitable for estimating personal exposure around the IOELV of 20 ppm. They do not measure the n-hexane isomer specifically. Other hydrocarbons will interfere. Direct-reading instruments are available, based on infra-red spectrophotometry (IR) and photoionization detection (PID). The IR detection limit for hexane isomers is <1 ppm at a wavelength of 3.4 µm. It is not possible to distinguish the n-hexane isomer by IR or PID separately from other hexane isomers. Personal exposure to the n-hexane isomer in air may be measured by pumped sampling on activated charcoal sorption tubes at 0.01-0.1 L min^{-1}, desorbing with carbon disulphide and analysing by gas chromatography with flame ionisation or mass spectrometry detection, for example, the general hydrocarbon method NIOSH 1500.[1,2] This method is based on an early validation [2] which did not address all the concerns of newer performance standards, however, NIOSH 1500 is likely to comply fully with EN 482 [3] with respect to overall uncertainty and with EN 1076 [4] with respect to desorption efficiency, storage and environmental factors, over the range 5-1000 ppm. The limit of quantitation (L_Q) is about 0.03 ppm for a 4 L air sample. A maximum safe sampling volume of 4 L on 100/50 mg tubes is recommended. Diffusive badge-type personal monitors intended for solvent desorption are available commercially from several suppliers. Sampling rate data for four commercial designs were summarised in MDHS 88. [5] At least one badge type (3M-3500) is fully compliant with the diffusive sampler performance standard EN 838 [6] with respect to n-hexane.[7] The diffusive thermal desorption method MDHS 80 [8] has been fully validated for n-hexane (with Chromosorb 106 sorbent) to EN 838. The L_Q for the diffusive methods is <0.1 ppm for an 8 hour TWA sample.

References

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MORPHOLINE

CAS 110-91-8
OES 20 ppm (72 mg m-3) 8h-TWA; 30 ppm (109 mg m^{-3}), STEL
IOELV 10 ppm (36 mg m-3) 8h-TWA; 20 ppm (72 mg m^{-3}), STEL

Self-indicating colourimetric tubes specifically calibrated for morpholine in air are not available. Tubes calibrated for aliphatic amines, such as the diethylamine tube from Kitagawa, may indicate morpholine but with a different sensitivity. Ammonia and many organic amines will interfere. Direct-reading instruments are available, based on infra-red spectrophotometry. The detection limit is <1 ppm at a wavelength of 9.0 µm. Personal exposure to morpholine in air may be measured by pumped sampling up to 20 L on silica gel sorption tubes at up to 0.2 L min^{-1}. Morpholine is desorbed from silica gel with 0.05M sulphuric acid and, after converting to the free base with alkali to > pH10, is analysed by gas chromatography with flame ionization detection (NIOSH method S-150 [1]). NIOSH S150 is an early validation with silica gel that may have been subject to batch variation. The desorption efficiency and storage stability is not stated but user guidance is given on measuring desorption efficiency. A diffusive badge sampling method included in MDHS 88 [2] reports a theoretical sampling rate of 33.1 mL min^{-1} on the carbon-based 3M 3500 badge. No validation details are available and in the absence of any stability and recovery data on carbons, this diffusive sampling method is not recommended for morpholine. NIOSH S150 was not validated according to the modern performance standards EN 482 [3] and EN 1076 [4], but a version adapted to capillary gas chromatography will be suitable for measurement at or around the IOELV, provided that a short guard column is fitted to protect the capillary stationary phase from a build up of sulphate residues. Alternatively, BIA method 8030 reports desorption of silica gel with methanol and analysis by gas chromatography with nitrogen/phosphorus detection.[5] The stability of morpholine on silica gel in storage remains to be determined. It is recommended that the tubes be refrigerated after sampling and analysed as soon as possible.

References

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NITRIC ACID

CAS	7697-37-2
OES	2 ppm (5.2 mg m-3) 8h-TWA; 4 ppm (10 mg m^{-3}), STEL
IOELV	0.5 ppm (1.3 mg m^{-3}), STEL

Self-indicating colorimetric tubes are available from Dräger and Gastec, calibrated for nitric acid or nitrous fumes in air. The limit of detection is in the range 0.2-1 ppm. All mineral acids will interfere. Direct-reading instruments for acid mists are not commercially available. Personal exposure to nitric acid may be measured by pumped sampling up to 100 L air at 0.2-0.5 L min^{-1} on specially cleaned 400/200 mg silica gel sorbent, desorption with 1.7 mM sodium bicarbonate/ 1.8 mM sodium carbonate and analysis by ion chromatography (IC) with conductometric detection. The methods NIOSH 7903 [1] and OSHA 165SG [2] describe the IC procedure for sampling and analysis of acid mists in general, with specific references to nitric acid. Over the range 1-10 mg m^{-3} for a 50 L air sample, the silica gel/IC method partially complies with the performance standards EN 482 [3] with respect to uncertainty and partially complies with EN 1076 [4] with respect to recovery in storage. However, performance characteristics with respect to temperature and humidity effects are not available. A colourimetric diffusion sampler is available from SKC Inc. The performance characteristics of this direct-reading diffusion sampler are not available and its compliance with the performance standard EN 838 [5] is unknown. It may unsuitable for short-term monitoring around the IOELV.

References

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2. US Occupational Health and Safety Administration*, OSHA Analytical Methods Manual, US Dept of Labour, Acid mist in workplace atmospheres,* method 165SG, 1985.
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PENTANES (N-, ISO, NEO-)

CAS	109-66-0, 78-78-0, 463-82-1
OES	600 ppm (1800 mg m^{-3}), 8h-TWA (proposed)
IOELV	1000 ppm (3000 mg m^{-3}), 8h-TWA

Self-indicating colourimetric tubes calibrated for pentane isomers in air are not available. Tubes calibrated for hexane will be suitable but will indicate with a different sensitivity. Some commercial tubes may not be suitable for indicating in excess of 1200 ppm. Other hydrocarbons will interfere. Direct-reading instruments are available, based on infra-red spectrophotometry (IR) and photoionization detection (PID). The IR detection limit for pentane isomers is <1 ppm at a wavelength of 3.4 µm. It is not possible to distinguish the n-, iso- or neopentane isomers by IR or PID. Personal exposure to the pentane isomers in air may be measured by pumped sampling on activated charcoal sorption tubes at 0.01-0.1 L min^{-1} , desorbing with carbon disulphide and analysing by gas chromatography with flame ionisation or mass spectrometry detection, for example, the general hydrocarbon method NIOSH 1500.[1,2] This method is based on an early validation [2] which did not address all the concerns of newer performance standards, however, NIOSH 1500 is likely to comply fully with EN 482 [3] with respect to overall uncertainty and with EN 1076 [4] with respect to desorption efficiency, storage and environmental factors, over the range 5-1000 ppm. The limit of quantitation (L_Q) is about 0.1 ppm for a 2 L air sample. A maximum safe sampling volume of 2 L on 100/50 mg tubes is recommended. Diffusive badge-type personal monitors intended for solvent desorption are available commercially from several suppliers. Sampling rate data for four commercial designs were summarised in MDHS 88. [5] For n-pentane at least one badge type (SKC-575) is compliant with the diffusive sampler performance standard EN 838 [6], subject to the limitation that the sampling time is restricted to 2 hours at concentrations exceeding 1000 ppm. The L_Q for the diffusive badge (solvent desorption) method is <0.1 ppm for an 8 hour TWA sample. The diffusive badge (solvent desorption) method has been specifically validated only for n-pentane. For other isopentane and neopentane there will be a small additional bias uncertainty in the diffusive sampling rate, but the compliance with EN 838 should be nearly equivalent to that of the n- isomer.

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PHOSPHINE

CAS	7803-51-2
OES	0.3 ppm, STEL
IOELV	0.1 ppm, 8h-TWA; 0.2 ppm, STEL

Self-indicating colourimetric tubes are available from Dräger, Gastec and Kitagawa calibrated for phosphine. Commercial tubes can measure down to about 0.01-0.05 ppm. Arsine is also indicated with about the same sensitivity if the reagent chemistry is based on mercuric chloride. Mineral acid fume or vapour may interfere and give a false positive indication. Direct-reading instruments based on electrochemical (EC) sensors and paper tape monitors are available. EC sensors have detection limits of the order of 0.05 ppm. They are cross-sensitive to other hydrides such as silane, diborane, germane, arsine, hydrogen selenide and hydrogen sulphide and also sulphur dioxide. Paper tape monitors can monitor down to single figure/10 ppb levels. Also, infra-red spectrophotometry (IR) or photoionization detection (PID) can be used, but they may not have the sensitivity (nor the selectivity for PIDs) required for short-term monitoring around the existing or proposed limit values. The IR detection limit for phosphine is 1.4 ppm at a wavelength of 10.1 μm or an unspecified detection limit at 8.95 μm.[1] Personal exposure to phosphine in air may be measured by pumped sampling at up to 1.0 L min^{-1} through a cassette containing a glass fibre pre-filter and a polyester filter treated with mercuric chloride, digesting with sulphuric acid and analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). This method has been validated as OSHA 1003 [2] and complies with the overall uncertainty requirement of EN 482.[3] The recommended sampling volume is up to 240 L when sampling at 1.0 L min^{-1}. The limit of quantification (L_Q) is about 0.03 ppm for a 240 L sample. ICP-AES is the preferred analysis technique, but if not available, there are alternative methods. OSHA method ID-180 [4] (superseded by OSHA 1003) involves sampling on carbon sorbent tubes impregnated with potassium hydroxide and analysis as phosphite by ion chromatography. These special sorbent tubes may be difficult to obtain commercially and it is likely that impregnated tubes designed for sulphur dioxide monitoring would be an acceptable substitute . NIOSH method 6002 [5], a reformatted version of S332 [6], involves sampling on silica gel sorbent tubes impregnated with mercuric cyanide at 0.01-0.2 L min^{-1} up to a maximum recommended volume of 16 L. After extraction with acidic permanganate solution and further treatment with a molybdate reagent, phosphate is determined spectroscopically at 625 nm as a phosphate-molybdate complex. The silica gel tubes are commercially available. NIOSH 6002 reports that limit of detection is 0.1 μg per sample. The estimated L_Q is equivalent to about 0.03 ppm for a 16 L air sample. There is insufficient data to assess whether NIOSH 6002 complies with the performance standard EN 1076 [7] with respect to desorption efficiency, storage and environmental factors. From the precision/accuracy data supplied, it is possible that NIOSH 6002 would not meet the overall uncertainty requirement of EN 482. Phosphates and any phosphorus compound capable of forming the molybdate complex will interfere.

References

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SULPHUR DIOXIDE

CAS	7446-09-5
OES	2 ppm, 8h-TWA; 5 ppm, STEL
IOELV	0.5 ppm, 8h-TWA; 1 ppm, STEL

Self-indicating colorimetric tubes are available from Dräger, Gastec and Kitagawa, calibrated for sulphur dioxide in air. The limit of detection is about 0.05-1 ppm. Acidic gases such as nitrogen dioxide will interfere, but the degree of interference depends on the reagent chemistry which is varied by manufacturers according to the required measuring range. Direct-reading instruments are available based on electrochemical sensors, infrared (photoacoustic) photometry, UV fluorescence photometry and colorimetry. The UV fluorescence and paper tape techniques can monitor down to around single figure ppb levels while the limit of detection of the electrochemical and photoacoustic techniques is around the 0.5 ppm level. Potential interferents for the electrochemical sensor, which is commonly used in portable instruments, include nitrogen dioxide and chlorine. Personal exposure to sulphur dioxide may be measured by pumped sampling up to 24 L air at 0.1 L min^{-1} on 100/50 mg impregnated activated beaded carbon sorbent, desorption with alkaline hydrogen peroxide and analysis as sulphate by ion chromatography (IC) with conductometric detection, according to OSHA method ID-200.[1] Suitable impregnated carbon tubes are commercially available with a low sulphate blank. Over a limited range around 1-4 ppm for a 12 L air sample, OSHA ID-200 complies with the performance standards EN 482 [2] with respect to uncertainty and partially complies with EN 1076 [3] with respect to recovery in storage and humidity effects. The limit of quantification for a 12 L air sample is 0.01 ppm. This method may be suitable for short-term monitoring down to 0.1 ppm over 15 minutes. However, it is necessary for users to check their own desorption efficiency at low concentrations because OSHA ID-200 reports that the desorption efficiency depends on load. This sampling method will not distinguish between sulphuric acid mist and gaseous sulphur dioxide. If necessary a PTFE pre-filter may be placed in front of the carbon tube to collect sulphuric acid. To analyse the sulphuric acid component the PTFE filter is best extracted with hot water. Glass fibre pre-filters must not be used because they adsorb some sulphur dioxide. NIOSH 6004 [4] is an alternate method which recommends sampling at 0.5-1.5 L min^{-1} on a dual-filter cassette comprised of a cellulose ester front filter and a sodium carbonate treated back filter impregnated with sodium carbonate. Any sulphuric acid aerosol collects on the front filter and should not interfere with sulphur dioxide adsorbed on the back filter. Sulphite/sulphate is extracted from the filters with dilute carbonate/bicarbonate solution and analysed by IC with conductometric detection. The validation data provided with NIOSH 6004 is limited and it is not possible from the information available whether the filter sampling method complies with EN 482 with respect to overall uncertainty.

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TOLUENE

CAS	108-88-3
OES	50 ppm (192 mg m^{-3}), 8h-TWA; 150 ppm (574 mg m^{-3}), STEL
IOELV	50 ppm (192 mg m^{-3}), 8h-TWA; 80 ppm (306 mg m^{-3}), STEL

Self-indicating colorimetric tubes are commercially available from Dräger, Kitagawa and other sources, calibrated for toluene in air. Many aliphatic and aromatic hydrocarbons will interfere. Direct-reading instruments are available, based on infra-red spectrophotometry (IR) and photoionization (PID). The IR detection limit is <1 ppm at a wavelength of 13.9 µm. Personal exposure to toluene in air may be measured by pumped sampling on charcoal sorption tubes at 0.05 L min^{-1}, desorbing with carbon disulphide and analysing by gas chromatography with flame ionisation or mass spectrometry detection, for example, NIOSH 1501[1] based on the earlier validation S343 [2]. The method S343 did not address all the concerns of later performance standards EN 482 [3] and EN 1076 [4] but is likely to comply with respect to uncertainty, desorption efficiency, storage and environmental factors over the range 1-100 ppm. Method OSHA 111 [5] is a full validation of a modified NIOSH 1501 using the synthetic carbon Anasorb 747 and dimethylformamide/carbon disulphide as desorption solvent. The limit of quantitation (L_Q) is about 0.02 ppm for a 8 L air sample. Diffusive badge personal monitors intended for solvent desorption are available commercially from several suppliers. Sampling rate data for several commercial designs were summarised in MDHS 88 [6] and a full validation of the 3M-3520 and SKC-575 badge sampler compliant with EN838 [7] was published in OSHA 111. The L_Q for the badge samplers is about 0.1 ppm for an 8-h TWA sample. The diffusive thermal desorption method MDHS 80 [8] has been partially validated for toluene (with Tenax TA sorbent) to EN 838 in field tests against a reference method. The L_Q for the diffusive thermal desorption method is about 0.01 ppm for an 8h-TWA sample. The pumped thermal desorption method MDHS 40 [9] is fully validated to EN 1076. A limitation of MDHS 40 is that it is too sensitive for concentrations exceeding 50 ppm. The sample volume should be restricted to less than 5 L with a flow-rate of 0.01-0.02 L min^{-1}, otherwise sorbent capacity may be exceeded at high concentrations.

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ACETONITRILE

CAS	75-05-8
OES	40 ppm (68 mg m^{-3}), 8h-TWA; 60 ppm (102 mg m^{-3}), STEL
IOELV	40 ppm, 8h-TWA

Self-indicating colourimetric tubes calibrated for acetonitrile in air are not available. Commercial tubes calibrated for acrylonitrile may give an indication for acetonitrile if the reaction principle is based on oxidation to hydrogen cyanide with Cr(VI), but manufacturers have not recommended alternatives for acetonitrile and should be consulted for advice. Direct-reading instruments are available, based on infra-red spectrophotometry (IR). The IR detection limit for acetonitrile is about 7 ppm at a wavelength of 9.7 µm. Personal exposure to acetonitrile in air may be measured by pumped sampling on charcoal sorption tubes at 0.01-0.2 L min^{-1}, desorbing with dichloromethane /methanol (85:15) and analysing by gas chromatography with flame ionisation or mass spectrometry detection as described in NIOSH method 1606.[1] NIOSH 1606 does not address all the concerns of newer performance standards, but it is likely to comply fully with EN 482 [2] and EN 1076 [3] with respect to overall uncertainty, desorption efficiency, storage and environmental factors, over the range 5-100 ppm. The limit of quantitation (L_Q) is about 0.1 ppm for a 10 L air sample. A maximum safe sampling volume of 25 L on 400/200 mg tubes is recommended. Diffusive badge-type personal monitors intended for solvent desorption are available commercially from several suppliers. Calculated sampling rates for three commercial designs were summarised in MDHS 88. [4] Experimental data for the Dräger ORSA, 3M-3500, SKC-575 devices are not available and they have not been fully validated to the performance standard EN 838.[5] However, provided the analysis method is based on NIOSH 1606, results uncertainty will only be subject to the additional systematic difference between actual sampling rates and calculated rates supplied by the manufacturers. The L_Q for the diffusive badge (solvent desorption) method is <0.2 ppm for an 8 hour TWA sample.

References

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BARIUM, SOLUBLE COMPOUNDS

CAS -
OES 0.5 mg m^{-3}, 8h-TWA
IOELV 0.5 mg m^{-3}, 8h-TWA

Self-indicating colourimetric tubes and direct-reading instruments are not appropriate for the measurement of metals and metal compounds. Personal exposure to barium (soluble compounds) may be measured by sampling air at 2.0 L min^{-1} through a filter mounted in an inhalable dust sampler operated according to MDHS 14/3.[1] Mixed cellulose ester 0.8 µm filters are suitable. Filters are digested using an aqueous dissolution procedure as described in the method NIOSH 7056 [2] that is based on earlier validation data published as report S198.[3] Ionization of barium is suppressed by addition of sodium chloride. The resultant acidified solution is analysed by aspiration into the nitrous oxide/acetylene flame of an atomic absorption spectrometer (AAS) measuring at 553.6 nm. The limit of quantification is about 0.1 mg m^{-3} for a 30 L air sample. OSHA method ID-121 [4] is a similar AAS procedure with equivalent performance. NIOSH 7056 complies with the performance standard EN 482 [5] with respect to overall uncertainty and is suitable for short-term monitoring. Alternative methods include inductively coupled plasma-atomic emission spectrometry (ICP-AES), X-ray fluorescence spectrometry (XRFS) and inductively coupled plasma-mass spectrometry (ICP-MS). The performance of dissolution procedures for barium by ICP-AES have not been assessed. NIOSH 7300 [6] and OSHA ID-125G [7] are two published versions of the generic ICP-AES method. However, barium data was not included in these two documents. The XRFS method is non-destructive and gives adequate sensitivity with a 960 L air sample. A generic method for metals analysed by the XRFS procedure is given in MDHS 91.[8] Barium by XRFS complies with EN 482 with respect to overall uncertainty, but validation is subject to certain limitations of particle size, matrix effects and sample load. ICP-MS is very sensitive and selective. Generic published standard methods for elements by ICP-MS are in preparation.

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BROMINE

CAS	7726-95-6
OES	0.1 ppm (0.66 mg m^{-3}), 8h-TWA; 0.3 ppm (2.0 mg m^{-3}), STEL
IOELV	0.1 ppm (0.66 mg m^{-3}), 8h-TWA

Self-indicating colourimetric tubes calibrated for bromine in air are available from Dräger, Gastec and Kitagawa. Their limit of detection is in the range 0.2-2 ppm. Tubes may indicate chlorine dioxide with twice the sensitivity of bromine. Chlorine and nitrogen dioxide may also interfere, but with a different colouration. Direct-reading instruments are usually based on electrochemical (EC) detection using chlorine sensors, which are cross-sensitive to bromine, or colorimetric methods such as paper tape monitors. The limit of detection for the EC method is around the 0.5 ppm level and potential interferents may include nitrogen dioxide, although this depends on the technology used. Limits of detection of tens of ppb are typically achievable using paper tape monitors. Personal exposure to bromine in air may be measured by pumped sampling up to 90 L at 0.3-1 L min^{-1} through a silver membrane filter and eluting as bromide with 0.25 mM sodium bicarbonate/ 4 mM sodium carbonate solution, followed by ion chromatography (IC) with conductometric detection, as described in NIOSH method 6011.[1] NIOSH 6011 complies with the performance standard EN 482 [2] with respect to overall uncertainty over the range 0.05-1 ppm for a 15 L air sample. It is suitable for short-term monitoring. The limit of quantitation is <0.01 ppm for a 90 L air sample. A liquid impinger version of the IC method is described in OSHA ID-108.[3]. Bromine disproportionates in a sodium bicarbonate/carbonate solution to bromide and bromate. ID-108 complies with the performance standard EN 482 [2] with respect to overall uncertainty over the limited range of 0.05-0.2 ppm for a 30 L sample at 0.5 L min^{-1} and a working range of 0.015-0.3 ppm is stated. However, where larger volumes in excess of 100 L are required to measure concentrations below the IOELV, liquid impinger methods are unlikely to comply with EN 482 in practice. Alternatively, a long-term self-indicating colourimetric chlorine tube is available from Dräger that indicates bromine with about the same sensitivity. The limit of detection is 0.1 ppm over 8 hours, or 1 ppm for 1 hour, when used with a dedicated pump. Information on bromine cross-sensitivity of the chlorine colourimetric diffusion tube supplied by SKC Inc is not available and it may lack sensitivity for bromine. The performance characteristics of diffusion or long-term pumped colourimetric tubes are not available and their compliance with the performance standard EN 838 [4] is unknown. They are unsuitable for short-term monitoring.

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CARBON DIOXIDE

CAS 124-38-9
OES 5000 ppm, 8h-TWA; 15,000 ppm, STEL
IOELV 5000 ppm, 8h-TWA

Self-indicating colourimetric tubes are available from Dräger, Gastec and Kitagawa, calibrated for carbon dioxide. Commercial tubes can measure down to about 100-1000 ppm depending on design. Direct-reading carbon dioxide analysers are usually based on either infra-red spectrophotometry (IR) or electrochemical (EC) detection. Both techniques can be employed in personal monitors. Typical detection limits are of the order of a few hundred ppm for IR and somewhat higher for EC. EC analysers are more susceptible to interference from other gases such as hydrogen sulphide and hydrogen chloride. However, the high value of the limit value compared to typical levels found for potential interferents reduces the effect of such gases on the EC carbon dioxide reading. IR analysers are available commercially in several forms. Typically they are dedicated to carbon dioxide with minimal user calibration or they may be capable of detecting a range of gases with carbon dioxide detection at a wavelength of 4.3 µm as one option. Personal exposure to carbon dioxide in air may be measured by pumped sampling into a multi-layer gas bag at about 0.02 L min^{-1} (time-weighted average) or 0.2-0.5 L min^{-1} (15-minute STEL) and analysing the contents by gas chromatography (GC) with thermal conductivity detection (TCD) as described in OSHA method ID-172 [1] or NIOSH method 6603.[2] Sample bags of 2-5 L capacity capable of retaining carbon dioxide for 14 days are commercially available. Suitable choices of GC column stationary phase might be Porapak QS, Porapak N or Chromosorb 102, operated with helium carrier gas. The GC-TCD method meets the performance standard EN 482 [3] with respect to overall uncertainty. It is advisable that sample introduction is via a fixed-volume loop system and not a manual syringe, otherwise it is possible for up to 5% extraneous air to be mixed with the sample. The TCD also detects water with about the same sensitivity as carbon dioxide. Water vapour at typical concentrations of 5000-15000 ppm will not interfere, provided time is allowed for the water peak to elute after carbon dioxide. There are no other existing performance standards that address the influence of storage and environmental factors in time-weighted average sampling of permanent gases.

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FORMIC ACID

CAS	64-18-6
OES	5 ppm (9.6 mg m-^{3}), 8h-TWA
IOELV	5 ppm (9.6 mg m-^{3}), 8h-TWA

Self-indicating colourimetric tubes are available from Dräger, Gastec and Kitagawa calibrated for formic acid. Commercial tubes can measure down to about 1 ppm. Acetic and propionic acids are also indicated, but with different sensitivity. Mineral acids will interfere and may indicate with a different colouration to that of the organic acids. Direct-reading instruments based on infra-red spectrophotometry (IR) may be suitable, depending on interference by other organic acids. The IR detection limit for formic acid is 0.2 ppm at 9.4 µm.[1] Personal exposure to formic acid in air may be measured by pumped sampling at up to 0.2 L min^{-1} on charcoal sorbent tubes, desorbing with 0.0015M sodium borate solution and analysis by ion chromatography (IC) with with conductivity detection. This method has been partially validated by OSHA as ID-186SG.[2] The safe sampling volume is at least 48 L for 100/50 mg tubes when sampling at 0.2 L min^{-1}. The limit of quantification (L_Q) is <0.01 ppm for a 48 L sample. Formic acid is not stable when stored on charcoal tubes. When refrigerated at 4°C, storage is acceptable up to 7 days but not at 14 days, therefore the method does not strictly comply with the performance standard EN 1076 [3] in this respect. The desorption efficiency of freshly sampled tubes is compliant with EN 1076. Since borate/formate solutions are stable for at least 14 days, sample tubes should be desorbed as soon as possible. NIOSH have published a modified version of the general acids method 7903 [4] as NIOSH 2011.[5] Formic acid in the range 0.1-12 ppm is sampled on silica gel tubes, desorbed with water and analysed by IC with conductivity detection. The desorption efficiency of freshly sampled tubes is about 96% and compliant with EN 1076. Storage stability is reported as 91% recovery after 7 days. Other organic acids may interfere with IC methods. Due to lack of data it is not possible to assess compliance of OSHA ID-186SG with the uncertainty requirement of the performance standard EN 482. [6]

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METHANOL

CAS	67-56-1
OES	200 ppm (266 mg m^{-3}), 8h-TWA; 250 ppm (333 mg m^{-3}), STEL
IOELV	200 ppm (266 mg m^{-3}), 8h-TWA;

Self-indicating colourimetric tubes are commercially available from Dräger, Gastec, MSA and Kitagawa. Direct-reading instruments are available, based on infra-red spectrophotometry (IR) including photoacoustic spectroscopy and possibly electrochemical sensors. Or photoionization detection (PID). The IR detection limit for methanol is < 1 ppm at a wavelength of 9.7 µm, with the photoacoustic technique having a detection limit approximately four times less than for 'standard ' IR detection, for example as used in the MIRAN ® IR spectrometer. Electrochemical sensors are based on the ethylene oxide sensor and are cross-sensitive to a wide range of 'reactive' organic vapours . The limit of detection is of the order of a few ppm. Personal exposure to methanol in air may be measured by pumped sampling on synthetic carbon sorption tubes (Anasorb 747) at 0.05 L min^{-1}, desorbing with carbon disulphide/dimethylformamide (50:50) and analysing by gas chromatography with flame ionisation or mass spectrometry detection as described in OSHA method 91.[1] OSHA 91 complies with the performance standards EN 482[2] and EN 1076[3] with respect to overall uncertainty, desorption efficiency, storage and environmental factors, over the range 50-500 ppm. It is likely that the validation would hold at concentrations considerably less than 50 ppm. The limit of quantitation (L_Q) is about 0.2 ppm for a 3 L air sample. The maximum safe sampling volume depends on relative humidity. At high humidity (> 50% R.H.) the safe sampling volume is 5 L on a 400 mg sorbent tube and is inversely related to humidity. Methanol migrates through the sorbent bed in storage, therefore OSHA 91 recommends that sampling is carried out using a 400 mg tube and 200 mg back-up tube in series. At completion the tubes are separated and sealed in order that any breakthrough onto the second tube during the sampling period is clearly distinguished from migration in storage. Alternatively, NIOSH method 2000[4] uses silica gel sorbent tubes, and desorption with water/isopropanol (95:5). NIOSH 2000 partially complies with EN 1076 with respect to desorption efficiency, storage and humidity effects. A report in OSHA Chemical Sampling Information[5] recommends a large silica gel tube (520/260 mg) and changes the desorption solvent to 0.02N sulphuric acid. Either OSHA 91 or NIOSH 2000 would be acceptable, subject to the user being aware of the effects of humidity on the various sorbents. There are no suitable diffusive sampling methods for methanol with published validation status.

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NICOTINE

CAS	54-11-5
OES	0.5 mg m^{-3}, 8h-TWA; 1.5 mg m^{-3}, STEL
IOELV	0.5 mg m^{-3}, 8h-TWA

Direct-reading instruments or self-indicating colourimetric tubes specifically calibrated for nicotine are not available. Nicotine has a short lifetime in the gas phase and some of the total may be present as aerosol or suspended particulate. Personal exposure to nicotine in air may be measured by various methods which differ according to the source and the environment. An environmental tobacco smoke (ETS) sampler which distinguishes vapour and particulate components is commercially available.[1,2] It consists of a 37 mm 1 µm PTFE filter backed by XAD-4 sorbent which is extracted and analysed by methods similar to NIOSH methods 2544 [3] and 2551. [4] NIOSH 2544 involved pumped sampling on XAD-2 sorbent tubes, desorption with ethyl acetate and analysis by gas chromatography with nitrogen/phosphorus detection. This was a version of the earlier method S293 [5] revised for format only. The validation of S293 did not address all the concerns of the later performance standards EN 482 [6] and EN 1076.[7] The effect of humidity was not assessed. Sample stability was 90-98% recovery up to 5 days. The range studied was 0.3-1.2 mg m^{-3} for a 100 L sample and the limit of detection was not determined. For improved performance at low concentrations, two amendments to S293 were suggested by the Association of Official Analytical Chemists and the American Society for Testing and Materials. Nicotine extracted from XAD-4 with ethyl acetate was stabilised with triethylamine to reduce adsorption on glass vials and quinoline was used as an internal standard. This is now published as NIOSH 2551. A similar approach was to fix nicotine on filters coated with sodium bisulphate and extract with alkaline aqueous ethanol followed by ammoniated heptane using ethylnornicotine as internal standard.[8] Active and diffusive sampling were compared at low concentrations. The diffusive method partially complied with the performance standard EN 838 [9] with respect to overall uncertainty. Data on storage and humidity effects were not reported. An alternative sampling method is collection on Tenax TA thermal desorption tubes followed by gas chromatography with mass spectrometry detection (TD-GC-MS). A partial validation of a TD-GC-MS method, addressing some of the issues in EN 1076, was reported by Rothberg et. Al.[10] The trend is for methods which measure indoor air concentrations at less than 1% of the proposed IOELV. Although compliance with EN 838 or EN 1076 has not been addressed in all respects, methods based on either NIOSH 2551 or TD-GC-MS will be satisfactory over the range 0.1 – 2 x IOELV.

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OXALIC ACID

CAS	144-62-7
OES	1 mg m^{-3}, 8h-TWA; 2 mg m^{-3}, STEL
IOELV	1 mg m^{-3}, 8h-TWA; 2 mg m^{-3}, STEL

Oxalic acid in air exists primarily as suspended particulate at ambient temperatures. Self-indicating colourimetric tubes and direct-reading instruments are not appropriate. Personal exposure to oxalic acid in air may be measured by pumped sampling on cellulose acetate filters.[1] The maximum sample volume is reported as 960 L when sampling at 2.0 L min^{-1}. A size-selective sampling head, such as the 25 mm IOM dust sampler, should be used and operated at 2.0 L min^{-1} according to MDHS 14/3.[2] The filters are analysed by suppressor-based ion chromatography (IC) with conductivity detection using a method similar to OSHA ID-186SG.[3] No other published details are available from OSHA or NIOSH agency sources and the limit of quantification (L_Q) is not stated. The IC method may be capable of detection of <0.1 mg m^{-3} oxalic acid in a 100 L air sample, however, performance depends to a large extent on which interfering anions are present. Some experimentation with column type and mobile phase may be necessary to avoid co-elution with monocarboxylates, dicarboxylates and the common mineral acid anions. Suggested conditions might be [4] a suppressor column with a 100 x 4.6 mm anion exchange column and mobile phase 0.85 mM sodium bicarbonate/0.9 mM sodium carbonate at 1.2 mL min^{-1}. Alternatively, INRS have validated an IC method for carboxylic acids, including oxalic acid.[5] Quartz fibre filters impregnated with sodium carbonate are recommended for sampling. Due to lack of published data it is difficult to assess compliance of the IC method with the uncertainty requirement of the standard EN 482 [6] and the characteristics of the method with respect to desorption efficiency and storage requirements are unknown at present. However the published INRS data indicates that compliance is likely.

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PHOSPHORUS PENTACHLORIDE

CAS 10026-13-8
OES 0.1 ppm (0.87 mg m^{-3}), 8h-TWA
IOELV 1 mg m^{-3}, 8h-TWA

Self-indicating colourimetric tubes or direct-reading instruments are not commercially available. Personal exposure to phosphorus pentachloride in air may be measured by pumped sampling at up to 0.2 L min^{-1} through a midget impinger (bubbler) containing deionized water and an attached PVC pre-filter. Analysis is by determination of the absorbance of a blue complex with sodium molybdate and hydrazine sulphate at 830 nm. This method was partially validated as NIOSH S257.[1] The detection limit was reported as 0.4 mg m^{-3} for a 48 L sample, however, this referred to the conditions of a 1976 determination and more sensitivity may be achievable with modern instrumentation. Liquid impinger methods are not normally suitable for personal monitoring and their use is restricted to substances for which there is no alternative published method. The liquid impinger method may not comply with the overall uncertainty requirement of the performance standard EN 482 [2] on the basis of the original validation for NIOSH S257.

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PHOSPHORUS PENTASULPHIDE

CAS	1314-80-3
OES	1 mg m^{-3}, 8h-TWA; 3 mg m^{-3}, STEL
IOELV	1 mg m^{-3}, 8h-TWA

Phosphorus pentasulphide in air exists as particulate. Self-indicating colourimetric tubes or direct-reading instruments are not commercially available. Personal exposure to phosphorus pentasulphide in air may be measured by pumped sampling at up to 2.0 L min^{-1} through a PVC filter, followed by ion chromatography with conductivity detection as phosphate.[1] A size-selective sampling head, such as the 25 mm IOM dust sampler, should be used and operated at 2.0 L min^{-1} according to MDHS 14/3.[2] The maximum sample volume recommended is 960 L. OSHA have identified the analysis procedure as ID-128SG, however, this is unpublished and the details cannot be verified at the time of writing.

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PHOSPHORUS PENTOXIDE

CAS	1314-56-3
OES	2 mg m^{-3}, STEL
IOELV	1 mg m^{-3}, 8h-TWA

Phosphorus pentoxide in air exists as particulate. Self-indicating colourimetric tubes or direct-reading instruments are not commercially available. Personal exposure to phosphorus pentoxide in air may be measured by pumped sampling at up to 2.0 L min^{-1} through a cellulose ester filter, followed by ion chromatography with conductivity detection as phosphate.[1] A size-selective sampling head, such as the 25 mm IOM dust sampler, should be used and operated at 2.0 L min^{-1} according to MDHS 14/3.[2] The maximum sample volume recommended is 480 L. OSHA have identified the analysis procedure as ID-111 (phosphoric acid as phosphate). The published version of ID-111 is a statement of measurement principle only and does not contain any validation data.

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RESORCINOL

CAS	108-46-3
OES	10 ppm (46 mg m^{-3}) , 8h-TWA; 20 ppm (92 mg m^{-3}) STEL
IOELV	10 ppm (46 mg m^{-3}), 8h-TWA

A significant proportion of resorcinol in air is present as aerosol or suspended particulate. Direct-reading instruments or self-indicating colourimetric tubes calibrated for resorcinol in air are not available. Personal exposure to resorcinol in air may be measured by pumped sampling at up to 1.0 L min^{-1} on XAD-7 sorbent tubes, desorbing with methanol and analysis by gas chromatography (GC) with flame ionisation (FID) or mass spectrometry (MS) detection. Sampling devices may consist of a filter backed by a sorbent bed, or the filter may be omitted. Typically but not exclusively, these devices are 13 mm in diameter and contain a glass-fibre or quartz filter over a sorbent bed of 200/100 mg XAD-7 in two sections (for example the OSHA Versatile Sampler or OVS). A method using a version of this sampler has been published by OSHA as partially validated method 2053.[1] OSHA PV2053 complies with the performance standard EN 482 [2] with respect to overall uncertainty and substantially complies with EN 1076 [3] with respect to storage and desorption efficiency. The limit of quantification (L_Q) with GC-FID detection is estimated at < 0.3 mg m^{-3} for a 60 L air sample. The recommended maximum sample volume is 180 L at 1.0 L min^{-1}. OSHA PV2053 found that the collection efficiency of the glass-fibre prefilter alone was 95-97% for a 60 L sample, decreasing to 93% for a 180 L sample when loaded with resorcinol equivalent to 30-100 mg m^{-3}. The collection efficiency at low concentrations, equivalent to 0.7-3 mg m^{-3} for a 60 L sample, was examined further in the NIOSH method 5701 [4], based essentially on OSHA PV2053. The recovery from the whole OVS sampler complied with EN 1076 down to 0.7 mg m^{-3} for a 60 L sample or down to 3 mg m^{-3} for a 15 L 15 minute STEL sample. Collection efficiency data for the glass-fibre pre-filter alone was about 50% at this concentration and suggests that a back-up sorbent tube is essential when not using the pre-assembled OVS sampler.

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SILVER, SOLUBLE COMPOUNDS

CAS	-
OES	0.01 mg m^{-3}, 8h-TWA (as Ag)
IOELV	0.01 mg m^{-3}, 8h-TWA (as Ag)

Self-indicating colourimetric tubes and direct-reading instruments are not appropriate for the measurement of metals and metal compounds. Personal exposure to silver (soluble compounds) may be measured by sampling air at 2.0 L min^{-1} through a filter mounted in an inhalable dust sampler operated according to MDHS 14/3.[1] Mixed cellulose ester 0.8 µm filters are suitable. Filters are digested using a nitric/hydrochloric acid dissolution procedure as described in the method OSHA method ID-121.[2] The resultant acidified solution is analysed by aspiration into the air/acetylene flame of an atomic absorption spectrometer (AAS) measuring at 328.1 nm. The limit of quantification is about 0.002 mg m^{-3} for a 240 L air sample. Alternatively, filters are digested using a nitric/perchloric acid dissolution procedure as described in the method NIOSH 7300.[3] The resultant acidified solution is analysed by aspiration into an inductively coupled plasma-atomic emission spectrometry (ICP-AES). The limit of quantification is about 0.002 mg m^{-3} for a 960 L air sample. OSHA method ID-125G [4] is a similar ICP-AES procedure with equivalent performance, but the text of OSHA ID-125G notes in this version that determination of silver is semi-quantitative. NIOSH 7300 complies with the performance standard EN 482 [5] with respect to overall uncertainty but is unsuitable for short-term monitoring. A generic method for metals analysed by the XRFS procedure is given in MDHS 91.[6] However, compliance with EN 482, with respect to overall uncertainty, has not been assessed for silver compounds in MDHS 91. Validation would be subject to certain limitations of particle size, matrix effects and sample load. An alternative method is inductively coupled mass spectrometry (ICP-MS). ICP-MS is very sensitive and selective. Generic published standard methods for elements by ICP-MS are in preparation.

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ACETIC ACID

CAS	64-19-7
OES	10 ppm (25 mg m^{-3}), 8h-TWA; 15 ppm (37 mg m^{-3}), STEL
IOELV	-

Self-indicating colourimetric tubes are available from Dräger, Gastec and Kitagawa calibrated for acetic acid. Commercial tubes can measure down to about 0.1-1 ppm. Formic and propionic acids are also indicated, but with different sensitivity. Mineral acids will interfere and may indicate with a different colouration to that of the organic acids. Direct-reading instruments based on infra-red spectrophotometry (IR) may be suitable, depending on interference by other organic acids. The IR detection limit for acetic acid is 0.3 ppm at 8.6 µm.[1] Personal exposure to acetic acid in air may be measured by pumped sampling at up to 0.2 L min^{-1} on charcoal sorbent tubes, desorbing with 0.0015M sodium borate solution and analysis by ion chromatography (IC) with with conductivity detection. This method has been partially validated by OSHA as ID-186SG.[2] The safe sampling volume is at least 48 L for 100/50 mg tubes when sampling at 0.2 L min^{-1}. The limit of quantification (L_Q) is <0.01 ppm for a 48 L sample. Desorption efficiency and storage of acetic acid on charcoal complies with the performance standard EN 1076.[3] The method is also suitable for formic acid, but the recovery of formic acid from charcoal is not acceptable after 7 days. Since borate/formate solutions are stable for at least 14 days, sample tubes should be desorbed as soon as possible if mixtures of acetic and formic acids are to be analysed. NIOSH have published a gas chromatography (GC) method as NIOSH 1603 [4] based on the earlier validation S169.[5] Acetic acid in air is sampled on charcoal tubes which are desorbed with formic acid and analysed by GC with flame ionization detection. The safe sampling volume is up to 300L at 0.01-1 L min^{-1}. The estimated limit of quantification (L_Q) is about 0.1 ppm for a 48 L sample. The validation of S169 did not address all the concerns of the modern performance standard EN 1076. Desorption efficiency complies with EN 1076 over a range equivalent to 2.5-65 ppm for a 48 L sample. Due to lack of data it is not possible to assess compliance of OSHA ID-186SG with the uncertainty requirement of the standard EN 482. [6]

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CRESOLS

CAS 1319-77-3 (all isomers)
OES 5 ppm (22 mg m^{-3}), 8h-TWA
IOELV -

Self-indicating colourimetric tubes calibrated for cresols in air are commercially available from Gastec and Kitagawa, capable of detecting down to 0.5 ppm. The Phenol 1/b tube manufactured by Dräger is effectively calibrated for cresols when a sensitivity factor of x 0.8 is applied to the phenol indication. Phenol will interfere with the cresol indication of all tubes. Direct-reading instruments are available, based on photoacoustic spectroscopy, infra-red spectrophotometry (IR) or possibly photoionization detection (PID). The detection limit for cresols with a portable IR instrument is about 0.2 ppm at a wavelength of 8.9 µm.[1] Personal exposure to cresols in air may be measured by pumped sampling on XAD-7 sorbent tubes (100/50 mg), followed by solvent desorption with methanol and analysis by liquid chromatography (LC) with UV detection (OSHA 32 [2]) or gas chromatography (GC) with flame ionization (FID) or mass spectrometry (MS) detection (NIOSH 2546 [3,4]). Both methods comply with the performance standard EN 482 [5] with respect to overall uncertainty and substantially comply with EN 1076 [6] with respect to sensitivity, storage and desorption efficiency. The limit of quantification (L_Q) with LC-UV detection is < 0.02 ppm for a 24 L air sample. The recommended maximum sample volume is 24 L at 0.1 L min^{-1}. The L_Q with GC-FID is similar, subject to the following important proviso. The GC column should be specifically for the chromatography of acidic polar compounds, coated with a stationary phase normally based on polyethylene glycol. Suitable phases are commercially available under proprietary names, for example, Carbowax, Stabilwax, CP-Wax and others. No diffusive sampling methods have been validated for cresols. A badge device containing a polymeric sorbent is potentially usable with LC or GC as the analysis method. However, most commercial devices are inappropriate, since cresols adsorbed by any membrane draught shields and other plastic parts would not be recovered in the desorption procedure. Diffusive sampling devices consisting of only metal or glass components may be suitable but no validation details are available.

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CYANAMIDE

CAS	420-04-2
OES	2 mg m-3, 8h-TWA
IOELV	-

Direct-reading instruments or self-indicating colourimetric tubes specifically calibrated for cyanamide are not available. Tubes calibrated for aliphatic amines may indicate cyanamide but with a different sensitivity. Ammonia and many organic amines will interfere. Personal exposure to cyanamide in air may be measured by pumped sampling on XAD-2 sorbent tubes coated with 1-naphthylisothiocyanate (NITC) and analysis by HPLC with UV detection (OSHA in-house file [1]). The desorption solvent is not stated. No validation details are available, however OSHA have reported a similar partially validated NITC method for diethanolamine (OSHA PV2018 [2]) with dimethylformamide as desorption solvent. This method complies with EN 1076 [3] with respect to 2-week storage and desorption efficiency of diethanolamine at low concentrations. In the absence of any further details, the performance of OSHA PV2018 for cyanamide is expected to be similar. The detection limit for diethanolamine is < 0.2 mg m^{-3} for a 10 L sample and OSHA PV2018 is the preferred method for any proposed cyanamide IOELV in the range 0.2 - 2 mg m^{-3}.

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DIETHYLAMINE

CAS	109-89-7
OES	10 ppm (30 mg m^{-3}), 8h-TWA; 25 ppm (76 mg m^{-3}), STEL
IOELV	-

Self-indicating colourimetric tubes, specifically calibrated for diethylamine are available from Kitagawa. Tubes from other suppliers, calibrated for triethylamine, may indicate diethylamine with similar sensitivity, subject to supplier advice. Other organic amines and ammonia will interfere. The detection limit with a portable infra-red instrument is about 1 ppm at 9.0 µm wavelength. Photoionization detectors are sensitive to the vapour but have a large number of interferents. Personal exposure to diethylamine in air may be measured by pumped sampling on XAD-7 sorbent tubes coated with the fluorescent reagent 7-chloro-4-nitrobenzo -2-oxa-1,3-diazole (NBD), followed by solvent desorption with alkaline tetrahydrofuran. The sample solution is heated to 60°C for 2.5 hours and analysed by liquid chromatography with fluorescence or UV detection. NBD-coated XAD-7 tubes are commercially available, but suppliers must be consulted about shelf-life recommendations. The method has been evaluated by Elskamp and Schultz [1] and incorporated in a method published as OSHA 41. [2] The method complies with the performance standards EN 482 [3] and EN 1076 [4] with respect to sensitivity, storage and desorption efficiency. The detection limit is reported as < 0.1 ppm for a 10 L air sample. NIOSH method 2010 [5] has been partially validated for diethylamine, but storage stability was not tested. Silica gel sorbent tubes are eluted with acidified methanol and analysed by gas chromatography with flame ionization or nitrogen/phosphorus detection. Due to potential storage problems of free aliphatic amines on silica gel, the method status of NIOSH 2010 is tentative and OSHA 41 is preferred. It has been proposed that primary and secondary amines sorbed on silica gel could be derivatized with m-toluoyl chloride in acetonitrile and analysed by gas chromatography.[6,7] This method showed promise, but measurement performance standards were not addressed in the evaluations. The amide derivatives were stable in acetonitrile for up to two months, though the stability of free underivatized amines on silica gel was not reported by Simon and Lemacon, which is the main disadvantage of NIOSH 2010.

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NAPHTHALENE

CAS	91-20-3
OES	10 ppm, 8h-TWA; 15 ppm, STEL (OES withdrawn)
IOELV	-

No details of self-indicating colourimetric tubes calibrated for naphthalene in air are available from manufacturers. Direct-reading instruments are available, based on photo-acoustic spectroscopy, infra-red spectrophotometry (IR) or photoionization detection (PID). The IR detection limit for naphthalene is < 1 ppm at a wavelength of 13.3 µm. Personal exposure to naphthalene in air may be measured by pumped sampling on porous polymer sorption tubes (Chromosorb 106) at 0.01-0.2 L min^{-1}, desorbing with carbon disulphide and analysing by gas chromatography with flame ionisation or mass spectrometry detection as described in OSHA method 35.[1] OSHA 35 does not address all the concerns of newer performance standards, but it is likely to comply fully with EN 482 [2] and EN 1076 [3] with respect to overall uncertainty, desorption efficiency, storage and environmental factors, over the range 1-20 ppm. The limit of quantitation (L_Q) is about 0.1 ppm for a 10 L air sample. A maximum safe sampling volume of 30 L on 100/50 mg tubes is recommended. The general NIOSH method for aromatic hydrocarbons (NIOSH 1501 [4] based on S292 [5]) is not suitable for naphthalene. Solvent desorption of naphthalene from charcoal with carbon disulphide does not meet the 75% criterion at a loading of less than 10 mg. Diffusive badge-type personal monitors intended for solvent desorption are available commercially from several suppliers, but badge-type devices containing carbon sorbents are not recommended because the 75% desorption efficiency criterion may not be achievable. A calculated sampling rate for the SKC 575-003 badge (containing the porous polymer Anasorb 727) is available.[6] Naphthalene on the SKC 575-003 badge has not been validated to the performance standard EN 838.[7] However, provided the gas chromatography method is based on OSHA 35, uncertainty in the result will only be subject to the additional systematic difference between the experimental sampling rate and the calculated rate supplied by the manufacturer. The L_Q for the SKC 575-003 device is about 0.3 ppm for an 8 hour TWA sample. NIOSH have published two pumped sampling methods for polyaromatic hydrocarbons: 5506 [8] (liquid chromatography with UV or fluorescence detection) and 5515 [9] (gas chromatography with FID detection. Both involve collection on XAD-2 sorbent tubes and desorption with acetonitrile. Validation details are limited and the 75% desorption efficiency criterion may not be achievable. Naphthalene has also been measured using the general thermal desorption (pumped) method MDHS 72.[10] Sampling was on Tenax TA sorbent tubes. The desorption efficiency was 100% at 250°C and the L_Q was estimated at 0.001 ppm for a sample volume of 5 L.[11] No published details of a validation to EN 1076 are available, but compliance is expected on the basis of experience with similar aromatic compounds. A diffusive sampling rate of 2.55 ng ppm^{-1} min^{-1} has been reported [11] for the tube-type sampler described in the general thermal desorption (diffusive) method MDHS 80.[12]

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NITROBENZENE

CAS 98-95-3
OES 1 ppm (5.1 mg m^{-3}), 8h-TWA; 2 ppm (10 mg m^{-3}) STEL
IOELV 1 ppm (5.1 mg m^{-3}), 8h-TWA

No details of self-indicating colourimetric tubes calibrated for nitrobenzene in air are available from manufacturers. Direct-reading instruments are available, based on photo-acoustic spectroscopy, infra-red spectrophotometry (IR) or photoionization detection (PID). The IR detection limit for nitrobenzene is about 1 ppm at a wavelength of 11.9 µm. Personal exposure to nitrobenzene in air may be measured by pumped sampling on silica gel sorption tubes at 0.1-1 L min^{-1}, desorbing with methanol and analysing by gas chromatography with flame ionisation or mass spectrometry detection as described in NIOSH method 2005.[1] NIOSH 2005 complies with EN 482 [2] and EN 1076 [3] with respect to overall uncertainty, desorption efficiency and storage over the range 0.4-2 ppm. Humidity effects are not specified. The limit of quantitation (L_Q) is <0.1 ppm for a 30 L air sample. A maximum safe sampling volume of 150 L on 100/50 mg tubes is reported in NIOSH 2005, but this volume must be reduced by a large unspecified factor at high humidity. For general conditions therefore, a maximum safe sampling volume of 30 L is recommended. Measurement of nitrobenzene using the general thermal desorption (pumped) method MDHS 72 [4] may be feasible on Tenax TA sorbent tubes. The desorption efficiency and other characteristics have not been determined. No published details of a validation to EN 1076 are available, but compliance is expected over the range 0.1-2 ppm for a 5 L sample.

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NITROGEN MONOXIDE

CAS	10102-43-9
OES	25 ppm, 8h-TWA; 35 ppm, STEL
IOELV	0.2 ppm, 8h-TWA (proposed)

Self-indicating colourimetric tubes calibrated for nitrous fumes (NO and NO_2) in air are available from Dräger, Gastec and Kitagawa with detection limits in the range 0.5-10 ppm. Tubes are cross-sensitive to ozone and/or chlorine, depending on reagent chemistry. The presence of very high concentrations of nitrogen dioxide (NO_2) can bleach the indication of the most sensitive range tubes. Direct-reading instruments are available, based on electrochemical sensors and chemiluminescence spectrometry, although open-path UV spectrometry is also used for environmental monitoring. Chemiluminescence detectors and UV spectrometers are generally used as fixed background instruments and are not easily portable. The limit of detection of electrochemical sensors is of the order of 1 ppm or less. Potential interferents include nitrogen dioxide and hydrogen sulphide depending on the technology. The limit of detection of chemiluminescent spectrometers, based on the reaction with ozone, is down to the single figure ppb level with essentially no interferents. Open-path UV spectrometry has a detection limit of the order of a few ppb, depending on the pathlength. Certain hydrocarbons may interfere with UV spectrometry. Personal exposure to nitrogen monoxide (NO) in air may be measured by pumped sampling through a 3-stage device, as described in OSHA method ID-190 [1], in which a primary tube impregnated with triethanolamine (TEA) removes any NO_2 present. A middle oxidiser tube containing a chromate salt converts NO to NO_2. The third tube contains TEA to convert NO_2 to nitrite which is desorbed with aqueous TEA solution and analysed by ion chromatography with conductometric detection. A concentration-dependent conversion factor is required to correct for the disproportionation of NO_2 to nitrite and nitrate. NIOSH method 6014 [2] is similar in principle, except that the nitrite is determined colourimetrically by the diazotisation of N-(1-naphthyl)ethylenediamine. From the published NIOSH and OSHA validation data, both methods would comply with the performance standard EN 482 [3] with respect to overall uncertainty, in the range 11-50 ppm. However, Laitinen et. al. found that the efficiency of NO oxidation in field trials was lower than in laboratory tests.[4] The detection limit may be as low as 0.1 ppm but no validation data exists below 10 ppm. The proposed IOELV of 0.2 ppm is likely to be around the limit of quantification of current personal monitoring methods.

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PICRIC ACID

CAS	88-89-1
OES	0.1 mg m^{-3}, 8h-TWA; 0.3 mg m^{-3}, STEL
IOELV	-

Picric acid in air exists primarily as suspended particulate at ambient temperatures. Self-indicating colourimetric tubes and direct-reading instruments are not appropriate. Personal exposure to picric acid in air may be measured by pumped sampling on cellulose acetate filters. A size-selective sampling head, such as the 25 mm IOM dust sampler, should be used and operated at 2.0 L min^{-1} according to MDHS 14.[1] The filters are analysed by extraction with methanol/water (70:30) followed by liquid chromatography with UV detection at 360 nm, as reported in NIOSH method S228.[2] The analysis method was originally validated over the range 0.04-0.2 mg for a 180 L air sample. From the reported detection limit in S228 it can be estimated that the limit of quantification (L_Q) is about 0.001 mg m^{-3}. S228 complies with the overall uncertainty requirement of the standard EN 482.[3] The desorption efficiency and storage characteristics of the method are acceptable.

References

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PYRETHRUM

CAS 8003-34-7
OES 5 mg m^{-3}, 8h-TWA; 10 mg m^{-3}, STEL
IOELV -

Pyrethrum is a mixture of three naturally occurring esters of chrysanthemic acid (pyrethrin I, cinerin I and jasmolin I) and three esters of pyrethrin acid (pyrethrin II, cinerin II and jasmolin II). The vapour pressure of pyrethrum is negligible and colourimetric detector tubes or direct-reading instruments are not available. Personal exposure to pyrethrum in air may be measured by pumped sampling at up to 1 L min^{-1} on XAD-7 sorbent tubes, desorbing with methanol and analysis by gas chromatography (GC) with with electron capture (ECD) or mass spectrometry detection (MS). Sampling devices may consist of a filter backed by a sorbent bed, or the backing sorbent may be omitted. Typically but not exclusively, these devices are 13 mm in diameter and contain a glass-fibre or quartz filter over a sorbent bed of 270/140 mg XAD-7 in two sections (for example the OSHA Versatile Sampler or OVS). A method using a version of this sampler has been published by OSHA as method 70.[1] The limit of quantification (L_Q) for the electron capture detector was estimated at 0.05 mg m^{-3} (8h-TWA) or 0.2 mg m^{-3} (15 min STEL) for 60 L and 15 L samples respectively.[2] In the OSHA 70 validation report, quantitation of pyrethrum was based on the summation of three peaks from cinerin I & II and jasmolin I. Pyrethrins I & II were thermally degraded in the injector or GC column and the electron capture detector response for jasmolin II was small. It may be possible to quantify on other peak selections with different GC conditions and MS detection. The ratios of the pyrethrum esters can vary according to source. Users must be cautious about such procedures unless they have a matched sample of the natural extract for calibration. OSHA 70 complies with EN 1076 [3] with respect to storage and desorption efficiency. NIOSH have published a liquid chromatography method with UV detection as NIOSH 5008 [4] which is a reformatted version of the earlier method S298.[5] Up to 400 L air at 1-4 L min^{-1} is sampled on glass fibre filters which are extracted with acetonitrile and analysed by liquid chromatography with UV detection at 225 nm. The estimated limit of quantification (L_Q) is about 0.2 mg m^{-3} for a 60 L sample. Desorption efficiency complies with EN 1076 over a range equivalent to 1.4-8.5 mg m^{-3} for a 132 L sample. Due to lack of data it is not possible to fully assess compliance of either OSHA 70 or NIOSH 5008 with the uncertainty requirement of EN 482 [6], however the OSHA GC method with either ECD or MS detection is preferred because it is more sensitive and selective. The collection of aerosol/particulate material on the OVS sampler is unlikely to fully comply with the size-selective requirements of MDHS 14 [7] due to compromises in air flow. There are no size-selective data available for the 13 mm OVS sampler, however, the 25 mm IOM dust sampler, operated at 2 L min^{-1} according to MDHS 14, should be satisfactory for collection of pyrethrum without any backup sorbent.

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ISBN 0 7176 1749 1, HSE Books (2000).

PYRIDINE

CAS	110-86-1
OES	5 ppm, 8h-TWA; 10 ppm, STEL
IOELV	-

Self-indicating colourimetric tubes calibrated for pyridine in air are available from Dräger, Gastec and MSA. Direct-reading instruments are available, based on photoacoustic spectroscopy, infra-red spectrophotometry (IR) or photoionization detection (PID). The IR detection limit for pyridine is about 1 ppm at a wavelength of 14.4 µm. Personal exposure to pyridine in air may be measured by pumped sampling on XAD-7 porous polymer sorption tubes at 0.1 L min^{-1}, desorbing with methanol and analysing by gas chromatography with flame ionisation or mass spectrometry detection as reported in OSHA Chemical Sampling Information.[1] This method is described as partially validated and no further published details are available, however, it is probable that a method using XAD-7 sorbent would partially comply with the performance standard EN 1076 [2] with respect to desorption efficiency and storage over the range 0.5-10 ppm. Compliance with EN 482 [3] with respect to overall uncertainty is unknown. The limit of quantitation (L_Q) is estimated at about 0.3 ppm for a 10 L air sample. A maximum safe sampling volume of 10 L on 100/50 mg tubes is recommended. The NIOSH method for pyridine (NIOSH 1613 [4] based on S161 [5]) requires large air volumes up to 150 L in order to meet the 75% desorption efficiency criterion of EN 1076. Solvent desorption of pyridine from charcoal with dichloromethane gave 81% recovery for a loading of 0.8 mg (2.6 ppm for a 100 L sample). The S161 tests were carried out with dry air. The effect of humidity on breakthrough volume and desorption efficiency was not evaluated. The requirement to sample large volumes conflicts with monitoring to a 15 min STEL. For these reasons NIOSH 1613 is not recommended. Diffusive badge-type personal monitors with calculated sampling rates for pyridine are available commercially as the Dräger ORSA, 3M-3500 and SKC-575 devices.[6] They have not been validated experimentally with pyridine. Badges containing carbon sorbents are not recommended if the gas chromatography analysis method is based on NIOSH 1613. They are unlikely to meet the 75% desorption efficiency criterion (EN 838 [7]) for compliance monitoring unless the pyridine concentration exceeds 2 ppm (8 hour TWA) or 60 ppm (15 min STEL).

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TIN, ORGANIC COMPOUNDS

CAS -
OES 0.1 mg m^{-3} 8h-TWA; 0.2 mg m^{-3}, STEL (as Sn)
IOELV -

The vapour pressures of organotin compounds (except some alkylstannanes) are mostly low or negligible and colourimetric detector tubes or direct-reading instruments are not feasible. The measurement of total tin in sampled air is not usually appropriate and a separation step must precede the detection of speciated tin compounds such as tributyltin oxide, tributyltin methacrylate or tributyltin fluoride. Separation is effected by gas (GC) or liquid chromatography (HPLC) and detection by atomic absorption spectrometry (AAS), flame photometry (FPD) or mass spectrometry (MS). Some combinations of separation step and detector are specialised and are not found in a general analytical laboratory. For example, NIOSH 5504 [1] involves sampling on a glass-fibre filter backed by XAD-2 sorbent followed by solvent extraction/sonication for 30 minutes with acetonitrile/0.1% acetic acid and analysis by HPLC-graphite furnace-AAS. A similar graphite furnace-AAS method (non-speciated total tin) is reported in OSHA Chemical Sampling Information.[2] *(Alkylstannanes, for example tetramethyltin, may be collected by adsorption on charcoal, solvent desorbed with carbon disulphide and analysed by GC with flame ionization detection [2] or preferably by GC-MS. No validation details are available.)* Because of the specialised nature of the HPLC-AAS technique and limitations in its sensitivity, a modified form of the NIOSH sampling procedure has been investigated by the UK Health and Safety Laboratory (HSL) in which the desorbed tin compounds are ethylated with sodium tetraethylborate and analysed by GC-MS with single ion monitoring (SIM).[3] The derivatization procedure is based on work outlined by Michel and Averty.[4] Sodium tetraethylborate is added to the acetonitrile/0.1% acetic acid solutions containing the desorbed tin compounds. After further sonication with isooctane the ethylated tin derivatives in the isooctane layer are analysed by capillary GC-MS-SIM. The modified HSL method complies with the performance standard EN 1076 [5] with respect to desorption efficiency and storage stability. The limit of quantitation (L_Q) varies according to the organotin species but is extremely low relative to any probable limit value. The L_Q values for many tributyl- and triphenyltin species are < 0.0001 mg m^{-3} (as tin) for a 15 L air sample. The ethylation of some compounds, for example tributyltin methacrylate (TBTM), gives multiple derivatives. However, the L_Q of TBTM is still <0.001 mg m^{-3} (as tin). The method as tested did not quite meet the overall uncertainty standard of EN 482 [6], although it may be optimised to comply with the standard.

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CYCLOHEXANE

CAS	110-82-7
OES	100 ppm, 8h-TWA; 300 ppm, STEL
IOELV	-

Self-indicating colourimetric tubes calibrated for cyclohexane in air are not available. Tubes calibrated for hexane will be suitable but may indicate with a different sensitivity. Other hydrocarbons will interfere. Direct-reading instruments are available, based on infra-red spectrophotometry (IR) and photoionization detection (PID). The IR detection limit for cyclohexane is <1 ppm at a wavelength of 3.4 µm. Personal exposure to cyclohexane in air may be measured by pumped sampling on activated charcoal sorption tubes at 0.01-0.1 L min^{-1} , desorbing with carbon disulphide and analysing by gas chromatography with flame ionisation or mass spectrometry detection, for example, the general hydrocarbon method NIOSH 1500.[1,2] This method is based on an early validation [2] which did not address all the concerns of newer performance standards, however, NIOSH 1500 is likely to comply fully with EN 482 [3] with respect to overall uncertainty and with EN 1076 [4] with respect to desorption efficiency, storage and environmental factors, over the range 10-200 ppm. The limit of quantitation (L_Q) is about 0.1 ppm for a 4 L air sample. A maximum safe sampling volume of 5 L on 100/50 mg tubes is recommended. Diffusive badge-type personal monitors intended for solvent desorption are available commercially from several suppliers. Cyclohexane sampling rate data for four commercial designs were summarised in MDHS 88. [5] The Dräger ORSA, 3M-3500, SKC-575 or Radiello devices are all either in full or near full compliance with the diffusive sampler performance standard EN 838.[6] The L_Q for the diffusive badge (solvent desorption) method is <0.1 ppm for an 8 hour TWA sample.

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2-(2-BUTOXYETHOXY)ETHANOL

CAS	112-34-5
OES	-
IOELV	10 ppm, 8h-TWA; 15 ppm, STEL

Self-indicating colourimetric tubes specifically calibrated for 2-(2-butoxyethoxy)ethanol are not available. In principle, tubes calibrated for alcohols will give an indication, but if the reagent chemistry is based on oxidation by chromium(VI), they will generally lack the sensitivity necessary to monitor around the proposed IOELV of 15 ppm (15 minute STEL). Many alcohols, esters, ketones and hydrocarbons will interfere. Direct-reading instruments are available, based on photoacoustic spectroscopy, infra-red spectrophotometry (IR) and photoionization (PID). The IR detection limit and wavelength would need to be established by the user since published details are not available. Personal exposure to 2-(2-butoxyethoxy)ethanol in air may be measured by pumped sampling on charcoal sorption tubes at up to 0.2 L min^{-1}, desorbing with dichloromethane/methanol (95:5) and analysing by gas chromatography with flame ionisation or mass spectrometry detection, as in the partially validated method OSHA PV2095.[1] The validation of OSHA PV2095 did not address all the concerns of later performance standards EN 482 [2] and EN 1076 [3] but is likely to comply with respect to uncertainty, desorption efficiency, storage and environmental factors over the range 3-60 ppm. The limit of quantitation (L_Q) is <0.5 ppm for a 10 L air sample taken on 100/50 mg tubes. Alternatively, a pumped thermal desorption method based on MDHS 72 [4] could be used if greater sensitivity was required. MDHS 72 has not been explicitly validated with 2-(2-butoxyethoxy)ethanol, however, with the closely related 2-butoxyethanol, MDHS 72 does comply with EN 482 on overall uncertainty and with EN 1076 with respect to desorption efficiency, storage and environmental factors over the range 0.01-20 ppm. Sampling rates for diffusive badge or tube devices have not been established in any validation study. In principle, carbon-based badges could be analysed using a method based on OSHA PV2095 if the sampling rates were known.

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MERCURY AND INORGANIC DIVALENT COMPOUNDS

CAS 7439-97-6 (Hg, metallic)
OES 0.025 mg m^{-3} (as Hg), 8h-TWA
IOELV 0.02 mg m^{-3} (as Hg), 8h-TWA, proposed

Self-indicating colourimetric tubes specifically calibrated for elemental mercury vapour are commercially available from Dräger, Kitagawa and Gastec with detection limits in the range 0.05-0.1 mg m^{-3}. Halogen gases interfere and reduce the indicated mercury concentration. Direct-reading instruments for elemental mercury vapour are available, based on atomic fluorescence, electrical conductivity of gold amalgam and UV photometry. Detection limits of less than 1 ng m^{-3} can be achieved using pre-concentration on gold amalgam followed by fluorescence analysis. Without preconcentration, detection limits of less than 0.5 µg m^{-3} may be achieved with either fluorescence or UV absorption. The limit of detection of the electrical conductivity method is typically around 3 µg m^{-3}. These methods do not have any major interferences. There are no direct-reading methods appropriate for particulate inorganic mercury. Personal exposure to mercury vapour may be measured by pumped sampling through a sorbent tube of mixed copper/manganese oxides on a ceramic substrate. These sorbent is commercially available from SKC Inc. as Anasorb C300. Other versions of this sorbent have been available under the proprietary names Carulite or Hydrar. If particulate inorganic mercury is present, the sorbent tube is preceded by a quartz filter. If it is known that no mercury vapour is present, the quartz filter may be used alone without a sorbent tube. Inhalable samplers suitable for particulates, and compliant with the provisions of EN 13205 [1], are described in MDHS 14/3.[2] After sample collection the sorbent and/or filter are treated with mixed nitric and hydrochloric acids to dissolve the mercury. Sample solutions are mixed with tin(II) chloride and the elemental mercury generated is measured in a cold vapour apparatus with either atomic absorption or fluorescence detection. The sampling and analysis procedure is detailed in MDHS 16/2 [3] and complies with the performance standard EN 482 [4] with respect to overall uncertainty and EN 1076 [5] with respect to concentration, temperature and humidity. The limit of quantification for a 12 L sample is about 0.003 mg m^{-3} and the safe sampling volume for mercury vapour is greater than 720 L at a concentration of 0.05 mg m^{-3}. The validation is described fully in the work of Foster et al.[6,7] Diffusive badge-type personal monitors for mercury vapour are available commercially from SKC Inc. Mercury vapour is collected by diffusion at a rate equivalent to 0.02 L min^{-1} onto Anasorb C300 (Hydrar) contained in a replaceable capsule within the badge housing. Analysis is by the dissolution and cold vapour generation procedure as previously described. The diffusive badge complies with the performance standards EN 482 with respect to overall uncertainty and EN 838 [8] with respect to storage and environmental factors [7,9] at around the limit value of 0.025 mg m^{-3}, subject to certain limitations. Diffusive badges meet the uncertainty requirements of EN 482 for sampling times around 8 hours, but not for times as short as 4 hours. They are unsuitable for measurement of mercury vapour in chloralkali works, due to the formation of particulate mercuric chloride. They may also be unsuitable when subjected to vibration or shock, due to fragmentation and escape of sorbent granules from the capsule. The limit of quantification for a 6 hour sample is about 0.006 mg m^{-3}.

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2-(2-METHOXYETHOXY)ETHANOL

CAS	111-77-3
OES	-
IOELV	10 ppm, 8h-TWA; Sk notation

Self-indicating colourimetric tubes specifically calibrated for 2-(2-methoxyethoxy)ethanol are not available. In principle, tubes calibrated for alcohols will give an indication, but if the reagent chemistry is based on oxidation by chromium(VI), they will generally lack the sensitivity necessary to monitor around the proposed IOELV of 15 ppm (15 minute STEL). Many alcohols, esters, ketones and hydrocarbons will interfere. Direct-reading instruments are available, based on photoacoustic spectroscopy, infra-red spectrophotometry (IR) and photoionization (PID). The IR detection limit and wavelength would need to be established by the user since published details are not available. Personal exposure to 2-(2-methoxyethoxy)ethanol in air may be measured by pumped sampling on charcoal sorption tubes at up to 0.2 L min^{-1}, desorbing with dichloromethane/methanol (95:5) and analysing by gas chromatography with flame ionisation or mass spectrometry detection, as in the partially validated method OSHA PV2095.[1] OSHA PV2095 has not been validated explicitly for 2-(2-methoxyethoxy)ethanol but, based on the validation for the closely related 2-(2-butoxyethoxy)ethanol, the method is likely to comply with performance standards EN 482 [2] and EN 1076 [3] with respect to uncertainty, desorption efficiency, storage and environmental factors over the range 3-60 ppm. The limit of quantitation (L_Q) is estimated at <0.5 ppm for a 10 L air sample taken on 100/50 mg tubes. BIA method 7832 also uses solvent desorption with dichloromethane/methanol.[4] Alternatively, a pumped thermal desorption method based on MDHS 72 [5] could be used if greater sensitivity was required. MDHS 72 has not been explicitly validated with 2-(2-methoxyethoxy)ethanol, however, with the closely related 2-butoxyethanol, MDHS 72 does comply with EN 482 on overall uncertainty and with EN 1076 with respect to desorption efficiency, storage and environmental factors over the range 0.01-20 ppm. Sampling rates for diffusive badge or tube devices have not been established in any validation study. In principle, carbon-based badges could be analysed using a method based on OSHA PV2095 if the sampling rates were known.

References

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SULPHURIC ACID MIST

CAS	7664-93-9
OES	1 mg m^{-3}, 8h-TWA
IOELV	-

Self-indicating colorimetric tubes are available from Dräger, calibrated for sulphuric acid in air. The limit of detection is in the range of 1 mg m^{-3}. All mineral acids will interfere. Direct-reading instruments for acid mists are not commercially available. Personal exposure to sulphuric acid may be measured by pumped sampling up to 100 L air at 0.2-0.5 L min^{-1} on specially cleaned 400/200 mg silica gel sorbent, desorption with 1.7 mM sodium bicarbonate/ 1.8 mM sodium carbonate and analysis by ion chromatography (IC) with conductometric detection. The methods NIOSH 7903 [1] and OSHA 165SG [2] describe the IC procedure for sampling and analysis of acid mists in general, with specific references to sulphuric acid. Over the range 0.5-2 mg m^{-3} for a 50 L air sample, the silica gel/IC method complies with the performance standards EN 482 [3] with respect to uncertainty and partially complies with EN 1076 [4] with respect to recovery in storage. However, performance characteristics with respect to temperature and humidity effects are not available. These sampling methods will not distinguish between sulphuric acid mist and gaseous sulphur dioxide. OSHA ID-200 [5] is an IC method primarily intended for sulphur dioxide monitoring. It allows for the presence of sulphuric acid mist by adding a PTFE filter before an alkali impregnated carbon tube. Sulphuric acid collects on the PTFE filter and sulphur dioxide is adsorbed by the sorbent tube which is then extracted with alkaline hydrogen peroxide. To analyse the sulphuric acid component the PTFE filter is best extracted with hot water. NIOSH 6004 [6] is an alternate method, also intended for sulphur dioxide, that recommends sampling at 0.5-1.5 L min^{-1} on a dual-filter cassette comprising a cellulose ester front filter and a sodium carbonate treated back filter impregnated with sodium carbonate. Any sulphuric acid aerosol collects on the front filter. Sulphite/sulphate is extracted from the filters with dilute carbonate/bicarbonate solution and analysed by IC with conductometric detection. Neither OSHA ID-200 or NIOSH 6004 have been specifically validated for sampling sulphuric acid mist and it is not possible to say from the information available whether the filter sampling methods comply with EN 482 with respect to overall uncertainty. Another approach may be to adapt the denuder/filter pack developed by Koutrakis et al.[7,8] Sulphur dioxide is adsorbed by a glass denuder coated with sodium carbonate/glycerol and acid aerosols are collected on a PTFE filter where the sulphate is extracted and analysed by IC. Although the portable equipment described in references 7 and 8 was a personal sampler, it was designed for ambient/indoor rather than workplace monitoring. It would need to be made lighter and more compact to be acceptable to the average wearer.

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CARBON DISULPHIDE

CAS	75-15-0
MEL	10 ppm, 8h-TWA
IOELV	-

Self-indicating colourimetric tubes calibrated for carbon disulphide in air are available from Dräger, Gastec and Kitagawa. Commercial tubes can monitor down to 1 ppm depending on design. Direct-reading instruments are available, based on photoacoustic spectroscopy, infra-red spectrophotometry (IR) and photoionization (PID). The limit of detection for photoacoustic spectrometry is of the order of 1 ppm while that for IR spectrometry is around 5 ppm, both at a 4.7 μm measurement wavelength. Personal exposure to carbon disulphide in air my be measured by pumped sampling on 100/50 mg charcoal sorbent tubes, solvent desorption and analysis by gas chromatography with flame photometric detection (FPD), as described in NIOSH method 1600. [1] NIOSH 1600 is based on an earlier validation S248 with toluene as desorption solvent.[2] A desiccant pre-tube is recommended when sampling at high humidity. The maximum sample volume is 25 L at a flow rate of 0.01-0.2 L min^{-1}. NIOSH 1600 may partially comply with the performance standards EN 1076 [3] with respect to storage and environmental factors. However, toluene as desorption solvent has severe limitations with respect to desorption efficiency that confine its use to a narrower range of conditions than the ones stated by NIOSH. Compliance with EN 482 [4] with respect to overall uncertainty is unlikely. Also the FPD has an exponential response to sulphur that restricts its dynamic range to a factor of about 100x. The mass spectrometer detector is preferred. Wright and Wickenden [5] evaluated the charcoal tube method and found that the desorption isotherm with toluene was a complex function of solvent volume and load. The 75% desorption efficiency criterion was not met below 10 ppm for a 25 L sample, therefore toluene is not recommended, particularly when sampling for short periods. OSHA Chemical Sampling Information [6] suggests dichloromethane/ methanol (95:5) as an alternate desorption solvent, but no further details are available and users must verify desorption efficiency under their own conditions. Diffusive badge personal monitors, intended for solvent desorption, are available commercially from several suppliers. Experimental sampling rate data for one commercial design is summarised in MDHS 88.[7] However, compliance with the performance standard EN 838 [8] has not yet been demonstrated because the measurement method and desorption solvent used in the validation is not documented. The FPD is not a suitable choice for analysis of diffusive samplers used in the field, due to its restricted dynamic range.

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ETHYL ACETATE

CAS	141-78-6
OES	200 ppm, 8h-TWA; 400 ppm, STEL
IOELV	-

Self-indicating colourimetric tubes calibrated for ethyl acetate in air are available from Dräger, Gastec and Kitagawa. Commercial tubes can monitor down to 20-200 ppm depending on design. If the tube reagent chemistry is based on oxidation by chromium(VI) a wide range of substances could interfere. Direct-reading instruments are available, based on photoacoustic spectroscopy, infra-red spectrophotometry (IR) and photoionization (PID). Personal exposure to ethyl acetate in air may be measured by pumped sampling up to 6 L on charcoal sorption tubes at 0.05-0.2 L min^{-1}, desorbing with carbon disulphide and analysing by gas chromatography with flame ionisation or mass spectrometry detection, for example, NIOSH 1457 [1] based on the earlier validation S49.[2,3] The method S49 with carbon disulphide desorption does not address all the concerns of the performance standards EN 482 [4] and EN 1076.[5] It is likely to comply with respect to uncertainty, desorption efficiency, storage and environmental factors over the limited range 100-400 ppm. The limit of quantitation (L_Q) is potentially about 0.1 ppm for a 6 L air sample, however, validation was not achievable when using pure carbon disulphide as desorption solvent at low concentrations. NIOSH 1457 suggests the addition of 2-(2-butoxyethoxy)ethanol to the carbon disulphide, based on work by Beck et al.[6] Alternatively BIA method 7365 uses diethyl ether as desorption solvent.[13] Diffusive badge personal monitors, intended for solvent desorption, are available commercially from several suppliers. Sampling rate data for at least three commercial designs, either in full or partially compliance with the performance standard EN 838 [7], were summarised in MDHS 88.[7] The L_Q for the badge samplers is about 0.1-0.2 ppm for an 8-h TWA sample. The diffusive thermal desorption method MDHS 80 [9] has been partially validated for ethyl acetate (with Chromosorb 106 sorbent) to EN 838 in field tests against a reference method.[10,11] A revised uptake of 0.43 cm^3 min^{-1} (1.77 ng ppm^{-1} min^{-1}) in refs 10 and 11 supersedes a value of 0.49 cm^3 min^{-1} quoted in MDHS 80. The L_Q for the diffusive thermal desorption method is about 0.01 ppm for an 8h-TWA sample. The pumped thermal desorption method MDHS 72 [12] is partially validated to EN 1076. A limitation of MDHS 72 is that it is too sensitive for concentrations exceeding 50 ppm. The sample volume should be restricted to less than 5 L with a flow-rate of 0.01-0.02 L min^{-1}, otherwise sorbent capacity may be exceeded at high concentrations.

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TETRAETHYL ORTHOSILICATE

CAS 78-10-4
OES 10 ppm (87 mg m^{-3}), 8h-TWA; 30 ppm (260 mg m^{-3}), STEL
IOELV -

Self-indicating colourimetric tubes are not available. Direct-reading instruments are available, based on photoacoustic spectroscopy, infra-red spectrophotometry (IR) and photoionization (PID). The IR detection limit is reported as 0.04 ppm at 9.1 µm.[1] Personal exposure to tetraethyl orthosilicate in air may be measured by pumped sampling on XAD-2 sorption tubes at up to 0.05 L min^{-1}, desorbing with carbon disulphide and analysing by gas chromatography with flame ionization or mass spectrometry detection, as in the partially validated method NIOSH S264.[2,3] This is an early validation and does not address all the concerns of the performance standards EN 482[4] and EN 1076[5] with respect to uncertainty, desorption efficiency, storage and environmental factors. In particular, the reference limit value used was 100 ppm and the desorption efficiency was determined only down to 50 ppm for a 9 L air sample. Storage was satisfactory for up to 5 days. The effect of humidity was not determined. The limit of quantitation (L_Q) was estimated at about 10 ppm for a 9 L air sample taken on 100/50 mg tubes, but the L_Q may have been limited by a signal recording system of low sensitivity. Modern capillary columns and improved signal detectors may increase sensitivity sufficiently for monitoring at the 1 ppm level and below. Other porous polymers could be used in principle to substitute for XAD-2 but further details are not available. Charcoal is unsuitable due to poor desorption efficiency with a wide range of solvents, including carbon disulphide.

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MONOCHLOROBENZENE

CAS	108-90-7
MEL	1 ppm (4.7 mg m^{-3}), 8h-TWA; 3 ppm (14 mg m^{-3}), STEL
IOELV	5 ppm (23 mg m^{-3}), 8h-TWA; 15 ppm (70 mg m^{-3}), STEL

Indicating colourimetric tubes for short-term measurements of chlorobenzene in air are commercially available and capable of detecting 0.5 ppm. Other chlorinated hydrocarbons can interfere with different sensitivities. Real-time instruments with infra-red or photo-acoustic detection that can detect less than 1 ppm are also available. Personal exposure to vapour in air can be measured by pumped sampling on charcoal tubes (solvent desorption method NIOSH 1003) [1] or Tenax (thermal desorption method MDHS 72 [2]) and analysis by gas chromatography. Earlier NIOSH data published as method S133 [3] suggest that the carbon tube method, with carbon disulphide and coconut shell charcoal, may not meet the >75% desorption efficiency criterion below 5 ppm at the maximum sample volume of 40 L. This factor is sensitive to the type of carbon and the addition of solvent modifiers. Synthetic carbons are better than coconut shell charcoal. OSHA have indicated a preference for 1% dimethylformamide in carbon disulphide .[4] With respect to other factors, solvent desorption methods would generally comply with EN 482 [5] on overall uncertainty and with EN 1076 [6] on environmental effects above 5 ppm. The pumped thermal desorption method MDHS 72 has a detection limit of <0.02 ppm for a 10 L sample. MDHS 72 has been partially validated for chlorobenzene and is likely to comply with EN 482 and EN 1076 for both long-term and short-term sampling at <1 ppm where desorption efficiency was >97%. Diffusive sampling is feasible on carbon-type badge devices with solvent desorption (MDHS 88).[7] However, diffusive uptake rates are generally lower than pumped flow-rates and the desorption efficiency criterion of >75% may not be met below 15 ppm for 8 hrs. Carbon-type diffusive badges are unlikely to be suitable for 15 minute sampling below 25 ppm. Users must verify the solvent desorption efficiency of chlorobenzene with their chosen collection medium, otherwise their procedure may not comply with EN 1076 or EN 838 [8] at low concentrations. Thermal desorption diffusive tube samplers are feasible (MDHS 80) [9] and have adequate sensitivity for the measurement of <0.1 ppm for 8-hr sampling and of <3 ppm for 15 minute sampling.

References

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CALCIUM DIHYDROXIDE

CAS	1305-62-0
OES	5 mg m^{-3}, 8h-TWA
IOELV	5 mg m^{-3}, 8h-TWA

Self-indicating colourimetric tubes and direct-reading instruments are not appropriate for the measurement of metals and metalloid compounds. Personal exposure to calcium compounds may be measured by sampling air at 2.0 L min^{-1} through a filter mounted in an inhalable dust sampler operated according to MDHS 14/3.[1] Mixed cellulose ester 0.8 µm filters are suitable. Filters are digested using a nitric/perchloric dissolution procedure as described in the method NIOSH 7020 [2], based on earlier validation data published as report S205.[3] Ionization of calcium is suppressed by addition of caesium chloride. The resultant acidified solution is analysed by aspiration into the nitrous oxide/acetylene flame of an atomic absorption spectrometer (AAS) measuring at 422.7 nm. The limit of quantification is about 0.02 mg m^{-3} for a 30 L air sample. OSHA method ID-121 [4] is a similar AAS procedure with equivalent performance. NIOSH 7020 is likely to comply with the performance standard EN 482 [5] with respect to overall uncertainty and is suitable for short-term monitoring.

References

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LITHIUM HYDRIDE

CAS	7580-67-8
OES	0.025 mg m^{-3}, 8h-TWA
IOELV	0.025 mg m^{-3}, 8h-TWA

Self-indicating colourimetric tubes and direct-reading instruments are not appropriate for the measurement of metals and metalloid compounds. Personal exposure to lithium hydride may be measured by sampling air at 2.0 L min^{-1} through a filter mounted in an inhalable dust sampler operated according to MDHS 14/3.[1] Mixed cellulose ester 0.8 µm filters are suitable. Filters are digested using a deionized water dissolution procedure as described in the method OSHA ID-121.[2] Ionization of lithium is suppressed by addition of potassium chloride. The resultant solution is analysed by aspiration into the nitrous oxide/acetylene flame of an atomic absorption spectrometer (AAS) measuring at 670.8 nm. Data from OSHA ID-121 indicates that the limit of quantification (L_Q) is about 0.003 mg m^{-3} for a 30 L air sample and the method is therefore suitable for short-term monitoring. OSHA ID-121 is likely to meet the requirements of the performance standard EN 482 [3] at or below the IOELV, although some validation data with respect to recovery from filters is lacking.

References

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PLATINUM (METALLIC)

CAS	7440-06-4
OES	5 mg m^{-3}, 8h-TWA
IOELV	1 mg m^{-3}, 8h-TWA

Self-indicating colourimetric tubes and direct-reading instruments are not appropriate for the measurement of metals and metalloid compounds. Personal exposure to platinum may be measured by sampling air at 2.0 L min^{-1} through a filter mounted in an inhalable dust sampler operated according to MDHS 14/3.[1] Mixed cellulose ester 0.8 µm filters are suitable. Filters are digested using a nitric/hydrochloric acid mixture (aqua regia) as described in the method MDHS 46/2. [2] The resultant acidified solution is analysed by electrothermal atomic absorption spectrometry (AAS) measuring at 265.9 nm, or by inductively coupled plasma-mass spectrometry (ICP-MS) at mass 195. For a 30 L air sample and solution volume of 10 mL the limit of quantification is about 0.004 mg m^{-3} for electrothermal AAS and 0.003 mg m^{-3} for ICP-MS. These procedures do not distinguish between different forms of platinum (the OES applicable to soluble platinum salts is 0.002 mg m^{-3} as platinum) but for the purpose of monitoring platinum metal at or around the IOELV the method is very sensitive. It complies with the performance standard EN 482 [5,4] with respect to overall uncertainty and is suitable for short-term monitoring. Alternative methods include X-ray fluorescence spectrometry (XRFS) and inductively coupled plasma mass spectrometry (ICP-MS). A generic method for metals analysed by the XRFS procedure is given in MDHS 91.[5] The XRFS method is non-destructive and may be feasible for platinum metal but validation details for platinum are not available in MDHS 91. ICP-MS is very sensitive and selective. Generic published standard methods for elements by ICP-MS are in preparation.

References

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GLOSSARY

3M-3500	3M diffusion sampler
AAS	Atomic Absorption Spectrometry
BIA	Berufsgenossenschaftliches Institut für Arbeitssicherheit
CAS	Chemical Abstracts Service
CEN	Comité Européen de Normalisation (European Committee for Standardisation)
DFG	Deutsche Forschungsgemeinschaft (German Research Council)
EC	Electrochemical
EH	Environmental Hygiene (series)
EN	Euronorm
ETS	Environmental Tobacco Smoke
FID	Flame Ionization Detector
FPD	Flame Photometric Detector
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ILV	Indicative Limit Value
INRS	Institut National de Recherche et de Sécurité
IOELV	Indicative Occupational Exposure Limit Value
IOM	Institute of Occupational Medicine
IR	Infra-red
ISO	International Standards Organisation
L	Litre
LC	Liquid Chromatography
L_Q	Limit of Quantification
MDHS	Methods for the Determination of Hazardous Substances
MEL	Maximum Exposure Limit
MS	Mass Spectrometry
NBD	7-Chloro-4-nitrobenzo-2-oxa-1,3-diazole
NIOSH	(US) National Institute of Occupational Safety and Health
NITC	1-Naphthylisothiocyanate
OES	Occupational Exposure Standard
ORSA	Dräger diffusion sampler
OSHA	(US) Occupational Safety and Health Administration

OVS	OSHA Versatile Sampler
PID	Photoionization Detector
PTFE	Polytetrafluoroethylene
SCOEL	(EU) Scientific Committee for Occupational Exposure Limits
SEG	(EU) Scientific Expert Group
SIM	Single Ion Monitoring
SKC	Commercial manufacturer
SKC-575	SKC Inc. diffusion sampler
STEL	Short-Term Exposure Limit
SUM	Summary document eg. SCOEL/SEG/SUM
TBTM	Tributyltin methacrylate
TCD	Thermal Conductivity Detector
TWA	Time-Weighted Average
UV	Ultra-violet
WATCH	Working group on Assessment of Toxic Chemicals
WEEL	ACTS Working group on European Exposure Limits
XAD	Porous polymer, trade name of Rohm and Haas Co.
XRFS	X-Ray Fluorescence Spectrometry