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The Workplace Analysis Scheme for Proficiency

(WASP)

Information for Participants

Preamble

This guide provides participants with information concerning the WASP PT scheme.

Issue status

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| 14.2 | 12/02/2013 | Sample types offered updated Statistical scoring protocol updated. Test sample homogeneity statement updated. Test sample stability statement updated References updated Typographic errors found in Issue 13 corrected. | O. Butler |
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Note: Latest issue supersedes all previous issues.

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WORKPLACE ANALYSIS SCHEME FOR PROFICIENCY (WASP)

1 Background

Proficiency testing (PT) is defined in ISO/IEC 17043[1] as the evaluation of participant performance against pre-established criteria by means of interlaboratory comparison.

The origins of the Workplace Analysis Scheme for Proficiency (WASP) lie in a small internal comparison that was set up to serve, at that time, the Health and Safety Executive's (HSE) regional laboratories that carried out occupational hygiene analysis. It was decided to then expand the scheme to external laboratories and the first round of WASP samples was issued in September 1988. Interested participants can find more about the origins of the scheme in a paper by Jackson and West [2].

2 Scope and Purpose

Historically, WASP was designed to provide external quality assurance for UK laboratories carrying out chemical analysis of air samples taken in the workplace environment.

In the United Kingdom, the Control of Substances Hazardous to Health (COSHH) Regulations [3] requires that where hazardous materials are used, a risk assessment be carried out to ensure that personal exposure is minimised. This may include measurement to assess exposures and to test the effectiveness of containment or ventilation. The results of these tests are often used to make decisions that have significant implications for the operation of a particular workplace. Occupational hygiene measurements are carried out elsewhere in the world for similar purposes.

It is therefore vital that the measurement results have sufficient integrity. Many factors contribute to a meaningful test, such as choice of where and when to sample, performance of sampling equipment and the analysis subsequently carried out in the laboratory. Control of all these factors is important and the WASP scheme provides a means of assessing the quality and performance of the analytical steps carried out in the laboratory.

More specifically the scheme is designed to help laboratories meet the criteria in European Standard EN 482 [4] for occupational hygiene measurements. This performance standard states that the contribution of the overall expanded measurement uncertainties (MU) for both sampling and analysis should not be greater than $\pm 30\%$ for measurements conducted around a workplace exposure limit value for long-term sampling (i.e. full 8 hour shift) and $\pm 50\%$ for measurements conducted at less than half the limit value for long term sampling or for short durations (typically 15-60 minutes).

In the WASP scheme the EN 482 criteria has been interpreted in the following way; the contribution of the errors in analysis can be expressed mathematically as:

$$\sigma_{Total} = \sqrt{(\sigma_A)^2 + (\sigma_S)^2}$$

where

σ_A is the analytical contribution and

σ_S is the contribution from sampling

If it is assumed the sampling uncertainty is large and constant, there will be a point above which any further improvements in analytical uncertainty will not significantly improve the total uncertainty. Mathematically this is about a quarter of the overall uncertainty. For an expanded uncertainty requirement of $\pm 30\%$, this level is about 8% rising to around 12% for an overall uncertainty requirement of $\pm 50\%$. Many performance limits (satisfactory performance) in WASP are therefore set around this range if they are analytically achievable.

Over time, WASP has expanded the scheme to provide analytes covering the indoor and environmental air testing arena. Here MU requirements are somewhat less codified or are linked to measurement performance requirements set out in specific regulation and directives. Where possible, performance limits in WASP for these analytes are set after consideration of relevant method/MU requirements.

Where such MU requirements are not codified a more pragmatic approach is taken wherein analytical performance limits (satisfactory performance) in WASP are set at levels that are deemed analytically achievable by 80-90% of laboratories that would participate on a routine basis. Here likely achievable analytical performance is gleaned from a variety of sources: analytical expertise within HSL, information sources such as published method validation and collaborative trial data and from performance requirements set out in other similar PT schemes.

It is important to realise that the scheme alone cannot monitor day-to-day quality; each laboratory needs to devise its own system for achieving this according to its own work pattern. WASP will, however, provide an externally verified indication of performance that analysts can use to satisfy themselves, their organisation, and their clients that the quality of their analyses are fit for purpose. It is also a requirement of accreditation to ISO/IEC 17025 [5] that laboratories take part in a suitable PT scheme where available.

Note: Participation in the WASP PT scheme does not constitute recognition or approval of a laboratory by the Health and Safety Executive (HSE) or the Health and Safety Laboratory (HSL). Likewise participation in the scheme does not confer accreditation upon a laboratory.

3 Organisation of the WASP PT scheme

3.1 Management of the WASP scheme

Internal Management

Responsibility for the day-to-day running of the scheme rests with the Health and Safety Laboratory (HSL) and includes the following activities

- the recruitment of new laboratories
- preparation and dispatch of test samples
- data processing of returned results
- reporting laboratory performance
- post-round liaison with participants

The scheme employs the use of a scheme administrator and a scheme technical manager.

The role of the administrator is to

- act as a conduit between HSL and participants and to co-ordinate all administrative issues associated with participation.

The role of the technical manager is to

- coordinate the production and the validation of test samples; prepare the proficiency test reports and deal with any technical issues or queries from participants.

External Steering Committee

The scheme does not have an external steering committee at present.

Note: Historically WASP was promoted by HSE's Committee on Analytical Requirements (CAR), and was guided by a Steering Committee, which was a sub-committee of CAR. The Steering Committee had an HSL chairman and representatives from the following interested organisations:

HSE (Health & Safety Executive)
BOHS (British Occupational Hygiene Society)
IOH (Institute of Occupational Hygienists)
RSC (Royal Society of Chemistry)

The demise of CAR and changing demographic makeup of WASP participations, wherein most participants now reside outside the UK, necessitates that a new approach be implemented. HSL is currently reviewing potential options on the reconstitution of a suitable steering committee.

3.2 Scheme Quality

HSL operates to the ISO 9001 standard [6] with an aspiration of operating the WASP scheme to the ISO/IEC 17043 standard [1].

All test samples, except the WASP NO₂, are prepared and validated in-house by experienced chemists using analytical procedures based upon published standard methods. Further details regarding the preparation and validation of test samples can be found in Appendix 1.

Participants requesting further information regarding HSL and its quality system are directed in the first instance to the HSL website.

Note: HSL is implementing a new WASP PT scheme software system in 2013 which meets key requirements set out in ISO 13528 [7] and by default to requirements set out in ISO 17043 [1].

Note: HSL Quality Information page can be accessed here at <http://www.hsl.gov.uk/about-hsl/business-assurance.aspx>

3.3 Scheme Confidentiality

All information held by WASP about participants is confidential (subject to exclusions noted below) and all paper and computer records are securely maintained by the HSL proficiency testing team. Access is strictly limited only to those HSL staff members directly involved in the delivery of the schemes.

To ensure confidentiality, each laboratory is uniquely identified by a HSL PT laboratory number known only to HSL staff directly involved in the administration of the scheme.

Three confidentially exceptions currently exist

- HSL is an agency of the Health and Safety Executive (HSE), the UK regulator for health and safety, and may be asked to provide pertinent information if requested as part of a criminal prosecution.

Note: A scenario where this may occur is if HSE were to be involved in a criminal prosecution against a UK based company wherein a laboratory, internally or contracted to this company, being a WASP participant, was used to provide occupational hygiene measurement data. In such a scenario, HSL, through the proficiency testing team, may be asked to provide, if available, any information regarding the quality of this laboratory performing measurements, which may form a part of the investigation.

- Round data from US AIHA accredited laboratories that participate in the WASP scheme is provided to the AIHA IHPAT proficiency testing management team on a biannual basis. AIHA IHPAT recommends participation in the WASP PT scheme for AIHA accredited laboratories for those samples/measurands not offered within their own PT scheme. As such, participation in the WASP scheme can be considered as an extension to participation in the AIHA IHPAT scheme.

- HSL has an arrangement with Defra wherein PT performance data from UK WASP laboratories that subscribe to the NO₂ sample is supplied to them. Such laboratories may undertake local authority air quality monitoring measurements, data from which can be collated in air quality reports, which are in turn are supplied to and used by Defra. In turn local authorities, air quality experts and other stakeholders need to have confidence in the analytical quality of such laboratories. To assist this process, summary laboratory performance in WASP NO₂ is therefore published on the Defra Local Air Quality Management (AQM) webpage.

Note: Defra AQM webpage can be found here at <http://laqm.defra.gov.uk/diffusion-tubes/qa-qc-framework.html>

3.4 Sample types, round composition, frequency and timescales, sample distribution, round lifecycle

Sample types

The range of test samples types currently offered as part of the WASP proficiency test service include

- Metals on filters
- Volatile organic carbon (VOCs) on charcoal and tenax sorbents
- Respirable crystalline silica (quartz) on filters
- Nitrogen dioxide (as nitrite) on passive Palmes-type diffusion samplers
- Formaldehyde (as DNPH-adduct) on filters
- Gravimetric (using sodium borate as a surrogate mass) on filters.

This range represents a good cross section of sample types derived from either a workplace, ambient or indoor air environment involving subsequent laboratory analysis.

Round composition

In each distribution (round) participants receive four test specimens of each sample type that they have subscribed to. Each test specimen can contain one or more measurands (analytes) prepared at various test loadings (spike levels) on appropriate sampling media. Appropriate numbers of blank media are also supplied.

Further details regarding these sample types, measurands, indicative loading ranges, how they are prepared and checked and references to suitable standard methods that may be employed to analyse such samples can be found in Appendix 1.

Round frequencies and timescales

Sample distributions (rounds) are typically every 3 months.

The exceptions are the gravimetric, material emission testing VOC and silica sample types which are currently distributed on a two round distribution per annum.

Distribution schedules are made available to participants upon joining and are tabulated on the HSL WASP Proficiency Testing webpage.

Note: Any changes to planned distribution schedules are emailed directly to participants.

Sample distribution

HSL currently use Royal Mail Parcel Force to distribute test samples to UK participants.

A specialised courier is used to distribute test samples to all non-UK participants. A courier charge is specified for this service on the scheme order form.

Note: Indicative Parcel Force transit times are as follows

- United Kingdom participants 2- 4 working days

Note: Indicative courier transit times are as follows

- Australia, Japan, New Zealand, South Africa, US: 2 – 5 working days
- Other countries: 2 – 8 working days

Note: Transit times in working days pending customs clearance

Round lifecycle

Each PT round consists of the following steps:

- Preparation of test materials (see Appendix 1)
- Dispatch of test materials
- Participants analyse test materials for selected measurands and report results back to HSL by a given date using reporting templates supplied by HSL. The schedule is such that laboratories have typically 20 working days upon receipt to analyse the samples and to report their results.
- Results are processed by HSL (according to statistical procedures set out in Appendix 2)
- Distribution of test reports to all participants. Generally reports are issued within three weeks of the PT round closing date

4 Participation in the WASP PT scheme

Who should participate?

WASP is open to any laboratory involved in the chemical analysis of air samples. The membership fee covers one-year subscription (April – March). New participants joining the scheme part way through this period pay on a pro-rata basis for the remainder of the particular subscription period.

Participants can subscribe to sample type/measurands that meet their particular needs. Participants are free to use whatever methods of analysis they wish but it is preferable to use methods commonly used on routine samples within the laboratory.

Responsibilities

Participants upon joining agree to abide by the rules and regulations of the scheme and the associated HSL terms and conditions. Details can be found in Appendix 3.

Note: With the gravimetric test sample, participants have to send back per weighed filters to HSL for spiking at their own expense.

Note: Upon completion of a PT round, participants are required to return Tenax sorbent tubes at their own expense.

5 Performance assessment and reporting

Performance assessment

The statistical approach used in the WASP PT is the Z-score statistic widely used in other PT schemes. Details are provided in Appendix 2.

Participant report

Following data analysis, participants will received a report containing

- Round cover letter
- Round group report

6 Queries and feedback

Administrative queries should be directed to the scheme administrator by email, phone or letter. Email is the preferred option.

Queries of a technical issue, including participants seeking measurement advice, should also be directed to the scheme administration. Once logged, the query is passed onto the scheme technical manager to progress.

Note: Technical queries by their nature may be complex. Hence the scheme technical manager may need to confer with other measurement experts from within HSL, which may add to the turnaround time in responding.

Note: The scheme welcomes feedback and suggestions regarding possible developments of new sample types, improvements in current sample types etc.

7 Complaint procedure

Complaints should be addressed to the scheme technical manager, in writing, via the scheme administrator. The technical manager will attempt to resolve any issues arising to the satisfaction of the participant. If the response is unsatisfactory, participants can request an appeal and the technical manager will escalate the concerns through the HSL complaints procedure detailed in HSL's quality system.

8 Copyright, advertising and endorsement

Copyright

Once reports are issued to participants they are regarded as being in the public domain but such reports issued by the WASP scheme are UK Crown Copyright, which cannot be assigned to other publishers. Anyone wishing to use data from WASP reports for their own external publications should first seek permission from HSL.

Advertising

It is recommended that any publicity and advertising material produced and distributed by a participant should describe the laboratory as '**a WASP PT participant**' and state the sample type / measurands for which they participate. Participants may wish to describe their level performance as '**WASP participant with satisfactory performance**' if they achieve this level of performance, but may only do so for the period of participation in which their laboratory achieved this status.

Endorsement

Participation in the WASP PT scheme does not constitute recognition or approval of the laboratory by the Health and Safety Executive (HSE) or the Health and Safety Laboratory (HSL). Likewise participation in the scheme does not confer accreditation upon a laboratory.

Note. Any misrepresentation could result in the removal of a participant from the scheme.

Note. In certain circumstances, publications exploiting WASP PT data may be produced and distributed without the prior knowledge or approval of HSL.

9 Advice, training and other information

Advice

The WASP PT scheme is a performance based scheme and does not specify any particular analytical method(s) to be used. A laboratory should ideally use the same analytical procedures when analysing the WASP samples that it would use when analysing routine air samples.

Suggested advice on method selection can be obtained from the scheme technical manager.

Note: Technical queries by their nature may be complex. Hence the scheme technical manager may need to confer with other measurement experts from within HSL, which may add to the response time.

Training

Training samples, surplus samples from previous WASP rounds, are also available for laboratories wishing to take corrective action and/or training of new staff. Please contact the scheme administrator for further details.

Other information

From time to time HSL publish scientific peer reviewed papers on various aspects of laboratory performance in WASP scheme using summary cohort data collated from a number of rounds. A listing of these papers is available on the HSL WASP webpage. Useful other PT related resources that may be of interested to WASP participants are also available here.

10 Scheme contact details

For all enquiries, including applications to join and changes in sample requirements, please contact:

WASP Scheme Administrator
Proficiency Testing Team
The Health & Safety Laboratory
Harpur Hill
Buxton
Derbyshire
SK17 9JN
United Kingdom

Telephone: +44 (0)1298 218553 (with answer phone)

Email:- proficiency.testing@hsl.gsi.gov.uk

Web:- <http://www.hsl.gov.uk/centres-of-excellence/proficiency-testing-schemes/wasp.aspx>

Appendix 1

Test Samples within the WASP scheme

Inorganic Test Samples

| Measurement arena | Sample type measurands | Medium | Indicative analyte loading range µg/sample (unless stated) ^[1] | Suitable analytical technique(s) Standard methods ^[2] |
|-------------------|-----------------------------------|---|---|--|
| Workplace Air | Metals spiked onto filters | | | AAS/ICP-AES/ICP-MS |
| | Cadmium | Measurands spiked onto 25-mm diameter membrane filters (mixed cellulose ester) | 5 - 50 | ISO 15202-2 (sample prep) |
| | Chromium | | 50 - 500 | ISO 15202-3 (ICP-AES) |
| | Cobalt | | 50 - 250 | ISO 30011 (ICP-MS) |
| | Copper | | 50 - 250 | ISO 11174 (Cd by AAS) |
| | Iron | | 50 - 250 | ISO 8518 (Pb by AAS) |
| | Manganese | | 50 - 250 | |
| | Nickel | | 50 - 250 | |
| | Lead | | 15 - 150 | |
| | Zinc | | 50 - 250 | |
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|----------------------|---|--|--------------|---|
| Workplace Air | Quartz sampled onto filters | | | FTIR/XRD |
| | Quartz | Respirable size quartz aerosolised in dust chamber and sampled onto 25mm diameter PVC filters (GLA5000) mounted in Higgins Dewell type cyclonic samplers | 60 to 460 | UK HSE MDHS 101 (Direct on filter analysis by FTIR or XRD) NIOSH 7500 (indirect analysis by XRD) NIOSH 7602 (indirect analysis via KBr disc and FTIR) |
| | | | | |
| Workplace Air | Gravimetric PT scheme | | | |
| | Sodium borate salt as mass surrogate spiked onto filter | Measurand spiked onto 25-mm or 37-mm diameter glass fibre filters (GFA) | 0.2 – 2.0 mg | UK HSE MDHS 14/3 |
| | | | | |
| Ambient air | NO₂ on diffusion tube | | | |
| | NO ₂ (as nitrite surrogate) spiked into diffusion tube | Sodium nitrite spiked into Palmes-type diffusion tubes | 0.4 - 3 | UK Guidance Document |

[1] loading ranges reflect mass quantities of analyte that would be collected, if they were real samples, over the range 0.2 – 2 x exposure limit at typical sampling volumes.

[2] suitable international standard method(s) cited. If no international standard method available then suitable national method(s) cited. Advice on suitability of analytical methods can be obtained from HSL.

Organic Test Samples

| Measurement Arena | Sample Type Measurand | Medium | Indicative Analyte Loading Range µg/sample unless stated ^[1] | Suitable Analytical Technique(s) Standard methods ^[2] | |
|----------------------|---|--|---|--|--|
| Workplace Air | Solvent vapour dynamically loaded onto tubes | | | | |
| | Analysis involving solvent extraction /GC analysis | | | GC-FID/MS | |
| | Benzene | Measurands loaded from gas-phase onto charcoal filled glass sorbent tube | 10 to 400 | ISO 16200-1 | |
| | Toluene | | 50 to 2500 | | |
| | Xylene (all isomers) | | 50 to 5000 | | |
| | Ethyl benzene | | 20 to 400 | | |
| | 111 trichloroethane | Measurands loaded from gas-phase onto charcoal filled glass sorbent tube | 250 to 12000 | ISO 16200-1 | |
| | n- Hexane | | 25 to 1000 | | |
| | n-Butyl acetate | | 250 to 12000 | | |
| | Trichloroethene | | 80-7000 | | |
| | Tetrachloroethene | | 100 to 4000 | | |
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|----------------------|--|---|--------------|---|
| Workplace Air | Analysis involving thermal desorption (occupational workplace levels) / GC analysis | | | TD-GC-FID/MS |
| | | | | |
| | Benzene | Measurands loaded from gas-phase onto Perkin Elmer type thermal desorption tube ^[3] filled with Tenax TA sorbent | 0.5 to 15 | ISO 16017-1 |
| | Toluene | | 2 to 200 | |
| | Xylene (all isomers) | | 2 to 200 | |
| Ethyl benzene | 0.5 to 50 | | | |
| | | | | |
| Workplace Air | Spiked Derivatives | | | |
| | Analysis involving HPLC analysis | | | HPLC-UV (PDA) |
| | Formaldehyde derivative 2,4,DNPH spiked onto filter | Measurand spiked onto 25-mm diameter Glass fibre filters | 1.5 to 30 | HSE MDHS 102 ISO 16000-3 |
| | | | | |
| Ambient Air | Analysis involving thermal desorption (environment air levels) / GC analysis | | | TD-GC-FID/MS |
| | | | | |
| | Benzene | Measurands loaded from gas-phase onto Perkin Elmer type thermal desorption tube ^[3] with Tenax TA sorbent | 15 to 300 ng | ISO 16017-1 |
| | Toluene | | | ISO 16017-2 |
| | Xylene (all isomers) | | | |
| Ethyl benzene | | | | |
| | | | | |
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|-----------------------------|---|--|--------------|--|
| Indoor / Chamber Air | Analysis involving thermal desorption Material Emission Testing (indoor / chamber air testing) / GC analysis | | | TD-GC-FID/MS |
| | Up to 13 components including n-Hexane, Benzene, MIBK, Toluene Butyl Acetate, Cyclohexanone p-Xylene, a-Pinene, Phenol, 124-TMB Limonene, 4-PCH, Hexadecane | Measurands loaded from gas-phase onto Perkin Elmer type thermal desorption tube ^[3] with Tenax TA sorbent | 50 to 300 ng | ISO 16000-6 ISO 16017-1 |
| | | | | |

^[1] loading ranges reflect mass quantities of analyte that would be collected, if they were real samples, over the range 0.2 – 2 x exposure limit at typical sampling volumes.

^[2] suitable international standard method(s) cited. If no international standard method available then suitable national method(s) cited. Advice on suitability of analytical methods can be obtained from HSL.

^[3] it may be possible to accommodate other TD tube designs – please contact the WASP scheme.

Overview of the preparation of the WASP PT test samples

All test samples are prepared in-house at HSL except where noted.

Metals spiked onto membrane filters

Metals are spiked onto individual filters with aliquots of a custom-made stock multi-element solution(s) using calibrated motorised repeater pipettes. The stock solutions are prepared in-house from commercially available metal powders or metal salts, of stated purity, and are cross-checked by ICP-AES analysis, following dilution, against NIST traceable multielement calibration solutions. Filter media used are 25-mm diameter cellulose nitrate all obtained from the same manufacturer's lot to ensure matrix consistency within the subscription year.

For homogeneity checking, ten filters, taken at random, from each sample loading are analysed. Filters are subjected to analysis by ICP-AES, to procedures set out in ISO 15202 part 3, after leaching the filters in dilute nitric acid, to procedures set out in ISO 15202 part 2, Annex B.

Spiked filters are individually packaged in labelled 50 mm Petri-dishes. Blank (unspiked) filters are also supplied.

Quartz on filters

Respirable sized quartz powder, Sikron F600 (HSE standard material quartz A9950) is re-aerosolised in a sealed test chamber and sampled onto 25-mm diameter PVC filters (GLA5000) mounted in BCIRA (British Cast Iron Research Association) of the Higgins-Dewell type respirable cyclonic sampler design. Currently test samples are prepared in lots of 45, using a multiport sampler with individual flow channels with matched flow rates (cohort precision < 1.5 %).

For batch homogeneity purposes, all charged filters are unloaded from the samplers and are screened using an FTIR measurement approach detailed in HSE MDHS 101.

Charged filters are packaged individually in labelled petri dishes.

Note: The HSE A9950 material has been certified against NIST SRM 1878a as described in a paper by Stacey *et al.* in *Ann.Occup. Hyg.*, 2009 53 6 639-649.

Note: The filters are suitable for participants using either FTIR or XRD "direct on measurements" approaches as exemplified in HSE MDHS 101. Participants using FTIR also received spectrum matched blank PVC filters. Please note that the geometry of the quartz deposited on the sample filters is characterised by the use of the specific BCIRA respirable sampler design employed for sampling. Participants are therefore requested to note this fact as (their) calibration filters generated using alternative sampler designs may generate a different dust deposition geometry that could potentially generate a bias in test results when using a "direct on filter" analytical procedure. Further technical advice can be obtained from HSL.

Note: Test samples can also be analysed using "indirect" methods such as NIOSH 7500 or 7602.

NO₂ (as nitrite) in diffusion tube

Samples are prepared by a sub-contractor. An aliquot of a stock custom made sodium nitrite solution is spiked onto sampling grids mounted in Palmes type diffusive samplers using a calibrated pipette. The spike value(s) are calculated based upon gravimetric and volumetric considerations taking into consideration the nitrite concentration in the prepared stock spiking solution which is checked using a titrimetric approach. The pipette used for sample spiking is routinely checked at intervals during sample production via a gravimetric check. As a cross check and also to assess end user sample homogeneity, ten spiked tubes, taken at random from each sample loading, are analysed for nitrite by ion chromatography. This additional check is carried out at a separate third party laboratory, which is accredited to ISO/IEC17025 for this particular assay.

Gravimetric filter samples

Glass fibre filters (25-mm or 37-mm glass fibre filters) are sent to participants to pre-weigh in individually labelled transport Petri dishes. Following weighing, to obtain the required tare weights, the filters are returned HSL. Upon return, filters are spiked with a sodium borate solution prepared in-house. The concentration of this solution is checked, following dilution, by ICP-AES. Filters are then subsequently dried in a HEPA filtered drying cabinet and dispatched for re-weighing by participants. In a similar fashion, for homogeneity checking, six filters, at each sample loading level, are weighed at HSL, spiked, dried and reweighed. Weighing procedures outlined in HSE MDHS 14/3 are followed.

VOC on sorbent samples

The VOC samples are prepared by sampling vapour onto sorbent tubes (charcoal or Tenax) from a dynamically generated vapour atmosphere. An atmosphere is generated by vapourising a solvent mixture into a heated chamber, using an automated syringe to continually inject at a controlled rate. The resultant vapour cloud is then mixed and diluted in a dilution chamber to provide the required standard atmosphere. This approach is based upon that described in ISO 6145 part 4.

With the current sample-loading rig, thirty sorbent tubes can be loaded simultaneously and all gas flows are metered using calibrated mass flow controllers. An on-line FID detector with adaptive feedback control is used to monitor the vapour concentration within the dilution chamber thus ensuring that batches of 30 tubes can be loaded, sequentially, with a very high degree of precision.

For homogeneity assessment, ten sorbent tubes from each production lot are taken at random for analysis. As a minimum, three sorbent tubes must be taken from each loading batch of 30 test samples for testing. In total up to a maximum of ten sample are tested.

Analysis is carried out using GC procedures described in HSE MDHS 72 (analysis following thermal desorption) or HSE MDHS 96 (analysis following solvent extraction).

Note: Analysis carried out using in-house analytical procedure based upon HSE MDHS 72 is an accredited method to ISO/IEC 17025 [5].

Formaldehyde on filter samples

Formaldehyde samples are prepared by spiking individual glass fibre filters with formaldehyde - 2,4-dinitrophenylhydrazine derivate solution using a calibrated pipette.

For homogeneity assessment, 10 spiked filters are randomly taken from each sample loading for analysis. The analysis is carried out by desorbing the filters in solvent and analyzing by a HPLC method described in HSE MDHS 102 and ISO 16000-3.

Note: HSL is accredited to ISO/IEC 17025 [5] for measurements conducted according to ISO 16000-3.

Test Sample Homogeneity Statement

WASP samples prepared in the manner described above are sufficiently homogeneous for use in the scheme. See Annex 2 for more detail.

Test Sample Stability Statement

WASP samples have been tested for the stability through a combination of in-house testing with supporting evidence from published stability studies conducted during the development of certain certified reference materials at national measurement institutes such as IRMM and NIST. These reference materials have typically been prepared in a similar fashion to the WASP approach in use today at HSL.

| Test Sample | Stability | Evidence |
|---|--------------------|--|
| Metals spiked on filters | At least 2 years | In-house from HSL studies NIST SRM 2676 series <i>spiked metal on filters</i> |
| VOC on charcoal tubes | At least 6 months | In-house from HSL studies* NIST SRM 2661/2662/2664/2666 <i>VOCs on charcoal</i> |
| VOC on tenax tubes | At least 2 years | In-house from HSL studies IRMM CRM 112 <i>Aromatic hydrocarbons on Tenax</i> IRMM CRM 555 <i>chlorinated hydrocarbons on Tenax</i> |
| Material Emission Testing VOC on tenax tubes | At least 18 months | In-house from HSL studies* |
| NO ₂ spiked into diffusion tubes | At least 9 months | In-house from HSL studies |
| Quartz on filters | At least 2 years | In-house from HSL studies NIST SRM 2950-2958 <i>Respirable alpha quartz on filters</i> |
| Formaldehyde derivative 2,4-DNPH spiked onto filter | At least 2 years | In-house from HSL studies IRMM CRM 553 <i>Formaldehyde 2,4-DNPH spiked on filters</i> |
| Gravimetric PT scheme | At least 6 months | In-house from HSL studies |

* stability/storage trials on-going at HSL

Packaging of Test Samples prior to dispatch

In each round, the four samples of each sample type are placed in plastic ziplock bags, placed in foam lined cardboard box within a transport envelope. The Tenax tube test samples are supplied in foam lined plastic transport boxes.

Participants receiving the environmental Tenax samples will note that the plastic zip lock bag may contain a segment of a carbon filled cloth material. The aim of this material is to mop up any VOC that may potentially ingress into the sample packaging during sample transport i.e. aviation fuel vapour.

Note. It is a mandatory requirement that Tenax tubes and associated plastic transport boxes are returned to HSL after every completed round. See Appendix 3.

Appendix 2

Z-score statistic

Scoring Protocol

The WASP scheme now makes use of the well-established Z-score used widely in chemical proficiency testing schemes

$$Z_{\text{score}} = \frac{(x_{\text{lab}} - x_{\text{ref}})}{SDPA}$$

where

x_{lab} = participant result

x_{ref} = assigned value

$SDPA$ = standard deviation for performance assessment

| Sample type | x_{ref} | SPDA |
|----------------------|-----------------------------------|------------------------------------|
| Inorganics | | |
| WASP spiked metals | Robust mean from participant data | Fixed at 5 % of x_{ref} |
| WASP silica (Quartz) | Robust mean from participant data | Fixed at 10 % of x_{ref} |
| WASP gravimetric | Robust mean from participant data | Fixed at 10 % of x_{ref} |
| WASP NO ₂ | Robust mean from participant data | Fixed at 7.5 % of x_{ref} |

| Sample type | χ_{ref} | SPDA |
|---|-----------------------------------|--------------------------------|
| Organics | | |
| WASP VOC on charcoal at workplace levels | Robust mean from participant data | Fixed at 5 % of χ_{ref} |
| WASP VOC on Tenax at workplace levels | Robust mean from participant data | Fixed at 5 % of χ_{ref} |
| WASP VOC on Tenax at environmental levels | Robust mean from participant data | Fixed at 7.5 % of χ_{ref} |
| WASP VOC on Tenax for Material Emission Testing | Robust mean from participant data | Fixed at 15 % of χ_{ref} |
| Formaldehyde derivative 2,4,DNPH spiked onto filter | Robust mean from participant data | Fixed at 5 % of χ_{ref} |

Assigned value

The assigned value is the best estimate available to WASP of the “true value”. Assigned values for WASP analytes are derived, where possible, from participant data using a robust winsorisation methodology.

Assigned values calculated in this way are cross-checked with either a formulation value or a measured value derived during the homogeneity testing of test samples. If participant data cannot be used to determine a satisfactory assigned value then WASP will default to the use of a HSL derived formulation or measured value.

Note: The algorithm corresponds to that described in two successive articles published in the RSC journal, *Analyst* 1989 114 12 1693-1699 and 1699-1702 and corresponds also to algorithm A published in ISO 5725 part 5.

SDPA

SDPA represents the “standard deviation for performance assessment” which is used to assess participant performance for the measurement of each sample/analyte combination. SDPA are set at values that reflects fitness-for-purpose for the analysis in question and are aligned, where possible, with performance requirements set out in relevant standards e.g. EN 482[4] (see section 2 of this handbook).

Test Sample Homogeneity Statement

The assigned value χ_{ref} has a standard uncertainty that depends upon the method(s) used to derive this value. When the assigned value is determined by the consensus of participants results, the estimated standard uncertainty u_x of the assigned value can be calculated by

$$u_x = 1.25 \times \frac{SD_R}{\sqrt{n}}$$

where SD_R = robust standard deviation
 n = number of results

Guidance in ISO 13528 [7] suggests that test samples can be considered sufficiently homogeneous if

$$u_x \leq 0.3 \times \text{SDPA}$$

where SDPA = standard deviation for performance assessment

Based upon data tabulated below the uncertainty of an assigned value can be considered negligible and need not be considered in the interpretation of results.

| Test Sample | Target sample production precision goal | Sample production precision typically determined ^[1] | SDPA | U_x | Comment |
|--|---|---|----------------------------|----------------------------------|---|
| Metals spiked on filters | < 2.5 % | < 1.5 % | 5 % | < 1.5 % | |
| VOC on charcoal tubes at workplace concentrations | < 2.5 % | < 1.5 % | 5 % | < 1.5 % | |
| VOC on tenax tubes at workplace concentrations | < 2.5 % | < 1.5 % | 5 % | < 1.5 % | |
| NO ₂ spiked into diffusion tubes | < 1.5 % | < 1 % | 7.5 % | < 1.5 % | Sample spike production precision derived from volumetric and gravimetric considerations |
| Quartz on filters | < 2.5 % | < 2.5 % | 10 % | 2.5 % | |
| VOC on tenax tubes at environmental levels at workplace concentrations | < 2.5 % | < 1.5 % | 7.5 % | 2 – 2.5 % | |
| Formaldehyde derivative 2,4,DNPH spiked onto filter | < 2.5 % | < 1.5 % | 5 % | < 1.5 % | |
| Gravimetric PT scheme | < 2.5 % | < 2 % | 10 % | < 1.5 % [25-mm] < 3 % [37-mm] | PT sample supplied on two different media sizes to two different laboratory cohorts |
| Material Emission Testing VOC on tenax tubes | < 2.5 % | < 2.5 % < 5.0 % [Phenol] | 15 % ^[2-target] | 3 – 8 % | Current U_x values reflect new scheme (participants) in its infancy. SDPA set as an initial target for this new test sample. |

^[1]The sample production precision is determined by the analysis at HSL of typically 6-10 randomly selected samples from each production lot. Values obtained reflect contributions from both potential sample heterogeneity and variability in the sample preparation/measurement steps.

^[2] New scheme, target SDPA aligned with similar sample type offered by IFA PT scheme.

Removal of errors and gross blunders

Extreme results should not be included in the statistical analysis of the data. For this reason, the assigned value will be calculated as above, but those results that are out of the range of the assigned value $\pm 5 \times \text{SDPA}$ will be excluded and a new assigned value recalculated. All reported results, including excluded results, will be given a Z-score performance.

Performance categories and classification

The general classification of a Z_{score} is

$Z_{\text{score}} < \pm 2$ – satisfactory result based upon the “fit for purpose” SDPA

$Z_{\text{score}} \geq \pm 2$ and $< \pm 3$ – questionable (warning) result

$Z_{\text{score}} \geq \pm 3$ – unsatisfactory result

The properties of a normal distribution are such that, over a number of PT rounds, ca. 95 % of results from participants should lie within the z score range of ± 2 . The probability of results falling between a z score of > 2 and < 3 is about 1 in 20. Occasional occurrences in isolated rounds may be of little importance but it is advisable to investigate the analytical system if the frequency of such scores increases or if such similar z-scores are obtained for a sample tested for multiple analytes. The probability of a z-score of > 3 is about 1 in 300 and as such reflects results which are probably not fit for purpose. Here such results should therefore be investigated and if necessary remedial action taken to improve performance.

Participant reports

A round report is issued for each WASP sample type. In summary these reports detail the following information

- details on how test samples are produced ,
- summary sample production validation data
- tabulation of returned participant data
- calculated Z-scores in tabular and/or graphic formats
- discussion and conclusion sections provide feedback on round performance
- if available, other useful information/news pertaining to a specific analytical test/performance requirements/published methodologies

Appendix 3

Responsibilities and terms and conditions

Summary

HSL will operate the WASP PT scheme in accordance with its obligations set out below. In turn, a condition of joining the WASP scheme, upon signing the subscription order form, is that participants abide by the rules and responsibilities of the scheme as set out in this handbook and in particular detailed below. Likewise participants comply with the HSL's standard conditions of business, which are available upon request.

Obligations of HSL

HSL will operate the WASP PT scheme in accordance with procedures and conditions set out in this handbook in particular offering the particular sample test types set out in Appendix 1; operating the statistical protocols as set out in Appendix 2 and applying any relevant actions detailed as noted below.

HSL undertakes to correct any mistakes attributable to errors on its part as quickly as possible. HSL also undertakes to follow up any technical queries relating to test samples and associated scores as quickly as possible.

Participant Responsibilities

Payment responsibilities

- The Client will pay the invoice in full, including any amount shown in respect of VAT, within 30 days of the date of the invoice.
- An invoice shall not be regarded as paid until funds (GBP) are received into a UK sterling bank account operated by HSL or by the Health and Safety Executive.
- Within a subscription period, HSL reserves the right to withhold PT reports until full payment is made.
- HSL reserves the right not to accept repeat subscriptions from participants who have unpaid invoices from a previous subscription period.

Communication responsibilities

- Laboratory number must be quoted in all correspondence.
- All queries should be directed in the first instance to the proficiency testing team. Contact details are detailed in section 10. Email communication is preferred.
- To ensure we can keep you updated with important information it is the participant's responsibility to inform the scheme of any changes to contact details.

- Technical queries relating to test samples and associated scores must be forwarded to HSL within the timescale as noted below.

Note: Failure to provide up to date contact details may result in additional expense and delays in sample shipment. Delays may also result in a laboratory missing participating in a selected round and/or missing result reporting deadlines.

Note: Participants are advised to check the WASP PT webpage on a frequent basis for latest information regarding round schedules.

Note: Participants are requested to bring technical enquires to the attention of the scheme within a reasonable timescale. WASP defines a reasonable timescale as test rounds conducted within the last 6 months.

Test sample transportation responsibilities

- Participants should ensure that any required paperwork/permit application is in place, if requested by HSL, to allow samples through national boundaries/customs.

Note: Failure to do so may result in a participant incurring additional courier costs arising from HSL attempting to deliver said samples or replacements. Delays may also result in a laboratory missing participating in a selected round and/or missing result reporting deadlines.

Responsibilities regarding lost, delayed, damaged or suspect samples

Participants are requested to contact HSL if

- Samples are not received as scheduled or if samples appear to be damaged in transit (indicative transit times below). The participant shall inform HSL within 15 working days of the advertised dispatch date.
- Samples are 'lost' during sample workup and/or during the analysis.

Royal Mail Parcel Force is used to distribute test samples to participants in the UK. A specialised courier is used to distribute test samples to participants elsewhere.

Note: Indicative Parcel Force transit times are as follows

- United Kingdom participants 2- 4 working days

Note: Indicative courier transit times are as follows

- Australia, Japan, New Zealand, South Africa, US: 2 – 4 working days
- Other countries 2 – 8 working days

Note: Transit times in working days pending customs

Note: Participants should ensure that any required paperwork/permit application is in place, if requested by HSL or its nominated courier, to allow samples through national boundaries/customs. Failure to do so may result in delays in sample shipment and hence participation.

Note: For samples lost or damaged in transit, HSL will attempt to supply replacement of test samples, at HSL's expense, on a best endeavours basis provided replacement test samples are available and provided adequate notification is given, as outlined above. HSL cannot guarantee shipment of replacement test samples if notification is received after this stated time period.

Note: If transport issues persist with a certain address/location, HSL reserve the right to dispatch future test samples by alternative means and where additional courier costs may therefore apply.

Note: For test samples suspected of being damaged in transit, HSL request that, in the first instance, photographic evidence be provided, if requested. HSL reserve the right to inspect said shipments. Therefore the participant should not dispose of any said test samples and associated packaging until confirmation is received from HSL. The participant shall, if requested, send them back to HSL for examination. HSL will reimburse the associated courier costs.

Note: In the eventuality of non delivery of test samples by HSL to a participant, the participant may elect for a refund of the fees paid for the PT round in question for said test samples or a credit note to the equivalent of one round for said test samples to apply in the next available subscription period.

Note: For test samples damaged and lost in the care of the participant, HSL will attempt to supply replacement of test samples on a “best endeavours” basis using an express courier service provided that replacement test samples are available. This is provided that adequate notification is given and within the constraints of the round schedule. HSL however cannot guarantee replacements if such notification is received within 5 working days from round result deadline. The participant will bear any additional express courier costs.

Test sample handling responsibilities

- VOC samples on sorbent tubes should be stored away from other potential solvent sources in the laboratory.
- WASP samples should be stored, prior to analysis, in the transport cassette provided to minimise potential from contamination.

Test sample reporting responsibilities

- It is the participant’s responsibility to ensure that scheme round results are submitted by the defined deadlines.
- Participants are requested to report results on the reporting forms/format provided and have access to certain mandatory IT facilities such as Microsoft Word and Excel; an email account and a web access facility.
- Results should be reported as clearly as possible if a handwritten format is provided/required. Thousands should be separated by a comma not a full stop.
- All results should be reported to a minimum of 3 significant figures unless otherwise requested.

Note: Generally results received after a round deadline will not be processed. The one exception is if a laboratory notifies HSL in advance of the round deadline of a particular issue e.g. instrument failure, delays in sample transit, sample loss or damage (see above). At the discretion of the WASP PT technical manager, a short time extension may be granted.

Note: HSL reserves the right to refuse results submitted on reporting forms/format alternative to those provided.

Note: Transcription errors and/or errors in reporting results in the correct units by participants is considered by HSL to be part of the proficiency testing assessment process. As such HSL will not amend or correct any submitted results if requested. Participants can however, report revised results, if such errors are noted, provided that they are received at HSL before the round reporting deadline.

Test sample and associated packaging returns responsibilities

- Participants subscribing to the VOC test samples on Tenax TD sorbent tubes **must** return said tubes and associated transportation box(es) to HSL within 4 weeks of the round results reporting deadline.
- Non-UK participants must follow the guidance in the supplementary note below.

Note: When returning the transportation boxes (including the sorbent tubes) please mark the parcels as **“Returned sample tubes for Proficiency Testing scheme, with no commercial value”**. If a mandatory value is required for the package then a statement such as **“declared nominal value of 5 Euro/Dollar”** should be added. Please ensure that these statements are clearly detailed on the outside packaging and that the package is returned with any associated shipment documentation as supplied/requested by HSL or its courier.

Note: Failure to do this can result in HSL incurring custom and excise importation charges. Any such fees will be passed onto the participant.

Note: HSL reserve the right to charge the full replacement costs for TD sorbent tubes and transport boxes not returned by the required deadline.

Renewal of membership

A renewal order form is sent to participants at the beginning of each year. Each laboratory must return a signed copy of this order form if it wishes to continue to participate.

Note: This signed order form constitutes the membership agreement between HSL and the participating laboratory. By signing the order form the participant agrees to their responsibilities set out in this handbook and agree to abide by the HSL’s standard conditions of business.

Closure of membership

Notification of a laboratory’s intent to withdraw from the scheme must be sent in writing to the Proficiency Testing Team. HSL will refund unused subscriptions after deducting a £50 administration fee. Closed participant data is then archived under the laboratory ID number that is then subsequently retired.

Change of ownership and laboratory mergers

Participants are requested to contact the scheme in the first instance.

Collusion and falsification of results by participants

The responsibility rests with each participant to behave in a professional scientific manner. Whilst maintaining confidentiality (see section 3.3 in the main handbook), HSL has in the past and will in future provide generic scientific feedback on likely achievable analytical performance to accreditation bodies and regulators where requested.

Appendix 4

References

- [1] ISO/IEC 17043:2010 Conformity assessment – General requirements for proficiency test.
- [2] West, N. and Jackson, H. *Initial experience with the workplace analysis scheme for proficiency (WASP)*, *Annals of Occupational Hygiene*, 1992, 36, 2 545-561.
- [3] COSHH <http://www.hse.gov.uk/coshh/>
- [4] EN 482: 2012 Workplace exposure - General requirements for the performance of procedures for the measurement of chemical agents.
- [5] ISO/IEC 17025:2005 General requirements for the competence of testing and calibration laboratories.
- [6] ISO 9001:2008 Quality Management Systems – Requirements.
- [7] ISO 13528:2005 Statistical methods for use in proficiency testing by interlaboratory comparisons.