

best @buchhi



www.buchi.com

Information Bulletin

Number 48/2007



Determination of airborne mineral oils: an inter-laboratory comparison

New methodologies for the determination of mineral oil in air samples are discussed. In inter-laboratory comparisons the Syncore® Polyvap proved to be a reliable tool showing excellent reproducibility and performance.

Authors: Robert Wolf¹, Maria Barbey¹ and Ruedi Hartmann²
¹: Schweizerische Unfallversicherungsanstalt SUVA, 6002 Luzern, Switzerland
²: Büchi Labortechnik AG, 9230 Flawil, Switzerland

Determination of airborne mineral oils: an inter-laboratory comparison

Metalworking fluid aerosols and vapors, occurring e.g. in the Swiss watch making industry, are generated under controlled laboratory conditions and determined using four different methodologies differing in sample preparation and analytical method. The reliability, reproducibility and performance of the Syncore® Polyvap parallel evaporator is scrutinized in an inter-laboratory comparison with five independent analytical laboratories in Switzerland.

Introduction

Metalworking Fluids (MWFs) are largely used in the metallurgical industry, and particularly the Swiss watch making sector. Despite the use of hooded ventilation and filtration systems to reduce the risk of oil mist exposure, there are various known respiratory ailments caused by dispersion of oil mists in the workplace atmosphere such as chronic cough, irritation of the airways, bronchitis and asthma.^[1]

It is estimated that 20'000 out of 120'000 registered Swiss workers are exposed to oil mist quantities of approximately 0.36 tons of oil per year per worker.^[2] Moreover, investigations performed in a group of 1811 employees at an automobile factory in Massachusetts, USA, revealed that the additional exposure to mineral oil mists during one year causes as much harmful effect as smoking one pack of cigarettes per day for a period of more than one year.^[3]

Presently, the national occupational exposure limits concerning oil mists are not standardized on an international level. However, the Swiss recommendations for the permissible exposure limits (PEL) are 0.2 mg/m³ for heavy oils with boiling points > 350 °C as aerosol, and/or 20 mg/m³ as oil aerosol plus vapor for medium or light oil.^[4]

Various techniques are available to determine the concentration of airborne oil mists. The standard method recommended by the Professional Association for Provisions on Labor (BGIA)¹ has some shortcomings

especially in the presence of hydrocarbon interferences (see later). A brief overview of the different methods in terms of sample preparation and analysis is given and the results are compared in an inter-laboratory round robin test with five independent analytical laboratories in Switzerland.

Experimental

Determination of the concentration of oil mists involves a sampling unit to collect the mist and vapors (see **Figure 1**), extraction with an organic solvent, and determination by spectrometric or gravimetric methods, respectively.



Figure 1: GSP sampler with a Ø 37 mm filter and 3 g XAD-2 cartridge used for the BGIA-modified procedure.

There are two inherent problems concerning the determination of MWFs in air samples, one regarding sampling and one regarding the analytical method. Firstly, the sampling procedure involves a constant air flow of 3.5 l/min for approximately 60 - 120 min through a sampler as depicted in Figure 1. Low-viscosity oil droplets² which are collected on the filter may evaporate due to constant contact with the air stream which acts as a carrier gas. The losses are mostly pertaining to aliphatic hydrocarbons (C₁₂ - C₂₄), but also to additives such as alkyl benzenes, esters, phenols and terpene odorants. This results in an underestimation of the MWFs concentration. To prevent this evaporative loss, the BGIA recommends placing an XAD-2 cartridge³ behind the filter to trap any vaporized mist samples (see **Figure 1**).

Secondly, volatile apolar cleaning solvents are frequently used in the metallurgical industry to degrease metal parts. These low-boiling contaminants are also trapped on the cartridge behind the filter and may interfere with the analysis resulting in an overestimation of the MWFs concentration. An independent determination of these contaminants (e.g. GC-MS analysis) or efficient separation in the sample work-up (e.g. fractional distillation) is required to overcome this problem.

Five inter-laboratory comparisons were organized based on the generation of oil mist under controlled laboratory conditions.⁴ The samples were collected on filters (glass fibre or PVC) and XAD-2 cartridges. White Spirit (Indurei, 60 - 100 mg/m³) was used as the chemical interference and polydispersed spherical glass particles (Spheringlass) as inert dust interference during aerosol generation in the test chamber. Four different procedures for the determination of MWF concentration were applied.

¹ BGIA, Berufsgenossenschaftliches Institut für Arbeitsschutz

² i.e. a kinematic viscosity less than 18 cSt at 40 °C

³ XAD-2 is a polymeric resin adsorbent that selectively scavenges hydrophobic organic contaminants from water and/or air samples.

⁴ MWFs were generated in a home-made glass nebulizer and the aerosol particles were characterized optically using an optical particle analyzer (Climet Model 208A), and gravimetrically using an impactor (Andersen 2000) equipped with 8 glass fibre filters. For further information see ref. [5, 6] and Figure 4.

Method A

Sampling was achieved with PVC filters and XAD-2 cartridges (1 g adsorbent). Oil mist on the filter was determined gravimetrically in a controlled humidity box. The volatile fraction on the cartridge was analyzed according to method B.

Method B

In contrast to Method A, glass fibre filters were used instead of PVC filters. In addition to the gravimetric analysis, adsorbed oil mist was extracted with CH_2Cl_2 (20 ml), followed by evaporation under nitrogen, and subsequent gravimetric determination of the extracts. The extracts of the volatile fraction adsorbed on the XAD-2 were determined according to the same method.

Method C

Determination of the mist fraction on the filter was achieved according to Method B. But instead of gravimetric evaluation, the XAD-2 extracts were analyzed by GC-MS and GC-FID in compliance with ISO 16703.

Method BGIA-modified

The standard BGIA method involves sampling with glass fibre filters and XAD-2 cartridges (3 g adsorbent), extraction with tetrachloroethylene (PER, 10 ml) and evaluation by IR absorbance at $3000 - 2800 \text{ cm}^{-1}$. The modified procedure is based on parallel fractional distillation of MWF samples in PER under vacuum at $60 \text{ }^\circ\text{C}$. In order to achieve reproducible conditions, a vacuum profile was optimized based on known mixtures of MWF contaminated with White Spirit in PER using the Buchi V-805 vacuum controller (see **Figure 2**). A defined pressure gradient was used to eliminate the delay in boiling and contamination of the apparatus. Buchi's Syncore® Polyvap with a 96 position rack was used for the simultaneous evaporation of all sample extracts from the filter and adsorbent (see **Figure 3**). This combined with the stored pressure program guaranteed equal treatment of all samples and reduced the time for sample handling during evaporation whilst minimising the amount of supervision.

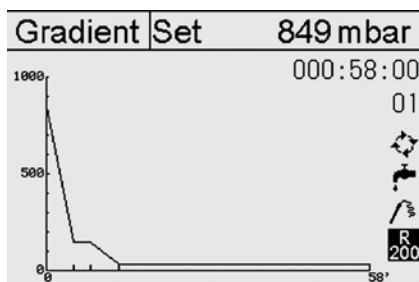


Figure 2: Vacuum profile for parallel evaporation of MWF samples in PER (4 ml) at $60 \text{ }^\circ\text{C}$. In the first ramping stage the pressure is linearly decreased from 850 to 150 mbar in 5 min and hold for 3 min. A second ramp was added to achieve a final vacuum of 35 mbar which was held for 45 min.

Results and discussions

The comparison procedure of the inter-laboratory runs was based on the International Organization for Standardization ISO 5725 to provide information about the repeatability (within laboratory variation) and the reproducibility of the measurements (between laboratory variations). To gauge the acceptability of the method performances, the results were compared with the requirements of the European Standard EN 482 Workplace atmospheres – General requirements for the performance of procedures for the measurement of chemical agents. This requires the Relative Overall Uncertainty (ROU) or bias plus twice the standard deviation, for comparison with limit values to be less than 30% when used in range 0.5 to 2 times a limit value, including sampling and analytical errors.

Table 1 shows an extract of the inter-laboratory results in terms of sum particulates and oil mist generated over two rounds. Round **A** was performed slightly higher than the SWISS PEL at 24.18 mg/m^3 . Round **B** involved chemical and particle interference at a MWF level of 1.64 mg/m^3 .

In the first round with generated oil mists slightly higher than the Swiss PEL (24.18 mg/m^3 , PEL = 20 mg/m^3), all laboratories complied with the ROU < 30% limit, irrespective of the sampling heads ($\varnothing 37 \text{ mm}$ BGIA head, $\varnothing 25 \text{ mm}$ IOM head, $\varnothing 37 \text{ mm}$ polystyrene cassette) or analytical methods (IR, gravimetry, GC-MS) used.

In round **B** an aliphatic hydrocarbon (White Spirit) and particle (polydispersed spherical glass particles, Spheriglass) interference were added. Laboratory 2 and 5 found good results. Very good reproducibility for the modified BGIA method (laboratory 5) was achieved due to equal sample treatment throughout the whole process including the parallel evaporation step.

Conclusions

The Syncore® Polyvap used in the modified BGIA method for the determination of metal working fluids (MWFs) in air samples showed excellent reliability in an inter-laboratory round robin test. In addition, the reproducibility was outstanding due to simultaneous evaporation of all sample extracts under identical conditions using a well-defined vacuum profile. Lastly, the time savings

	Method	N	Mean	STD	ROU
A	MWF, ref. value: $24.18 \pm 0.69 \text{ mg/m}^3$				
1	B	5	24.72	0.86	9.3
2	A	4	23.43	0.91	10.6
3	B	3	23.63	0.76	8.5
4	BGIA	3	24.25	1.21	10.1
5	BGIA	3	24.87	0.38	6.0
B	MWF, ref. value: $1.64 \pm 0.33 \text{ mg/m}^3$ plus interference with 100 mg/m^3 of White Spirit and 5 mg/m^3 of inert dust (Spheriglass)				
1	B	5	1.74	0.17	26.6
2	C	5	1.66	0.05	7.3
3	A	5	1.69	0.20	38.5
4	B	5	0.95	0.04	46.8
5	BGIA-mod	5	1.72	0.03	9.3

Table 1: Inter-laboratory round robin results

yielded by simultaneous parallel evaporation in comparison to sequential rotary evaporation are impressive, taking into account that 30 samples were worked up within one hour with a minimum of sample manipulation compared to several days with the conventional method.

References

- [1] J. Ameille, P. Wild, D. Choudat, G. Ohl, J. F. Vaucouleur, J. C. Chanut, P. Brochard, American J. of Ind. Med. **1995**, 27, 247– 256.
- [2] Swiss Accident Insurance Fund, SUVA, Health Protection Department Prevention Services, Luzern.
- [3] E. A. Eisen, T. J. Smith, D.Kriebel, S. R. Woskie, D. J. Myers, S. M. Kennedy, S. Shalat, R. R. Monson, American J. of Ind. Med. **2001**, 39, 443 – 453.
- [4] Swiss Accident Insurance Fund, SUVA, : "Valeur limites d'exposition aux postes de travail", Switzerland, **2003**.
- [5] C. K. Huynh, T. Vu Duc, H. Savolainen, AIHA Journal **1992**, 53, 157 – 162.
- [6] C. K. Huynh, T. Vu Duc, H. Savolainen, Ann. Occup. Hyg. **1989**, 33, 573 – 581.



Figure 3: Laboratory equipment used for parallel evaporation under vacuum according to the modified BGIA method. The Syncore® Polyvap with a 96 position rack was used to heat the samples to 60 °C and to generate a vigorous vortex at 400 rpm. In order to avoid cross-contamination due to condensation, the vacuum cover was heated to 45 °C. A vacuum was generated using the V-500 vacuum pump and controlled with a pressure profile programmed with the V-805 vacuum controller (see Figure 2).



Figure 4: Round robin inter-laboratory sampling exercise in an experimental chamber of 10 m³. Oil mist was generated with light, medium and heavy mineral oils based MWF (Somentor 29, Blaser VP 1006 or Blasomil 22 and Blaser 220 respectively) in a home-made glass nebulizer. The generated range of oil mist can be regulated in the range of 0.1 to > 20 mg/m³ and can be held constant at least for 6 hours within a deviation standard of < 5%. The spatial uniformity of the aerosol inside the test chamber was in the range of 2 - 3% reported by 5 point test.

BÜCHI Labortechnik AG
Postfach
9230 Flawil 1
Schweiz
T +41 71 394 63 63
F +41 71 394 65 65
buchhi@buchhi.com
www.buchhi.com

BÜCHI Labortechnik GmbH
Postfach 10 03 51
45003 Essen
Deutschland
Freecall 0800 414 0 414
T +49 201 747 490
F +49 201 237 082
deutschland@buchhi.com
www.buechigmbh.de

BÜCHI Labortechnik GmbH
Branch Office Netherlands
Postbus 142
3340 AC Hendrik-Iso-Ambacht
The Netherlands
T +31 78 684 94 29
F +31 78 684 94 30
netherlands@buchhi.com
www.buchhi.nl

BÜCHI Italia s.r.l.
Centro Direzionale, Milano Fiori
Pal. A-4, Strada 4
20090 Assago (MI)
Italia
T +39 02 824 50 11
F +39 02 57 51 28 55
italia@buchhi.com
www.buchhi.it

BUCHI (Thailand) Ltd.,
77/175, Sin Sathon Tower,
39th FL, Unit F
Krunghthonburi Rd.
Klongtsonai, Klongsan
Bangkok 10600
Thailand
T +66 2 862 08 51
F +66 2 862 08 54
bacc@buchhi.com
www.buchhi.com

BUCHI SMP
Services Private Ltd.
201, Magnum Opus
Shantinagar Industrial Area
Vakola, Santacruz (East)
Mumbai 400 055,
India
T +91 22 66 98 94 50 / 51
F +91 22 66 98 94 52
smp@buchhi.com
www.buchhi.com

BUCHI Corporation
19 Lukens Drive, Suite 400
New Castle
Delaware 19720
USA
T +1 302 652 3000
F +1 302 652 8777
Toll Free: +1 877 692 8244
us-sales@buchhi.com
www.mybuchhi.com

BUCHI Hong Kong Ltd.
1810 Fortress Tower
250 King's Road
North Point, Hong Kong
China
T +852 2389 2772
F +852 2389 2774
china@buchhi.com
www.buchhi.com

BUCHI Shanghai Trading LLC
21/F Shanghai Industrial
Investment Building
18 Caoxi Bei Road
200030 Shanghai
China
T +86 21 6468 1888
F +86 21 6428 3890
china@buchhi.com
www.buchhi.com

BUCHI UK Ltd
5 Whitegate Business Centre
Jardine Way
Chadderton
Oldham OL9 9QL
United Kingdom
T +44 161 633 1000
F +44 161 633 1007
uk@buchhi.com
www.buchhi.co.uk

BUCHI Sarl
5, rue du Pont des Halles
Z.A. du Delta
94656 Rungis Cedex
France
T +33 1 56 70 62 50
F +33 1 46 86 00 31
france@buchhi.com
www.buchhi.fr

Nihon BUCHI K.K.
3F IMON Bldg.,
2-7-17 Ikenohata, Taito-ku,
Tokyo 110-0008
Japan
T +81 3 3821 4777
F +81 3 3821 4555
nihon@buchhi.com
www.nihon-buchi.jp

We are represented by more than 100 distribution partners worldwide. Find your local representative at www.buchhi.com

Quality in your hands