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Optimized determination of airborne mineral oils

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.
Determination of airborne mineral oils: an inter-laboratory comparison

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/m\(^3\) for heavy oils with boiling points > 350 °C as aerosol, and/or 20 mg/m\(^3\) 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.

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 droplets\(^2\) 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 (C\(_{12}\) – C\(_{24}\)), 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 cartridge\(^3\) 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 over-estimation 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/m\(^3\)) was used as the chemical interference and polydisperse spherical glass particles (Spheriglass) as inert dust interference during aerosol generation in the test chamber. Four different procedures for the determination of MWF concentration were applied.

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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 homemade 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 CH₂Cl₂ (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 gravimetrical 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 (1 g adsorbent), extraction with tetrachloroethylene (PER, 10 ml) and evaluation by IR absorbance at 3000 – 2800 cm⁻¹. The modified procedure is based on parallel fractional distillation of MWF samples in PER under vacuum at 60 °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.

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/m³. Round B involved chemical and particle interference at a MWF level of 1.64 mg/m³. In the first round with generated oil mists slightly higher than the SWISS PEL (24.18 mg/m³, PEL = 20 mg/m³), all laboratories complied with the ROU < 30% limit, irrespective of the sampling heads (Ø 37 mm BGIA head, Ø 25 mm IOM head, Ø 37 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

Table 1

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Figure 2: Vacuum profile for parallel evaporation of MWF samples in PER (4 ml) at 60 °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.

Figure 3: A defined vacuum profile.

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**


**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.