Occupational Exposure to Mineral Oil Metalworking Fluid (MWFs) Mist: Development of New Methodologies for Mist Sampling and Analysis. Results from an Inter-laboratory Comparison

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Abstract. Metalworking Fluids (MWFs) are largely used in the sector of undercutting, a large professional activity in Switzerland, in particular in the fine mechanic and watch making industry. Various respiratory pathologies are caused by the production and dispersion of oil mists in the workplace.

1. Introduction

Metalworking Fluids (MWFs) are largely used in the metallurgical industry, especially in undercutting, a widely exercised professional activity in the Swiss watch making industry. Various respiratory pathologies are caused by the production and dispersion of oil mists in the workplace.
In this paper, we suggest a new approach designed to overcome the drawbacks of both techniques.

Conventional methods recommend the use of a filter to quantify oil mists but this is only reliable for common use MWFs that form stable airborne mists. Oil with viscosities inferior to 18 centi-Stokes (cSt) at 40°C, which is commonly used in Switzerland, loses more than 70% of its weight on the filter for periods up to 6 h at 2 l.min⁻¹ of standard sampling conditions [11]. The losses from the MWFs were mostly aliphatic hydrocarbons (C₁₂-C₂₄), but additives such as alkyl benzenes, esters, phenols and terpenes were also lost. The problem of exposure underestimation and inappropriate exposure sampling could be widespread.

To prevent evaporative loss, the BGIA standard [5] involves the placing of a XAD-2 absorbent cartridge behind the filter. The method seems perfect for MWFs in an occupational interference free from light vapour solvent such as White Spirit (C₅-C₇), which has a high Swiss PEL (525 mg.m⁻³). In fact, in machine shops atmosphere usually contaminated with traces of White Spirit, the BGIA method over-estimated the MWFs levels. Simpson [13] in another recent study proposed a similar method using both filter and cartridges of XAD-2 to measure the total airborne oil (i.e. mist and vapour). Any mist sample that is vaporized should be trapped as vapour by the absorber charcoal tube and XAD-2 cartridge. A gas chromatographic with flame ionization detector (GC-FID) technique was used to determine the vapour fraction.

In this paper, we suggest a new approach designed to overcome the drawbacks of both techniques.
2. Materials and Methods

2.1. Oil mist generation

Oil mist was generated with light, medium and heavy mineral oils based MWF (Somentor 29, Blaser VP1006 or Blasomil 22 and Blaser 220 respectively) in a home-made glass nebulizer \cite{17} using compressed-air inside first, a small cylindrical experimental chamber (130 cm x 50 cm \( \varnothing \text{id} \)) during a previous isocyanate study \cite{16, 17} and second, in an experimental chamber of \( 10 \text{ m}^3 \). The compressed air flow rate was automatically controlled between 0 and 10 \( \text{l.m}^{-1} \) by a mass flow control valve (Hi-tech MFC model F200). The size characteristics of the aerosol were determined using optical method and gravimetric method: an optical particle analyser (Climet Model 208A, USA) equipped with its dilution system (Climet CI-294-1, USA) which counted the particles in the diameter range of <0.3 to 10 \( \mu \text{m} \) and classified them into seven categories; an impactor (Ambient Particle Sizing Sampler, model 2000, Andersen Inc., USA) equipped with 8 glass fibre filter stages and a backup filter (Glass fibre filter 934AH, \( \varnothing 81 \text{ mm} \), Whatman) which collected aerosols in the aero-dynamic diameter range of <0.4 to >11 \( \mu \text{m} \). The granulometry distribution of aerosol was computerized using “in house” software, based on Andersen individual calibrated penetration curve of each stage.

To test the performance of oil mist methods, interference was introduced in the test chamber during aerosol generation: Industrial solvent vapour of White spirit (Indurei) at 60 -100 mg.m\(^{-3}\), 1/5 of PEL (Swiss MAK: 100 ppm or 525 mg.m\(^{-3}\)). This interference induced no effect on standard aerosol-on-filter methods, but gives an over-estimation by the BGIA-like methods, using absorbers cartridges and IR method. To check the real target value, one round of pure oil mist was generated and during a second round, with identical level of oil mist, White Spirit interference was introduced. In round 5, we also introduced in the experimental chamber other interference, inert dust (glass polydispersed spherical particles, Spheriglass, 0-15 \( \mu \text{m} \), 5 mg.m\(^{-3}\) level).

2.2. Proposal methods

The principal aim of this work was to investigate sampling and analyze methods for measuring both mist and vapour, to comply with the new Swiss regulation (2003) and to demonstrate the robustness of the proposals during a mini inter-laboratory comparison. Our laboratory (IST) developed two new methods and proposed to other participants for adaptation during an “inter-laboratory comparison”:

2.2.1. Gravimetric determination method. Based on the French INRS method \cite{6} for particular fraction and BGIA method \cite{5} for vapour fraction, the new proposal method tries to determine the oil vapour fraction with controlled evaporation under nitrogen and correct the interference from vapour solvent. As to the analytical method, we developed a new technique because the Infrared (IR) method used in Germany, BGIA method \cite{5} does not distinguish the vapours from White Spirit or from the others cleaning solvents. This fact results in an overestimation of the true exposure level to the oil vapours.

The new method consists in initially extracting the filter and XAD-2 cartridge with \( \text{CH}_2\text{Cl}_2 \), then determining the residual fraction by gravimetric measurement after evaporation of the extracting solvent according to French method from INRS \cite{6}. A detailed attention is devoted to the level of evaporation to make it possible the elimination of \( \text{CH}_2\text{Cl}_2 \) and other solvents, the cleaning solvents or collected White Spirit on XAD2 cartridges, without loss of oil vapour. After extraction of XAD-2 cartridge by organic solvents, \( \text{CH}_2\text{Cl}_2 \) or tetrachlorethylene (PER), a GC-FID or gravimetric method of evaporated residues were used to determine the vapour oil fraction. The figures 1 to 3 show the determination of \( \text{CH}_2\text{Cl}_2 \), White Spirit and vapour oil fraction by gravimetric with gentle evaporation of extract solution, repetitive weigh of residue on vial and calculate the theoretical amount of volatile fraction. The real amount of volatile fraction was calculated using regression method and intercept at time \( t=0 \) (start time, 0 min). This approach was better than conventional constant weighing technique, avoiding loss of oil evaporation. By this technique, we can confirm the possibility to analyse the vapour oil fraction without interference, even at very high level. This technique was proposed for
validation in an “inter-laboratory comparison” as shown in this study, and can be applied by any laboratories without special instruments or costly apparatus.

2.2.2. GC-FID or GC-MS method. Based on ISO16703 [18] for the determination of hydrocarbon content in soil, the total signal of FID detector in the retention range of White Spirit against oil volatile fraction or the Single Ion Monitoring (SIM) signal of ion m/z 57 of respective fractions, representing the hydrocarbon molecules were integrated and computed. Quantification was done by comparing the total signal of sample to the standard, in this case, a solution of oil diluted in CH₂Cl₂ or PER. The figure 4 shows the determination of vapour oil fraction by GC-MS method with quantification by summing aliphatic chromatographic area peaks corresponding to oil vapour fraction (C₁₂ to C₂₄ in this case). The interference compound, the White Spirit fraction of C₅ to C₁₁ is separated and discarded.

This technique was also validated in an inter-laboratory comparison as shown in this study, but it required more costly instruments like GC-MS or GC-FID.

2.3. Participants
The principal aim of this work was to prove the inefficiency of actual official methods to measure the oil mist and to suggest Swiss official laboratories for adaptation of new proposals. There is not a real inter-laboratory comparison with certified methods but a tentative work-team to check the feasibility of new proposals. To achieve the objectives, five inter-laboratory comparisons were organised based on generation of oil mist in an experimental chamber, under controlled conditions.

In the beginning, each participant used its own conventional and official method, without modifications. By the introduction of interference during the oil mist generation, we can point out the lack of official methods against interferences and the loss-by-evaporation during samplings. After a few round, each participant will be asked for modification if necessary to overcome the loss-by-evaporation during sampling or White Spirit interference problem. IST laboratory proposed two methods: gravimetry with controlled evaporation rate (method C) and GC-MS (method D).

The adopted sampling techniques for aerosol and oil vapour were: glass fibre filters + XAD-2 adsorbent cartridges [7]. Gravimetric, Fourier Transform Infrared Spectroscopic (FTIR), gas chromatography with flame ionisation detection (GC-FID) and gas chromatography with mass spectrometric detection (GC-MS) analytical methods were considered for quantitative determination of collected oil mist and vapour. The sampling time (2 to 8 hours) was determined in function of the concentration level of oil mist, the capacity load of aerosol samplers and the Limit of Quantification (LOQ) of the methods (at least 0.2 mg) on the filters for accuracy gravimetric determination. Briefly, the different adopted methods by participants were described herewith, and summarized in table 1:

2.3.1. Method BGIA. Standard BGIA method [5] with GSP samplers were used with minor modifications for lab 5: 1 l/min sampling flow rate instead of 3.5 l/min with a modified entry orifice of Ø 2 mm. This modification tries to minimize the evaporation loss of droplet oil collected on the filters, but no effects was observed and finally, lab 5 reused the original BGIA GSP sampler. After sampling, the filter and the cartridge of absorber (3g of XAD-2) were eluted with 10 ml of PER and the total oil mist weight was done by measuring IR absorbance at 3000-2800 cm⁻¹ of desorbed solution with 10 mm path length. Quartz cell comparing to standard solution of oil in PER freshly prepared. Blank correction was done with extracted blank glass fibre filter solution of PER.

2.3.2. Method BGIA mod. The determination of volatile oil fraction can also be done by gentle evaporation of extract PER solution, elimination of interfering solvents and determination of the amount of volatile oil fraction by FTIR. Before analyzing the samples, the evaporation method is optimized with known mixtures of the used MWF and the interfering solvents in PER. With this adjusted method all extracts of filters and adsorbents and all calibration solutions are treated in the same way, advantageous simultaneously by a multi-rotavapor device. The quantitative determination is done by FTIR.
2.3.3. **Method B.** Standard NIOSH method 5026 [20] was applied, using PVC filters with modification for volatile fraction by adding sorbent cartridge (1g of XAD-2) as backup vapour sampler. IOM heads were also tested at 2 l/min during few rounds. Gravimetric determinations of oil mist on the filters were done after conditioning during 24 hours in controlled humidity box (52 % RH ± 5 %) before weighing by microbalance (Model M5P, Sartorius). The determination of volatile fraction on XAD-2 cartridges was done by similar procedure described in method C.

2.3.4. **Method C.** Based on French INRS method [6] for particular fraction and BGIA method [5] for vapor fraction, the new proposal method tries to correct the interference from vapour solvent. The sampling train was Ø 37 mm closed-face polystyrene cassette containing glass fibre filters, (GF/B, Whatman), coupled with a Solid Phase Extraction (SPE) cartridge (6 ml Polypropylene tube and frits, ref 57242 and 57181, Supelco) containing 1 g of XAD-2 (ref 1-0357, Supelco). The flow rates were 2 l/min for all round tests. For particular fraction, gravimetric methods were done with filters conditioned before and after sampling in the same glow box as method B. Extraction of oil mist on the filter with 20 ml CH₂Cl₂ followed by evaporation under gentle nitrogen stream (200 ml/min of N₂ at 40°C), and gravimetric determination of extracted fraction was also applied to avoid non-oil mist dust in the real situation. Volatile fraction on XAD-2 cartridges was extracted by elution of 20 ml of distilled CH₂Cl₂. After evaporation to small volume (5 ml), under gentle nitrogen stream, the final solution was transferred into a small vial and gravimetric determination of volatile oil fraction can also be done by gentle evaporation of extract solution, repetitive weigh of residue on vial and calculate the theoretical amount of volatile oil fraction (see result section).

2.3.5. **Method D.** Volatile fraction on XAD-2 cartridges was extracted by elution of 20 ml of distilled CH₂Cl₂. After evaporation to small volume (5 ml), under gentle nitrogen stream, a amount of extract was injected into a GC-MS for determination of interference (White Spirit, C₅-C₁₁) and volatile oil fraction, C₁₂-C₂₄. The method was based on ISO 16703 [18] for the determination of hydrocarbon content in soil. Briefly, 1-2 µl of extracted solution were injected in a GC-FID or GC-MS instrument and the oil volatile fraction (C₁₂-C₂₄) fraction was quantified by using the total signal of FID detector or the Single Ion Monitoring (SIM) signal of ion m/z 57 of GC-MS detector in their retention range were integrated and computed. Fraction representing White Spirit (C₅-C₁₁) was ignored. Calibration curve was computed with standard solution of oil at different concentrations.

It seem that there are a plenty of methods applied by participants, but in fact, the general approach was based on both IST proposals: gravimetric with controlled evaporation under nitrogen and by GC technique.

2.4. Quality control

The comparison procedure was based on the International Organisation for Standardization [14] (ISO 5725), to provide information about the repeatability (within-laboratory variation) and the reproducibility of measurements (within- and between-laboratory variation). 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 [15]. It requires the Relative Overall Uncertainty (ROU) or bias plus twice the standard deviation, for comparison with limit values to be less than 30 percent, when used in range 0.5 to 2 times a limit value, including sampling and analytical errors. The reference level was computerized with all individual data of each participating lab.

3. Results and discussions

3.1. Generated WMFs oil mist performances

Oil mist was generated with light, medium and heavy mineral oils based MWF (Somentor 29, Blaser VP1006 or Blasomil 22 and Blaser 220 respectively) in a home-made glass nebulizer [17] using compressed-air in a experimental chamber of 10 m³. The generated range of oil mist can be regulated...
in the range of 0.1 to > 20 mg.m\(^{-3}\). After a 15-min stabilization time, the aerosol concentration of commercial machine cutting oil (Blaser VP1006) can be held constant for more than 6 hr 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 a 5 points test. This clearly illustrates the good stability and spatial uniformity of the aerosol concentration, ready for an inter-laboratory comparison. The granulometry distribution of aerosol was computerized and show an aerodynamic diameter means of 2.74 \(\mu\)m \(\pm\) 1.8 \(\mu\)m. This size distribution of oil mist corresponds to the observed aerosol distribution in machining shop atmosphere.

3.2. Loss of oil mist during sampling

Table II shown the loss of oil vapour fraction spiked on filter in function of the Boiling Point (BP) or the Flash Point of respectively light, medium and heavy oil during the sampling, using a flow rate of 2 l/min and a total air volume of 480 l through the filters. The amount of evaporated vapour oil was collected on XAD2 cartridges mounted in serial after the filter. With light oil (flash point: 74°C), all the aerosol fraction was evaporated and moved to XAD2 cartridge, with medium oil, the vapour-liquid repartition is 50% and with the heavy oil (flash point: > 250°C), only 25% vapour fraction was evaporated during the sampling. Depending the nature of oil, the problem of exposure underestimation and inappropriate exposure sampling could be widespread.

To prevent evaporative losses of sampled oil, the BGIA standard [5] proposed a XAD-2 absorbent cartridge behind the filter. The method seem perfect for MWFs in an occupational interference free of light vapour solvent such as White Spirit (C\(_5\)-C\(_{11}\)) with a very high Swiss PEL (525 mg.m\(^{-3}\)). In reality, in machine shops atmosphere, we uncounted usually high level of White Spirit or others cleaning solvents, and the BGIA method overestimates the MWFs levels.

3.3. Gravimetric determination of oil vapour

As to the analytical method, we developed a new technique because the IR method used in Germany, BGIA method [5] does not distinguish the vapours from White Spirit or from the others cleaning solvents. This fact results in an overestimation of the true exposure level to the oil vapours.

The new gravimetric method consists in initially extracting the filter and XAD-2 cartridge with CH\(_2\)Cl\(_2\), then determining the residual fraction by gravimetric measurement after evaporation of the extracting solvent according to French method from INRS [6]. A detailed attention is devoted to the level of evaporation to make it possible the elimination of CH\(_2\)Cl\(_2\) and other solvents, the cleaning solvents or collected White Spirit on XAD2 cartridges, without loss of oil vapour. Contrarily to the French method, we are not going to evaporate until dryness to constant weight, but we try to monitor the evaporation rate of the oil fraction to avoid losses. The determination of vapour oil fraction by gravimetric with gentle evaporation of extract solution was done by repetitive weigh of residue on vial and calculation of the theoretical amount of volatile oil fraction. The real amount of vapour oil was calculated using regression method and intercept at time t=0. After extraction of XAD-2 cartridge by organic solvents (CH\(_2\)Cl\(_2\) or PER), a GC-FID or gravimetric method of evaporated residues were used to determine the vapour oil fraction. The figures 1 to 3 show the determination of CH\(_2\)Cl\(_2\) (theoretical added value 3.98 g, founded: 3.656 g), White Spirit (theoretical added value: 100 mg, founded: 105.2 mg) and vapour oil fraction (theoretical added value: 10 mg, founded: 9.58 mg) by gravimetric with gentle evaporation of extract solution, repetitive weigh of residue on vial and calculate the theoretical amount of volatile fraction. The precision of the method was better than \(\pm\) 20 \(\mu\)g by weighing for oil determination. The errors for interference White Spirit and solvent CH\(_2\)Cl\(_2\) were much more higher but this is not important for MWFs determinations. Other conventional sampling methods (Coconut Charcoal tubes, GC method) can be used simultaneously to perform White Spirit level in air. This approach was better than conventional constant weighing technique, avoiding loss of oil evaporation. By this technique, we can confirm the possibility to analyse the vapour oil fraction without interference, even at very high level. This technique was validated in an inter-laboratory comparison as shown in this study, and can be applied by any laboratories without special instruments or costly apparatus.
3.4. GC-FID or GC-MS determination of oil vapour

Based on ISO16703 [18] for the determination of hydrocarbon content in soil, the total signal of FID detector in the retention range of White Spirit against oil volatile fraction or the Single Ion Monitoring (SIM) signal of ion m/z 57 of respective fractions, representing the hydrocarbon molecules were integrated and computed. With the high resolution of the GC capillary columns, the separation of dissolvent and oil vapour fraction was made without difficulties. Quantification was done by comparing the total signal of sample to the standard, in this case, a solution of oil diluted in CH₂Cl₂ or PER. The figure 4 shows the determination of vapour oil fraction by GC-MS method with quantification by summing aliphatic chromatographic area peaks corresponding to oil vapour fraction (C₁₂ to C₂₄ in this case). The interference compound, the White Spirit fraction of C₅ to C₁₁ is separated and discarded. This technique was also validated in an inter-laboratory comparison as shown in this study, but it required more costly instruments like GC-MS or GC-FID.

3.5. Round-Robin test results

The figure 5 shows the experimental chamber of 10 m³ during Round Robin inter-laboratory sampling exercise. Each participant was asked to bring their own sampling devices, pumps, sampling heads, cartridges, etc. All participants applied the combined sampling devices (filters+cartridges XAD2) to eliminate the loss of oil vapour. Table III shown the all laboratory results in term of sum of particulates and vapour of oil mist generated over 5 rounds. First of all, as show the fig 6, we observed that at 24.18 mg/m³ level of pure oil mist (Switzerland 2003 PEL = 20 mg.m⁻³), all laboratories complied with the ROU<30%, no matter the sampling heads used (⌀47 mm BGIA sampling head, ⌀25 mm IOM sampling head, ⌀25 mm IOM sampling head, and ⌀37 mm closed-face polystyrene cassette), nor the used methods (IR, gravimetry or GC-MS). The overall performance of all laboratories remained very good for lower levels: 14.75, 3.32 mg/m³, excepted lab 5, with a ROU slightly higher than 30. The potential explanations for slightly high ROU (56.3) of lab 5 in this round were high blank level, contamination and eventually technical problems. At 3.32 mg.m⁻³ of pure oil mist level of round 4, we introduced interference, White Spirit at 1/5 of PEL level (100 mg.m⁻³), We observed, as show the fig 7, a bias on results of lab 4 and 5 using standard BGIA method and IR technique to measure the total oil mist. The interference, a family of aliphatic hydrocarbons, absorbs in a same IR range than oil mist and the results were overestimated. Other labs (1 to 3) using gravimetric with controlled evaporation under nitrogen or GC-MS technique, found the correct result. 4. At 1.64 mg.m⁻³ level of pure oil mist + interferences (White Spirit and Spheriglass) of round 5, lab 3 lost vapour oil during evaporation and weighing. Lab 4 used BIA mod method and found good results. For the determination of volatile fraction of oil, GC-FID, GC-MS or gravimetric methods worked well, except that some special oils containing polar or thermo sensible “non-chromatographed” compounds by GC. In this case, only gravimetric method was applied.

4. Conclusions

In this study, we propose two new and validated methods of measuring mixed mist and vapour oil and to overcome the difficulties of loss of vapour oil during sampling and interference problems: by determining separately the aerosol fraction on filter and by adding a absorber cartridge (XAD2) for trapping vapour fraction of oils, completed by a selective determination of vapour oil fraction (C₁₂-C₂₄) against interferences such as cleaning solvent fraction White Spirit like (C₅-C₁₁).

Two techniques to quantify the oil vapour fraction can be used: by gravimetric with controlled evaporation under nitrogen, by FTIR, by GC-FID and by GC-MS:
1. The gravimetric method, using controlled evaporation under nitrogen technique was proposed as standard method. This method is easy to apply successfully by any laboratories without the needs of special instruments or costly apparatus.
2. Alternative techniques, using GC-FID or GC-MS methods were also validated in this inter-laboratory comparison.
For low viscosity oils, it may be appropriate to measure both the mist and vapour, as requested by the new Swiss regulation. The inter-laboratory circuit to validate sampling and analytical approaches was helpful and the accuracy results of developed methods give more reproducible results suitable for assessment or survey of real oil mist exposure for future epidemiological studies.

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Figure 1. Gravimetric determination of CH$_2$Cl$_2$ extracting solvent fraction was presented by gentle evaporation of 3ml of CH$_2$Cl$_2$ solution and repetitive weighing of residue on vial (N=4). The theoretical value of CH$_2$Cl$_2$ was 3.98 g and the experimental value was 3.656 g. This experiment suggests gentle evaporation of CH$_2$Cl$_2$ extracting solvent to avoid losses, without exact determination of solvent amount. Under 200 ml.min$^{-1}$ flow rate of N$_2$ at 40°C, the evaporation rate of CH$_2$Cl$_2$ was 101 mg.min$^{-1}$. 

\[ y = -101.35x + 3656.3 \]

\[ R^2 = 0.99 \]
Figure 2. Determination of interference White Spirit fraction by gravimetric with gentle evaporation of extract solution, repetitive weigh of residue on vial and calculate the theoretical amount of White Spirit fraction. The real amount of White Spirit (100 mg) was calculated using regression method and intercept at time T=0 (N=4) and the experimental value was 105.2 mg. The evaporation rate of White Spirit was 0.9 mg.min$^{-1}$. Again, this experiment tends to suggest gentle evaporation of White Spirit interference to avoid losses, without exact determination of White Spirit amount.
**Figure 3.** Determination of vapour oil fraction by gravimetric with gentle evaporation of extract solution, repetitive weighing of vial residue and calculating the theoretical amount of volatile oil fraction. The real amount of vapour oil (10 mg) was calculated using a regression method and intercept at time t=0 (N=4) and the experimental value was 9.58 mg. The evaporation rate of oil was very low, 0.003 mg.min$^{-1}$, but not negligible. Contrary to the INRS method assuming constant residual weight over time, the determination of the oil fraction was made using the slope of evaporation.
Figure 4. Determination of vapour oil fraction by GC-MS method with quantification by summing aliphatic chromatographic area peaks corresponding to oil vapour fraction (C$_{12}$ to C$_{24}$ in this case). The interference compound, the White Spirit fraction of C$_5$ to C$_{11}$ is separated and discarded.
Figure 5. The picture shows the various sampling devices inside the experimental chamber of 10 m$^3$, during inter-laboratory sampling exercise. Oil mist from light, medium and heavy mineral oils based MWF (Somentor 29, Blaser VP1006 or Blasomil 22 and Blaser 220 respectively) was generated in a homemade glass nebulizer. The generated range of oil mist can be regulated in the range of 0.1 to > 20 mg.m$^{-3}$ and can be held constant at least for 6 hr within an deviation standard of < 5 %. The spatial uniformity of the aerosol inside the test chamber was in the range of 2-3 % reported by 5 test points.

Each participant used five to six sampling heads to perform reproducible results.
Figure 6. All laboratories round 1 results of medium oil mist generated at 24.18 mg.m$^{-3}$. We observed an excellent correlation of results independently of laboratory method and sampling technique, dotted lines mean ±30% of the Relative Overall Uncertainty (ROU) or bias plus twice the standard deviation, for comparison with limit values to be less than 30 percent, when used in range 0.5 to 2 times a limit value, including sampling and analytical errors.
Figure 7. All laboratories round 4 results of medium oil mist generated at 3.32 mg/m$^3$ in presence of interference, White Spirit at 1/5 of PEL level (100 mg.m$^{-3}$). We observed a bias on results of lab 4 and 5 using BGIA method and IR technique to measure the total oil mist. The interference, a family of aliphatic hydrocarbons, absorbs in a same IR range than oil mist and the results were over estimated. Other labs (1 to 3) using gravimetric with controlled evaporation under nitrogen or GC-MS technique, found the correct results.
Table 1. Summary of methods used by participating laboratories (N=5).

| Method | Lab | Sampling devices | Flow rate l/min | Filter nature | XAD-2 g | Extraction solvent | Measurement |
|--------|-----|------------------|-----------------|---------------|---------|-------------------|-------------|
| BGIA   | 4, 5| GSP sampler      | 3.5             | Glass fibre filter Ø 47 | 3       | PER               | FTIR        |
| BGIA mod | 5   | GSP sampler      | 3.5             | Glass fibre filter Ø 47 | 3       | PER               | FTIR + multi-rotavapor |
| B      | 2   | IOM              | 2               | PVC Ø 37       | 1       | CH₂Cl₂            | Gravimetry  |
| C      | 1, 3| Closed-face polystyrene cassette | 2 | Glass fibre filter Ø 37 | 1       | CH₂Cl₂            | Gravimetry  |
| D      | 1   | Closed-face polystyrene cassette | 2 | Glass fibre filter Ø 37 | 1       | CH₂Cl₂            | Gravimetry + GC-MS |

Table 2. Loss of oil vapour fraction collected on filter in function of the Boiling Point (BP) or the Flash Point of respectively light, medium and heavy oil during the sampling. With light oil, the entire aerosol fraction is evaporated and moved to XAD2 cartridge, with medium oil, the repartition is 50% and with the heavy oil, only small vapour fraction is evaporated. Since 2003, the new Swiss recommendations for PEL (MAK) [4] would be 0.2 mg.m⁻³ for heavy oil with Boiling Point (BP) >350°C of aerosol and/or 20 mg.m⁻³ of oil aerosol + vapour for medium or light oil. In some cases, we have not founded the BP, because the thermo degradation of heavy oils and Flash Point unit was more usually reported in oil industries.

| Oil                        | Flash Point | Oil amount (mg) spiked on filter (N=3) | 480 l of air at 2 l/min |
|----------------------------|-------------|----------------------------------------|-------------------------|
|                            |             | Filter (mg)                            | XAD2 (mg)               |
| Light oil (Somentor 29)    | 74°C        | 4.91 ± 0.05                            | 5.04 ± 0.17             |
| Medium oil (Balser VP1006 or Blasomil 22) | 180°C | 2.05 ± 0.05                            | 0.96 ± 0.08             | 0.82 ± 0.03 |
| Heavy oil (Blaser 220, BP>350°C) | >250°C | 0.22 ± 0.05                            | 0.16 ± 0.002            | 0.08 ± 0.006 |
### Table 3. All laboratory Round-Robin results of generated oil mist.

| Laboratory | Method | N  | Mean  | STD  | ROU |
|------------|--------|----|-------|------|-----|
| Round 1:   | Medium oil, reference value: 24.18 ± 0.69 mg.m\(^{-3}\) |    |       |      |     |
| 1          | C      | 5  | 24.72 | 0.86 | 9.3 |
| 2          | B      | 4  | 23.43 | 0.91 | 10.6|
| 3          | C      | 3  | 23.63 | 0.76 | 8.5 |
| 4          | BGIA   | 3  | 24.15 | 1.21 | 10.1|
| 5          | BGIA   | 3  | 24.87 | 0.38 | 6.0 |
| Round 2:   | Medium oil, reference value: 14.75 ± 0.44 mg.m\(^{-3}\) |    |       |      |     |
| 1          | C      | 5  | 14.58 | 0.80 | 12.1|
| 2          | B      | 4  | 14.38 | 1.83 | 27.3|
| 3          | C      | 2  | 11.58 | 0.48 | 27.9|
| 4          | BGIA   | 3  | 15.96 | 0.18 | 10.7|
| 5          | BGIA   | 3  | 16.43 | 1.82 | 36.0|
| Round 3:   | Medium oil, reference value: 3.32 ± 0.10 mg.m\(^{-3}\) |    |       |      |     |
| 1          | C      | 4  | 3.18  | 0.10 | 10.5|
| 2          | B      | 4  | 3.17  | 0.31 | 23.2|
| 3          | C      | 3  | 2.84  | 0.23 | 28.6|
| 4          | BGIA   | 3  | 3.35  | 0.30 | 18.6|
| 5          | BGIA   | 3  | 4.17  | 0.51 | 56.3|
| Round 4:   | Medium oil, reference value: 3.32 ± 0.10 mg.m\(^{-3}\) + interference 100 mg.m\(^{-3}\) of White Spirit (1/5 of Swiss PEL) | |     |      |     |
| 1          | C      | 5  | 3.09  | 0.28 | 24.2|
| 2          | B      | 2  | 1.90  | 0.02 | 44.2|
| 3          | C      | 3  | 4.08  | 0.58 | 58.0|
| 4          | BGIA   | 3  | 103.12| 3.65 | 2838.0|
| 5          | BGIA   | 3  | 85.57 | 3.52 | 2364.5|
| Round 5:   | Medium oil, reference value: 1.64 ± 0.33 mg.m\(^{-3}\) + interference 100 mg.m\(^{-3}\) of White Spirit (1/5 of Swiss PEL) + 5 mg.m\(^{-3}\) inert dust (Spheriglass) | |     |      |     |
| 1          | C      | 5  | 1.74  | 0.17 | 26.6|
| 1          | D      | 5  | 1.66  | 0.05 | 7.3 |
| 2          | B      | 5  | 1.69  | 0.20 | 38.5|
| 3          | C      | 5  | 0.95  | 0.04 | 46.8|
| 4          | BGIA mod | 5  | 1.72  | 0.03 | 9.3 |

Remarks:
1. Round 1, at 24.18 mg.m\(^{-3}\) level of pure oil mist (PEL = 20 mg.m\(^{-3}\), Switzerland 2003), all laboratories complied with the ROU<30%, no matter the sampling heads used (Ø47 mm BGIA head, Ø25 mm IOM head, and Ø37 mm closed-face polystyrene cassette), nor the used methods (IR, gravimetry or GC-MS).
2. The overall performance of all laboratories remained very good for lower levels, rounds 2 and 3: 14.75, 3.32 mg.m\(^{-3}\), excepted lab 5, with a ROU slightly higher than 30.
3. At 3.32 mg.m\(^{-3}\) of pure oil mist level of round 4, we introduced interference, White Spirit at 1/5 of PEL level (100 mg.m\(^{-3}\)). We observed a bias on results of lab 4 and 5 using standard BGIA method and IR technique to measure the total oil mist.
4. At 1.64 mg.m\(^{-3}\) level of pure oil mist + interferences (White Spirit and Spheriglass) of round 5, lab 3 lost vapour oil during evaporation and weighing. Lab 4 used BGIA mod method and found good results.