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Alternative Method for the Analysis of Water-Based Metalworking Fluids Using Fourier Transform Infra-Red Spectroscopy

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ABSTRACT

Mists of water-based metalworking fluids (MWFs) as a kind of lubricants mineral oil are reported as a respiratory irritant with having carcinogenic compounds such as formaldehyde. Due to the widespread exposure of Iranian metal machining workers to water-based MWFs and limitations of advanced analytical balance in Iran, which is required by the National Institute of Occupational Safety and Health (NIOSH) conventional method No5524, the purpose of this study was set to develop a new analytical method using Fourier-transform infrared (FTIR) spectrometry instead. In this study, the spiked standards in the range of 0.96 to 960 µg/sample were dried and extracted with carbon tetrachloride and scanned by FTIR in the range of 2700 to 3200cm^{-1} for the best absorption. FTIR and Gas chromatography analysis of formaldehyde as a toxic ingredient of MWFs was examined and its presence was confirmed. For establishing the validation, the merits of the analysis of the FTIR and NIOSH method No.5524, such as precision, accuracy, LOD, LOQ, and bias were obtained that were 1.49%, 103%, 0.0004, 0.0014 µg/sample, -3%, and 10.87%, 111%, 14.9, 49.1µg/sample and 11% respectively. Regression coefficients (r^2) of the calibration line with the spiked standards (0.96-960µg/sample) were in the range of 0.997 to 0.999. Since the merits of the analysis of the FT-IR method for water-based MWFs were comparable to the respective NIOSH method, the developed method could be very useful in monitoring lathe workers, especially in developing countries. However, collaborative examination for full validation of the method is recommended.

Keywords: Air-Borne, Water- Soluble Oil, Analysis, Fourier Transform Infrared Spectroscopy, Validation Study

ABBREVIATION:

ACGIH: American Conference of Governmental Industrial Hygienist
ASTM: American Society for Testing and Materials
HSE: Health and Safety Executive
FTIR: Fourier Transform Infrared Spectrometry
GC: gas chromatography
LOD: Limit of Detection
LOQ: Limit of Quantitation
MWFs: water-based metalworking fluids
NIOSH: National Institute for Occupational Safety and Health
OSHA: Occupational Safety and Health Administration
PTFE: Polytetrafluoroethylene
REL: Recommended Exposure Limit
TLV: Threshold Limit Value

INTRODUCTION

Metalworking fluids (MWFs) as a kind of lubricant mineral oils, derived from the refining of crude oil, composed of mixed compounds with diverse hydrocarbon chain length [1]. MWFs are used in industrial processes, such as lathe operations, cutting and metal shaping. These processes are involved in friction and heat production, contribute to rising of mists in the workroom environment [2, 3]. NIOSH

(1977) organization estimated that more than 1.2 million workers are exposed to the mists of MWFs [4]. MWFs are classified into four categories: pure, soluble, synthetic and semi-synthetic compounds [5, 6]. Specific methods for the analysis of each of them has been proposed [7, 8]. Water-based MWFs as a superior coolant and lubricant is a mixture of oil, emulsifier, and water [9]. MWFs additives such as formaldehyde in the form of formalin, nitrosamines, triethanolamine, diethanolamine and derivatives alkanolamines, which are added for the prevention of corrosion and suppression of microbiological organism growth [10, 11].

Occupational exposure of workers in the auto engine manufacturing industries to MWFs and its components such as formaldehyde was reported to be accompanied by complications such as irritation of the eyes and respiratory tract, shortness of breath, asthma, bronchitis and pneumonitis sensitivity [12-14]. In addition, the risk of cervical cancer for female workers exposed to MWFs was reported [15, 16]. In another study, an increased risk of bladder cancer was reported with increased cumulative exposure to soluble MWFs [17]. Epidemiological studies of workers exposed to MWFs reported an increased risk of cancer [18-20].

The American Conference of Governmental Industrial Hygienist (ACGIH) has also classified the mists of unrefined mineral oil as the carcinogenic substance in the category A_2 designated as a suspected human carcinogen [21]. However, this organization has not recommended a threshold limit value (TLV) for the mists of water-based MWFs in their publications.

NIOSH organization has presented recommended exposure limit (REL) for the thoracic and total particles of metalworking fluids at 0.4 mg/m^3 and 0.5 mg/m^3 respectively [8]. The standard level of occupational exposure to mists of mineral oil according to the British Health and Safety Executive (HSE) and Iran's Ministry of Health was set at 1 mg/m^3 [22, 23].

Few methods of the analysis have been presented for MWFs [7, 24-26]. The most applicable method used by health authorities has been the NIOSH method No. 5524, which was recently reviewed in 2014. In this method, MWFs are extracted by ternary solvents and finally, the weight difference of the filter (amount of extracted soluble oil by solvents) was calculated gravimetrically by micro-balance [8]. The American Society for Testing and Materials (ASTM) offered a method number PS 42-97 dated at 1997 for the sampling and analysis of the mists of MWFs. The principles of the ASTM method are fairly similar to NIOSH Method No. 5524 [24].

ASTM offered another method with the code of D664903, this method is similar to the earlier method by ASTM. However, this method has added an extra extraction step to improve the analysis by removing non-soluble aerosols [27]. Verma and colleagues compared a direct read instrument (DustTrak) against the ASTM method PS42-79 and it was concluded that the ASTM method should be preferred for assessing MWFs [28].

NIOSH presented another method No. 5026 for sampling and analysis of airborne mist of mineral oil in the MWFs [29]. In this method, mists of mineral oil were sampled by a personal sampler equipped with a membrane filter and then the mineral oil was extracted by carbon tetrachloride. Samples and blanks were scanned for the best absorption using IR spectrophotometry in the range of 3200-2700cm^{-1} and the amount of mineral oil with consideration of blank sample absorbance were calculated. Historically, organic compounds were analyzed by IR spectrometry [30]. Recently, Fourier Transform-Infra Red (FT-IR) spectrometry is used for the analysis of such chemicals in many studies due to better accuracy, precision, elimination of interferences caused by stray radiation and speed of analysis [31]. FT-IR technique was just presented for the analysis of pure and poorly refined mineral oil [32].

Considering the importance of the occupational exposure to water-based MWFs on the health of the working population and many countries with limited occupational hygiene resources, microbalances with the sensitivity of 0.001 mg required by NIOSH Method 5524 may not be available in laboratories, the aim of this study was to develop a less complex alternative method for quantification of water-based MWFs by using Fourier Transform Infra-Red spectrometry along with possible detection of formaldehyde as an additive by using gas chromatography.

MATERIALS AND METHODS

The soluble oil samples were obtained from a manufacturer of auto engine industry. Soluble mineral oil samples were centrifuged twice at 6000 RPM for 10 minutes for clarification of particulate materials. Then 1ml of soluble oil was weighed by analytical balance (Sartorius: TE 124S model/ 10^{-5}gr precision) and its density was determined. The clarified soluble mineral oil sample was mixed with double distilled, deionized water to produce the stock solution of 1mg soluble oil/10ml water. The fibreglass filter (25 mm) obtained from the Whatman Co. with 1.6 µm pore size was used for producing spiked standards according to the NIOSH Method 5026. Standards in the range of 0.96 to 960 as µg soluble oil/filter were prepared by adding 10, 25, 50, 75, 100, 250, 500, 1000 µl of stock solution to each filter. Elimination of water from spiked standard samples was explored in this study through drying in a desiccator containing silica gel of

time periods of 1, 2 and 6 hours for obtaining the most efficient elimination of water. In this study, 2 hours drying time as reported by NIOSH method 5524 [8], was the best drying time period. All dried samples were transferred to 15ml Falcon tubes and 10ml carbon tetrachloride (Merck Co. with a purity of 99.98%) were added to each tube. Extracted samples were scanned for the best absorption by FT-IR spectrometry in the range of 2700-3200 cm^{-1} in accordance with the NIOSH Method No.5026 [29]. Dried samples containing soluble oil were quantified in accordance to the calibration line obtained from the standards in the range of 0.96 to 960 as µg/sample.

The validity of the method for the analysis of water-based MWFs by FT-IR analysis in this study was investigated in three phases according to the criteria proposed by Mitra *et al.* [34].

The first phase of validation of the FT-IR method for soluble oil the following parameters such as; bias, precision, linear range concentration, the limit of detection (LOD), and limit of quantification (LOQ) was determined.

The second phase of validation, the results of the identical sets of spiked standards analyzed by FT-IR and reference NIOSH method No. 5524, were compared according to the following steps:

a- Two sets of dried spiked standards in the range of 0.96 to 960 as µg soluble oil/filter as described earlier were considered.

b- The first set of spiked standards was prepared and analyzed by FT-IR as described earlier and their mass per sample was calculated according to linear calibration range of 0.96 to 960 µg/sample and equation No.1.

$$M(\mu g/sample)=(W-B) \quad (1)$$

Where:

W= mass of MWFs as determined by FT-IR (mg)

B = mass of MWFs in the blank sample as determined by FT-IR (mg)

c-The second set of spiked standards was analyzed according to the NIOSH method No. 5524. In this method, all dried samples were weighed and then extracted by ternary solvents (toluene, methanol, and dichloromethane with 1:1:1 based on volume) and a double solution (deionized water and methanol with 1:1 as volume). After drying the samples again under laboratory hoods for 2 h, they were weighed and soluble oil in the standards was measured according to the weight differences of pre and post-extraction with ternary solvents with consideration of 5 blank samples per set of a standard sample (Equation No. 2).

$$M(mg/sample)=(W_1-W_2)-(B_1-B_2) \quad (2)$$

Where:

W_1= mean post-sampling weight (pre-extraction weight) of sample-containing filter (mg)

W_2 = mean post-extraction weight of sample-containing filter (mg)

B_1 = mean post-sampling weight of all blank filters (mg)

B_2 = mean post-extraction weight of all blank filters (mg)

The third phase of validation of FT-IR method, a group of lathe operators (n=8) with the same work task were personally monitored by using an open face filter holder equipped with pre-weighed 37mm, Polytetrafluoroethylene (PTFE) filter (SKC Co.) connected to SKC personal sampler pump (SKC EX44-244) with the flow of 2 l/min for total sampling according to the method described by NIOSH method 5524. All samples were dried and weighed in the Sartriuse TE124S analytical balance (10^{-5}gr precision). Subsequently, all dried filters were cut in half and each half was weighed by analytical balance (10^{-5}gr precision). Each set of samples was analyzed by NIOSH 5524 and FT-IR spectrometry methods as described earlier. The weight of the soluble oil for each sample was calculated proportionally in accordance with a total weight of the full and halved filter, in order to eliminate probable cutting errors.

This study also focused on the analysis of formaldehyde in poorly refined soluble oil used in the routine lathe operations. The used water-based MWFs sample was obtained from the auto engine manufacturer, it was analyzed for its formaldehyde content by gas chromatography-flame ionization detector according to the NIOSH method No.2541 [33] and FT-IR spectrometry. The sampling for the analysis formaldehyde content of water-based MWFs was conducted from aerosolized water-based MWFs under a chamber, by using an open face filter holder equipped with a 37 mm, PTFE filter (SKC Co.) connected to SKC personal sampler pump with the flow of 2 l/min for a total sampling according to the method NIOSH method under a chamber. Subsequently, samples (n=8) were dried and prepared for FT-IR spectrometry as described earlier. Qualitative detection of formaldehyde was accomplished through comparison of FT-IR spectrum with a typical spectrum of IR absorption of formalin solution obtained from Merck Co. Since, commercial formalin solution with 37% formaldehyde, 10% methanol [34, 35], was scanned for IR absorption of an aldehyde functional group of C-H (2800-2950cm^{-1}) [36] and a methanol functional group of O-H (3000-3700cm^{-1}) [37, 38].

Since FT-IR analysis of formaldehyde content of water-based MWFs is not specific, another method by NIOSH method No.2541 was also considered [33]. In this method, samples (n=8) were taken from

aerosolized water-based MWFs (Super Care nebulizer) in range of 0.5-5 µl under a chamber, by using a solid sorbent tube (10% (2-hydroxymethyl) piperidine on XAD-2, 120 mg/60 mg (SKC Co.) connected to a personal pump with a flow of 50ml/min. After the termination of sampling, the two sections of the XAD-2 tube were poured into two closed vials and 1ml of toluene (99.9% Merck Co.). The vials were sonicated in an ultrasonic bath for 60 minutes. Upon the termination of the extraction period, 1µl of each vial was injected into gas chromatography-flame ionization detector (GC-FID, Shimadzu GC-17A, made in Japan) with the splitless mode of injection. GC-FID was equipped with a capillary column (BP 20 with 30 m× 0.1 mm× 0.1 µm) was set for 2ml/min for the flow of carrier gas (N_2 gas with a purity of 99.999% purchased from (Mahan Gas Co.). The temperature of the injection port and the detector was 280 and 290 as ^oC, respectively. The thermal programming of the GC oven for initial temperature was 40 ^oC with a gradient temperature rise of 15^oC/min to final 180^oC [40]. In this method, the detection of formaldehyde and methanol was achieved through a comparison of retention times of standards prepared from formalin (Merck Co.) with the peaks observed with the MWFs samples.

The agreement of the analytical results of spiked standards and personal samples for lathe machine operators, analyzed by two methods (FT-IR of this method and NIOSH method 5524), were examined by the Bland-Altman plot. The agreement could be true when the differences between the two sets of data obtained from the two methods fall within two standard deviations (2SD) from the average of the differences [29, 39].

RESULTS AND DISCUSSION

The best absorption of the soluble oil used for water-based MWFs was in the range of 2796-3031cm^{-1} (Fig. 1). The merits of the analysis of FT-IR and NIOSH method 5524 as accuracy, precision, linear range concentrations, LOD, LOQ and bias were 103%, 1.49%, 0.96-960 µg/sample, 0.0004, 0.0014 µg/sample, -3%, and 111%,10.87%, 48-960 µg/sample, 14.9, 49.1 µg/sample and 11% respectively (Table 1).

Table 1: Comparative study of the merits of MWFs analysis by the FT-IR and NIOSH method No. 5542

Method of analysis	Linear Dynamic Range (µg/sample)	Accuracy (%)	R^2	Precision (%)	LOD (µg/sample)	LOQ (µg/sample)	Bias %
NIOSH 5542	48-960	11	0.9917	10.87	14.9	49.1	-11
FT-IR	0.96-960	3	0.998	1.49	0.0004	0.0014	-3
NIOSH 5542*	50-900	14	Not determined	7	0.03	Not determined	Not determined

*Established by NIOSH standard method No. 5524

The agreement of results obtained using two analytical methods (FT-IR in this study and NIOSH method No. 5524), analyzing four sets identical spiked standards (n=32) by each method and along with of personal sampling obtained from industry (n=8) were examined separately by Bland and Altman graph. Since the differences of identical samples were less than two standard deviations in each graph, the agreement of the FT-IR method of analysis with NIOSH method 5524 applied in this study was established.

Qualitative analysis of formaldehyde by FT-IR analysis was checked by the absorption of the standard formalin solution against FT-IR spectrum of water-based MWFs in various ranges of the IR spectrum for the aldehyde functional groups of C-H (2850cm^{-1}) and a methanol functional group of O-H (3680cm^{-1}) (Fig. 1). Direct detection of formaldehyde functional groups by FT-IR method was not possible and only methanol content of formalin could be detected through the O-H functional group. The presence of formalin (as a mixed solution of formaldehyde and methanol compounds) in MWFs was also examined by NIOSH method No.2541 and qualitative presence of formaldehyde and methanol was confirmed (Fig. 2).

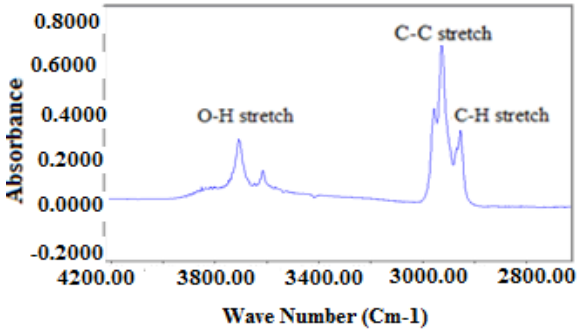

Fig.1: FT-IR spectrum of used water-based MWFs with functional group of O-H, C-H and C-C stretch

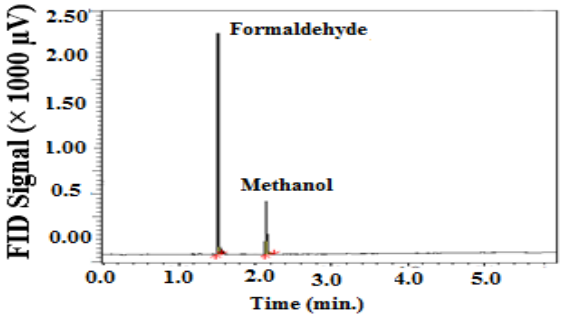

Fig. 2: GC chromatograph of formaldehyde and methanol as an additive in the poorly refined water-based MWFs

Water-based MWFs are widely used in metal machining industries and workers' health risks in the form of respiratory irritants and even various cancer types were reported [40]. Despite the use of formaldehyde in form of formalin solution as a biocide in MWFs [11], the occupational exposure of metal machinists is just expressed as the soluble oil according to reference NIOSH method No. 5524 [8]. The same time the efficiency of the NIOSH method No. 5524 in Iran and possibly other developing countries, due to limited availability of advanced analytical balance with 10^{-6}gr precision could be compromised.

The merits of analysis of the NIOSH method No 5524 which were experimentally obtained in this study, did not produce as good results in terms of overall precision and accuracy, LOD and LOQ as reported in the original manuscript of NIOSH method. These differences could be due to the application of lesser precision analytical balance (10^{-5}gr) instead of microbalance (10^{-6}gr). Generally, despite the agreement of four sets spiked standards and along with actual personal samples of lathe workers analyzed by either FT-IR method of this study or NIOSH reference method, the developed method of this study demonstrated comparable performances compared with data obtained by using the reference NIOSH method No. Since, water-based MWFs were reported to contain toxic compounds such as formaldehyde [41], PAHs and endotoxin [42], analysis of toxic, carcinogenic substances such as formaldehyde could upgrade the monitoring program. Due to the toxicity of water-based MWFs and especially having formalin as a preservative, installation of the industrial ventilation system according to the standard of the ACGIH's industrial ventilation document [43] required by executive organizations such as OSHA [44] and HSE [45], is recommended as a mandatory protective action the health of Iranian lathe workers.

CONCLUSION

This study offers an alternative method of analysis for water-based MWFs instead of NIOSH Method No. 5524 in the developing countries, which may not have precision analytical balance. Generally, the presence of formaldehyde in water-based MWFs, rationalize the need for a more precise technique in future studies and justification of installation of the industrial ventilation system.

ETHICAL ISSUES

Ethical issues such as plagiarism and chemical safety protocols for the laboratory personnel were observed by the authors of this study.

CONFLICT OF INTEREST

Authors have no conflict of interests

AUTHORS CONTRIBUTIONS

The experimental work of this study under the supervision of Azari, Zendehdel and respective advisors. The task of preparing this manuscript was carried out by Kamalifar and Rafieepour under the supervision of Azari.

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