Received: 24 February 2020 | Revised: 20 March 2020 | Accepted: 22 March 2020
DOI: 10.1111/cod.13533

ORIGINAL ARTICLE

CONTACT DERMATITIS WILEY

Metals in used and unused metalworking fluids: X-ray fluorescence spectrometry as a screening test

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Funding information
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Abstract

Background: Exposure to metalworking fluids (MWFs) is a well-known cause of occupational contact dermatitis.

Objectives: We aimed to (1) determine the amount of nickel, chromium, and cobalt in large samples of used and unused MWFs collected from metalworking plants in Denmark, and (2) evaluate a handheld x-ray fluorescence (XRF) device as a screening instrument for metals in MWFs.

Methods: A handheld XRF device was used to screen for metals in MWFs. All samples were also analyzed for concentrations of nickel, chromium, and cobalt using graphite furnace atomic absorption spectroscopy (GFAAS).

Results: GFAAS analysis showed that 13 of 80 samples (16.3%) contained >1 mg/kg (ppm) nickel (range: 6.4-17.7 mg/kg), 3 of 80 (3.8%) contained >1 (range: 1.4-3.1) mg/kg chromium, and 1 of 80 (1.3%) contained 1.3 mg/kg cobalt. XRF-screening detected nickel in eight samples (range: 2.5-15.5 mg/kg), but only one sample with 3.0 (±0.5) mg/kg was found subsequently to contain 9.9 (0.02) mg/kg nickel by GFAAS. Although no chromium was found by XRF analysis, cobalt was found in two samples with 6 (±1.5) mg/kg and 5 (±1.5) mg/kg, subsequently found to contain 0.1 (±0.01) mg/kg and 0.08 (±0.01) mg/kg by GFAAS. Similar concentrations of nickel were found in used (N = 6, range: 6.4-17.7 mg/kg) and unused MWFs (N = 7, range: 9.1-17.3 mg/kg).

Conclusion: Considerable levels of nickel, chromium, and cobalt were found in some used and unused MWFs indicating that these might represent a source of metal allergy. The XRF device is a poor screening test for these metals in MWFs.

KEYWORDS
allergic contact dermatitis, chromium, cobalt, metals, metalworking fluids, nickel, X-ray fluorescence

1 | INTRODUCTION

Occupational contact dermatitis (OCD), mainly irritant contact dermatitis (ICD) and allergic contact dermatitis (ACD), is estimated to constitute 90%-95% of all cases of occupational skin diseases.[1] In Europe, OCD has an estimated incidence of 0.5 to 1 per 1000 workers annually and is generally associated with major socioeconomic impacts.[1]

Metals, including nickel (Ni), chromium (Cr), and cobalt (Co), are well-recognized occupational allergens. According to British occupational surveillance schemes, Cr and Co caused, respectively, 6% and 4%, respectively, of all OCD cases recorded during 1993-2004.[2] Exposure to metalworking fluids (MWFs) among metal workers is a well-known cause of occupational skin diseases.[3] MWFs consist of various chemicals and fall into classes of straight (mineral oil, neat), soluble (emulsion of oil and water), semisynthetic (lower oil concentrations), and synthetic (no mineral oil) MWFs.[4] In metal manufacturing processes, MWFs are applied as coolants and lubricants sprayed on the metal surfaces to reduce friction and heat generated with the machining, grinding, and fabrication of metal products. In a Finnish study including 1027 metalworking machinists, 279 cases of occupational skin diseases were recorded, of which 144 (53%) were ICD and 107 (39%) were ACD.[5] Previous studies from the 1970s have shown the presence of metals in MWFs, elucidating a potential important source of exposure causing ACD.[6,7]

In the present survey, we determined and quantified the metallic composition in a large sample of MWFs from several metalworking plants located in Copenhagen, Denmark. Furthermore, we evaluated the benefit of a handheld x-ray fluorescence (XRF) device as a screening instrument for metals in MWFs.

2 | MATERIALS AND METHODS

2.1 | Sample collection

Twenty metalworking plants were contacted in Copenhagen, Denmark. A consultant from the Danish Union of Metalworkers provided a list on plants assumed to use MWFs. A metalworking plant was defined as a factory working with metals to create individual parts, assemblies, or large-scale structures. Participating plants were visited and samples of both used and unused MWFs were collected (Table SS1). Used samples consisted of MWFs that had been used for metalworking processes such as stamping, grinding, and milling. Furthermore, we recorded the name of the plant, numbered the samples chronologically, and retrieved the safety data sheet for the MWFs. Materials processed at the plants included steel, stainless steel, aluminum alloys, brass, iron, copper alloys, palladium alloys, silver alloys, chromium-nickel alloys, and plastic alloys (Table SS1).

2.2 | XRF screening

A handheld XRF device (X-MET8000 Series, Uedem, Germany) was used to measure the content of Ni, Cr, and Co in predesigned polyethylene sample cups. The XRF device bombards the material with high-energy x-ray beams, capturing the emitted secondary characteristic radiation of each element contained in the material. The manufacturer recommended applying the analytical mode “FP-Plastic” to screen for metals in mg/kg (ppm) using an energy source of 50 kV and 60.5 seconds of measuring time. All samples were shaken manually for 10 seconds before XRF screening. The results were presented as an average of two replicates.

2.3 | Digestion

Prior to elemental analysis, all samples were digested using a microwave digestion system (Multiwave GO Plus, Anton Paar, Graz, Austria), digesting up to 12 samples simultaneously. Then 350 μL of each sample was pipetted into a sealed vessel and the weight was recorded. Furthermore, 400 μL of 30% ultrapure H_2O_2 and 7 mL of 65% ultrapure HNO_3 were added to the vessel before starting the digestion for 55 minutes at 190°C. Subsequently, the digested samples were transferred to test tubes and diluted with ultrapure water (resistivity of 18.2 MΩ cm), and the total volume was noted. The final volume in milliliters (mL) was divided by the initial weight in grams (g) to obtain the individual dilution factor for each sample. Except for regular samples, known amounts of Ni, Cr, and Co were added to unused MWFs as quality controls and blank samples (for no added metal). These were digested and treated as the regular samples.

2.4 | Elemental analysis

Quantitative elemental analysis was done by graphite furnace atomic absorption spectroscopy (GFAAS, μg/L range) (Perkin Elmer AAnalyst 800) at KTH Royal Institute, Stockholm. The calibration curve was based on 1% HNO_3 (0 μg/L) and standards with known concentrations: 10, 30, and 60 μg/L for Ni; 10, 30, 60, and 80 μg/L for Cr; and 10, 30, 60 ,and 90 μg/L for Co. All samples were shaken by a vortex shaker for 10 seconds before elemental analysis. All results were presented as an average of three replicate readings. Furthermore, the measured metal concentrations of blank samples were subtracted from the metal concentrations found in the MWFs. The limit of detection (LOD) was estimated as three times the standard deviation (SD) of the blank solutions. Accordingly, the LOD was 2.1 μg/L for Ni, 0.6 μg/L for Cr, and 0.4 μg/L for Co. The quality control samples spiked with 10 μg/L of either metal showed acceptable recoveries of 107% for Ni, 101% for Cr, and 101% for Co. Consequently, there were no matrix effects (systematic analytical errors induced by other components in the MWFs) or interferences detected.

3 | RESULTS

Eight metalworking plants were included yielding a response rate of 40%. Overall, 80 samples were collected, including 61 used and 19 unused samples. Table SS1 presents an overview of the MWFs and materials processed at each metalworking plant. Table 1 provides a summary of the main findings from XRF screening and GFAAS analysis.

3.1 | XRF screening

According to the XRF screening, 9 of 80 samples (11.2%) contained Ni, Cr, or Co. Despite detecting Ni in eight samples (range: 2.5-15.5 mg/kg), only one sample with 3.0 (±0.5) mg/kg was subsequently found to contain 9.9 (0.02) mg/kg Ni by GFAAS while no Cr was found by XRF analysis, Co was found in two samples with 6 (±1.5) mg/kg and 5 (±1.5) mg/kg subsequently found to contain 0.1 (±0.01) mg/kg and 0.08 (±0.01) mg/kg by GFAAS.

TABLE 1 All samples with metal content ≥1 mg/kg analyzed by GFAAS and XRF screening

			XRF (±SD)[a] mg/kg			GFAAS (±SD)[b] mg/kg		
MWF type	Used/unused	Sample number	Ni	Cr	Co	Ni	Cr	Co
Semisynthetic	Unused	1	-	-	-	11.2 (1.5)	-	-
Semisynthetic	Used	2	-	-	-	10.0 (0.3)	-	-
Semisynthetic	Used	3	-	-	-	11.1 (0.4)	-	-
Semisynthetic	Used	4	3.0 (0.5)	-	-	9.9 (0.02)	-	-
Semisynthetic	Used	5	-	-	-	9.9 (0.5)	-	-
Neat	Unused	6	-	-	-	9.4 (1.5)	-	-
Neat	Unused	7	-	-	-	9.1 (0.9)	-	-
Neat	Unused	8	-	-	-	10.6 (2.0)	-	-
Semisynthetic	Used	9	3.5 (1)	-	-	0.01 (0.02)	-	-
Soluble	Used	17	2.5 (0.5)	-	-	-	-	1.3 (0.04)
Semisynthetic	Used	32	-	-	-	17.7 (0.4)	-	-
Soluble	Unused	33	-	-	-	17.3 (1.9)	-	-
Neat	Unused	34	-	-	-	17.1 (0.6)	-	-
Soluble	Unused	35	-	-	-	14.7 (1.8)	-	-
Semisynthetic	Used	44	-	-	-	-	1.4 (0.3)	-
Soluble	Used	49	2.5 (0.5)	-	-	-	3.1 (0.03)	-
Soluble	Used	54	15.5 (1.5)	-	6 (1.5)	0.8 (0.01)	-	0.1 (0.01)
Soluble	Used	56	5.5 (1)	-	-	-	-	-
Soluble	Used	60	-	-	5 (1.5)	-	-	0.1 (0.01)
Soluble	Used	64	-	-	-	-	1.8 (0.2)	-
Soluble	Used	68	-	-	-	6.4 (0.2)	-	-
Semisynthetic	Used	73	3 (0.5)	-	-	-	-	-
Semisynthetic	Used	76	3 (1)	-	-	-	-	-

[a]Mean and standard deviation of two replicate measurements.
[b]Mean and standard deviation of triplicate measurements.

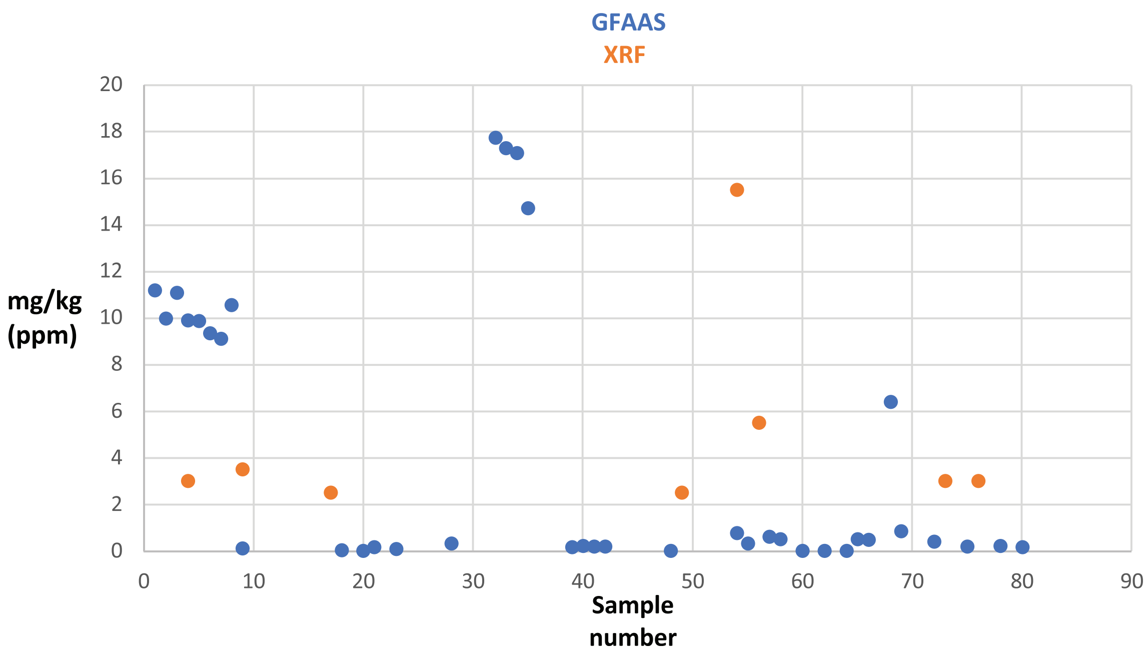

FIGURE 1 Scatter plot illustrating the poor relationship between XRF screening and GFAAS analysis for Ni contents (mg/kg) in all samples. Samples with amounts below LOD are not shown

3.2 | GFAAS analysis

GFAAS analysis showed that 13 of 80 samples (16.3%) contained >1 mg/kg Ni (range: 6.4-17.7 mg/kg), 3 of 80 (3.8%) contained >1 mg/kg Cr (1.4-3.1 mg/kg), and 1 of 80 (1.3%) contained 1.3 mg/kg Co. Overall, the mean concentrations of Ni, Cr, and Co were 2.0 (±0.2), 0.22 (±0.02), and 0.05 (±0.01) mg/kg, respectively. Ni was found in both used (N = 6, range: 6.4-17.7 mg/kg) and unused MWFs (N = 7, range: 9.1-17.3 mg/kg), whereas Cr and Co were found only in used ones (Table 1). Overall, 17 of 80 samples (21.3%) contained ≥1 mg/kg of Ni, Cr, or Co.

3.3 | Sensitivity and specificity calculations

Applying a cut-off value of ≥1 mg/kg for GFAAS, XRF screening detected 1 true positive and had 12 false negatives for Ni, yielding a sensitivity of 7.7%, whereas the specificity was 89.4% based on 59 true negatives and 7 false positives. Regarding Cr and Co, no true-positive event was recorded, yielding zero sensitivity. Furthermore, the specificity of the XRF screening was 96.3% for Cr based on 77 true negatives and 3 false positives, whereas it was 97.4% for Co based on 76 true negatives and 2 false positives. Figure 1 demonstrates the poor correlation between XRF-screening and GFAAS analysis for Ni.

4 | DISCUSSION

All three metals were found in in the MWFs, with Ni being the most prevalent. Cr and Co were found only in used oils, whereas Ni occurred in unused ones as well. Furthermore, the XRF device was a poor screening instrument for metals in MWFs.

Despite the overall low amounts of metals found in the MWFs, it is important to highlight that these levels might induce ACD. Fischer et al assessed the elicitation threshold in 20 nickel-allergic patients, reporting that 16.7% of the individuals reacted to an Ni dose of 0.035 μg/cm^2 (15.8 mg/kg) applied twice daily during 3 weeks of a repeated open application test.[8] Furthermore, 1% and 10% reacted to 0.048 μg/cm^2 (1.6 mg/kg) and 0.78 μg/cm^2 (26 mg/kg) Ni, respectively, through patch testing.[8] The latter findings illustrate the allergic capacity of the Ni levels found in our study, with 13 of 80 of MWFs containing 6.4-17.7 mg/kg. Regarding trivalent and hexavalent Cr, previous dose–response patch test studies have reported minimum 10% elicitation thresholds of 0.18 μg/cm^2 (6 mg/kg) and 0.03 μg/cm^2 (1 mg/kg), respectively,[9] elucidating the allergic potential of the Cr levels found in 3 of 80 samples (range: 1.4-3.1 mg/kg). Generally, very low levels of Co were found in our study, with only one sample containing more than 1 mg/kg (1.3 mg/kg), suggesting that this hapten occurs rarely in MWFs. The low levels of Co might also be due to the lack of Co as an alloying element in the materials processed (Table SS1). In a recent case report involving a patient with severe hand dermatitis, a machine oil was assessed as the causative hapten containing 2.4-2.7 mg/kg Co.[10] In line with this, previous studies detected Co levels at 300-550 mg/kg in MWFs used for processing of hard metal alloys, thus indicating that high levels of cobalt might occur in MWFs.[6,7] In addition, the oils and additives in the MWFs might act as surfactants and irritants, disturbing the skin barrier and thus facilitating the penetration of the metals, and resulting in lower sensitization and elicitation thresholds. The ability of some oils to enhance transdermal penetration has been described previously.[11,12] The risk of ACD might further be increased because many metal workers refuse to use protective gloves due to reduced dexterity and risk of accidents, entailing an increased risk of microtraumatic skin lesions that might facilitate the passage of metal particles or ions.

The most common causes of occupational ACD in machinists due to MWFs have been ascribed to alkanolamines, formaldehyde, and colophonium.[13] However, among metals, Ni has been suggested as the most prevalent hapten.[14] The occurrence of metals in MWFs has been attributed to contamination from machining operations, entailing a dissolution of metals in the fluids from the workpiece. Stainless steel and Ni-Cr alloys were processed at some plants, which might explain the occurrence of Ni and Cr in the used MWFs. Nevertheless, we found Ni in unused MWFs containing concentrations similar to those of the used ones. The latter finding suggests that the contamination might originate from a source other than machining operations. In some plants, we noted that the MWFs were carried in steel drums, which might present a putative source of contamination, as it is possible that metals are released from the inner surface of the steel to the fluids. In line with this, it has been postulated that the principal source of exposure in metal workers is contact with metal objects themselves at the workplace and elsewhere, thus questioning the significance of MWFs as clinically relevant exposure sources. The latter is further stressed by the lack of reaction to patch testing with MWFs that had been in use for 11.5 months in a study population of metal workers sensitized to metals.[14] Furthermore, an insight into the level of metal release from the MWFs and skin bioavailability is necessary for an accurate evaluation of the allergic potential of these haptens.

The XRF device was a poor screening instrument given the low sensitivity estimates. The advent of the XRF device has greatly improved exposure analysis in patients with ACD, particularly pertaining to metallic alloys and possibly leather products.[15] However, despite the low accuracy, it is important to emphasize that the occurrence of all three metals was either low or nonexistent in the fluids, especially regarding Co and Cr given by mean values of 0.05 (±0.01) mg/kg and 0.22 (±0.02) mg/kg, respectively. In addition, the metal concentrations found in the MWFs might be too low for the LOD of the XRF device, further explaining the poor accuracy and the high rate of false positives (10.6% for Ni). It is important to mention that XRF screening was performed on undigested organic samples comprising oil–water mixtures and other auxiliary substances, including biocides, preservatives, fragrances, and emulsifiers, thus creating a complex background scatter that might interfere with the readings of the XRF device. Furthermore, these undigested fluids might contain metal particles, which were also clearly visible to the eye in used MWFs, whereas the digested samples analyzed by GFAAS were homogeneous and particle-free. The presence of particles is suggested to interfere with the XRF measurement if higher concentrations of particles are present in the detection volume.[16]

Strengths of this study are the large MWF sample, pretreatment of the organic samples with digestion, and empirical calibration of GFAAS with standard solutions of known metal concentrations. The study was limited by a possible bias of the contributing metalworking plants; it is possible that noncontributing metalworking plants or plants from other locations have MWFs with higher concentrations of Ni, Co, and Cr, depending on the materials processed. Another important limitation includes the lack of knowledge regarding the specific materials processed on the day of MWFs collection. This study is further limited by not examining the inner surface of the steel drums as a potential source of Ni contamination.

In conclusion, considerable levels of Ni, Cr, and Co were found in some used and unused MWFs, indicating that these might represent a source of metal allergy. The XRF device is a poor screening test for these metals at these low concentrations in MWFs.

ACKNOWLEDGEMENTS

Aage Bangs Fond, Miljøstyrelsen. Zheng Wei, KTH Royal Institute of Technology, is acknowledged for analytical assistance.

AUTHOR CONTRIBUTIONS

Farzad Alinaghi: Data curation; formal analysis; investigation; writing-original draft; writing-review and editing. **Yolanda Hedberg:** Investigation; methodology; resources; supervision; writing-review and editing. **Claus Zachariae:** Conceptualization; supervision; writing-review and editing. **Jacob Thyssen:** Conceptualization; supervision; writing-review and editing. **Jeanne Duus Johansen:** Conceptualization; investigation; methodology; resources; supervision; validation; writing-review and editing.

CONFLICT OF INTERESTS

None declared.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Alinaghi F, Hedberg YS, Zachariae C, Thyssen JP, Johansen JD. Metals in used and unused metalworking fluids: X-ray fluorescence spectrometry as a screening test. *Contact Dermatitis*. 2020;83:83–87. https://doi.org/10.1111/cod.13533