Critical Evaluation of Sequential Leaching Procedures for the Determination of Ni and Mn Species in Welding Fumes

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In this work, welding fume samples were collected in a welding plant, where corrosion-resistant steel and unalloyed structural steel were welded by gas metal arc welding (GMAW) and manual metal arc welding (MMAW) techniques. The welding fumes were sampled with a fixed-point sampling strategy applying Higgins–Dewell cyclones. The following solutions were used to dissolve the different species of Ni and Mn: ammonium citrate solution [1.7% (m/v) diammonium hydrogen citrate and 0.5% (m/v) citric acid monohydrate] for 'soluble' Ni, 50:1 methanol–bromine solution for metallic Ni, 0.01 M ammonium acetate for soluble Mn, 25% acetic acid for Mn^0 and Mn^{2+} and 0.5% hydroxylammonium chloride in 25% acetic acid for Mn^{3+} and Mn^{4+}. 'Insoluble' Ni and Mn contents of the samples were determined after microwave-assisted digestion with the mixture of concentrated (cc). HNO_3, cc. HCl and cc. HF. The sample solutions were analysed by inductively coupled plasma quadrupole mass spectrometry and inductively coupled plasma atomic emission spectrometry. The levels of total Ni and Mn measured in the workplace air were different because of significant differences of the fume generation rates and the distributions of the components in the welding fumes between the welding processes. For quality control of the leaching process, dissolution of the pure stoichiometric Mn and Ni compounds and their mixtures weighing was investigated using the optimized leaching conditions. The results showed the adequacy of the procedure for the pure metal compounds. Based on the extraction procedures, the predominant oxidation states of Ni and Mn proved to be very different depending on the welding techniques and type of the welded steels. The largest amount of Mn in GMAW fumes were found as insoluble Mn (46 and 35% in case of corrosion-resistant steel and unalloyed structural steel, respectively), while MMAW fumes contain mainly soluble Mn, Mn^0 and Mn^{2+} (78%) and Mn^{3+} and Mn^{4+} (54%) in case of corrosion-resistant steel and unalloyed structural steel, respectively. According to the results of the leaching procedures, GMAW fumes are rich in oxidic Ni (79%), while Ni compounds in welding fumes generated during MMAW are mainly in easily soluble form (44%). The crystalline phases were identified in each welding fume by X-ray powder diffraction (XRPD) technique as well. From the XRPD spectra, it is clear that GMAW fumes contain predominantly magnetite ($FeFe_2O_4$). In case of structural steel welding, there was a little amount of ferrite (α-Fe) also found. Welding fume generated during MMAW of structural steel contained a complex alkali–alkali earth fluoride phase ($KCaF_3$–CaF_2) and some magnetite and jakobsite ($MnFe_2O_4$). The XRPD results did not fully confirm the ones obtained from the extraction experiments. However, some results, for example the rate of soluble Ni and Mn compounds compared to the total, can be useful for further investigations of welding fumes.

Keywords: leaching; manganese; nickel; speciation; welding fume

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INTRODUCTION

The metal-mechanic sector (turnover 970 billion € a year) represents 8% of the total European Union economy. Welding is the most important joining technique in this sector. In Europe, there are ∼730 000 full-time jobs in welding and 5.5 million other jobs related to it. Welding has a significant impact on health: it is physically high demanding, which leads to a high percentage of sick leave, ∼160 working hours per welder yearly (source: http://www.ewf.be/econweld).

According to our present knowledge about welding fume effects on human health, it can be counted on a higher incidence of respiratory illness—e.g. pneumoconiosis, chronic bronchitis and ventilatory function, fibrosis of the lung, occupational asthma and different diseases of the upper respiratory tract—among welders (Flechsig, 1988; McNeilly *et al.*, 2004). Stern (1983) had concluded that the excess risk of lung cancer in welders is ∼30% greater than it is in the non-welding population. It was suggested that the greater risk of lung cancer found among stainless steel welders could be related to the high concentrations of nickel (Ni) and hexavalent chromium (Cr) in stainless steel welding fumes. Increased mortality due to ischemic heart disease among welders was observed as well (Sjögren *et al.*, 2006). Nowadays, there is an increasing concern about the possible neurological risk for welders, which is assigned to the relatively high manganese (Mn) content of some welding fumes (Fored *et al.*, 2006; Park *et al.*, 2006).

The chemical forms of the elements influence their bioaccessibility (Ruby *et al.*, 1999) and therefore they influence uptake, and subsequently, bioavailability (Gibaldi, 1984), toxicity and in some cases detoxification. For the study of welding fumes from a toxicological point of view, determination of toxic metal species in welding fumes generated by different welding processes is a fundamental problem. The analytical techniques for the determination of Cr species in welding fumes were developed in the early 1980s (Blomquist *et al.*, 1983; Gray *et al.*, 1983; Moreton *et al.*, 1983; Cox *et al.*, 1985), while chemical speciation of Ni and Mn has been less investigated. Some recent publications deal with chemical speciation of Ni (Füchtjohann *et al.*, 2001; Oller and Bates, 2003) and Mn (Thomassen *et al.*, 2001; Ellingsen *et al.*, 2003) in urban and workplace aerosols, but we still do not know enough about the chemical forms of Mn and Ni in welding fumes.

Gas metal arc welding (GMAW) and manual metal arc welding (MMAW) are the most commonly used welding techniques in the metal industry. Therefore, it is reasonable to get as much information as possible about the health-damaging factors of these techniques, especially about the compounds of the welding fumes generated in these processes. Two different chemical fractionation procedures were applied for the determinations (one for Ni and one for Mn), based on the methods first described by Zatka *et al.* (1992) and Tessier *et al.* (1979), later developed by Oller and Bates (2003) and Thomassen *et al.* (2001), respectively.

The above-mentioned procedures were mainly applied for aerosols, which were formed during certain industrial processes and contained species in relatively well-defined compounds, like pure oxides. The particles' size distributions were also presumed based on the investigated industrial process in most of the applications. These facts has to be taken into consideration when applying a formerly developed method, in spite of the fact that some authors like Oller and Bates (2003) used the sequential extraction procedure for urban particulate matter while Füchtjohann *et al.* (2001) developed and applied a similar procedure for the determination of Ni species in ambient aerosols. However, these two attempts can encourage other researchers to use sequential extraction methods for the speciation analysis of very different aerosols without any consideration, which can lead to questionable results.

In this study, leaching procedures were used for the quantification of the chemical species of Ni and Mn in welding fumes generated during the welding of corrosion-resistant steel and unalloyed structural steel applying both the welding techniques mentioned above. The respirable fraction of the fumes was collected, as welding fume particles are primarily respirable with a particle aerodynamic diameter of <1 μm (Hewett, 1995). For the chemical characterization of the collected aerosol samples, X-ray powder diffraction (XRPD), inductively coupled plasma quadrupole mass spectrometric (Q-ICP-MS) and inductively coupled plasma atomic emission spectrometric (ICP-AES) techniques were applied.

MATERIALS AND METHODS

Sampling

The welding fume samples were collected in a welding plant, where corrosion-resistant steel (X8CrNi1810) and unalloyed structural steel were welded by GMAW and MMAW techniques during normal workplace conditions. The gas mixtures used during GMAW in case of corrosion-resistant steel and structural steel contained 97% Ar–3% O_2 and 82% Ar–18% CO_2, respectively. For sampling of respirable aerosols, 'fixed-point' Higgins–Dewell plastic cyclone (SKC Inc., Eighty Four, PA, USA) samplers were used at flow rate of 2.2 ± 0.1 dm^3 min^{-1}. Millipore cellulose ester membrane filters (Millipore Corp., Bedford, MA, USA) with diameter of 25 mm and pore size of 0.8 μm were used. For

collecting samples for the determination of the crystalline phases in the welding aerosols by XRPD technique, conical inhalable samplers (Casella, Bedford, UK) were applied at flow rate of 3.5 ± 0.1 dm^3 min^{-1}. The conical inhalable sampler cassettes were equipped with polyvinyl chloride (PVC) membrane filters (Millipore Corp.) with diameter of 37 mm and pore size of 5.0 μm. These differences from the other filters used for sample collection were required by the XRPD measurements because filters with greater diameter can be placed into the sample holders more easily and X-ray diffraction scans of blank filters exhibited a significantly higher intensity from cellulose ester filters than from PVC ones. Length of sampling times varied between 15 and 45 min. The air sampling durations were determined from pilot sampling data. Sampling equipment was put as near to the emission source as it was possible, but not further than 1 m.

Sequential extraction procedures

Both Ni and Mn can exist in various chemical forms with different oxidation states and solubility, therefore with potential for different biological activity. It was reasonable to follow the formerly established practice in the selection of the analysed components. The extraction procedures for Ni and Mn were performed separately within a few days after sampling.

Three different fractions of Ni ('soluble', metallic and oxidic/'non-soluble') were separated by the sequential extraction summarized in Table 1. For the determination of the non-soluble Ni species, the leached filters were transferred into digestion vessels made of poly(tetrafluoroethylene) (PTFE) and digested with the mixture of 2.0 ml HNO3 (69% v/v), 1.0 ml HF (40% v/v) and 1.0 ml HCl (37% v/v). A total

of 0.2 g solid H_3BO_3 was also added into each vessel before the digestion to avoid the attack of the Pyrex spray chamber in the sample introduction system of the ICP-AES by formation of BF_4^- complex (Gasparics *et al.*, 1997).

The sequential extraction procedure for Mn consisted of four steps (shown in Table 1). The digestion of the 'insoluble' Mn was carried out similarly to the procedure described for determination of oxidic Ni.

It has to be mentioned that during the first step of the extractions 37°C was applied instead of 20°C (Thomassen *et al.*, 2001) to create similar temperature conditions as it is in the human body in order to get more adequate results for a further bioaccessibility study. Some international standards for workplace air measurements, like ISO 15202:2000, also recommend the use of this temperature when the soluble fraction of metals is determined.

Reagents and instrumentation

The deionized water used throughout was prepared by an ELGA Purelab System (18.2 MΩ cm). Nitric acid and hydrochloric acid were for trace analysis (Fluka, Buchs, Switzerland) while hydrofluoric acid, hydroxylammonium chloride, diammonium hydrogen citrate, citric acid and acetic acid had analytical grade quality produced by Merck (Darmstadt, Germany). Powdered Mn metal (50 mesh, ~10 μm), MnO (60–170 mesh), Mn_2O_3 (325 mesh, ~3 μm), MnO_2 (60–230 mesh) and NiO (<10 μm) were all of ≫99% purity and obtained from Sigma–Aldrich (Milwaukee, WI, USA) while powdered Ni metal (~10 μm, 99+) was purchased from Merck.

For the sequential leaching procedure, 50 ml volume Maxi-Spin polypropylene tubes with 25 ml filter cup inserts equipped with 0.2 μm polyvinylidene

Table 1. Leaching conditions for Ni and Mn compounds in welding fumes

Step	Components	Reagents	Conditions	MDL[a], μg l^{-1}	MQL[b], μg l^{-1}
1	Soluble Ni	1.7% Diammonium hydrogen citrate and 0.5% citric acid solution (10 ml)	60 min, 37°C	0.3	0.9
2	Metallic Ni	50:1 Methanol–bromine solution (10 ml)	3 h, 20°C	2	5
3	Oxidic Ni	2.0 ml cc. HNO_3 – 1.0 ml cc. HF – 1.0 ml cc. HCl, 0.2 g boric acid	Closed PTFE vessel microwave-assisted digestion	8	27
1	Soluble Mn	0.01 M ammonium acetate (10 ml)	60 min, 37°C	0.03	0.1
2	Mn^0 and Mn^{2+}	25% Acetic acid (15 ml)	60 min, 75°C	0.2	0.5
3	Mn^{3+} and Mn^{4+}	0,5% Hydroxylammonium chloride in 25% acetic acid (15 ml)	90 min, 75°C	0.2	0.5
4	Insoluble Mn	2.0 ml cc. HNO_3—1.0 ml cc. HF—1.0 ml cc. HCl, 0.2 g boric acid	Closed PTFE vessel microwave-assisted digestion	2	6

[a]Method detection limit.
[b]Method quantification limit.

membranes and glass–fiber pads on the top of the membranes (Alltech, Deerfield, IL, USA) were used.

All centrifugations were done at 2500 revolutions min^{-1} (1272 g) with Eppendorf 5804 centrifuge (Eppendorf AG, Hamburg, Germany). For the digestion procedure, MARSX microwave-assisted digestion system (CEM, Matthews, NC, USA) was used. Fourteen samples were simultaneously digested by applying a two-step heating program (ramp to 11 bar pressure limit at 600 W for 25 min and hold at 600 W for 5 min). The solutions were filled up to 50 ml with deionized water. For the ICP-AES measurements as internal standard, yttrium was added to each solution in a concentration of 1.0 mg l^{-1}. The analysis of the extracts was performed by Q-ICP-MS (Agilent 7500a, Agilent Technologies) system after 10- to 50-fold dilution and addition of Sc internal standard in a concentration of 50 μg l^{-1}. Solutions obtained from the digestion were analysed by ICP-AES (Optima 3200 DV, Perkin Elmer Inc.) system. Although the ICP-MS as well as the ICP-AES method can be used for the measurement of Ni and Mn in welding fumes (Berlinger *et al.*, 2007), the ICP-MS seemed to be a better choice for the analysis of the leach extracts because Ni and Mn were expected to be present in lower concentrations in the extracts. Operating conditions of the ICP-MS and ICP-AES methods were as described previously (Berlinger *et al.*, 2007).

XRPD patterns were obtained in a Philips model PW 3710-based PW 1050 Bragg-Brentano parafocusing goniometer using CuKa radiation ($l = 0.15418$ nm), graphite monochromator and proportional counter. The XRPD scans were digitally recorded with a step size of 0.04° and evaluated with profile fitting methods.

RESULTS AND DISCUSSION

Quality control

The dissolution of the pure stoichiometric Mn and Ni compounds and their mixtures weighing 0.2–2 mg of them was investigated using the optimized leaching conditions. All Mn compounds were quantitatively recovered in the range of 96–100% during the leaching steps. However, 54–74% of the metallic Mn and 9–11% of the MnO dissolved in 0.01 M ammonium acetate during Step 1 due to the increased temperature. Recoveries of Mn_2O_3 and MnO_2 during Step 3 amounted to 95–100%. The recoveries were 83–89% and 91–103% for metallic Ni and NiO, respectively. Although 3–7% of the metallic Ni was not dissolved during Step 2, the selectivity of the leaching procedure for Ni compounds can still be rated as adequate. More details about the selectivity and the accuracy of the leaching procedures can be found in Tables 2 and 3. For quality control of the microwave-assisted digestion, commercially available 37-mm cellulose ester membrane filter samples (Standard Reference Material A 2, Oslo, Norway) were analysed which were prepared by spiking each filter with an aqueous solution containing 24 elements with concentrations gravimetrically traceable

Table 2. Leaching recoveries[a] in % of pure Ni compounds with well-defined stoichiometries, $n = 5$

Compound	Component 1, soluble Ni	Component 2, metallic Ni	Component 3, oxidic Ni
Ni	<1	86–89	3–7
NiO	<1	<1	91–99
Ni + NiO	<1	83–87	98–103

[a]The calculation of the recoveries is based on the weights of the added compounds.

Table 3. Leaching recoveries[a] in % of pure Mn compounds with well-defined stoichiometries

Compound	Component 1, soluble Mn	Component 2, Mn^0 and Mn^{2+}	Component 3, Mn^{3+} and Mn^{4+}	Component 4, insoluble Mn
Mn	54	44	<1	<1
MnO	9	87	<1	<1
Mn_2O_3	<1	<1	97	<1
MnO_2	<1	<1	97	<1
Mn + Mn_2O_3	67 (Mn^0)	32 (Mn^0)	98 (Mn^{3+})	<1
MnO + Mn_2O_3	10 (Mn^{2+})	86 (Mn^{2+})	99 (Mn^{3+})	<1
Mn + MnO_2	74 (Mn^0)	25 (Mn^0)	100 (Mn^{4+})	<1
MnO + MnO_2	10 (Mn^{2+})	86 (Mn^{2+})	100 (Mn^{4+})	<1
(Mn + MnO) + Mn_2O_3	41 (Mn^0, Mn^{2+})	50 (Mn^0, Mn^{2+})	99 (Mn^{3+})	<1
(Mn + MnO) + MnO_2	40 (Mn^0, Mn^{2+})	51 (Mn^0, Mn^{2+})	98 (Mn^{4+})	<1
Mn + (Mn_2O_3 + MnO_2)	64 (Mn^0)	32 (Mn^0)	95 (Mn^{3+}, Mn^{4+})	<1
MnO + (Mn_2O_3 + MnO_2)	11 (Mn^{2+})	89 (Mn^{2+})	99 (Mn^{3+}, Mn^{4+})	<1
(Mn + MnO) + (Mn_2O_3 + MnO_2)	26 (Mn^0, Mn^{2+})	69 (Mn^0, Mn^{2+})	98 (Mn^{3+}, Mn^{4+})	<1

[a]The calculation of the recoveries is based on the weights of the added compounds.

to ultrapure metals or stoichiometrically well-defined oxides. The recoveries of Ni and Mn were 96.3–99.4 and 96.1–99.8%, respectively.

Determination of Ni and Mn species in the different welding fumes

The levels of total Ni and Mn measured in the workplace air are listed in Table 4. Background corrections were made by using field and laboratory blanks. It is well known from the literature (Heile and Hill, 1975; Hewitt and Gray, 1983) that the fume generation rates and the distribution of the chemical compounds in the welding fumes strongly depend on the welding technology.

The Ni and Mn speciation results expressed as a percentage of total Ni and Mn are summarized in Table 5. Background corrections were made by using field and laboratory blanks which were sufficiently below the concentration levels studied. The statistical calculations are based on the cited literature (Green and Margerison, 1978). Since during the first step considerable amount of metallic Mn and MnO could have been already extracted, the results for the first two stages of the procedure were added together. However, dissolved Mn in the first step is discussed separately as well because of the possible biological relevance. It was proved by McNeilly *et al.* (2005) that the soluble transition metals present in welding fumes are responsible for inflammation of the lungs of rats because removal of the soluble fraction by chelation or washing the welding fume particles abolished the ability to cause inflammation. The most obvious feature of the speciation results is that in MMAW fumes less insoluble Ni and Mn compounds were found than in GMAW fumes. When we applied these two technologies for welding of corrosion-resistant and unalloyed structural steel, the distributions of the chemical forms of Ni and Mn proved to be very different in the different welding fumes. However, it is an important finding that in MMAW of corrosion-resistant steel, more Ni and Mn compounds were in soluble form than in GMAW. Therefore in case of Ni, we may suggest that welders working with MMAW technique are exposed to Ni compounds having higher bioaccessibility in spite of the fact that total concentration of Ni in the workplace air is lower.

Based on our experience, dissolution reagents influence solubility of metal components in welding

Table 4. Total Mn and Ni concentrations in the workplace air within 1 m of the emission source of the welding fume obtained as a sum of species concentrations determined by ICP-MS and ICP-AES, background corrected as appropriate using field and laboratory blanks

	Corrosion-resistant steel		Unalloyed structural steel	
	GMAW	MMAW	GMAW	MMAW
Total Mn concentration				
n^a	20	15	11	12
Mean[b] (mg m^{-3})	1.1	3.0	2.7	7.5
SD[c] (mg m^{-3})	0.4	1.1	1.0	2.1
Min[d] (mg m^{-3})	0.3	1.2	1.5	2.9
Max[e] (mg m^{-3})	2.0	4.6	4.4	10.9
Total Ni concentration				
n	17	10	—	—
Mean (mg m^{-3})	0.52	0.19	—	—
SD (mg m^{-3})	0.25	0.03	—	—
Min (mg m^{-3})	0.16	0.14	—	—
Max (mg m^{-3})	0.95	0.26	—	—

[a]Number of air filters collected.
[b]Arithmetic mean.
[c]Standard deviation of the mean.
[d]Minimum concentration.
[e]Maximum concentration.

Table 5. Proportions in % of Mn and Ni components in welding fumes generated by GMAW and MMAW processes, background corrected as appropriate using field and laboratory blanks

	Corrosion-resistant steel				Unalloyed structural steel			
	GMAW		MMAW		GMAW		MMAW	
	Mean[a]	95% CI[b]	Mean	95% CI	Mean	95% CI	Mean	95% CI
Mn compounds	n^c = 20		n = 15		n = 11		n = 12	
Dissolved Mn in the first step	10	9–10	31	30–33	16	15–17	9.3	9.0–9.7
Soluble Mn + Mn^0 and Mn^{2+}	45	40–50	78	74–80	39	36–41	33	31–35
Mn^{3+} and Mn^{4+}	9	8–10	19	18–19	27	24–29	54	52–55
Insoluble Mn	46	42–50	3.9	3.7–4.2	35	31–38	14	12–16
Ni compounds	n = 17		n = 10		—		—	
Soluble Ni	15	14–16	44	40–49	—	—	—	—
Metallic Ni	6.0	5.7–6.3	23	21–24	—	—	—	—
Oxidic Ni	79	78–80	33	30–36	—	—	—	—

[a]Arithmetic mean.
[b]95% Confidence interval of the mean.
[c]Number of measurements.

fumes. For example, ammonium citrate can dissolve a greater amount of metal components than the ammonium acetate solution in case of welding aerosols. Therefore, it is advisable to use always the appropriate solutions for each metal in such measurements and to develop methods for measuring the biosoluble/bioinsoluble fractions of welding and other workplace aerosols.

Identification of the crystalline phases by XRPD

The crystalline phases that could be identified in the different welding fumes by XRPD are listed in Table 6. The few milligrams of the aerosols that were collected on the 37-mm PVC membrane filters were enough for the semiquantitative analysis of the welding fume samples by the XRPD method. Neither the 37-mm PVC nor the 25-mm cellulose ester filters were gravimetrically analysed because gravimetric data were not important from the point of view of the speciation analysis. There was also not enough time to perform accurate gravimetric analysis because the sample preparation was made within a few hours after sampling to reduce the possibility of transformation of the compounds.

From the XRPD spectra (Fig. 1), it is clear that GMAW fumes contain predominantly magnetite ($FeFe_2O_4$). In case of structural steel welding, there was a little amount of ferrite (α-Fe) also found. Welding fume generated during MMAW of structural steel contained a complex alkali–alkali earth fluoride phase ($KCaF_3$–CaF_2) and some magnetite and jakobsite ($MnFe_2O_4$). These results are in good agreement with previous XRPD studies of welding fumes (Jenkins and Eagar, 2005).

There were no well-defined narrow peaks in the spectra of welding fume generated during MMAW of corrosion-resistant steel. However, sodium fluoride, potassium sodium chromium/titanium fluoride and potassium permanganate were qualitatively identified as crystalline phases in the welding fume. It can be also suggested that there are amorphous or non-well crystallized phases present like SiO_2 or some kind of silicates. Since the welding fumes are mainly formed from the electrode materials, the coating of the welding electrode was also investigated in order to help the identification. The following phases were detected: microcline ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$), fluorite (CaF_2), rutile (TiO_2), calcite [$Ca(CO_3)$], quartz (SiO_2) and eskolaite (Cr_2O_3). However, these results did not help us in the more exact identification of the phases of this fume.

Comparison of the results obtained from the leaching procedures to the XRPD results

The XRPD results cannot fully confirm the ones obtained from the sequential extractions because of several reasons: most of the amounts of Ni and Mn were found to be insoluble in case of GMAW fumes. But it is not likely that Ni can be in a pure NiO form in higher amounts and it is also unlikely that such insoluble compounds of Mn (FeMn and SiMn) can appear in welding fumes as in the aerosol characterized by Thomassen *et al.* (2001). At the same time, 'non-solubility' of Ni and Mn in case of GMAW can be explained by the XRPD measurements that could identify magnetite as the main crystalline phase in these kind of welding fumes. $Mn^{2,3+}$ and Ni^{2+} ions can be easily built in the magnetite crystal lattice, which is quite stable and cannot be dissolved easily. The first statement is based on the properties of the magnetite crystal lattice rather than the XRPD spectra, as differences of the detected magnetite peaks locations from the reference pattern were not observable. However, it does not preclude the possibility of the replacement in the crystal lattice structure by Mn and Ni because Mn increases while Ni decreases the lattice parameter (Henderson *et al.*, 2007). In case of MMAW, mainly fluorides were identified as crystalline phases by the XRPD. The presence of fluorine in high amounts in MMAW fumes elucidates the relatively good solubility of Ni and Mn in MMAW fumes (Voitkevich *et al.*, 1984). Nevertheless, the XRPD determinations do not give any evidence of the observed rates of the other Ni and Mn compounds found in the leaching procedures.

Not only the XRPD results question the adequacy of the method of sequential extractions in case of welding fume characterization. X-ray photoelectron spectroscopic (XPS) and secondary ion mass spectrometric (SIMS) analysis of individual welding fume particles proved that most welding fume particles have a complex morphology and consist of

Table 6. Crystalline phases identified by X-ray diffraction of GMAW and MMAW fumes generated by corrosion resistant and unalloyed structural steel welding

Corrosion-resistant steel		Unalloyed structural steel	
GMAW	MMAW[a]	GMAW	MMAW
Magnetite, $FeFe_2O_4$ (100%)[b]	Sodium fluoride, NaF; potassium sodium chromium fluoride, K_2NaCrF_6; potassium sodium titanium fluoride, K_2NaTiF_6; potassium permanganate, K_2MnO_4	Magnetite, $FeFe_2O_4$ (95%); ferrite, α-Fe (3%)	Potassium calcium fluoride, $KCaF_3$ (50%); jakobsite, $MnFe_2O_4$ (20%); magnetite, $FeFe_2O_4$ (15%); fluorite, CaF_2 (8%)

[a]Qualitative results.
[b]The approximate amount of the crystalline phase compared to the whole amount of crystalline phases.
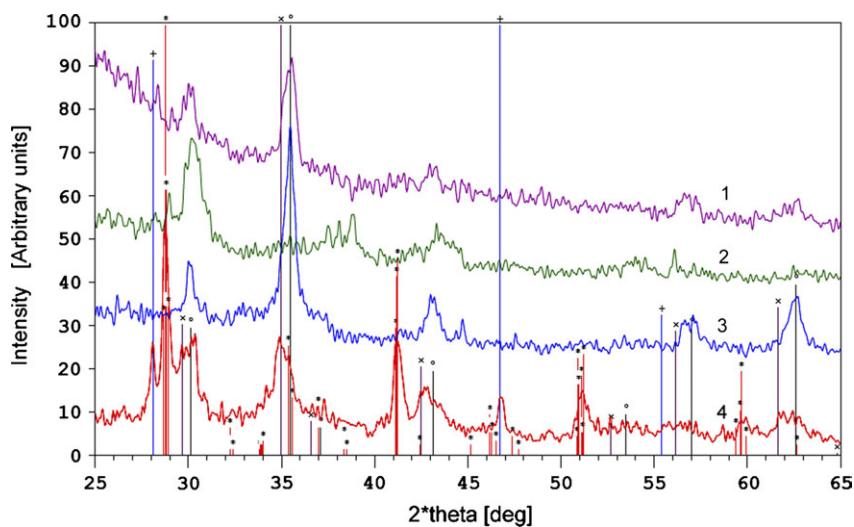
Fig. 1. XRPD spectra of the different welding fumes: 1, MMAW—unalloyed structural steel; 2, GMAW—unalloyed structural steel; 3, GMAW—corrosion-resistant steel; 4, MMAW—corrosion-resistant steel. Reference patterns: asterisk indicates potassium calcium fluoride (KCaF$_3$), plus sign indicates fluorite (CaF$_2$), open circle indicates magnetite (FeFe$_2$O$_4$) and times symbol jakobsite (MnFe$_2$O$_4$).

a core and shell regardless of the type of welding technique (Minni *et al.*, 1984; Konarski *et al.*, 2003). This kind of structure necessitates a leaching procedure, which is able to extract the compounds of the surface at first than dissolve the compounds, which build the core.

CONCLUSIONS

The main conclusion of this study is that the limitations of the sequential extraction methods developed for certain metal compounds in industrial processes should always be considered when they are applied for other complex matrixes like welding aerosols.

Several techniques are needed for the speciation analysis of the elements in welding fumes at the same time—including methods like XRPD, which allows the identification of the crystalline phases, and SIMS or XPS, which give the unique opportunity of individual particle characterization—in order to eliminate the possible errors that can be based on inadequately chosen methods. A promising method in these days for characterization of the morphology, chemical composition and microstructure of the ultrafine (<100 nm) particles is provided by the combined technique of high-resolution transmission electron microscopy, energy-dispersive X-ray spectroscopy and electron diffraction (Chen *et al.*, 2005). This method also gives the unique opportunity of analysing the welding fume particles.

The examination of the solubility of different elements is essential for the investigation of biosoluble/bioinsoluble fractions of welding fumes, if we would like to form a reliable database for risk as-

sessment. From this point of view, the efforts done by applying sequential extraction to get more data about chemical speciation of welding fumes were not completely profitless. Besides putting the adequacy of the leaching methods into question, some results of soluble Ni and Mn compounds in different welding fumes and with different solvents were provided, and these results can be used in a further bioaccessibility study.

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