

2. Welding Fumes and Gases

2.1 Introduction

Welders are exposed to a variety of airborne contaminants arising from the welding process and other operations in the work place. In the literature, the term 'welding fume' is applied variously to some or all of the emissions from welding. In this monograph, the term is applied only to the particulate emissions intrinsic to the various welding processes, to distinguish these from gaseous emissions. Incidental particulate emissions, for example, from the pyrolysis of paint on metal being welded, are excluded from this definition.

The chemical composition and physical properties of welding fumes and gases and details of occupational exposures of welders in the work place have been reviewed (American Welding Society, 1973; Ulfvarson, 1981; Tinkler, 1983; Stern, R.M. *et al.*, 1986; National Institute for Occupational Safety and Health, 1988). The aerosol contains contributions from a number of sources: (a) vaporization of the wire, rod or metallic/alloying coatings; (b) decomposition and vaporization of the flux materials; (c) spatter from the arc region and weld pool and fumes therefrom; and (d) evaporation from the molten weld metal.

The consumable is the major source of fume, the workpiece making only a minor contribution unless it bears a surface coating.

The elemental composition of a welding aerosol reflects the composition of the consumable used, while the relative abundance of the elements in the aerosol is a function of the physics and chemistry of the arc and geometry of the weld: low-melting-point metals are relatively enriched in the fume (Mn by a factor of 2-6, Cu and Pb by a factor of 3-5), while the more refractory metals are depleted by factors of e.g., 0.07-0.5 for Fe, 0.2-0.7 for Cr and 0.03-0.4 for Ni (when present) (see e.g., Malmqvist *et al.* 1986).

Potential occupational exposure to fumes from a given consumable can be estimated by combining information on the relative elemental abundance of the aerosol, as determined from a chemical analysis of welding fumes produced in the laboratory under controlled conditions, with the total aerosol concentration expected on the basis of work-place measurements. Actual elemental exposures can be determined on the basis of fume samples collected at the work place by stationary samplers placed on the shop floor or by personal samplers placed in the breathing zone. Detailed descriptions of standard sampling methods have been proposed by a number of sources (e.g., American Welding Society, 1973; British Standards Institution, 1986), and the general characteristics of welding fumes have been studied under controlled conditions (e.g., American Welding Society, 1973; Evans *et al.*, 1979; Mayer & Salsi, 1980). Although a welder usually works for long periods with a single type of consumable, changing conditions may result in variations in the chemical composition of the fume with time over a working shift. In addition, the presence of other process applications in the vicinity contributes to the chemical composition of the background: under certain conditions, e.g., TIG (see below), the background may contribute significantly to the fume collected in the breathing zone, although typically the background fume concentration as measured with stationary samplers is about one-tenth that found in the breathing zone (Ulfvarson, 1981). Hence, the presence of specific elements determined by chemical analysis of samples obtained in the work place may not be corroborated by laboratory measurements of nominally the same welding process.

Each consumable produces a unique fume in terms of elemental composition (see, e.g., Mayer & Salsi, 1980), particle size distribution and identifiable stoichiometric compounds (see, e.g., Fasiska *et al.*, 1983). Since there are thousands of different consumables, the only way to review data on composition and exposure derived from laboratory and work-place measurements is by use of tables of ranges of elemental concentration for very general classes of processes, applications and consumables. This technique has the disadvantage that one cannot determine from the tables the actual composition of a specific welding fume; on the other hand, since welders use many consumables during a working week, their actual exposure is properly reflected in the logarithm of the median values so obtained.

Not only particulate matter but also a wide range of gaseous pollutants is produced by welding, either through decomposition of compounds in the flux coating or core of the consumable or through oxidation, dissociation or other chemical reactions in the air mixed into the arc or surrounding the arc region.

Estimates of exposure to potentially toxic gases (ozone, carbon monoxide, nitrogen oxides) based on production rates measured in the laboratory may be unreliable because of the influence of local ventilation and work-place design on the actual concentrations found in the welders' breathing zone. Determination of occupational exposures to gases must be based on work-place measurements.

2.2 Chemical composition and physical properties of welding fumes

(a) *Elemental composition*

Fasiska *et al.* (1983) identified 38 individual types of covered electrodes (MMA/steel) and 20 classes of MIG/Al fume, the fumes from which contain one or more elements in high abundance. The detailed chemical composition of a number of classes of welding fume are summarized in Table 2. The range (when available) of elemental distributions is given, together with an indication of the analytical method used. Fumes for chemical analysis are typically produced in a 'fume box', standards for which have been reviewed recently (Moreton, 1986).

A description of work-place exposures and the chemistry of welding fumes can be considerably simplified by recognizing that each couplet of process technology-application represents a source of a broad class of welding fume that is similar in constituents if not in concentration. Three major process technologies (MMA, MIG/MAG, TIG) applied to two classes of metal (mild steel (MS) and stainless steel (SS)), plus a few additional couplets (e.g., MIG/Al), however, account for perhaps 80% of all exposures in welding (Stern, 1983). In addition, MIG/Ni and MMA/Ni processes, with wire or electrodes (i.e., consumables) containing high levels of nickel, are used on cast iron and low-alloy steel. MIG/MAG processes produce fume with components from the metal/alloy wire alone, while fume from flux-producing

Table 2. Average or range (%) of elemental distribution of welding fumes by type

Element	Manual metal arc fume		Metal inert gas fume		Method ^a	Reference
	Mild steel	Stainless steel	Mild steel	Stainless steel		
Si	2.7-8.1	2.9-5.6	1.6-3.3	0.9	XRF	Mayer & Salsi (1980)
	-	10	-	1.7	XRF	Moreton <i>et al.</i> (1986)
F	7-14	16-24	ND	ND	PIXE	Malmqvist <i>et al.</i> (1986)
	-	14.9	-	-	XRF	Moreton <i>et al.</i> (1986)
	0.6-17	7-11.5	0.05-14	-	XRF	Mayer & Salsi (1980)
Cl	ND-0.54	ND-0.34	ND	ND	PIXE	Malmqvist <i>et al.</i> (1986)
K	9-19	18-22	ND	ND	PIXE	Malmqvist <i>et al.</i> (1986)
	-	19.9	-	<0.1	XRF	Moreton <i>et al.</i> (1986)
	5.1-15	8.7-15.4	0.11-5.7	-	XRF	Mayer & Salsi (1980)
Ca	0.62-2.6	1.3-10	ND	ND	PIXE	Malmqvist <i>et al.</i> (1986)
	-	0.4	-	<0.2	XRF	Moreton <i>et al.</i> (1986)
	0.09-10.8	3.8-6.8	0.01-13.6	-	XRF	Mayer & Salsi (1980)
Ti	ND-0.54	0.62-2.3	ND	ND	PIXE	Malmqvist <i>et al.</i> (1986)
	-	2.1	-	0.1	XRF	Moreton <i>et al.</i> (1986)
	0.6-2.4	7.7-12.7	0.006-2.8	-	XRF	Mayer & Salsi (1980)
Cr	ND-0.07	3.0-3.4	0.07	10-12	PIXE	Malmqvist <i>et al.</i> (1986)
	-	5.0	-	13.4	XRF	Moreton <i>et al.</i> (1986)
	0.11-0.7	6.5-9.2	0.2-0.6	-	XRF	Mayer & Salsi (1980)
Mn	2.8-5.9	2.4-14	7.3	4.8-5.3	PIXE	Malmqvist <i>et al.</i> (1986)
	-	5.0	-	12.6	XRF	Moreton <i>et al.</i> (1986)
	2.7-5.6	4.3-5.0	3.9-7.0	-	XRF	Mayer & Salsi (1980)
Fe	11-32	3.3-3.7	45	28-31	PIXE	Malmqvist <i>et al.</i> (1986)
	-	5.1	-	33.3	XRF	Moreton <i>et al.</i> (1986)
	14.4-31.8	6.0-15.9	33-55	-	XRF	Mayer & Salsi (1980)
Ni	ND	0.22-0.44	ND	4.5-4.8	PIXE	Malmqvist <i>et al.</i> (1986)
	-	0.4	-	4.9	XRF	Moreton <i>et al.</i> (1986)
	0.01-0.32	0.48-2.9	0.01-0.06	-	XRF	Mayer & Salsi (1980)
Cu	ND-0.08	ND-0.01	0.26	0.06-0.09	PIXE	Malmqvist <i>et al.</i> (1986)
	-	<0.1	-	0.6	XRF	Moreton <i>et al.</i> (1986)
	0.04-0.24	0.09-0.14	0.01-0.18	-	XRF	Mayer & Salsi (1980)
Zn	0.04-0.29	0.11-0.25	0.04	0.17-0.18	PIXE	Malmqvist <i>et al.</i> (1986)
	0.04-0.07	0.007-0.10	0.08-0.40	-	XRF	Mayer & Salsi (1980)

Table 2 (contd)

Element	Manual metal arc fume		Metal inert gas fume		Method ^a	Reference
	Mild steel	Stainless steel	Mild steel	Stainless steel		
As	ND-0.06	ND	ND	ND	PIXE	Malmqvist <i>et al.</i> (1986)
	0.005-0.05	0.003-0.01	0.009-0.12	-	XRF	Mayer & Salsi (1980)
Rb	ND	ND-0.02	ND	ND	PIXE	Malmqvist <i>et al.</i> (1986)
Zr	ND-0.54	ND	ND	ND	PIXE	Malmqvist <i>et al.</i> (1986)
Mo	ND	ND-0.09	ND	0.92-0.95	PIXE	Malmqvist <i>et al.</i> (1986)
	-	< 0.02	-	0.6	XRF	Moreton <i>et al.</i> (1986)
	0.005-0.3	0.2-1.4	0.1-0.2	-	XRF	Mayer & Salsi (1980)
Pb	< 0.07	ND-0.04	ND	ND	PIXE	Malmqvist <i>et al.</i> (1986)
	0.03-0.28	0.08-0.55	0.05-0.22	-	XRF	Mayer & Salsi (1980)

^aXRF, X-ray fluorescent spectrometry; PIXE, proton-induced X-ray spectrometry; -, no data; ND, not detected

processes (flux-cored electrode welding, MMA) contains significant contributions from the vaporization and decomposition of the flux-forming components of the filler or coating. For simplicity, the following list indicates the elements that occur in more than trace (i.e., 1%) quantities in the respective fumes of general-purpose electrodes:

MIG/Al	Al
MIG/Ni	Ni, Fe
MIG-MAG/MS	Fe, Mn, Si
MIG-MAG/SS	Fe, Mn, Cr, Ni
MIG/MS	Fe, Mn, Si, K
MMA/Ni	Ni, Fe, Ba
MMA/MS	Fe, Mn, Ca, K, Si, F, Ti
MMA/SS	Fe, Mn, Ca, Si, F, K, Ti, Cr, Ni

In addition to the elements listed above and in Table 2, many other trace elements (e.g., Ag, Ga, Nb, Se, Sn, Sr) have been identified in special-purpose welding fumes (Pedersen *et al.*, 1987).

(b) Oxidation state of chromium

Considerable attention has been given to the oxidation state of chromium in welding fumes. (See Pedersen *et al.*, 1987, for a recent review.) The only soluble species of chromium in welding fumes is Cr[VI]. (For a discussion of the definition

of solubility for Cr[VI] compounds, see p. 55 of the monograph on chromium, and the General Remarks, pp. 42-43). Table 3 gives information on the solubility and oxidation state of chromium in MMA/SS, MIG/SS and TIG/SS welding fumes. For all practical purposes, the (long-term) insoluble Cr[VI] content of SS welding fumes is less than 0.5% and is more typically of the order of 0.2-0.3%, and is thus negligible from the point of view of exposure. The high Cr[VI] content of MMA fumes is attributed to the presence of alkaline metals in the flux coating; hence, flux cord electrode fume resembles MMA fume with regard to chromium chemistry due to the presence of the flux forming materials in the core, although the technique resembles MIG. Numerous attempts have been made to alter the Cr[VI] content of MMA/SS fume; in a recent approach, potassium was replaced by sodium in a modified electrode (Kobayashi & Tsutsumi, 1986), resulting in a significant reduction in the relative Cr[VI] content (see below).

The concentration of Cr[VI] and the Cr[VI]/Cr (total) ratio in MIG(MAG)/SS welding fumes has been the subject of considerable discussion. Stern *et al.* (1984) showed that collection of MIG/SS fume in an impinger can result in fixation of 30% and more of the total Cr as Cr[VI] (compared to a maximum of 3% in membrane-collected fumes). The Cr[VI]:Cr(total) is heavily dependent on welding parameters (current, voltage, arc length) and time after welding (Thomsen & Stern, 1979; Stern, 1983). Maximal concentrations of Cr[VI] occur after about 10 s and then fall by about a factor of 3 within 3 min (Hewitt & Madden, 1986).

Occupational exposure to Cr[VI] also occurs in stainless-steel processes other than welding. Sawatari and Serita (1986) showed that the fumes from plasma spraying contain 27% Cr[VI]. Flame spraying, electric arc spraying and plasma spraying of additives containing mixtures of Fe, Cr and Ni produced fumes with approximately 6-8% Cr, of which 22-69% was Cr[VI] (Malmqvist *et al.*, 1981).

A problem with respect to chromium speciation has been lack of standardized collection and analytical methods. Reduction of fume during dry membrane collection and reduction or oxidation of fume during analysis could lead to under- or over-reporting of Cr[VI] concentrations (Pedersen *et al.*, 1987).

(c) Crystalline materials

Chemical analysis of welding fume is usually based on methods which allow determination only of the elemental content. Frequently, composition is given in terms of the putative oxide (e.g., Fe_2O_3 , Fe_3O_4 , CrO_3) although such assignment of compound is not justified without additional crystallographic evidence. Recently, a number of authors have begun to investigate the presence of crystallographic compounds in a range of welding fumes.

Fasiska *et al.* (1983) found Fe_3O_4 , $(\text{Fe}, \text{Mn})_3\text{O}_4$, KF-CaF_2 , CaF_2 , MnFe_2O_4 , $(\text{Fe}, \text{Cu})\text{Fe}_2\text{O}_4$, K_2CrO_4 , K_2FeO_6 , NaF , K_2FeO_4 , $\text{K}_2(\text{Cr}, \text{Fe})\text{O}_4$, $(\text{Fe}, \text{Ni})\text{Fe}_2\text{O}_4$ and

Table 3. Distribution (%) of chromium by oxidation state and solubility and of nickel as a function of type of welding fume

Type of fume ^a	Cr (total)	Cr[VI]			Cr[VI]: Cr (total)	Cr[VI] soluble: Cr (total)	Ni (total)	Reference
		Total	Soluble	Insoluble				
MMA/SS	2.9–4.4	–	1.5–3.2	< 0.5–0.92	–	0.50–0.73	0.22–0.44	Malmqvist <i>et al.</i> (1986)
MMA/SS	5.0	4.1	3.8	0.3	0.82	–	0.4	Moreton <i>et al.</i> (1986)
MMA/SS	3.0–5.3	1.8–3.9	–	–	0.36–1.0	–	0.3–1.3	Eichhorn & Oldenburg (1986)
MMA/SS (modified) ^b	4.9–7.3 ^c 11.4	– –	4.4–5.4 0.66	0.4–1.8 11.2	– –	0.74–0.91 0.056	0.03–0.6 ^d 0.9	Kobayashi & Tsutsumi (1986)
MMA/SS	2.4–6.4	–	2.2–4.3	0.03–0.42	–	0.7–0.9	0.38–1.9	Stern (1980b)
MMA/Ni ^e	0.02	–	–	–	–	–	1.4	Stern (1980b)
MIG/SS	12	–	0.23	< 2	–	0.019	4.5	Malmqvist <i>et al.</i> (1986)
MIG/SS	13.4	–	0.2	< 0.1	–	0.015	4.9	Moreton <i>et al.</i> (1986)
MIG/SS	4.1–15.6	0.02–2.9	–	0.01–0.42	0.005–0.19 ^f	–	3.5–6.7	Stern (1980b)
FCW/SS	5.1	2.7	2.5	0.2	0.53	–	1.3	Moreton <i>et al.</i> (1986)
MIG/Ni	0.04	–	< 0.004	0.04	–	–	53–60	Stern (1980b)

^aMMA, manual metal arc; SS, stainless steel; MIG, metal inert gas; FCW, flux-cored electrode

^bCovering comprises modified lime–titania

^cTotal Cr₂O₃

^dTotal NiO

^e[Ba = 40%; 6% water-soluble]

^f[Impinger collection]

PbCrO₄ in a wide range of MMA fumes; and Kobayashi and Tsutsumi (1986) found the following compounds in different MMA welding fumes:

Non-lime MMA/MS	Fe ₃ O ₄ , MnFe ₂ O ₄ , Fe ₂ O ₃
Lime-type MMA/MS	K ₂ CO ₃ , Fe ₃ O ₄ , MnFe ₂ O ₄ , NaF, CaF ₂ , KCaF ₃ , KCl (and MgO and Na ₂ CO ₃ in a modified type)
MMA/SS	K ₂ CrO ₄ , Fe ₃ O ₄ , NaF, CaF ₂ , Na ₂ CrO ₄ (and LiF in a modified type)

Combined X-ray diffraction analysis and Mössbauer spectroscopy showed that Fe in welding fume occurs as α -Fe (metallic) as well as in an iron oxide spinel (Fe₃O₄) with some degree of impurities and imperfection. MIG/MS and MIG/SS welding fumes contained approximately 7% α -Fe and 12% γ -Fe, respectively (Stern *et al.*, 1987). Although welding fumes contain considerable amounts of silicium in oxidized form, the presence of crystalline silica has not been reported; only amorphous silica is observed (Mayer & Salsi, 1980), presumably because the physical/chemical conditions for the formation of crystalline silica are not met during welding (Fasiska *et al.*, 1983; Kobayashi & Tsutsumi, 1986; Stern *et al.*, 1987). Previously asbestos and currently clays are used to provide elemental Al, Mg and Si; however, these originally crystalline materials are decomposed in the high temperature of the arc, and corresponding crystalline substances do not appear in the fumes.

(d) *Physical properties*

The most important physical characteristic of welding fumes is their particulate size distribution, as this property determines the degree to which fumes are respirable and how they are deposited within the respiratory tract. Aerodynamic mass median diameters of welding fumes have been determined with cascade impactors; typical values are as follows: MMA fumes: 0.35-0.6 μ m for total fume (Malmqvist *et al.* 1986); 0.23-0.52 μ m aerodynamic diameter (Eichhorn & Oldenberg, 1986); 0.2 μ m for metallic parts (Mn, Fe) and 2.0 μ m for slag components (Ca) (Stern, 1982); MIG fumes: < 0.2 μ m (Stern, 1980b) and 0.11-0.23 μ m aerodynamic diameter (Eichhorn & Oldenburg, 1986). Stern *et al.* (1984) and Malmqvist *et al.* (1986) showed by means of electron spectroscopy for chemical analysis and transmission electron microscopy that the outer layers of the amorphous matrix of MMA/SS fume particles are soluble in water and contain only Cr[VI]. With most digestion procedures, there is almost always an insoluble residue consisting of refractory cores from MIG/SS fume (Pedersen *et al.*, 1987). Transmission electromicroscopy showed that the particles of MIG fumes can be very crystalline and tend to form long chains, clusters and rafts, most of which, however, break up in solution (Stern, 1979; Grekula *et al.*, 1986; Farrants *et al.*, 1988). For MMA fumes, the situation is complex, since there are several sources of the aerosol. Slag particles make up a separate aerosol with a relatively large median diameter, and a certain fraction

consists of particles similar to those found in MIG fumes. A third class of particles consist of an amorphous matrix containing droplets of metal-rich material, which in turn can contain a large number of crystalline precipitates, mostly of an impure, imperfect iron oxide (magnetic) spinel (Stern *et al.*, 1984).

Studies using energy dispersive analysis of X-rays in the electron microscope (Stern, 1979; Minni *et al.*, 1984; Grekula *et al.*, 1986; Gustafsson *et al.* 1986) show that individual particles, especially of MMA fume, can have widely varying chemistry; the particles of MIG fumes may be somewhat more homogeneous, the average particle chemistry resembling that of the fume.

Studies of the chemistry of fumes collected in liquid-filled impingers indicate that the elemental distribution varies as a function of particle size (Stern *et al.*, 1984).

2.3 Occupational exposures of welders

Exposures of welders that have been evaluated for carcinogenicity in previous IARC Monographs are listed in Table 4.

(a) *Exposures to welding fumes*

Occupational exposures in the welding industry have been measured for decades. Ambient concentrations of welding fumes are determined by the rates of formation of fume during the process and the extent of ventilation. Steady-state concentrations of fumes in work-room/work-space air are determined by the ratio of fume formation rate (in mg/s) to the ventilation rate (m^3/s). In small, confined spaces with poor ventilation, the concentration increases with time: a single welder working with a process producing 10 mg/s of fume in a ship double-bottom section or container with a volume of 10 m^3 will be exposed to an environment containing $60 \text{ mg}/\text{m}^3$ fume after 1 min of arcing time. Typical 4-mm diameter electrodes produce 0.5-4 g total fume and have a burning time of 30-45 s. In most contemporary shops in industrialized countries, ventilation rates are designed to maintain the background level well below $5\text{-}10 \text{ mg}/\text{m}^3$; present levels usually average $2\text{-}4 \text{ mg}/\text{m}^3$ and have been decreasing by a factor of two per decade since the 1940s, as can be seen from a comparison of recent data with measurements of working place concentrations in the 1960s (e.g., Caccuri & Fournier, 1969).

In order to compare fume production from different welding techniques, two entities can be defined — total fume emission rate, E (g/min), and the relative fume formation index, R , which is the total mass of emitted fume standardized to the mass of the deposited consumable (excluding slag) in mg/g (Malmqvist *et al.*, 1986).

Table 4. Occupational exposures of welders, other than to nickel and chromium compounds (evaluated elsewhere in this volume) that were evaluated for carcinogenicity in *IARC Monographs Volumes 1-48*

Agent	Degree of evidence for carcinogenicity ^a		Overall evaluation ^a	Occurrence
	Human	Animal		
Lead and lead compounds				Welding fumes from special-purpose electrodes
Inorganic	I	S	2B	
Arsenic and arsenic compounds	S	L	1*	Impurity in some mild stainless-steel welding fumes
Asbestos	S	S	1	Insulation material, e.g., in shipyards
Toluene	I	I	3	Welding fumes from painted steel
Xylene	I	I	3	Welding fumes from painted steel
Phenol	I	I	3	Welding fumes from painted steel
Benzene	S	S	1	Welding fumes from painted steel
1,4-Dioxane	I	S	2B	Welding fumes from painted steel
Formaldehyde	L	S	2A	Welding fumes from painted steel
Acetaldehyde	I	S	2B	Welding fumes from painted steel
Acrolein	I	I	3	Welding fumes from painted steel
Methyl methacrylate	ND	I	3	Welding fumes from painted steel

^aS, sufficient evidence; L, limited evidence; I, inadequate evidence, ND, no adequate data. For definitions of the overall evaluations, see Preamble, pp. 36-37.

*This evaluation applies to the group of chemicals as a whole and not necessarily to all individual chemicals within the group.

For a particular welding technique and typical welding parameters, the rate of fume formation does not vary by more than a factor of 3 from the average. In MMA, the amount of fume produced per electrode is independent of the current but roughly proportional to the length of the arc, and hence welding voltage. Poor welding technique can result in twice the fume production per rod. The burn time of an electrode is inversely proportional to the current, so welding at twice the current produces twice the fume formation rate (see Stern, 1977; Malmqvist *et al.*, 1986). Under most open and shipyard conditions, exposure is determined by the relationship between the position of the welder's face mask and the rising plume; typically, the mask effectively reduces exposure by a factor of 3-6 (American Welding Society, 1973).

One way of describing welders' exposures is to present data in terms of cumulative distribution curves for various welding processes. Stern (1980a) generalized the data for Swedish and Danish workplaces (Ulfvarson *et al.*, 1978a,b,c; Ulfvarson,

1979, 1981) and found that the median reported 8-h TWA total dust concentration in the breathing zone was 10 mg/m³ for MIG/Al; that for MMA and MIG processes was 1.5-10 mg/m³. Within the 10-90% range, the distribution curves are parallel: the 90% limit is typically four times greater than the 50% value. Ulfvarson (1986) reviewed many of the general principles that relate to fume concentrations and pointed out that actual fume formation rates are quite similar in different welding processes (with the exception of TIG) and that most of the variation comes from differences in arcing time, which can be as low as 20% for certain MMA operations requiring considerable work-piece preparation, and close to 85% for certain MIG operations. Rutile electrodes emit higher fume concentrations than do basic electrodes, and, with the exception of ozone formation during MIG welding, working postures do not affect fume emissions from mild steel. General ventilation affects exposure considerably: low ventilation rates in the winter lead to a strong seasonal variation (by a factor of 2-3) in Scandinavian work places. Local exhaust, on average, reduces fume concentrations by only 58% in MMA welding and 35% in MIG welding, and by much less if not used properly (close to the arc) or if poorly maintained (Ulfvarson, 1986).

An indication of the range of exposures to total particles was provided by Ulfvarson (1981): the 50% and 90% exposures (in mg/m³) were: TIG/Al, 1 and 4; MIG/Al, 9 and 43; MMA/SS, 4 and 10; TIG/SS, 2 and 6; MMA/Ni, 2 and 10; MMA/MS, 10 and 28; MIG(MAG)/MS, 7 and 18; and MIG/SS, 2 and 5. Most of the results of studies in factories and shipyards are in agreement with the upper limits, as can be seen in Tables 5 and 6. Table 5 also shows total chromium, hexavalent chromium and nickel concentrations in various stainless-steel welding processes. The concentration of hexavalent chromium (mostly water-soluble) ranged from 25 to 1550 µg/m³ in MMA/SS, from < 1 µg/m³ to < 20 µg/m³ in MIG/SS and was ≤1- < 6 µg/m³ in TIG/SS. The nickel levels were 10 to 970 µg/m³, 30 to < 570 µg/m³ and 10 to < 70 µg/m³, respectively. Higher levels of chromium and nickel occur during special process applications and during welding in confined spaces. The levels of other air contaminants are summarized in Tables 5-7 for mild-steel and stainless-steel welding.

(b) *Biological monitoring of exposure* (see also pp. 484-485)

(i) *Chromium*

Both blood and urine levels of chromium are found to be elevated in stainless-steel welders compared to control populations (Gylseth *et al.*, 1977; Tola *et al.*, 1977; Kalliomäki *et al.*, 1981; Rahkonen *et al.*, 1983; Sjögren *et al.*, 1983a; Welinder *et al.*, 1983; Littorin *et al.*, 1984; Cavalleri & Minoia, 1985; Gustavsson & Welinder, 1986; Schaller *et al.*, 1986). Typical levels of chromium in biological fluids of stainless-steel welders are presented in Table 8.

Table 5. Occupational exposures within the stainless-steel welding industry by process and application (average and/or range)

Reference (country)	Process ^a	Total fume (mg/m ³)	Total Cr (µg/m ³)	Cr[VI] (µg/m ³ or % of total Cr)	Ni (µg/m ³)	Cu (µg/m ³)
Åkesson & Skerfving (1985) (Sweden)	MMA/SS	-	101 (26-220)	-	440 (70-970)	-
van der Wal (1985) (Netherlands)	MMA/SS	2-40	30-1600	25-1550	10-210	-
	MIG/SS	1.5-3	60	< 1	30	-
	TIG/SS ^b	0.8-4.2	10-55	< 1	10-40	-
	Background	0.5-1.2	-	-	-	-
	TIG/Monel	1.3-5	-	-	330	215
	MMA,TIG/Cu-Ni-Fe	0.6-5.5	-	-	20-120	40-320
Froats & Mason (1986) ^b (Canada)	MIG/SS (1st plant)	0.3-2.25	-	0.1-0.6	-	-
	MIG/SS (2nd plant)	0.67-8.32	8-37	1-3.4	-	-
	SS grinders	1.6-21.6	17-108	1-3	-	-
Coenen <i>et al.</i> (1985, 1986) (German Democratic Republic)	MMA/SS ^b	90%, < 13.4	90%, < 350	90%, < 400	90%, < 240	-
	Small MMA/SS	-	90%, < 210	90%, < 30	90%, < 70	-
	Large MMA/SS	-	90%, < 1200	90%, < 980	90%, < 570	-
	Background	90%, < 8	90%, < 170	90%, < 60	90%, < 220	-
	TIG/SS ^b	90%, < 5.4	90%, < 40	90%, < 6	90%, < 70	-
	Background	90%, < 1	90%, < 40	90%, < 2	90%, < 26	-
	MIG/SS ^b	90%, < 12.8	90%, < 190	90%, < 20	90%, < 160	-
	Background	90%, < 3.5	90%, < 80	90%, < 10	90%, < 80	-
	MAG/SS ^b	90%, < 41	90%, < 340	90%, < 30	90%, < 190	-
	Background	90%, < 14.4	90%, < 30	90%, < 3	90%, < 20	-
Ulfvarson <i>et al.</i> (1978b) (Sweden)	MMA/SS	75%, < 6.3	75%, 400	98%	75%, < 40	-
	Background	75%, < 4	75%, < 50	11.5%	75%, < 22	-
	MIG/SS	75% < 2.65	75%, < 94	-	-	-
	Background	75%, < 2	75%, < 50	-	-	-
van der Wal (1986) ^b (Netherlands)	PC/SS	1.0-7.5	30-440	< 1-40	< 10-260	-
	PW/SS	0.2-1.1	20-30	< 1	1-20	-

^aMMA, manual metal arc; SS, stainless-steel; MIG, metal inert gas; TIG, tungsten inert gas; AIB, aluminium bronze; PC, plasma cutting; PW, plasma welding

^bBreathing zone

Table 6. Occupational exposures of welders during various processes and applications in the mild-steel and non-ferrous industry

Reference (country)	Process ^a	Total fume (mg/m ³)	CO (ppm)	NO ₂ or NO _x (mg/m ³)	F (mg/m ³)	Cu (mg/m ³)	Mn (mg/m ³)
Casciani <i>et al.</i> ^c (1986) (Italy)	MMA/MS:						
	No exhaust	8.8-90.6	1-47	0-6.5 ^d			
	Average	32.0	6.0	1.09	0.83		
	With exhaust	1.3-7.9					
	Average	4.34					
Ulfvarson <i>et al.</i> (1978c) (Sweden)	MMA/MS	1.3-53	< 5-10	< 0.5-2.5		0.007-0.094	0.089-0.77
	Average	7.7				0.016	0.26
	MAG, MIG, TIG/MS	1.3-52	< 5-150	< 0.5-0.5		0.008-0.14	0.066-1.8
	Average	7.0	3			0.027	0.30
van der Wal (1985) (Netherlands)	MMA/MS ^c	1.3-13.2		0.09 ^b			
	Average	5.3					
	Background	0.6-3.1					
	MIG-MAG/MS ^c	0.9-12.9		0.09			
	Average	4.4					
	Background	0.4-6.7					

^aMMA, manual metal arc; MS, mild steel; FCW, flux-cored electrode; MAG, metal active gas; MIG, metal inert gas

^bNO₂

^cBreathing zone

^dNO_x

Table 7. Concentrations of gaseous pollutants in welding fume

Reference (country)	Process ^a	CO	O ₃	NO ₂	NO _x	NO	Ni(CO) ₄
Sipek & Smårs (1986) (Sweden)	TIG/SS		0.97 ppm	0.21 ppm		0.005 ppm	
	TIG/SS		0.31 ppm	2.0 ppm		0.44 ppm	
Hallne & Hallberg (1982) (Sweden)	MMA/Ni	15-100 ppm		0.1-0.2 ppm		0.6-2.6 ppm	0.02 ppm
Wiseman & Chapman (1986) (Canada)	TIG/Ni						≤0.00011 ppm
	MIG/Ni						< 0.0001 ppm
	MIG/SS						< 0.0001 ppm
	TIG/SS						< 0.0001 ppm
van der Wal (1985) (Netherlands)	MMA/MS			(breathing zone)		(background)	
	MIG-MAG/MS		< 5 µg/m ³	ND-0.4 mg/m ³		ND-0.7 mg/m ³	
	TIG/SS		< 5 µg/m ³	ND-0.3 mg/m ³		ND-0.7 mg/m ³	
	MIG/SS		< 5 µg/m ³	ND-0.8 mg/m ³		ND-1.1 mg/m ³	
	MIG/Al bronze		≤100 µg/m ³	ND-1.7 mg/m ³		ND-0.6 mg/m ³	
	MIG/Al		> 1000 µg/m ³	ND-0.1 mg/m ³		ND-0.1 mg/m ³	
van der Wal (1986) (Netherlands) (breathing zone)	PC/SS			< 0.01-2 mg/m ³			
	PW/SS			0.03-0.2 mg/m ³			
Ulfvarson (1981) (Sweden)			(50%,90%)		(50%,90%)		
	TIG/Al		≤0.02, 0.08 ppm		≤1, 7.6 ppm		
	MIG/Al		≤0.08, 0.43 ppm		≤0.5, 3.2 ppm		
	MMA/MS				≤0.2, 1.1 ppm		
	MMA/SS		< 0.01 ppm		≤0.5, 3.0 ppm		
	MIG-MAG/SS		≤0.02, 0.2 ppm		≤0.5, 2.0 ppm		
MIG-MAG/MS		≤0.03, 0.08 ppm		≤0.5 ppm			

^aTIG, tungsten inert gas; SS, stainless-steel; MMA, manual metal arc; MIG, metal inert gas; MAG, metal active gas; PC, plasma cutting; PW, plasma welding

Table 8. Concentrations of chromium in biological fluids from stainless-steel welders

Reference (population) ^a	Concentration of chromium		
	In urine	In serum (plasma)	In erythrocytes
<i>Verschoor et al. (1988)^b</i>			
MMA/SS welders	3 (1-62) µg/g creatinine	0.2 (0.04-2.9) µg/l	-
SS Boilermakers	1 (0.3-1.5) µg/g creatinine	0.2 (0.07-0.7) µg/l	-
Controls	0.4 (0.1-2.0) µg/g creatinine	0.2 (0.01-0.9) µg/l	-
<i>Angerer et al. (1987)^b</i>			
MMA-MIG/SS welders	33 (5.4-229) µg/l	9 (2.2-69) µg/l	0.3 (<0.6-39) µg/l
<i>Gustavsson & Welinder (1986)^c</i>			
MMA/SS welders	15.6-61.1 µmol/mol creatinine	52-190 nmol/l	27-188 nmol/l
After summer vacation	2-11.3 µmol/mol creatinine	< 13-58 nmol/l	< 20-65 nmol/l
<i>Schaller et al. (1986)^d</i>			
MMA + TIG + MIG/SS welders	8.3 (0.4-67.4) µg/g creatinine	2.5 (0.4-7.8) µg/l	-
<i>Zschiesche et al. (1987)^e</i>			
MMA/SS welders	6.7 (2.2-34.8) µg/g creatinine 11.6 (2.4-42) µg/l		
MAG-MIG/SS welders	4.9 (3.2-10.9) µg/g creatinine 6.3 (3.4-21.9) µg/l		
TIG/SS welders	2.7 (2.3-4.5) µg/g creatinine 4.5 (4.1-8.6) µg/l		
Controls	1.4 (0.8-2.4) µg/g creatinine 1.6 (0.8-3.4) µg/l		
<i>Emmerling et al. (1987)^e</i>			
MMA/SS welders	28 (8.1-54) µg/l	10.7 (5.3-20.8) µg/l	3.6 (1.3-12.5) µg/l
MIG-MAG/SS welders	14.8 (4.9-30.7) µg/l	5.7 (2.7-13.3) µg/l	0.6 (0.4-1.4) µg/l
TIG welders	8.7 (4.7-14.5) µg/l	5.5 (3.0-8.1) µg/l	1.5 (0.6-3.4) µg/l

^aMMA, manual metal arc; SS, stainless-steel; MIG, metal inert gas; TIG, tungsten inert gas; MAG, metal active gas

^bGeometric mean, range

^cRange

^dMedian, 90% range

^eMedian, 68% range

(ii) *Nickel*

Consistent results have been difficult to obtain with regard to the levels of nickel in blood and urine of persons exposed during welding, although levels are elevated when compared to unexposed individuals (Table 9).

Table 9. Concentrations of nickel in work-room air and in the urine of stainless-steel welders

Reference (population) ^a	Concentration of nickel		
	In air ($\mu\text{g}/\text{m}^3$)	In plasma ($\mu\text{g}/\text{l}$)	In urine ^a (mean \pm SD or range)
Åkkeson & Skerfving (1985) ^b MMA/SS welders Monday morning before work MMA/SS welders Thursday p.m.	440		12 (4.2–34) $\mu\text{g}/\text{l}$; 8.8 (3.1–14.1) $\mu\text{g}/\text{g}$ creatinine 18 (8.1–38 $\mu\text{g}/\text{l}$); 12.4 (4.1–50.4) $\mu\text{g}/\text{g}$ creatinine
Zschiesche <i>et al.</i> (1987) ^c MMA/SS welders post-shift	19		7.5 (2.5–15) $\mu\text{g}/\text{l}$; 4.5 (2.5–12) $\mu\text{g}/\text{g}$ creatinine
MIG/SS welders	66		11.2 (4.1–28) $\mu\text{g}/\text{l}$; 8.1 (3.5–21.4) $\mu\text{g}/\text{g}$ creatinine
Controls	–		2.3 (1.2–5.1) $\mu\text{g}/\text{g}$ creatinine; 1.8 (1.1–5.0) $\mu\text{g}/\text{g}$ creatinine
Angerer & Lehnert (1990) ^d MMA/SS welders	72 \pm 82 (< 50–260)	4.3 \pm 3.9 (< 1.8–18.1)	13.2 \pm 26.5 (0.6–164.7) $\mu\text{g}/\text{l}$
MIG/SS welders	100 \pm 82 (< 50–320)	3.9 \pm 4.2 (< 1.8–14.6)	26.8 \pm 53.6 (1.2–209.4) $\mu\text{g}/\text{l}$
MMA/SS and MIG/SS welders	–	5.6 \pm 4.1 (< 1.8–19.6)	20.3 \pm 18.3 (0.1–85.2) $\mu\text{g}/\text{l}$
Controls	–	< 1.8	0.9 \pm 1.4 (< 0.1–13.3) $\mu\text{g}/\text{l}$

^aMMA, manual metal arc; SS, stainless-steel; MIG, metal inert gas; TIG, tungsten inert gas

^bMedian and range; welding of high-nickel alloy (75% Ni)

^cMedian and 68% range

^dMean \pm SD (range)

(iii) *Manganese*

Most ferrous welding fumes contain manganese, and the range of manganese concentrations in blood and urine of exposed welders is considerably higher than the range in unexposed individuals, although there is considerable overlap (Järvisa-

lo *et al.*, 1983; Zschiesche *et al.*, 1986). Cutters of manganese steel had elevated plasma levels of Mn (up to 28 nmol/l) compared to baseline levels (11 nmol/l) (Knight *et al.*, 1985).

(iv) *Fluoride*

Increased urinary fluoride excretion levels were detected in arc welders using basic electrodes; the fluoride levels correlated with the total dust exposures (Sjögren *et al.*, 1984; see Table 6).

(v) *Lead*

High blood lead concentrations may occur after thermal cutting or welding of lead oxide-coated steel (Rieke, 1969). Increased concentrations of lead in blood were seen in welders in a ship repair yard (Grandjean & Kon, 1981).

(vi) *Aluminium*

Welders utilizing the MIG/Al technique had elevated blood and urinary levels of aluminium (Sjögren *et al.*, 1983b). After exposure to air concentrations of 1.1 (0.2-5.3) mg/m³ aluminium, the urinary aluminium level was 82 (6-564) µg/l (54 (6-322) µg/g creatine); after an exposure-free period, the concentration had decreased to 29 (3-434) µg/l among welders with more than ten years' exposure (Sjögren *et al.*, 1988).

(vii) *Barium*

Barium is found as a constituent in the coating of electrodes with a high nickel content for use on cast iron, and fumes from MMA/Ni welding can contain up to 40% barium (Stern, 1980b). Oldenburg (1988) found that up to 60% of barium in welding fumes was water-soluble. The concentration of barium in poorly ventilated spaces was about 20 mg/m³ (Zschiesche *et al.*, 1989); increased exposure to barium resulted in higher urinary excretion of barium (Dare *et al.*, 1984).

(c) *Exposures to welding gases*

Welding processes produce not only particulate matter but also some gaseous pollutants. The high temperature of the arc and the presence of large surface areas of metal at temperatures above 600°C lead to the production of various oxides of nitrogen from the atmosphere. Decomposition of carbonates present in MMA electrode coatings and flux cores produces a protective shield of active carbon dioxide; this gas is also used in MIG/MAG welding as a shield component. Carbon monoxide is also produced, and in some cases has been used as an experimental shield gas component, together with either argon or helium (American Welding Society, 1973, 1979). It has been postulated that the presence of carbon monoxide in the vicinity of welding in which nickel is present, either in the work piece or in the consumable,

could result in the formation of nickel carbonyl, which is extremely toxic (see pp. 387-388). Measurements with an instrument with a detection limit of 0.0001 ppm, however, indicated that nickel carbonyl is produced only occasionally in amounts that just exceed the detection threshold (Wiseman & Chapman, 1986).

Occupational exposures to gases have been described for the US industry by the American Welding Society (1973) and for the Swedish industry by Ulfvarson (1981). The results of the latter (see Table 7) reveal that most exposures to ozone arise during MIG and TIG welding of aluminium. Electric arc welding, and particularly MIG/SS, TIG/SS and MIG/Al welding, produce ozone by the ultra-violet decomposition of atmospheric oxygen; high concentrations are found mostly within 50 cm of the arc. The highest exposures to ozone are found in MIG welding of AlSi alloys: emission rates are 5-20 times those for MIG/SS. The presence of nitrogen monoxide, produced in large amounts by MMA welding, acts as a sink for ozone ($\text{NO} + \text{O}_3 = \text{NO}_2 + \text{O}_2$) so that little or no residual ozone is produced in this process (Sipek & Smårs, 1986).

Tables 6 and 7 provided an indication of the ranges of gases found with various processes and working conditions. A major problem in interpreting occupational measurements is that sometimes continuous recording instruments are used to sample concentrations behind the face shield, and sometimes grab samples are taken using sampling tubes placed in front of the shield.

(d) *Exposures to organic constituents of welding fumes*

Welding is frequently performed on mild-steel base plates coated with shop primer, and although welders are usually instructed to remove the primer from the welding zone, this is frequently not done. Welding on primed plate can significantly increase the total fume concentration, especially if a zinc-based primer has been used. Primers frequently contain organic binders based on alkyl, epoxy, phenolic or polyvinyl butyral. A significant amount of organic material occurs in the fumes originating from pyrolytic decomposition of the plastic. Benzo[*a*]pyrene is frequently found, its distribution being approximately log-normal: 50% of observed values lie below 10 ng/m³, while 98% lie below 1000 ng/m³ (Ulfvarson, 1981). Table 10 gives a summary of the concentrations of some of the organic substances identified in welding fume.

(e) *Other exposures*

Because welding can be performed under a wide variety of industrial settings, welders (or those engaged in welding) are potentially exposed to a great number of substances derived from the welding process itself or from other industrial activities being performed in the immediate vicinity (bystander effect). The range of incidental exposures during welding was reviewed by Zielhuis and Wanders (1986).

Table 10. Organic substances found during welding of painted mild steel

Paint type	Organic compound identified	Mean concentration (mg/m ³)	Reference
Not reported	Aldehydes, ketones, methylbenzofurane, phenol, dioxane, 2,4-hexadienal, 2-hexanone, alcohols, naphthalene, cresol, pyridine, saturated and unsaturated aliphatic and aromatic hydrocarbons (C ₆ -C ₁₄), etc.		Bille <i>et al.</i> (1976)
Not reported	Toluene	0.07	Ulfvarson <i>et al.</i> (1978c)
	Methylethylketone	0.02	
	Ethanol	0.2	
	Xylene	2.8	
	Benzene	< 0.05	
	Ethylbenzene	1.2	
	Isobutanol	< 0.006	
	<i>n</i> -Decane	0.1	
Epoxy	Alkylated benzenes ^a , aliphatic alcohols (C ₁ -C ₄) ^a , bisphenol A ^a , phenol ^a , aliphatic ketones (C ₃ -C ₅), acetophenone, aliphatic aldehydes (C ₁ -C ₄), aliphatic amines (C ₁ -C ₂)		Engström <i>et al.</i> (1988)
Ethyl silicate	Aliphatic alcohols (C ₁ -C ₄) ^a , butyraldehyde ^a , butyric acid, aliphatic aldehydes (C ₆ -C ₉), formaldehyde, acetaldehyde, acetic acid		
Polyvinyl butyral	Aliphatic alcohols (C ₁ -C ₄) ^a , butyraldehyde ^a , butyric acid ^a , formaldehyde ^a , acetaldehyde, acetic acid, phenol		
Modified epoxy ester	Aliphatic aldehydes (C ₁ -C ₉) ^a , aliphatic acids (C ₅ -C ₉) ^a , methyl methacrylate ^a , butyl methacrylate ^a , phenol ^a , bisphenol A ^a , alkylated benzenes, aliphatic alcohols (C ₁ -C ₄), phthalic anhydride, acrolein, aliphatic hydrocarbons (C ₆ -C ₇)		
Modified alkyd	Aliphatic aldehydes (C ₆ -C ₉) ^a , acrolein ^a , phthalic anhydride ^a , aliphatic acids (C ₅ -C ₉) ^a , alkylated benzenes, aliphatic alcohols (C ₁ -C ₄), formaldehyde, benzaldehyde		

^aMajor compound

Ultra-violet radiation is produced during all electric arc welding. The ranking order for emission is MIG > MMA > TIG, with typical fluxes of the order of 22 W/m² for MIG (at 1 m from the arc) and 0.7-2.5 W/m² for MMA welding (American Welding Society, 1979; Moss & Murray, 1979). Infra-red radiation is also produced, and emissions in excess of 3500 W/m² were found in a number of allied processes

(Grozdenko & Kuzina, 1982). Extremely low frequency and radio frequency radiation are produced by the 50-60-Hz currents used in welding, the interruption of current by metal transfer in the arc, and by the radio frequency generators used for igniting MIG and TIG arcs. Typical magnetic flux densities near welding generators range from 2 to 200 μT (Stuchly & Lecuyer, 1989), and current pulses of up to 100 000 A have been found to produce magnetic flux densities of upward of 10 000 μT at distances of 0.2-1.0 m from cables of transformers (Stern, 1987).

Most welders prepare their own work piece by mechanical grinding. This produces an aerosol which, although it has a relatively large aerodynamic diameter, is frequently directed towards the face of the welder. Aerosols from stainless-steel grinding can contain appreciable amounts of metallic nickel and chromium (Koponen *et al.*, 1981).

Asbestos may be encountered by welders in shipbuilding and construction, either from the spraying of asbestos coatings (as a fireproofing measure) or during repair and removal of insulation from pipes, ducts and bulkheads (Sheers & Coles, 1980; Stern, 1980a; Newhouse *et al.*, 1985). Asbestos gloves and heat-protective cloth have been traditionally used by welders.

Sand blasting, as used extensively in the past for surface preparation, can contribute to exposure to free silica, although such exposures have not been studied systematically; glass beads are usually now used.

(f) *Regulatory status and guidelines*

Occupational exposure limits for airborne chromium and nickel in various forms are given in the respective monographs. The occupational exposure limit (time-weighted average) in the USA for welding fume (total particulate) is 5 mg/m^3 (American Conference of Governmental Industrial Hygienists, 1988).

2.4 Chemical analysis of welding fumes and gases

Within recent years, standard practices have been developed for monitoring exposures in order to comply with occupational exposure limits for elements, compounds and nuisance dusts. Most measurements are made using personal monitoring systems with a small battery-driven pump at a flow of about 1 l/min connected to a cassette containing a membrane filter, which is mounted on the lapel or behind the face mask of welders for one or two periods of 3 h. Values are derived for time-weighted average concentrations of total fumes by weighing the filter before and after exposure; elemental concentrations are determined by chemical analysis of the filters (see American Welding Society, 1973; British Standards Institution, 1986). Attempts have also been made to make time-resolved analyses of exposures using special techniques (Barfoot *et al.*, 1981).

A wide range of methods has been used to analyse welding fumes. Proton-induced X-ray emission fluorescence energy analysis has been used for total analysis of the elements (Malmqvist *et al.*, 1986; Pedersen *et al.*, 1987). This is an inexpensive method for providing information on all elements heavier than phosphorus, but one disadvantage is that special calibration methods are necessary which are not always accurate, and no detailed comparison has been reported between the results of this method and wet chemical methods. Special methods can be used to determine specific elements: Malmqvist *et al.* (1986) used a nuclear reaction to determine fluorine and electron spectroscopy to determine the relative distribution of Cr[VI] to total Cr on particle surfaces. The diphenyl carbazide technique, sometimes as adapted by Thomsen and Stern (1979), has been used widely to determine the Cr[VI] content of soluble fractions (Abell & Carlberg, 1984; National Institute for Occupational Safety and Health, 1985). Energy dispersive X-ray analysis has been used to identify the elemental content of individual particles under the electron microscope (Grekula *et al.*, 1986), and X-ray diffraction methods have been used to identify crystalline species. X-Ray photoelectron spectroscopy and Auger electron spectroscopy have been used to identify chemical species on the surface of particles and, together with argon sputtering, to analyse deeper within the particles (Minni, 1986).

In only a few cases have systematic comparisons been made of the results of various techniques on the same fume samples. Oláh and Tölgyessy (1985) showed that the results of X-ray fluorescence and neutron activation methods with regard to MMA fume composition agreed to within 5%.

It is becoming common practice to collect two filters for analysis of SS fumes — one for speciation of chromium and analysis of nickel and the other for total elemental analysis. Gas fibre filters without organic binders or polyvinylchloride filters are recommended (e.g., van der Wal, 1985; Pedersen *et al.*, 1987) to avoid reduction of Cr[VI], which can be as much as 95% if cellulose acetate filters are used. Typical procedures for the analysis of SS fumes are as follows. One part of the filter is leached with distilled water or 1% sodium carbonate at room temperature for 30 min to extract the soluble fraction. Soluble Cr[VI] in the leachate (filtered through a 0.45- μ M Duropore membrane) is then determined by the diphenyl carbazide method (or by atomic absorption spectrometry). A second part of the filter is leached with 3% sodium carbonate and 2% sodium hydroxide in water (heated with a cover glass and avoiding formation of white fumes), and total Cr[VI] content is determined by the diphenyl carbazide method in the leachate. A third part of the filter is leached with nitric and hydrochloric acids for 1 h at 175°C and analysed by atomic absorption spectrometry to determine other elements and total chromium. A fourth part of the filter is fused with sodium carbonate for determination of total chromium in the melt solution (van der Wal, 1985).

Digestion of MIG/SS fumes in phosphoric acid:sulfuric acid (3:1) avoids the formation of insoluble residues, which can be as much as 20% of total fume mass for certain types, prior to analysis by atomic absorption spectroscopy for total metallic content (Pedersen *et al.*, 1987).