

METHODS FOR DETERMINING SOLUBLE AND INSOLUBLE Cr III AND Cr VI COMPOUNDS IN WELDING FUMES

WANDA MATCZAK, MSc and Jadwiga CHMIELNICKA, DSc

Department of Chemical Hazards, The Nofer Institute of Occupational Medicine, Lodz, Poland

Key words: Determination of chemicals in the air, Stainless steel welding fumes, Elements, Chromium

Abstract. An analytical procedure for simultaneous determination of soluble and insoluble Cr III and Cr VI compounds in welding fumes has been proposed. In the welding fume samples collected on a membrane filter, total chromium was determined with atomic absorption spectrophotometry (AAS). Glass filters with collected samples were divided into two parts. In one part of the sample, soluble and insoluble chromium was determined by means of AAS. The separation of soluble chromium III and VI was carried out on diphenylcarbazide resin. In the second part of the sample total chromium VI was determined by means of the colorimetric method with s-diphenylcarbazide. The difference in the results of these determinations allowed the calculation of the content of total Cr III, Cr III insolub. and Cr VI insolub. The results of determining chromium compounds in welding fumes samples collected in the welder's breathing zone and in experimental chambers are also presented in this paper. The content of total chromium in the fumes determined by AAS (from a membrane filter) and that calculated from the sum of soluble and insoluble chromium (from a glass filter) were concordant and within the limits of the admissible error for the method. Total chromium content in welding fume samples collected individually was found to range from 2.4—4.2%. The percentage of particular chromium compounds as compared to total chromium (100%) amounted: total Cr III — 34%, total Cr VI — 66%, soluble chromium — 66% and in this Cr III — 20% and Cr VI — 43%, insoluble chromium — 34% and in this: Cr III — 14% and Cr VI — 20%.

INTRODUCTION

The fumes which arise during manual metal arc welding of stainless steel (MMA/SS) and metal inert gas welding (MIG/SS) and tungsten inert gas welding (TIG/SS) contain chromium compounds of different solubility and at different level of oxidation. Among them, Cr VI insolub. is suspected of having carcinogenic potential (2, 7, 12, 26, 27).

In order to determine total chromium in the workplace atmosphere

Address reprint requests to W. Matczak, Department of Chemical Hazards, The Nofer Institute of Occupational Medicine, 8 Teresy Str., P.O. Box 199, 90-950 Lodz, Poland



the following methods are used most frequently: atomic absorption spectrophotometry, AAS (4, 15, 21, 28, 32), inductively-coupled plasma-atomic emission spectroscopy, ICP-AEC (23), x-ray fluorescence spectroscopy, XRF (22, 29), particle-induced x-ray emission, PIXE (3, 13), neutron activation analysis, NAA (9, 34).

Moreover, x-ray photoelectron spectroscopy, XDS (17, 34) and electron spectroscopy for chemical analysis, ESCA (3, 11, 34) techniques can be used for independent determination of Cr III and Cr VI. However, these methods are disadvantageous in that they require special instrumentation, which may not be readily available and they do not always allow simultaneous determination of soluble and insoluble chromium compounds at different oxidation levels.

Soluble chromium is usually determined by means of AAS in the samples collected by means of an impinger or in water (32), 1% Na_2CO_3 (32, 37), or 0.5n H_2SO_4 (24, 32) extracts from filters. The separation of soluble Cr III from soluble Cr VI is performed using ion exchange of diphenylcarbazide resins (16, 20).

For determining Cr VI (total or insoluble) the method by Thomsen and Stern is used (31). Some modifications of the method allow the elimination of the influence of the oxidation of Cr III to Cr VI which occurs during alkaline extraction either using sample aeration with nitrogen (24) or magnesium addition (0.5—1 mg Mg II per sample) (37) or, possibly, standard compound addition (5, 14, 25).

In view of the variety of existing methods for chromium determination, such aspects as air sampling, filter media, sample treatment and parallel determination of Cr III and Cr VI have not been considered here. For detailed discussion see references (1, 10, 14, 18, 19, 32, 36).

The aim of the present study was to establish an analytical procedure for determining soluble and insoluble trivalent and hexavalent chromium compounds in welding fumes.

MATERIAL AND METHODS

Sample collection and preparation:

1) Welding fumes samples from the MMA/SS welding of stainless steel (18% Cr, 8% Ni) and mild steel MS (1% Cr). Two air samples per working shift were collected in the welders' breathing zone (behind the face guard), each over a period of about 7 h. A two-stage Personal Air Sampling was applied (Casella AFC-123, flow-rate, 1.9 liters per minute). The respirable fraction of dust was collected on a membrane filter (Sartorius 11304, 0.8 μm Φ 37 mm) and a glass filter Whatman GF/A, Φ 37 mm).



2) Standard samples of MMA/SS welding fumes (I — 18% Cr, 8% Ni; II — 20% Cr, 24% Ni) from an experimental chamber, supplied by the Welding Institute, Gliwice.

3) Model samples containing 0.16 mg of Cr III solub. (CrCl_3 solution); 0.48 mg of Cr VI solub. ($\text{K}_2\text{Cr}_2\text{O}_7$ solution) and 0.16 mg of Cr VI insolub. (weighed portion of PbCrO_4), placed on membrane and glass filters.

Mineralization

In order to select the acids appropriate for mineralization of welding fumes samples, several acid mixtures were examined: HNO_3 ; $\text{HNO}_3/\text{HClO}_4$ (4 : 1); $\text{HNO}_3/\text{HClO}_4/\text{HF}$ (4 : 1 : 2) and $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (2 : 3).

The AAS analyses involving different types of mineralization were performed for two types of standard welding fumes samples (MMA/SS — I and MMA/SS — II) (3 samples each).

Simultaneously a standard chromium sample was prepared; 0.08 mg Cr solub. as $\text{K}_2\text{Cr}_2\text{O}_7$; spiked on a filter containing 5 mg PbCrO_4 i.e. 0.805 mg Cr insolub.

Analytical procedures

Determination of welding fumes by the gravimetric method

Before and after sampling, both the membrane and glass filters were dried at 105°C for one hour, then cooled in a desiccator (over CaCl_2) and weighed. Next, the dry substance mass was calculated by comparing filter mass before and after the sampling.

Methods of determining of welding fumes components

An outline of the method is shown in Fig. 1.

Membrane filter

One part of the sample from membrane filter was mineralized with concentrated HNO_3 , then diluted with 10% HNO_3 containing La, Cs, NH_4Cl salts (1 mg/ml), and Fe, Mn, Ni, Cr were determined by AAS (Zeiss Spectrophotometer) (15).

In the other part of the membrane filter, sample fluorides were determined after microdiffusion, using a colorimetric method with a zirconium-SPADNS complex (6).



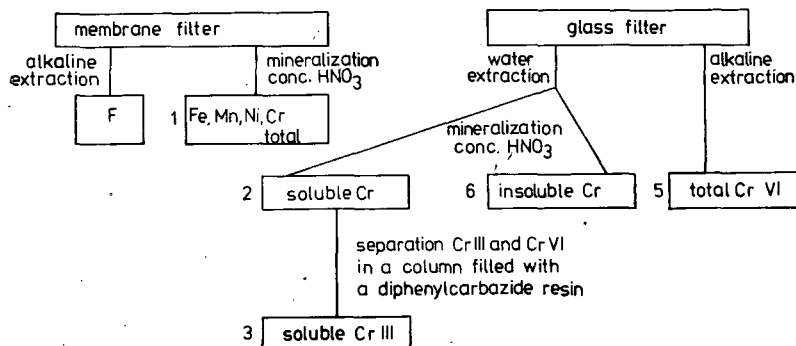


Fig. 1. Analytical procedure for determination welding fume elements.

Glass filter

In one part of the glass filter, after water extraction, total Cr solub. was determined by AAS. Cr III solub. was separated from Cr VI solub. in a column filled with diphenylcarbazide resin which retains Cr VI. Cr III solub. was determined in the eluat. The insoluble residue underwent mineralization with concentrated HNO_3 and then total Cr insolub. was determined by AAS (15). The second part of residue from the glass filter was used to find the content of total Cr VI by the colorimetric method with s-diphenylcarbazide (DPC) after alkaline extraction of the sample (14, 25).

All other chromium extracts were calculated as follows (Tables 2, 3):

- Cr VI solub. (column 4): as the difference between total Cr solub. and Cr III solub.,
- total Cr III (column 9): as the difference between total Cr and total Cr VI,
- Cr VI insolub. (column 8): as the difference between total Cr VI and Cr VI solub.,
- Cr III insolub. (column 7): as the difference between total Cr III and Cr III solub.,
- total Cr insolub. (column 6): as the difference between total Cr and total Cr solub.

RESULTS

Table 1 shows the percentage of particular welding fume components (x), with relative standard deviation of the values (RSD) in standard dust from experimental chambers (MMA/SS — I and MMA/SS — II).

As revealed by the study the acids used in the following configurations: HNO_3 , $\text{HNO}_3/\text{HClO}_4$, $\text{HNO}_3/\text{HClO}_4/\text{HF}$ are most suitable for the



TABLE 1. The Percentage (x) and Relative Standard Deviation ($\pm$ RSD) of Particular Components in the MMA/SS Wel-
ding Fumes Samples After Mineralization With Various Acids

No Mineraliza- tion with	% content (x) $\pm$ RSD (n = 3)						% recovery Cr * $\pm$ RSD (n = 4)	
	Sample I			Sample II				
	Fe	Mn	Cr	Ni	Fe	Mn	Cr	Ni
1 HNO ₃	11.1 $\pm$ 0.01	4.8 $\pm$ 0.02	5.9 $\pm$ 0.06	0.74 $\pm$ 0.14	9.8 $\pm$ 0.11	3.0 $\pm$ 0.19	7.7 $\pm$ 0.14	3.1 $\pm$ 0.17
2 HNO ₃ /HClO ₄	10.9 $\pm$ 0.06	4.9 $\pm$ 0.02	5.7 $\pm$ 0.05	0.73 $\pm$ 0.10	8.3 $\pm$ 0.04	3.0 $\pm$ 0.08	8.1 $\pm$ 0.08	2.9 $\pm$ 0.03
3 HNO ₃ /HClO ₄ /HF	10.1 $\pm$ 0.10	4.9 $\pm$ 0.02	5.9 $\pm$ 0.04	0.88 $\pm$ 0.18	8.8 $\pm$ 0.10	3.1 $\pm$ 0.03	7.5 $\pm$ 0.10	2.8 $\pm$ 0.11
4 H ₂ SO ₄ /H ₃ PO ₄	7.5 $\pm$ 0.02	4.6 $\pm$ 0.11	5.1 $\pm$ 0.14	0.65 $\pm$ 0.08	8.3 $\pm$ 0.15	3.8 $\pm$ 0.12	8.3 $\pm$ 0.11	3.3 $\pm$ 0.17

* — in standard chromium samples

TABLE 2. Evaluation of Methods for Determining Different Chromium Compounds According to Suggested Procedure

No	Chromium compound	Limit of determination µg per sample	Amount Cr placed on filter in mg (n = 10)	Cr recovery %	Calculation	Standard deviation SD	Relative standard deviation RSD
1.	Cr total		0.800	102.9	0.972	0.074	0.09
2.	Cr soluble		0.640	86.3	1.16	0.032	0.05
3.	Cr III soluble		0.160	89.3	1.12	0.017	0.10
4.	Cr IV soluble		0.480	85.4	1.17	0.035	0.07
5.	Cr VI total		0.640	102.3	0.978	0.033	0.08
6.	Cr insoluble		0.160	98.4	1.016	0.021	0.13
7.	Cr III insoluble			102.5	—	0.046	0.28
		1—2 **				0.080 *	0.49 *
		/1—5/—3 **	0		—	0.017	—
						0.093 *	
8.	Cr VI insoluble		0.160	101.9	—	0.026	0.16
		5—4 **				0.064 *	0.39 *
9.	Cr III total		0.160	100	—	0.032	0.20
		1—5 **				0.091 *	0.57 *

* — estimated for an individual result, according to formula $SD^* = \sqrt{SD_i^2 + SD_j^2}$

** — calculated as the difference

mineralization of dust from the welding of highly alloyed chromium-nickel steels. The average content of dust components was found to be similar. For the mixture of H_2SO_4 and H_3PO_4 a wide dispersion of results, low recovery and low precision in determining particular components was found.

Therefore, the mixture is not recommended for mineralization. Fig. 1 shows a suggested procedure for determining soluble and insoluble trivalent and hexavalent chromium compounds in the welding fumes.

Table 2 presents data from the analysis drafted in Fig. 1. The methods for determining total Cr, soluble Cr, Cr III solub., Cr VI solub. and total Cr VI have been found to be in accordance with the requirements for air analysis (recovery exceeding 80%, RSD — 10%).

The calculations of other chromium forms: Cr insolub., Cr III insolub., Cr VI insolub., total Cr III, can be regarded only as tentative, due to the wide dispersion of results (RSD: 10%).

Fig. 2 presents the content of particular components in individual and standard samples of welding fumes which underwent mineralization with concentrated HNO_3 as shown in Fig. 1. The percentage of chromium in the fumes varied from 2.4% to 4.2% but in the standard samples it amounted to 5.9% (sample I) and 7.7% (sample II).

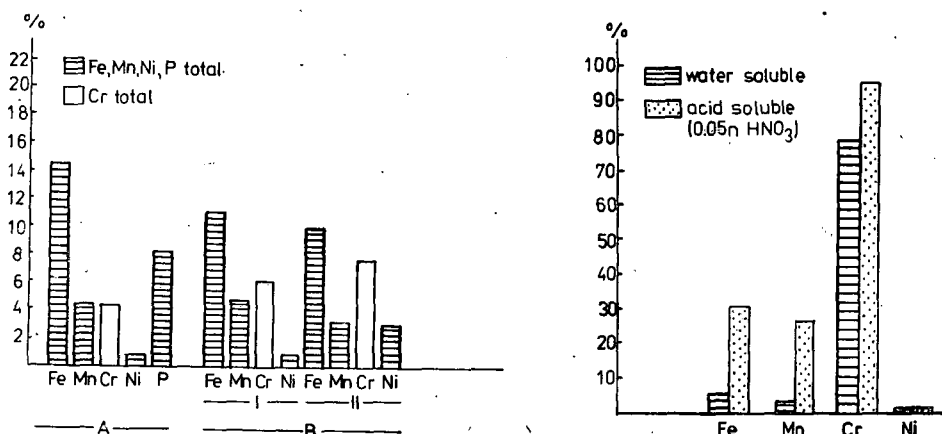


Fig. 2. The percentage content of the elements in MMA/SS welding fumes. A — the samples collected in the breathing zone of welders; B — the standard samples the laboratory arrangement — collected in the exposure chamber (samples I, II).

Fig. 3. The relative content of the soluble elements in the MMA/SS welding fumes.

Fig. 3 displays relative content of soluble chromium compounds in individual samples from the welders breathing zone. The high content

TABLE 3. The Ratio Between the Percent Content of Particular Chromium Compounds and Total Chromium in MMA/SS Welding Fumes

% Particular chromium compounds/total chromium													
Sample	Column No	Total Cr	Soluble			Total Cr VI	Insoluble			Total Cr III			
			Cr	Cr III	Cr VI		Cr	Cr III	Cr VI				
1	2 + 6	2	3	4	5	1-2 */6	7 = 9 - 3 */**8 = 5 - 4	9 = 1 - 5 */**					
100/3.5/	100/3.7/	64.8	18.9	45.9	70.3	35.2/31.4	10.8/11.4	24.3	29.7/25.7				
collected in the welders breath- ing zone	100/3.1/	71	16.2	54.8	80.1	29	0	32.2	12.9				
	100/3.0/	63.3	26.6	36.7	40	36.7	33	3.7	60				
	100/5.9/	69.1	16.4	52.7	72.7	30.9/33.3	10.9/14.6	20	27.3/29.8				
from an experi- mental chamber	100/5.5/												
	100/7.7/	64.3	5.7	58.6	80	35.7	14.3	21	20				
	100/7.0/					39.2	18.9		24.3				

* — value calculated according to column 1.

/ — % content of total Cr in welding fumes

** — value calculated to column (2 + 6)

of chromium compounds soluble either in water or in 0.5n HNO₃ should be emphasized. The ratio between Cr solub. and total Cr amounted to 66.40% (water extraction) and 93.00% (acid extraction). The ratio between soluble and total iron was 5.00% for water and 30.00% for acid extraction. For manganese compounds the values were 2.00% and 24.00%, respectively.

In contrast to the previous results nickel compounds were found to be insoluble (the soluble nickel compounds were below the limit of detection in all determinations).

Table 3 presents the ratio between the content of particular chromium compounds in total chromium determined as shown in Fig. 1. The percentages of total Cr in welding fumes determined in the membrane filter (column 1) i.e. 3.50% for individual sample, 5.90% for standard sample I and 7.70% for standard sample II, corresponded to the sums of soluble and insoluble chromium found in the glass filter (column 2+6) i.e. 3.70%, 5.50% and 7.00%, respectively. The differences between the results were less than the permissible error for the analytical method applied. The comparison between relative contents of Cr insolub. which were calculated as a result of subtracting column 2 from column 1 and determined directly by AAS (column 6), produced similar values i.e. 35.2 and 31.4 for individual sample, 30.9 and 33.3 for standard sample I, 35.7 and 39.2 for standard sample II, respectively. As regards the content of Cr III in total Cr — the values calculated from total Cr determined directly (column 1) or as the sum of soluble and insoluble chromium fractions (column 2 + 6) for particular samples were also found to be similar and amounted to, respectively;

for Cr III insolub. — 11.40% and 10.80%; 14.00% and 10.90%; 18.90% and 14.40%;

for Cr III total — 25.70% and 29.70%; 29.80% and 27.30%; 24.30% and 20.00%.

As shown by the data, individual samples of MMA/SS welding fumes, Cr VI solub. ranged from 36.70%—54.80%, Cr VI insolub. from 3.30% to 32.20% and Cr III insolub. — from 0 to 33% of the total Cr. The wide range of the concentrations of Cr VI insolub. may be due to the variability of welding parameters and redox processes. As for the standard samples from experimental chambers, the findings were slightly different. Cr VI insolub. amounted to 20.00% and 21.40% while Cr III insolub. — to 10.90% and 14% of total Cr.

The content of particular chromium compounds in MMA/SS welding fumes was found to be: 66% for Cr solub. and 20% for Cr VI insolub. or, alternatively, 77% for Cr solub. and 10% for Cr VI insolub. if the recovery coefficient is taken into account (Table 2, Fig. 4).



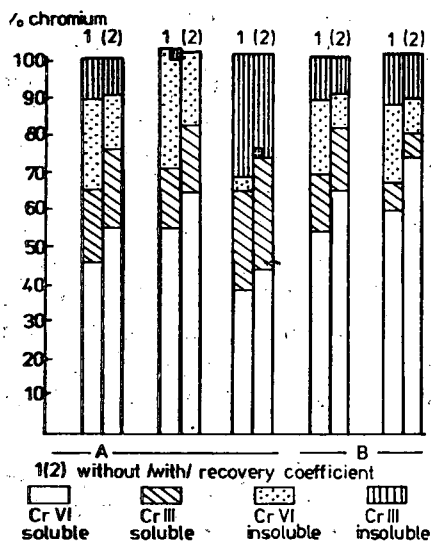


Fig. 4. The relative content of the different chromium compounds in the MMA/SS welding fumes.

DISCUSSION

According to the literature, the two methods of sampling on a glass filter and of collecting two samples on glass and membrane filters at the same time are recommended for the determining of concentrations of different chromium fractions.

* In the case when two samples are collected, the sample from the membrane filter is used for the determination of total Cr (3, 18, 36) whereas, particular chromium fractions are determined in the glass filter sample (4, 15, 30, 32).

For analytical procedures that have been described, neither the complete estimation of recovery nor the precision of all the components analysed has not been published.

The procedure developed in the present study allows determination of the content of total Cr, Cr solub., Cr III solub., total Cr VI, Cr insolub. and to calculate, from the differences between the results, the amounts of all the other chromium fractions, i.e.: Cr VI solub., Cr III insolub., Cr VI insolub. and total Cr III. As revealed by the study results the limit of quantitation for particular chromium fractions amounted to 2 μg per sample for total Cr and total Cr VI, and 10 μg per sample for Cr solub., Cr III solub. and Cr VI solub.

The recovery of chromium fractions from the filters was found to exceed 80% with the relative standard deviation less than 10% (Table 2).

The content of chromium fractions that has been calculated as the

difference between particular results can be regarded only as tentative due to the wide dispersion of results (RSD 10%).

Most of the authors (3, 8, 9, 10, 13, 20, 27, 28, 33, 36) regard Cr VI compounds in MMA/SS welding fumes as soluble whereas they see Cr III (and/or Cr⁰) as insoluble. Nonetheless, according to Thomsen and Stern (22, 32), Dare (8) and Malmqvist (13) the proportion of particular fractions is dependent on the welding parameters, the amount of chromium determined and the actual methods applied.

The findings indicated that it was Cr VI that prevailed among soluble Cr compounds. With reference to Cr VI insolub., different values were found in the samples from the welders' breathing zone. In the samples from the experimental chamber Cr VI insolub. constituted up to 20% of total Cr.

It can be concluded that the determination of Cr VI insolub. calculated as a difference between total Cr VI and Cr VI solub. involved considerable error which implies a necessity to modify the method.

In view of the carcinogenic potentials of Cr VI insolub. a more rational analytical procedure should be developed. Moreover, the inconsistency of reports on the presence Cr VI insolub. in MMA/SS welding fumes makes it necessary to undertake further investigations.

REFERENCES

1. Bhargava O. P. (et al): Study of Analytical Method for Hexavalent Chromium. *Am Ind Hyg Assoc J* 44, 433, 1983. — 2. Becker N., Claude J., Frenzel-Beyme R.: Cancer risk in arc welders exposed to chromium-nickel-containing fumes. Proceedings of the International Conference on Health Hazards and Biological Effects of Welding Fumes and Gases: Copenhagen 19–21 February 1985, Excerpta, Medica, Amsterdam-New York-Oxford 1986. — 3. Bohgard M., Jangida B. L., Akselsson K. R.: An analytical procedure for determining chromium in samples of airborne dust. *Ann Occup Hyg* 22, 241–251, 1979. — 4. British Standard: Fume from welding and allied processes. Part 1. Guide to methods for the sampling and analysis of particulate matter, 1983. — 5. Carelli G. (et al): Interferences in the spectrophotometric *s*-diphenyl-carbazide determination of environmental hexavalent chromium in a chromium and zinc plating plant. *Scand J Work Environ Health* 7, 56–61, 1981. — 6. Ciosek A., Kesy-Dąbrowska I.: Determination of fluorine compounds in the air. *Med. Pracy* 23, 6, 5, 1982 (in Polish). — 7. Criteria for a Recommended Standard ... Occupational Exposure to Chromium VI. 171–176, US Department of Health, Education and Welfare, Publ. NIOSH, 76–129, 1976. — 8. Dare P. R. M. (et al): Letters to the editor: Analysis of chromium in welding fume. *Am Occup Hyg* 28, 2, 275–277, 1984. — 9. Fishbein L.: Overview of analysis of carcinogenic and mutagenic metals in biological and environmental samples. I. Arsenic, beryllium, cadmium, chromium and selenium. *Int J Environ Anal Chem* 17, 2, 123, 1984. — 10. Gray C. N. (et al): The Evolution of hexavalent Chromium in Metallic Aerosols. *Am Ind Hyg Assoc J* 44, 384–388, 1983.



11. Lautner G. M. (et al): Measurement of chromium VI and chromium III in stainless steel welding fumes with electron electroscopy for chemical analysis. *Am Ind Hyg Assoc J* 39, 8, 1978. — 12. Malczewska B. (et al): Carcinogenic substances in work environment. Chromium and some chromium compounds. V. 3, Institute of Occupational Medicine, Lodz, 1987. — 13. Malmqvist K. G. (et al): Process — dependent characteristics of welding fume particles. Proceedings of the International Conference on Health Hazards and Biological Effects of Welding Fumes and Gases, Copenhagen 18–21 February 1985, Excerpta, Medica, Amsterdam-New York-Oxford, 1986. — 14. Matczak W., Rogaczewska T., Solnica J. T.: Determination of hexavalent chromium compounds in air. *Med Pracy* 37, 3, 197–205, 1983 (in Polish). — 15. Matczak W., Chmielnicka J.: Method and Evaluation of exposure to welding fumes of nickel-chromium steel. *Med Pracy*, 39, 3, 175, 1988 (in Polish). — 16. Matczak W., Chmielnicka J.: Method for simultaneous determination of soluble Cr III and Cr VI compounds in air. *Chem Anal* (in press) (in Polish). — 17. Minni E. (et al): A study of the chemical structure of particles in the welding fumes of mild and stainless steel. *J Aerosol Sci*, Vol. 15, No 1, 57–68, 1984. — 18. Moons A. M. M.: A selective quantitative analytical method for hexavalent, trivalent and total chromium in welding fumes. IMG-TNO Report F 1984. — 19. Moreton (et al): Investigation of techniques for the analysis of hexavalent chromium, total chromium and total nickel in welding fume: a co-operative study. *Ann Occup Hyg* 25, 137, 1983. — Naranjit D., Thomassen Y., Van Loon J. C., *Anal Chim Acta* 110, 307, 1979.

21. NIOSH Manual of Analytical Methods: Chromium and compounds, as Cr. 3rd ed, V. 1, Method 7024, US Department of Health and Human Services. Publ. NIOSH, 84–100, 1984. — 22. NIOSH Manual of Analytical Methods: Welding and brazing fume, 3rd ed., V. 2, Method 7200, US Department of Health and Human Services, Publ. NIOSH, 1984. — 23. NIOSH Manual of Analytical Methods: Elements (ICP), 3rd ed., Vol. 1, Method 7300, US Department of Health and Human Services. Publ. NIOSH, 1984. — 24. NIOSH Manual of Analytical Methods: Chromium, hexavalent, 3rd ed., V. 1, Method 7300, US Department of Health and Human Services Publ. NIOSH, 1984. — 25. Polish Standard: PN-87/Z-04126.03. Determination of hexavalent chromium at work places by colorimetric method with alkaline extraction of sample. PKNMiJ, 1987 (in Polish). — 26. Reuzel P. G. J. (et al): Carcinogenicity and in vitro genotoxicity of the particulate fraction of two stainless steel welding fumes. Proceedings of the International Conference on Health Hazards and Biological Effects of Welding Fumes and Gases. Copenhagen 18–21 February 1985, Excerpta, Medica Amsterdam-New York-Oxford, 1986. — 27. Stern R. M.: A chemical, physical and biological assay of welding fumes. In: The Hungarian-Finish-Scandinavian symposium on industrial dust problems. Institute of Occupational Health, Helsinki, pp. 44–58, 1977. — 28. Stern R. M. (et al): Health Hazards and biological effects of welding fumes and gases. Proceedings of the International Conference on Health Hazards and Biological Effects Welding Fumes and Gases, Copenhagen 18–21 February 1985, Excerpta Medica, Amsterdam-New York-Oxford, 1986. — 29. Takada T. (et al): Simultaneous determination of multielement in air borne particulate samples by x-ray fluorescence spectrometry. *Jap J Industr Health*, 25, 4, 235, 1983. — 30. TGL 3261/01 Messung und Bewertung von Schweißrauch und gasen. Sumanische Grenzwerte für ausgewählte werkstoffe und Verfahren.

31. Thomsen E., Stern R. M.: A Simple Analytical Technique for the Determination of Hexavalent Chromium in Welding Fumes and other Complex Matrices.



Scand J Work Environ Health 5, 386—403, 1979. — 32. Thomsen E., Stern R. M., Pedersen B.: Exposure monitoring and chemical analysis of welding fume. Proceedings of the International Conference on Health Hazards and Biological Effects of Welding and Gases, Copenhagen 18—21 February 1985, Excerpta Medica, Amsterdam-New York-Oxford 1986. — 33. Toła S. (et al): Urinary chromium as an indicator of the exposure of welders to chromium. Scand J Work Environ and Health, 3, 192—202, 1977. — 34. Tuomisari M. (et al): Characterisation of Stainless Steel Welding Fumes. International Institute of Welding Annual Assembly, Trondheim 1983, IIW/IIS, doc. VIII-2037-83, 1983. — 35. Vorpahl K. W. (et al): Chrome alloy welding study. Am Ind Hyg Assoc J 37, 566—569, 1976. — 36. Wal J. F. van der.: Exposure of welders to fumes Cr, N, Cu and Gases in Dutch Industries. Ann Occup Hyg, Vol. 29, No 3, ipp. 377, 1985. — 37. Zatká V. J.: Speciation of Hexavalent Chromium in Welding Fumes. Interference by Air Oxidation of Chromium. Am Ind Hyg Assoc J 46, 6, 327—331, 1985.

Received for publication: 9.08.1989

Accepted for publication: 30.11.1989

