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Application of high performance liquid chromatography with inductively coupled plasma mass spectrometry (HPLC–ICP-MS) for determination of chromium compounds in the air at the workplace

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A B S T R A C T

The toxicity and bioavailability of chromium species are highly dependable on the form or species, therefore determination of total chromium is insufficient for a complete toxicological evaluation and risk assessment. An analytical method for determination of soluble and insoluble Cr (III) and Cr (VI) compounds in welding fume at workplace air has been developed. The total chromium (Cr) was determined by using quadruple inductively coupled plasma mass spectrometry (ICP-MS) equipped with a dynamic reaction cell (DRC®). Soluble trivalent and hexavalent chromium compounds were determined by high performance liquid chromatography with inductively coupled plasma mass spectrometry (HPLC–ICP-MS). A high-speed, reversed-phase CR C8 column (PerkinElmer, Inc., Shelton, CT, USA) was used for the speciation of soluble Cr (III) and soluble Cr (VI). The separation was accomplished by interaction of the chromium species with the different components of the mobile phase. Cr (III) formed a complex with EDTA, i.e. retained on the column, while Cr (VI) existed in the solutions as dichromate. Alkaline extraction (2% KOH and 3% Na_2CO_3) and anion exchange column (PRP-X100, PEEK, Hamilton) were used for the separation of the total Cr (VI). The results of the determination of Cr (VI) were confirmed by the analysis of the certified reference material BCR CRM 545 (Cr (VI) in welding dust). The results obtained for the certified material (40.2 ± 0.6 g kg^{-1}) and the values recorded in the examined samples (40.7 ± 0.6 g kg^{-1}) were highly consistent. This analytical method was applied for the determination of chromium in the samples in the workplace air collected onto glass (Whatman, Ø 37 mm) and membrane filters (Sartorius, 0.8 μm, Ø 37 mm). High performance liquid chromatography with inductively coupled plasma mass spectrometry is a remarkably powerful and versatile technique for determination of chromium species in welding fume at workplace air.

1. Introduction

In environmental samples, chromium occurs most frequently in two oxidation states, trivalent chromium Cr (III) and hexavalent chromium Cr (VI). The toxicity of Cr depends primarily on its chemical form. Cr (III) compounds are much less toxic than those of Cr (VI) [1–5]. The International Agency for Research on Cancer (IARC) has classified hexavalent chromium compounds as carcinogenic to humans (Group 1). That is why it is very important, from the point of view of the assessment of sanitary conditions, to determine both Cr (VI) and Cr (III) with different solubility present in dust emissions at the workplace.

Regulators and legislators are becoming increasingly aware that the toxicity of trace elements is more dependent on the amount and character of their chemical forms than on the total concentration. The American Conference of Government Industrial Hygienists (ACGIH®) has set threshold limit values (TLV®)—time weighted average (TWA) for water-soluble Cr (VI), water-insoluble Cr (VI) and Cr (III) compounds at the following levels: 0.05 mg/m^3, 0.01 mg/m^3 and 0.5 mg/m^3 of air, respectively [6]. In Poland, the maximum admissible concentration (MAC) for occupational exposure to total (both soluble and insoluble) Cr (VI) compounds in dust and aerosols amounts to 0.1 mg/m^3 of air and for Cr (III) compounds to 0.5 mg/m^3 of air [7]. Based on the differences in their toxicity, speciation analysis is needed to distinguish between the different forms of chromium. Water-insoluble Cr (VI) compounds are carcinogenic (lung cancer), water-soluble Cr (VI) compounds also appear to be carcinogenic and allergenic [5,8–9]. Insoluble chromium Cr(VI) compounds can be a cause of an increased risk of development of lung tumors in the exposed group, whereas soluble chromium Cr(VI) compounds may lead to an increased risk of cancer of the upper respiratory tract, such as nasal septum cancer [6]. In the conditions of occupational exposure, chromium compounds are absorbed mainly in the respiratory tract.

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The absorption performance is not exactly known and depends on the solubility of the various compounds in water. High concentrations of chromium in the lungs of persons occupationally exposed to chromium indicate that at least a part of chromium is deposited in the water-insoluble form. Cr (III) compounds are not carcinogenic (IARC, Group 3) [5].

The main processes that involve exposure to Cr (VI) compounds are stainless steel welding, chrome plating and other processes. Welding is the predominant source of exposure to chromium compounds in occupational settings. Worldwide, millions of employees are exposed to welding fumes either as professional or occasional welders. The International Agency for Research on Cancer (IARC) has classified welding fumes as “possibly carcinogenic to humans” (Group 2B) [5]. Welders are occupationally exposed to airborne chromium compounds as constituents of welding fumes. Depending of the welding technique and the metal content of the base material, e.g. an electrode, welding fumes contain different amounts of various chromium species, e.g. hexavalent chromium such as $K_2Cr_2O_4$ and CrO_3 soluble in water, $ZnCr_2O_4$, $Na_2Cr_2O_4$, $PbCrO_4$ insoluble in water, trivalent chromium such as K_2NaCrF_6. Stainless steel welders may be exposed to all chemical forms of chromium. During the welding process, different levels of Cr may be present in the atmosphere [10–13]. The fumes which are formed during manual metal arc welding of stainless steel (MMA/SS) and metal inert gas welding of stainless steel (MIG/SS) contain chromium compounds of different solubility and different levels of oxidation.

The most popular techniques for the determination of the total concentration of chromium compounds in the workplace air have been flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GF-AAS), electrothermal atomic absorption spectrometry (ET-AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). However, these methods do not allow for the quantitative determination of various forms of chromium compounds [2–4]. Therefore, the hyphenated technique of HPLC–ICP-MS has become a popular technique for chromium speciation analysis [14–22].

The aim of this study was to develop a method to conduct determination of soluble and insoluble chromium species in workplace air by HPLC–ICP-MS.

2. Experimental

2.1. Instrumentation

An ELAN DRC-e ICP-MS with a Dynamic Reaction Cell (PerkinElmer SCIEX, Waltham, MA, USA) was used for the chromium determination. A cyclonic spray chamber (PerkinElmer, Inc., Shelton, CT, USA), a Meinhard® Type A quartz nebulizer and a four-channel peristaltic pump were used. A Series 200 HPLC (PerkinElmer, Inc., Shelton, CT, USA) was used to separate the chromium chemical forms. A high-speed, reversed-phase CR C8 column (PerkinElmer Inc., Shelton, CT, USA) was used for the speciation of soluble Cr (III) and soluble Cr (VI)—method 1. An anion exchange, Hamilton PRP-X100 column (150 × 4.6 mm, 5 μm, PEEK, Hamilton, USA) was used for the separation of the total Cr (VI) compounds—method 2. For the purpose of the separation of the total Cr(VI) we applied the Hamilton PRP-X100 column, because it has a wider range of pH, namely 1–13, and it is better suited for the analysis of samples which are eluted with highly alkaline solutions with a relatively high pH. Detailed parameters are presented in Tables 1 and 2.

Table 1
Instrument parameters for the separation of soluble Cr (III) and Cr (VI) species—method 1.

HPLC	PerkinElmer Series 200
Column	3 × 3™ CR C8 (Part no. 0258-0191) PerkinElmer, Inc., Shelton, CT, USA [14]
Column temperature	Ambient 25 °C [14]
Autosampler flush solvent	5% methanol/95% HPLC-grade water [14]
Mobile phase	1 mM TBAH (Tetrabutylammonium hydroxide)+0.6 mM EDTA (potassium salt); pH=7.2–7.4. The pH was adjusted by adding 10% HNO_3
Flow rate	1.5 mL/min isocratic [14]
Run time	3 min [14]
Sample preparation	Dilute with mobile phase
Sample injection volume	50 μL [14]
Total analysis time	3 min [14]
Detection ICP-MS	PerkinElmer SCIEX ELAN DRC-e ICP-MS
Nebulizer	Meinhard® Type A quartz
Spray chamber	Quartz Cyclonic
RF power	1100 W
Plasma air flow	15 L/min
Monitored ion m/z	$^{52}Cr^+$
Dwell time	1000 ms
Reaction gas	Methane (CH_3)
Methane flow	1.0 mL/min

Table 2
Instrument parameters for the separation of the total Cr (VI)—method 2.

HPLC	PerkinElmer Series 200
Column	Hamilton PRP-X100 (150 × 4.6 mm, 5 μm)
Column temperature	Ambient 25 °C
Autosampler flush solvent	5% methanol/95% HPLC-grade water
Mobile phase	50 mM CH_3COONH_4+10 mM $ClNaO_4$; pH=9
Flow rate	1.4 mL/min isocratic
Run time	6 min
Sample preparation	Dilute with mobile phase
Sample injection volume	200 μL
Total analysis time	6 min
Detection ICP-MS	PerkinElmer SCIEX ELAN DRC-e ICP-MS, conditions ICP-MS such as shown in Table 1.

2.2. Reagents

Soluble chromium Cr (VI) standard stock solutions (10 mg Cr/mL) were prepared from potassium dichromate ($K_2Cr_2O_7$, Sigma-Aldrich, A.C.S. reagent) by dissolution in water. The insoluble chromium Cr (VI) standard was prepared from lead dichromate ($PbCrO_4$, Merck, 107512) by weighing 0.32 mg of $PbCrO_4$ containing 50 μg of insoluble Cr. Soluble Cr (III) standard stock solutions were prepared from a commercially available standard solution (Merck 9948, $CrCl_3$). For the extraction, concentrated nitric acid HNO_3 (J.T. Baker® Instra-analyzed 69–70% for trace metal analysis) was used. All intermediate and working standards were prepared in the pH-adjusted TBAH/EDTA mobile phase and allowed to stand for approximately 1 h prior to the use.

The mobile phase for soluble Cr (III) and Cr (VI) was prepared by dissolving the appropriate amounts of tetrabutylammonium hydroxide (TBAH, J.T. Baker Analyzed® HPLC reagent, 1.0 mM solution in methanol) and the dipotassium salt of ethylenediaminetetraacetic acid (0.6 mM EDTA, Sigma-Aldrich) in methanol [14,15]. This solution was then adjusted to a pH of 7.2–7.4. All standard solutions containing Cr (III) were kept at room temperature of 20 °C for 45 min prior to the analysis to allow the Cr (III)–EDTA complex to form [14,15].

For the total Cr (VI), the mobile phase was prepared by dissolving the appropriate amounts of ammonium acetate (J.T. Baker®, Baker HPLC Analyzed, 50 mM solutions in methanol) and sodium perchlorate (Sigma-Aldrich, 10 mM solutions in methanol). Unless noted, reagent grade chemicals were used without further purification. The determination of the total chromium concentration was performed with the multi-element reference standard solution for ICP-MS (Multi-Element Calibration Standard 3, PerkinElmer). Deionized water (18 MΩ) (Milli-Q Plus, Millipore Corp., Billerica, MA, USA, water-purification system) was used to prepare all working stocks, standards and spiking solutions.

Certified Reference Material: BCR CRMs 545 (Cr (VI) in welding dust Community Bureau of Reference, Brussels, Belgium) was used as a quality control sample for the evaluation of the analytical results of the total Cr and Cr (VI) determination [23]. The laboratory participates in the Interlaboratory Quality Control Program For Metals On Filters (PICC-MET), organized by the National Center of Conditions of Work in Barcelona, Spain.

2.3. Samples and standards preparation for analytical procedure

Membrane filters Sartorius (Goettingen, Germany), 0.8 μm, cellulose nitrate membrane filters of 37 mm diameter and glass microfiber filters Whatman (Buckinghamshire, UK), of 37 mm diameter were used. Calibration standards for the determination of chromium species were prepared by spiking the standards on the filters. The membrane and glass filter samples were spiked with mixtures of 50 μg of soluble Cr (III) and Cr (VI) and insoluble Cr (VI) by weighing 0.32 mg of CrO_4Pb containing 50 μg of insoluble Cr (VI), and allowed to dry for 24 h at ambient temperature.

2.3.1. Samples and standards preparation for determination of total chromium compounds

Calibration standards were prepared at 0.01, 0.05, 0.1, 0.5 and 1 μg/mL levels using the 10 μg/mL Multi-Element Calibration Standard 3, PerkinElmer. The membrane filter samples were spiked with mixtures of 100 μg of soluble Cr (III) and Cr (VI) and 50 μg of insoluble Cr (VI) by weighing 0.32 mg of $PbCrO_4$. Next, the membrane filters were mineralized on a hotplate at about 150 °C using concentrated HNO_3. The samples were diluted in 0.1 M HNO_3 to 1000 mL. The diluted samples were analyzed for the total chromium content directly by the ICP-MS technique.

2.3.2. Samples and standards preparation for determination of soluble Cr (III) and Cr (VI)

Calibration standards were prepared at 2.5, 5, 10, 25 and 50 μg levels using 500 μg/mL of mixed species of working stock solutions of soluble Cr (III) and Cr (VI) that were spiked on the glass filters. In addition to the reference scale, some samples were also prepared to determine the accuracy of the method. The glass filter samples were spiked with mixtures of 50 μg of soluble Cr (III) and 50 μg of soluble Cr (VI). The filters were washed with 0.05 M nitric acid and water 1/1 (v/v) to 10 mL (pH –4) and subjected to agitation in ultrasonic bath for 30 min at ambient temperature. For the elution of soluble compounds of Cr (VI) and Cr (III) we used a solution with pH—4, so that we could avoid the effect of the transformation of Cr (VI) into Cr (III). Afterwards, the content was quantitatively filtered through membrane filters and diluted ten times with de-ionized water. Next, the samples were diluted ten times with a mobile phase (1.0 mM TBAH and 0.6 mM EDTA) and allowed to sit at room temperature for 30–40 min prior to analysis, to allow the Cr (III)–EDTA complex to form [14,15]. The prepared samples were placed in a glass vial and 50 μL was injected on the column and analyzed with the HPLC–ICP-MS technique.

2.3.3. Samples preparation for determination of the total Cr (VI)

The calibration standards were prepared by spiking the glass filters with mixtures of soluble and insoluble compounds of Cr (VI). The soluble compounds were in the form of solutions, i.e. 2.5, 5, 12.5, 25 and 50 μg of Cr (VI). The insoluble compounds were in the form of powder weighed in the amount of 2.5, 5, 12.5, 25 and 50 μg of insoluble Cr (VI) on the filters. The glass filter was washed with a 10 mL mixture of an alkaline buffer (2% KOH-3% Na_2CO_3-pH—9.5) and subjected to agitation in a heated (70 °C) ultrasonic bath for 30 min. Afterwards, the content was quantitatively filtered through a membrane filter and diluted with a mobile phase (50 mM, ammonium acetate CH_3COONH_4 and 10 mM sodium perchlorate $NaClO_4$) a hundred times and 200 μL was injected on the column and analyzed with the HPLC-ICP-MS technique. Elution of the total chromium (VI) requires the application of a strong alkaline environment, the solution (2% KOH-3% Na_2CO_3) used for elution has pH 9.5. The Hamilton PRP-X100 (150 ± 4.6 mm, 5μm) column used for the separation of the total Cr(VI) works better at higher pH, its pH range is 1–13.

2.3.4. Determination of insoluble Cr (VI) and Cr (III)

The total content of chromium (III) in a sample was determined based on the difference between the content of the total chromium and the total chromium (VI). The content of water-insoluble chromium (VI) in a sample was determined based on the difference between the content of the total chromium (VI) and soluble chromium (VI).

3. Results and discussion

3.1. Determination of soluble chromium Cr (III) and Cr (VI)

The detection of chromium species was accomplished with ELAN DRC-e (PerkinElmer SCIEX, Waltham, MA, USA). Methane was used in the dynamic reaction cell (DRC®) to effectively reduce the $^{40}Ar^{12}C^+$ interference on $^{52}Cr^+$. Typical HPLC–ICP-MS chromatograms for reagent standard containing 50 μg/L of soluble chromium Cr (III) and Cr (VI) are shown in Fig. 1. The data was acquired in less than 3 min under the conditions stated above. For this study, the 1 mM TBAH and 0.6 mM EDTA concentrations appeared to be optimal [14]. The separation was accomplished by interaction of the chromium species with the different components of the mobile phase. Cr (III) formed a complex with EDTA, i.e. retained on the column, while Cr (VI) existed in the solutions as dichromate [14–17]. All calibrations were linear with the concentration range of 2.5–50 μg/L for soluble Cr (III) and Cr (VI) and the concentration range of 5–100 μg/L for the total Cr (VI) with the correlation coefficients higher than 0.998 for each form of chromium. Limit of detection (LOD) calculated on a 3 s basis (a value of three times standard deviation of the blank) ranged from 0.4 to 0.6 μg/L. Limit of quantification (LOQ) calculated on a 6 s basis (a value of six times standard deviation of the blank) ranged from 0.9 μg/L to 1.2 μg/L. Analytical parameters characteristics of the proposed method are summarized in Table 3.

3.2. Determination of the total Cr (VI)

According to the literature, in order to leach the Cr (VI) compounds, a mixture of solutions of 2%NaOH+3%Na_2CO_3 [23–27] may be used. In the studies dealing with the determination of Cr(VI) compounds in the urban dust samples (urban particulate matter) and in soil samples, solution 2% KOH+3% Na_2CO_3 was used for the elution of Cr(VI) [28].

In order to select the extraction reagent for alkaline extraction of a welding fumes sample, two mixtures were examined: 2% KOH+3%

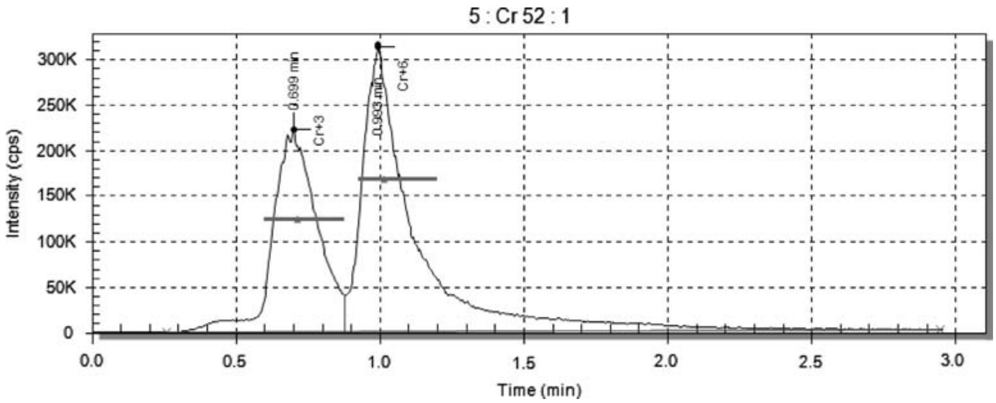

Fig. 1. HPLC–ICP-MS Typical chromatogram of chromium species—50 μg/L standard, a high-speed, reversed-phase CR C8 column (Perkin–Elmer, Inc., Shelton, CT, USA) was used.

Table 3
Analytical parameters of the proposed method for determination of chromium compounds.

Forms of chromium	Range (μg/L)	Regression line $y \equiv ax+b$	Correlation coefficient (r), $p \leq 0.05$	Limit of detection (LOD) calculated on a 3 s basis (a value of three times standard deviation of blanc) (μg/L)	Limit of quantification (LOQ) calculated on a 6 s basis (a value of six times standard deviation of blanc) (μg/L)
Cr(III) soluble	2.5–50	$y=20713\ x+1161.5$	0.999	0.5	1.0
Cr(VI) soluble	2.5–50	$y=25742\ x+216.5$	0.998	0.6	1.2
Cr(VI) total	1–100	$y=7516.8\ x+9924.6$	1.000	0.4	0.9

Table 4
Results of the recoveries of the total Cr (VI) determined after alkaline extraction from filters using different alkaline solutions.

Sample/extraction	Concentration of soluble Cr (VI) on the filter (μg)	Concentration of insoluble Cr (VI) on the filter (μg)	Concentration of the total Cr (VI) on the filter (μg)	Recovery (%)
I/After extraction 2%NaOH+3%Na_2CO_3 (n=6)	25	25	49.2 ± 0.7	98.4
II/After extraction 2%KOH+3%Na_2CO_3 (n=6)	25	25	49.6 ± 0.5	99.2

Table 5
Results of the certified reference material BCR®-545, determination value.

Component	Certified reference material value (g kg^{-1} dust)	Determined value (n=6) (g kg^{-1} dust)
Cr (VI)	40.2 ± 0.6	40.7 ± 0.6
Total leachable chromium	39.5 ± 1.3	38.9 ± 0.5

Na_2CO_3 and 2% NaOH+3% Na_2CO_3. The results of the study on these two mixtures are shown in Table 4. Based on the comparison of the two solutions for the extraction of the total Cr(VI), we can conclude that both work well and can be used. In order to verify the method, reference material was analyzed BCR 545—welding dusts loaded on a glass filter [23]. The concentrations of Cr (VI) and the total Cr were consistent with the values obtained for the certified reference material (Table 5 and Fig. 2).

3.3. *Determination of various chromium compounds*

In order to test the applicability of the method for chromium compounds speciation, the filters were spiked with a mixture of soluble chromium compounds in the amount of 50 μg of soluble Cr (III) and 50 μg of soluble Cr (VI) and 50 μg of Cr (VI) in the form of insoluble compounds˙. The recoveries for individual chromium species ranged from 91.4 to 99.6%. The results of the accuracy of determination for various chromium species according to the elaborated procedure are presented in Table 6.

4. The application of the proposed procedure of determination of chromium in occupational settings

The proposed procedure for the determination of the total chromium and chromium species was applied to conduct the analysis of real samples collected in occupational settings. Welding fumes samples were collected from the Manual Metal Arc (MMA), Metal Inert Gas (MIG) during the process of welding stainless steel (18% Cr, 8% Ni). The samples were collected on 37 mm glass filters (G/FA Whatman, Ø 37 mm) and membrane filters (Sartorius 11304, 0.8 μm, Ø 37 mm) at a nominal flow rate of 2 l min^{-1}. The filters were not subjected to the pre-treatment process. In order to check the possible contamination, a clean filter was analyzed as a blank sample. No impregnation was applied either to the filters, because in case of welding processes we mainly deal with chromium compounds contained in welding fumes. To verify the usefulness of the proposed analytical procedure, an analysis was performed of the reference material BCR 545 - welding dusts loaded on a glass filter—and it provided positive results [23]. The total dust was collected by placing, simultaneously, two filters in the employees' breathing zone. The filters after collection were suitably secured and stored at room temperature until analysis. The analysis was performed within 48 h of the collection. The fumes/dust collected on the membrane filters were/was mineralized on a hotplate at about 150 °C using concentrated HNO_3 and diluted in 0.1 M HNO_3. The total chromium compounds were analyzed in the obtained solutions of the samples with the use of the ICP-MS technique. The analyses were performed in the laboratory with the quality system

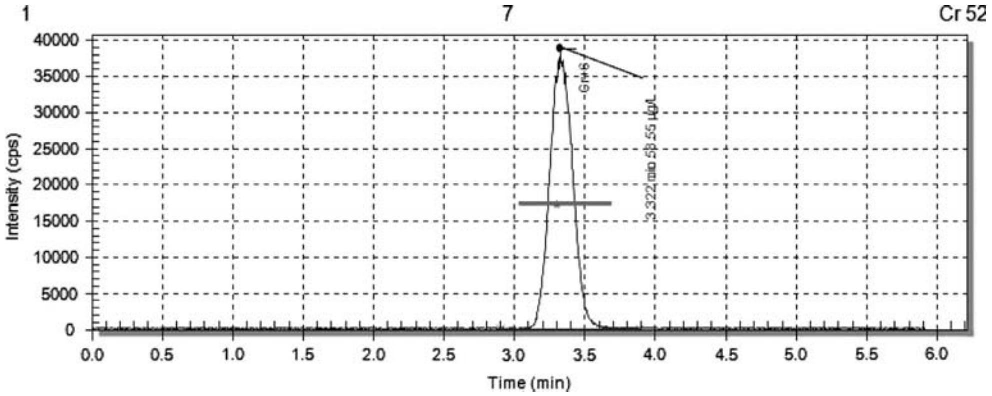

Fig. 2. HPLC–ICP-MS Chromatogram of the total hexavalent chromium species, BCR® -545, an anion exchange, Hamilton PRP-X100 column (150 × 4.6 mm, 5 µm, PEEK, Hamilton, USA) was used.

Table 6
Results of the accuracy of determination of chromium species according to the proposed procedure.

Chromium compound	Technique used for determination	Added on filter (µg) ($n=6$) $\bar{x}$	Determined value (µg) $\pm\bar{x}+s_r$	Relative Error (%) $x-\bar{x}/x100\%$	Recovery (%) $\bar{x}/x100\%$	Repeatability (%) $s_r/x \cdot 100\%$
Cr total	ICP-MS	150	144.8 ± 4.0	3.4	96.6	2.7
Cr total soluble	ICP-MS	100	98.4 ± 2.0	1.7	98.3	2.0
Cr (III) soluble	HPLC–ICP-MS	50	48.6 ± 1.5	2.8	97.2	1.5
Cr (VI) soluble	HPLC–ICP-MS	50	49.8 ± 2.5	0.4	99.6	1.2
Cr (VI) total	HPLC–ICP-MS	100	99.2 ± 1.1	0.9	99.2	1.1
Cr (VI) insoluble	Calculated as the difference	50	49.4 ± 1.9	1.3	98.7	1.9
Cr (III) total	Calculated as the difference	50	45.7 ± 3.5	8.6	91.4	3.5

Table 7
Concentrations of soluble Cr (VI) and Cr (III) the total Cr(III) and the total Cr in welding fumes samples obtained from different welding methods.

Welding method	No sample	Total Cr (µg/m^3)	Cr (III) soluble (µg/m^3) determined-method 1	Cr (VI) soluble (µg/m^3) determined-method 1	Total Cr (VI) (µg/m^3) determined-method 2	Total Cr (III)[a] (µg/m^3)
MIG/SS metal inert gas/stainless steel	Sample 1	105.2	35.3	–[b]	3.0	102.2
	Sample 2	172.5	52.3	5.0	20.5	152.0
	Sample 3	50.2	5.0	–[b]	4.1	46.2
	Sample 4	223.4	62.6	17.4	29.3	194.1
	Sample 5	184.5	59.8	–[b]	21.3	163.2
	Sample 6	182.4	58.3	–[b]	27.5	154.9
	Sample 7	106.5	37.2	–[b]	22.9	83.6
	Sample 8	350.0	66.3	20.1	32.1	318.0
	Range	50.2–350.0($n=8$)	5.0–66.3($n=8$)	5.0–20.1($n=3$)	3.0–32.0($n=8$)	46.2–318.0($n=8$)
MMA/SS manual metal arc/ stainless steel	Sample 1	215.3	70.4	30.8	55.1	160.2
	Sample 2	186.0	10.1	10.0	12.0	174.0
	Sample 3	412.0	95.8	42.4	62.0	350.0
	Sample 4	360.2	88.6	40.5	60.2	300.0
	Range	186.0–412.0($n=4$)	10.1–95.8($n=4$)	10.0–42.4($n=4$)	12.0–62.0($n=4$)	160.2–350.0($n=4$)

Total Cr (III)

[a] The total content of chromium Cr(III) in a sample was determined based on the difference between the content of the total chromium and total chromium Cr(VI).

[b] Results below the limit of detection (LOD).

in place conforming to the standard EN 482:2009 and ISO/IEC 17025:2005 [29–31]. The glass filters were cut into two equal parts. One part of the filter was transferred to a glass beaker, and then water was added (5 mL) and 0.05 M nitric acid (5 mL), and placed in an ultrasonic bath, without raising the temperature, for 30 min. After the removal from the bath, the solution was filtered through a membrane filter, and then transferred to a flask and diluted with a mobile phase (1.0 mM TBAH and 0.6 mM EDTA) 1/100 (v/v). In this sample, soluble forms of Cr (III) and Cr (VI) were determined with the use of the HPLC–ICP-MS technique—method 1. The other part of the filter was washed with a mixture of an alkaline buffer (2% KOH-3% Na_2CO_3). Next, the samples were diluted with a mobile phase (50 mM, ammonium acetate CH_3COONH_4; and 10 mM, sodium perchlorate $NaClO_4$). In this sample, the total Cr (VI) was determined with the use of the HPLC–ICP-MS technique—method 2. The content of the total chromium (III) in a sample was determined based on the difference between the content of the total chromium and the total chromium (VI). The content of insoluble chromium (VI) in a sample was determined based on the difference between the content of the total chromium (VI) and soluble chromium (VI).

The results summarized in Table 7 show that in occupational settings one can expect the presence of soluble as well as insoluble chromium Cr (VI) and Cr (III). However, the concentration of Cr (VI) in none of the cases exceeded the highest recommended exposure limit in Poland (100 µg/m^3) [7]. The content of various chromium compounds depends largely on the type of material, the method and the welding parameters used in the welding processes.

5. Conclusions

High performance liquid chromatography with inductively coupled plasma mass spectrometry was shown to be a good technique with easy sample preparation process and short time of analyses for the determination of soluble Cr (III) and Cr (VI) and for the determination of the total Cr (VI) compounds in the samples obtained from the work environment. This procedure offers an alternative to spectrophotometric methods of determination of hexavalent chromium with diphenylcarbazide (DPC) [24–25,32], when the chromium species of interest are soluble and insoluble. Methods for determination of chromium (VI) compounds based on the complex formation of Cr(VI) with DPC and spectrophotometric measurement techniques require complex sample preparation procedures. Moreover, spectrophotometric techniques have a much higher sensitivity than ICP-MS. For the elution of soluble compounds of Cr (VI) and Cr (III) we used a solution with pH—4, so that we could avoid the effect of the transformation of Cr (VI) into Cr (III) [33]. Moreover, extraction of hexavalent chromium compounds from welding fumes samples may be carried out with two types of alkaline mixtures (Table 4).

From the obtained results, it can be seen that in welding environment one can expect the presence of different chromium species, both the soluble and insoluble ones. Speciation of various chemical forms of chromium compounds gives an opportunity to assess the toxic influence of the particular chemical form, which is of great significance for work environment in which there occur chromium compounds of various oxidation levels and of various solubility.

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