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Monitoring of chromium species and 11 selected metals in emission and immission of airborne environment

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Abstract

Monitoring of chromium species as hexavalent chromium (Cr(VI)) and the determination of the total chromium concentration as well as the concentration of 11 selected metals (Al, Ca, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sb, Zn) in industrial emission of a foundry and immission studies of the nearby airborne environment were carried out. The samples were taken as industrial exhaust directly by the outlet and as airborne sample in the environment with distances between some hundred meters and 2 km from the industrial factory.

Wherefore two methods of sampling, sample pre-treatment and mass spectrometric measurement were developed and applied. With respect to different sampling duration different volumes of air were sampled and analysed. For the determination of Cr(VI) sampling in impingers (filled with carbonate-buffer) was used. A procedure of selective complex forming and extraction was developed and measured by double focussing sector field inductively coupled plasma mass spectrometry (ICP-SFMS).

For the determination of the total chromium concentration as well as of 11 metals sampling was done by using quartz-filters. After microwave digestion in the medium of aqua regia the samples were analysed by quadrupole inductively coupled plasma mass spectrometry (ICP-QMS).

The maximum concentration of Cr(VI)-species in emission samples was determined as 180 ng/m^3 air which is about 2% of total Cr. The lowest concentration of Cr(VI)-species in immission was determined as 0.5 ng/m^3 air.

Keywords: Chromium; Speciation; Air; Inductively coupled plasma mass spectrometry

1. Introduction

An important example of analytical speciation with respect to correlating species via oxidation states are the two chromium species Cr(VI) and Cr(III). Cr(III) is essential for higher plants, animals and the human body. Details about the function of Cr(III) in the glucose tolerance factor are well-known. Cr(III) has influence on the forming and the efficacy of insulin. This is contrary to Cr(VI) which is toxic and carcinogenic [1,2]. The contrast in toxicities of Cr(III) and Cr(VI) has become the reason for applying speciation analysis. Speciation of various oxidation states of a metal in a sample is not always easy. Even after an analytical method has been developed the question, whether or not sampling or sample pre-treatment has altered the relative concentration of the species of interest, still remains. Accurate sampling with the stability of the different species prior to analysis is of great importance. It is also important that the species are stable and that no species-transformation takes place. There are several parameters that control the species-transformation. These include the presence of oxidising and reducing agents, the electrochemical potential of oxidation and reduction reactions, UV light and acid–base reactions [3].

In water the existence of different Cr(VI)-species is greatly depending on the pH. Primarily chromic acid (H_2CrO_4) and its salts, hydrogen chromate ion ($HCrO_4^-$) and chromate ion (CrO_4^{2-}) exist. The predominant species present, as a function of the pH, are H_2CrO_4 at a pH less than 1, $HCrO_4^-$ at a pH between 1 and 6 and CrO_4^{2-} at a pH above 6. The dichromate ion ($Cr_2O_7^{2-}$) is a dimer of $HCrO_4^-$ after condensation, which is formed when the concentration of chromium exceeds approximately 1 g/L [4].

Since more than 20 years, performing speciation of Cr in liquid matrices (like river, drinking and wastewater as well as salt solutions and urine) is a great issue. Preferred sample pre-treatments are complex formation and pre-concentration by

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column/ionic exchange [5,6]. In the matrices of river and reservoir water selective complex formation is applied, e.g., with 8-hydroxyquinoline immobilised polyacrylonitrile (PAN) fiber: Cr(III) can be chelated whereas Cr(VI) cannot [7]. For the determination of Cr(VI) in buffered filtrates of wastewater and sludge liquid anion exchange by Amberlite LA-2 (LAES) and extraction into an organic phase of MIBK can be used [6,8]. Measurements are mainly carried out by graphite furnace atomic absorption spectrometry (GFAAS) [5,8] as well as inductively coupled plasma (ICP)-techniques. The limits of detection are mainly below the 0.1 μg/L and often below 0.01 μg/L [5]. Especially the measurement of Cr by inductively coupled plasma mass spectrometry (ICPMS) brings several problems due to interferences. Interferences on $^{52}\mathrm{Cr}^+$ and $^{53}\mathrm{Cr}^+$ are mainly C-based ($^{40}\mathrm{Ar}^{12}\mathrm{C}^+$, $^{40}\mathrm{Ar}^{13}\mathrm{C}^+$) and/or Cl-based ($^{37}\mathrm{Cl}^{16}\mathrm{O}^+$, $^{35}\mathrm{Cl}^{16}\mathrm{O}^{1}\mathrm{H}^+$). Therefore advanced ICPMS-techniques are often applied. By using dynamic reaction cell (DRC−) ICPMS with $\mathrm{NH_3}$ as reaction cell gas [3,6,9] and by using double focussing sector field (ICP-SFMS) Cr is measured in the medium resolution ($R = 4000$) [this work].

Hyphenated techniques can be used for the determination of Cr species. Examples: ion chromatography (IC) [10] or anion-exchange high-performance liquid chromatography (HPLC) coupled to inductively coupled plasma atomic emission spectroscopy (ICPAES) or ICPMS are also applied [11]. Anion-exchange chromatography was also coupled with ICPMS by using a special hydraulic high pressure nebulisation (HHPN) for sample introduction with high aerosol efficiency. Within this application it is possible to use nitric acid as eluent, which keeps the risk of interferences (see above) in ICPMS to a minimum in comparison with any other possible eluents [12]. Another example is the hyphenation of a microbore anion exchange column to double focussing sector field (ICP-SFMS) for Cr speciation in industrial process solutions [13]. Furthermore ion-pair chromatography using tetrabutylammonium hydroxide (TBAH) as ion-pair reagent and the detection of Cr species by DRC-ICPMS may also be applied [9].

About the speciation of Cr in the matrix air fewer publications are available and wherefore different techniques are applied. Examples: Cr(VI) is determined in atmospheric particulate samples by selective extraction and ion chromatographic determination. The detection of Cr(VI) is based on colorimetric absorbance measurement at 520 nm. The elution process was performed by complex formation of Cr(VI) with pyridine-2-6-dicarboxylic acid (PDCA) followed by post-column derivatisation reaction of the effluent with 1,5-diphenyl carbohydrazide (DPC) [14]. A comparison of three sampling and analytical methods for the determination of airborne Cr(VI) is carried out with samples from a hard chrome electroplating facility and in a jet engine manufacturing facility. The range of detected concentrations of Cr(VI) in working areas are from 0.6 to 960 $\mu\mathrm{g/m^3}$ air. For a very sensitive determination thermal ionisation isotope dilution mass spectrometry was applied. The limits of detection are 0.03 $\mathrm{ng/m^3}$ for Cr(III) and 0.008 $\mathrm{ng/m^3}$ for Cr(VI) [15,16]. The selective determination of airborne Cr(VI) is carried out after 24 h sampling of air in potassium hydroxide solution, followed by silica gel column separation of Cr(VI), then pre-concentration by complexation and solvent extraction. The Cr(VI) complex is dissolved in nitric acid and analysed for Cr by DRC-ICPMS [3].

Within this study a method was developed for sampling Cr(VI) from air in impingers by using four parallel systems. Sample pre-treatment by selective complexation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction as well as sensitive measurement by ICPMS, in this case ICP-SFMS. A high concentration of organic solvent is not optimal for ionisation and a lot of carbon-based interferences disturb the measurement and may suppress the signal intensity [17]. The procedure of pre-treatment is optimised to keep the concentration of organic solvent as low as possible and the extract is in diluted nitric acid. Especially quality control aspects like control of trueness by analysing certified standard reference material, recovery experiments by standard addition to samples and controls with respect to species-transformation of Cr(III) and Cr(VI) are investigated. The developed analytical method is applied for sampling and analysis of emission of industrial exhaust and immission in airborne environment in closed living areas.

Different mass spectrometric methods are suitable for the general determination of metals in airborne particles. With direct introduction of particulate matter into glow discharge atomic emission and mass spectrometric source was studied closely for elements like Fe, Na and V, while low detections limits of a few ng per element were achieved [18]. Routinely microwave digestion of airborne particulate matter collected on filters is applied prior measurements by various spectrometric methods [19]. Various techniques like ICPAES, ICPMS and laser ablation (LA)-ICPMS were used for the indirect characterisation of airborne particulates and associated trace metals by analysing them as deposited on, e.g., tree barks [20].

Within this study the emission of the total Cr concentration as well as the concentration of 11 metals (Al, Ca, Cd, Co, Fe, Mn, Ni, Pb, Sb, Zn) in industrial emission were also controlled. For this purpose an internal standard operation procedure, by using microwave digestion and ICP-QMS, was applied.

2. Experimental

2.1. Instrumentation

The measurements for the determination of the Cr(VI) concentration were performed with the ICP-SFMS ELEMENT2 (ThermoFinniganMAT, Bremen, Germany) [21,22]. ThermoFinniganMAT, Bremen, Germany, also supplied the sample introduction system. The details of this sample introduction system as well as instrumental operating conditions and the measuring parameters are summarised in Table 1.

The measurements for the determination of the total Cr concentration and the concentration of 11 other selected metals (Al, Ca, Cd, Co, Fe, Mn, Ni, Pb, Sb, Zn) were performed with the ICP-QMS HP4500plus (Agilent former Hewlett Packard, Amstelveen, the Netherlands). The details of this sample introduction system as well as instrumental operating conditions and the measuring parameters are summarised in Table 2. Interference correction was performed by a MS Excel calculation

Table 1
Sample introduction system, instrumental operating conditions and measuring parameters of ICP-SFMS

Sample introduction system	
Nebulizer	100 μL/min, PFA quality, self-aspiration mode
Spray chamber	Scott type
Cones	Nickel
Instrumental operating conditions	
RF power	1290 W
Cool gas flow	16 L/min Ar
Auxiliary gas flow	0.9 L/min Ar
Sample gas flow	1.11 L/min Ar
Measuring parameters	
Isotope (resolution mode)	$^{52}Cr^+$ ($R = 4000$; medium resolution)
Sample time	0.025 s
Samples per peak	20
Acquisition/“mass” window	150%
Search window	75%
Integration window	70%
Number of replicates	25

External calibration at 0, 10, 25 and 50 ng (abs.) Cr(VI).

procedure which was set up to calculate the correction factors that are part of elemental equations used to correct for polyatomic and doubly charged in interferences [23].

With respect to the availability two ICPMS-instruments were used within this study. ICP-SFMS was used for new measurements at low concentrations levels while ICP-QMS was applied for routine measurements.

Table 2
Sample introduction system, instrumental operating conditions and measuring parameters of ICP-QMS

Sample introduction system			
On-line mixing of sample and internal standard solution[a]: 1:5.5			
HP V-groove nebulizer			
Quartz spray chamber cooled at 2 °C			
Nickel cones			
Instrumental operating conditions			
RF power			1350 W
Plasma gas flow			15 L/min Ar
Auxiliary gas flow			1 L/min Ar
Carrier gas flow			1.18 L/min Ar

Measured isotope(s)	Integration time per point (s)	Integration time per mass (s)	Internal standard
Measuring parameters			
$^{27}Al^+$	0.03	0.09	$^{72}Ge^+$
$^{44}Ca^+$	0.03	0.09	$^{72}Ge^+$
$^{52}Cr^+$	0.1	0.3	$^{72}Ge^+$
$^{55}Mn^+$	0.03	0.09	$^{72}Ge^+$
$^{57}Fe^+$	0.03	0.09	$^{72}Ge^+$
$^{59}Co^+$	0.1	0.3	$^{72}Ge^+$
$^{60}Ni^+$	0.1	0.3	$^{72}Ge^+$
$^{63}Cu^+$	0.1	0.3	$^{72}Ge^+$
$^{66}Zn^+$	0.1	0.3	$^{125}Te^+$
$^{114}Cd^+$	0.3	0.9	$^{103}Rh^+$
$^{121}Sb^+$	0.1	0.3	$^{72}Ge^+$
$^{206–208}Pb^+$	0.1	0.3	$^{185}Re^+$

[a] Internal standard solution: 100 μg/L Ge, 20 μg/L Re and Rh, 200 μg/L Te in 0.7% HNO_3.

2.2. Reagents, standards and reference materials

All chemicals were of analytical grade or of higher purity. Concentrated HNO_3 and HCl, Na_2CO_3, $NaHCO_3$, ammonium pyrrolidine dithiocarbamate (APDC) and methyl-iso-butylketon (MIBK) were supplied by Merck, Darmstadt, Germany. A standard solutions of Cr(VI) was prepared from $K_2Cr_2O_7$ (Merck, Darmstadt, Germany), while standard stock solutions with a concentration of 1000 μg/mL (atomic spectroscopy standard; PE pure) of all other elements including Cr(III) were supplied from PerkinElmer, Oosterhout, The Netherlands. Deionised water was purified by a Millipore Milli-Q system.

As reference material a lyophilised solution of Cr(III) and Cr(VI) (CRM 544) from BCR, IRMM, Geel, Belgium was analysed in each series. The reference material is reconstituted according to the supplier’s instruction with 20 mL of HCO_3^-/H_2CO_3 buffer, pH 6.4, see also [24].

2.3. Sampling locations

Ten sampling locations were chosen whereof three refer to emission and seven to immission. Emission was controlled from halls with different activities of welding and founding. Immission was controlled next to the halls of the factory as well as in the surroundings (living areas). The sampling periods varied between a few hours and 1 day. Parameters which might influence the sampling procedure like wind direction and wind speed were also registered. All information is summarised in Table 3
.

2.4. Sampling, sample preparation and determination of Cr(VI)-species

The sampling unit for Cr(VI) consisted of impinger-sets (see Fig. 1). Wherefore four sets of two impingers were connected in series with a pump and flow regulation (around 8 L/min air) was used. With this set-up gas as well as particles was collected. Details about the composition of the impingers are given in Table 4.

Cr(VI)-species were determined by selective complexation, extraction and sensitive measurement by ICP-SFMS. The procedure is given in Fig. 2.

2.5. Sampling, sample preparation and measurement of metals

For the determination of the concentration of total Cr and of other metals (Al, Ca, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sb, Zn) sampling was carried out with a so-called Kleinfiltergeraet and the airborne matter was collected on quartz filters. The sampling period was around 24 h and with a flow rate of 90 L/min air. The loaded quartz-filters were digested with diluted aqua regia in a microwave system. Details about sampling and sample preparation are given in [25].

After dilution multi-element determinations were carried out by ICP-QMS, see also Table 2.

Table 3
Detailed information about the sampling locations

Location	Sample characteristic	Period (h)	Wind direction	Wind speed (m/s)
C1	Immission reference area[a]	20.3	NW to ESE[b]	0–2
C2	Immission living area[c]	4.5	SSE	3–5
C3	Emission hall welding[d]	1.5	SSE	5–7
C4	Immission living area[c]	5	ENE to E	4–6
C5	Immission lining area[c]	24	NE to E[b]	4–6
C6	Immission reference area[a]	23	ENE to ESE	3–6
C7	Immission living area[c]	22.5	NE to SE[b]	3–6
C8	Immission reference area[a]	22	NE to SE	3–6
C9	Emission hall founding	24.5	NE	9
C10	Emission hall welding	24.75	N to NE	1

[a] Imissions in living area as reference locations (C1, C6 and C8): distance to emission locations: between 0.25 and 0.5 km.
[b] During several samplings the wind direction changed several times.
[c] Imissions in living area (C2, C4, C5 and C7): distance to emission locations: less than 0.2 km.
[d] Sampling next to/not exactly at exhaust (compare with C10: sampling exactly at exhaust); analysis not evaluated.

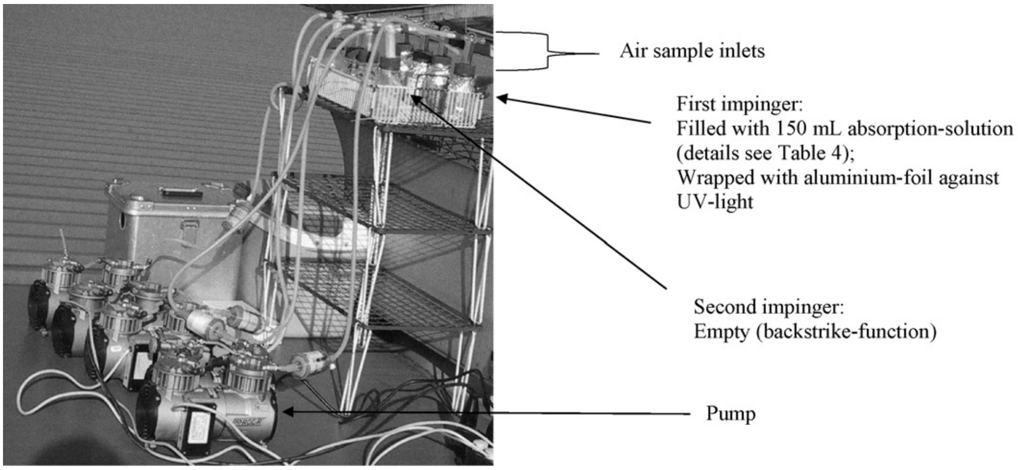

Fig. 1. Sampling unit with four sets of two impingers.

Table 4
Set-up of the sampling unit with impingers for chromium(VI)

Nr.	Impinger-1	Impinger-2
1. Sampling 1 of 2 (duplicate)	150 mL 0.05 mM Na_2CO_3/$NaHCO_3$-buffer	Empty (backstrike-function)
2. Sampling 2 of 2 (duplicate)	150 mL 0.05 mM Na_2CO_3/$NaHCO_3$-buffer	Empty (backstrike-function)
3. Quality control: recovery of Cr(VI)	50 ng Cr(VI) in 150 mL 0.05 mM Na_2CO_3/$NaHCO_3$-buffer	Empty (backstrike-function)
4. Quality control: species-transformation Cr(III) → Cr(VI)	500 ng Cr(III) in 150 mL 0.05 mM Na_2CO_3/$NaHCO_3$-buffer	Empty (backstrike-function)

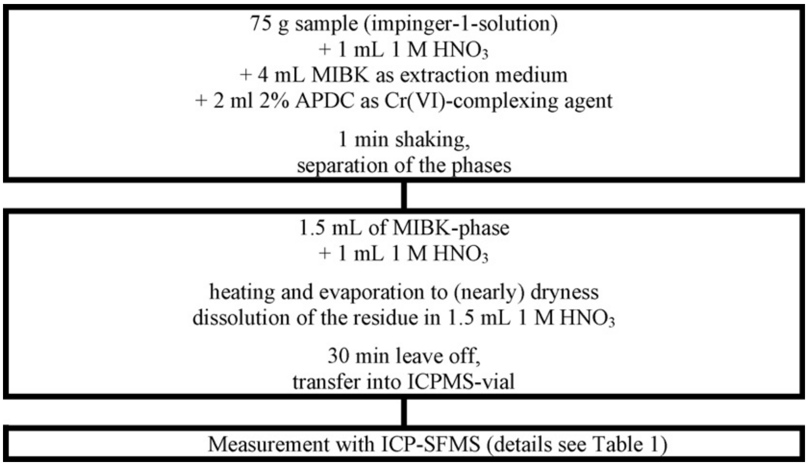

Fig. 2. Procedure for the determination of Cr(VI).

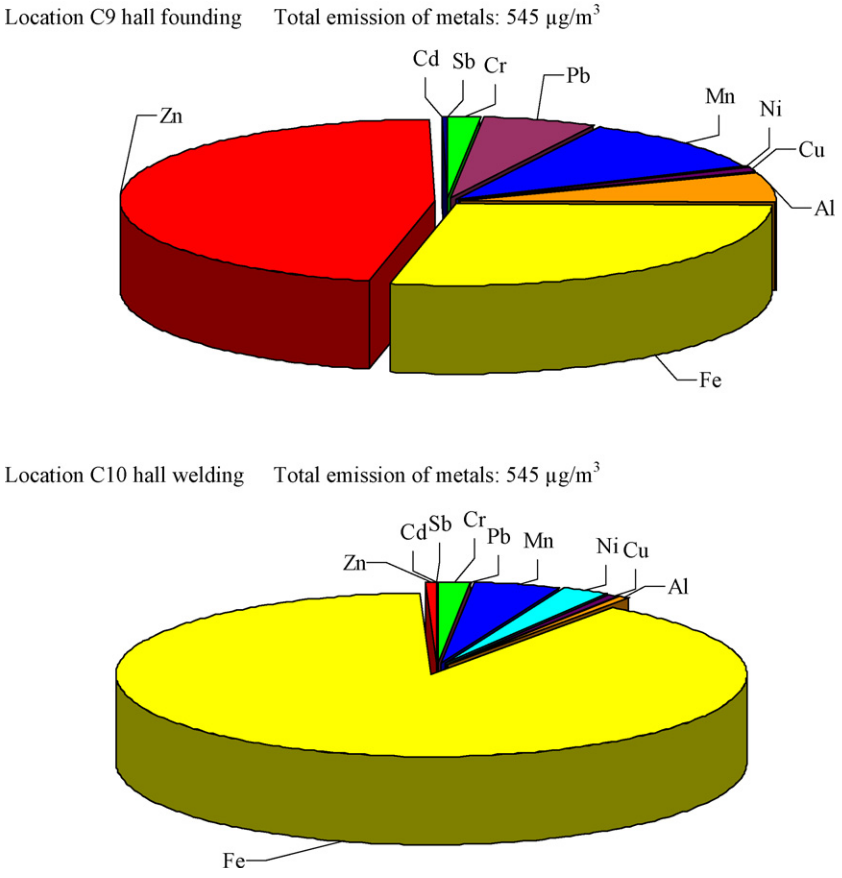

Fig. 3. Results of the concentration of the other metals in emissions from halls. Depending on the performed activities (founding and welding) different metals were emitted.

3. Results and discussion

3.1. *Emission in general*

With respect to emission it is significant that different metals are emitted depending on the performed activities—in this case of founding and welding. The results of emission are graphically presented in Fig. 3. The total emission of metals is in both processes comparable (545 $\mu g/m^3$). During founding nearly half of the emission consists of Zn and more than one quarter is of Fe, while during welding more than three quarters consist of Fe. In welding the contribution of Zn is with around 2% significant

Table 5
Results of the Cr(VI) concentration and the total Cr concentration

Location	*c*Cr(VI)[a] (ng/m³)	*c*(total Cr) (ng/m³)	Part (Cr(VI)) (%)	*c*(TSP[b]) (μg/m³)
Emissions from halls of foundry				
C9 (founding)	5	8740	<0.1	4100
C10 (welding)	180	9200	2	1950
Imissions in living area next to foundry				
C2	20.3	312	6.5	48.5
C4	0.7	139	0.5	115
C5	1.3	153	0.8	103
C7	0.5	32.4	1.5	91
[3][c]	0.2–1.3			
Imissions in living area as reference locations				
C1	1.5	7.3	21	30.8
C6	0.4	<2.0	20	43
C8	0.5	4.7	11	45.2
[3][c]	≤0.2			

[a] Average of duplicate determination.

[b] Total suspended particles.

[c] Comparable location in literature.

low. In both processes the emissions of total Cr is around 8–9% (see Fig. 3).

3.2. Emission and immission of Cr-species

All analytical results for total Cr as well as for Cr(VI) are given in Table 5.

The investigations of emissions led to various results. A significant higher ratio of Cr(VI) to total Cr was emitted by welding activities (C10) compared to founding activities (C9). While the emission of total suspended particles (TSP) is around a factor of two higher in founding areas.

The immission studies led to important results, e.g., measured concentrations of Cr(VI) in living areas are much lower than its emission. With regard to the concentration of Cr(VI) there is no significant difference between living area next to the foundry and reference places. Nevertheless for total Cr there is a significant difference between living areas next to the foundry and reference locations. In living areas next to the foundry concentrations of total Cr were found in the range between 32.4 and 312 ng/m^3. The difference between the four living areas next to the foundry is that C2 is in another direction than C4, C5 and C7. It is obviously that not only the effective distance from the emission point but also the direction of the wind is of great influence on the contribution of the emission. In comparison the concentration of reference locations are in the lower range of less than 2.0 and 7.3 ng/m^3. The obtained concentration levels of Cr(VI) in living areas and reference locations are in agreement with results in the literature (see Table 5).

For Cr the difference in toxicity and bioavailability of the two species Cr(III) and Cr(VI) is well known. With respect to workplaces the amount of Cr in the indoor air is regulated according to the species. The occupational exposure limit (OEL) for water soluble and certain water insoluble compounds in indoor air is set at 0.5 mg/m^3 for Cr(III) and 0.05 mg/m^3 for Cr(VI) [26].

From the results of the study it was concluded that the maximum permissible risk concentration of Cr(VI) in the Netherlands (2.5 ng/m^3) is probably not exceeded—apart of the result from location C2 where 20.3 ng/m^3 Cr(VI) were found. Further, the ratio of Cr(VI) to total Cr was determined to be at most 5%, except near sources [25].

3.3. Immission in general

Eleven metals of immission which were collected in living areas next to the foundry (C2, C4 and C5) as well as in a living area as reference location (C8) are given in Fig. 4. At the reference location C8 significantly lower concentrations for all metals were found than for the locations next to the foundry (C2, C4 and C5). The two main metals are Fe and in one case also Zn (see Fig. 4) which is in agreement which the main emission of metals (see Fig. 3). Nevertheless for the reference location (C8) the concentration levels of both metals are significantly lower than for the three living areas next to the foundry.

For the metals Cu and Mn the same significant pattern is present. The concentration levels of these two metals are significantly higher in living areas next to the foundry.

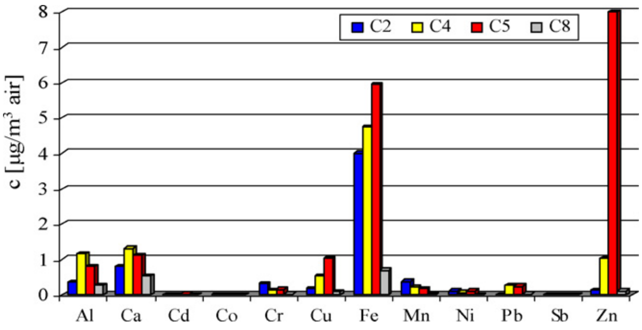

Fig. 4. Results of the concentration of the other metals in immissions.

Al and Ca show a comparable pattern (see Fig. 4). Generally the results of these two metals are due to the local background concentration and not used for direct relations with respect to this emission- and immission-study.

3.4. Quality control aspects and comparisons

Within this analytical study quality control aspects played an important role. Four different criteria were involved in each series of sample pretreatment and measurement. The criteria are

- Recovery after spiking a certain amount of Cr(VI) to the sample matrix.
- Recovery by analysing the standard reference material CRM 544 with regard to Cr(VI).
- Control of species-transformation from Cr(III) to Cr(VI).
- Control of species-transformation from Cr(VI) to Cr(III).

All obtained results for the quality control criteria are summarised in Table 6. Furthermore the results are compared with literature and in the case of the standard reference material with the certificate. Good agreement was obtained for both recovery studies (see Table 6). In comparison with [3] a significant better result was obtained for the stability of Cr(III)-species which in

Table 6
Results of the quality control experiments

Recoveries with regard to spike-experiments of Cr(VI)	
This work ($n = 4$)[a]	88 ± 15%
[3]	95 ± 9%
Recoveries with regard to certified reference materials CRM 544	
This work ($n = 4$)[a]	21.3 ± 2.6[b] µg/L Cr(VI)
Certification	22.8 ± 1.0[c] µg/L Cr(VI)
Species-transformation Cr(III) → Cr(VI)	
This work ($n = 4$)[a]	<2%
[3][d]	10% (maximum 17% for 17 days sampling)
Species transformation Cr(VI) → Cr(III)	
This work ($n = 4$)[a]	<10% (during sampling)
[3][d]	No conversion found
Measurement uncertainty (sampling included)	≤20%

[a] Number of replicate determinations.
[b] Standard deviation from replicate determinations.
[c] Uncertainty.
[d] Absorbing media potassium hydroxide solution.

this study led to less than 2% transformation to Cr(VI). Species-transformation of Cr(VI) to Cr(III) may occur during sampling which led to a maximum of 10%. The measurement uncertainty of the whole procedure including "natural" variations of sampling up to analysis is less than 20% for all results.

4. Conclusion

The results of this study show that the Cr(VI)-method is applicable for the ultra-trace determination of Cr(VI) in air. The obtained results were well-founded by the determination of the quality control aspects as well as the comparison of them to other literature, e.g. [9].

The results showed significant different Cr(VI)-concentration levels with respect to emission depending on the performed activity in the foundry as well as to immission depending on the distance from the foundry. From the obtained results in this study it was concluded that the maximum permissible risk concentration of Cr(VI) in the Netherlands (2.5 ng/m^3) is probably not exceeded. Further, the ratio of Cr(VI) to total Cr was determined to be at most 5%, except near sources.

The total elemental study delivered supplementary information which was useful for the interpretation of the Cr(VI)-results. The deposition of heavy metals in the surroundings of the foundry was found to be increased. The exposure of residents through inhalation of toxic compounds in the air did not exceed the tolerable limit values [25].

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