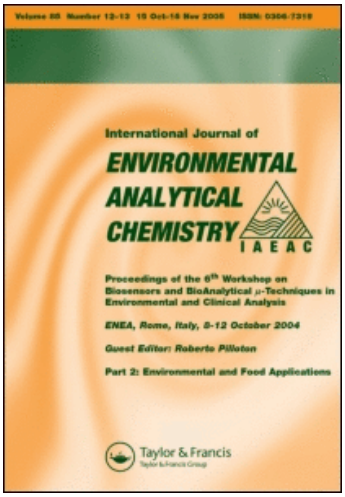

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Biological Monitoring of Occupational Exposure to Different Chromium Compounds at Various Valency States†

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Chromium concentrations in the air were measured in seven different workroom environments, where exposure to water soluble hexavalent or trivalent compounds was expected. Urinary excretion of chromium was measured before and after the same arbitrarily chosen working day. End-of-shift urinary chromium and its increase above pre-exposure levels were closely related to the concentration of water soluble chromium (VI) in the air. The values corresponding to 50 $\mu g\, m^{-3}$ in the air, which is the current threshold limit value in most countries, were 29.8 and 12.2 $\mu g\, g^{-1}$ of

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creatinine, respectively. Urinary chromium in workers exposed to water insoluble chromates or to water soluble chromic (III) sulphate was definitely higher than that observed in subjects not occupationally exposed to chromium compounds, but it cannot be recommended as short-term exposure test for evaluation of the job-related hazard.

KEY WORDS: Chromium metabolism; urine; chromium (III) sulphate; chromium (VI) trioxide; potassium dichromate; lead chromate; zinc chromate; welding fumes; plating mists; painting aerosols.

INTRODUCTION

Adverse effects of chromium compounds are mainly due to the hexavalent form of the element, whereas trivalent compounds seem to be less hazardous to occupationally exposed workers.[1]

Exposure to water soluble chromium(VI) compounds can be monitored by evaluating the urinary excretion of chromium. On the basis of the relationships occurring between exposure intensity and urinary concentration, biological limit values have also been proposed for the chromium plating and stainless steel welding industry.[2,3]

So far, no information is available about the absorption and excretion rate of chromium, either tri- or hexa-valent, contained in aerosols different from welding fumes and plating mists.

The present study was aimed to evaluate the role of valency and solubility of chromium compounds in its absorption and excretion rate in occupationally exposed workers.

MATERIALS AND METHODS

The study involved 137 workers employed in seven different industries where exposure to chromium compounds was expected. Urine samples were collected before and at the end of the same arbitrarily chosen workshift using acid washed polyethylene bottles. Particular care was taken to avoid contamination. Total chromium was measured by atomic absorption spectroscopy following an electrothermal method.[4] Urinary creatinine was determined by Jaffe's reaction using a Technicon Auto Analyzer.

Air samples were collected on PVC or cellulose nitrate (for welding fumes only) filters with mean pore size of 0.8 or 0.45 μm connected to personal (Dupont 4,000) or stationary (Gelman EC 3,000) samplers, respectively. Flow rates ranged 10–15 L min^{-1} for stationary pumps and 3–4 L min^{-1} for personal samplers, respectively. Accordingly, sampling time varied from 30 to 60 min.

Total chromium in the airborne particulate was measured by X-ray fluorescence and atomic absorption spectroscopy. Chromium(VI) assays were performed according to the method No. P & CAM 319 of 8.29.80 "Hexavalent Chromium" reported in the NIOSH Manual of Analytical Methods. The water and acid soluble fractions of chromium in welding fumes were measured following the method described elsewhere.[2]

RESULTS

The typical concentrations and the characterization of exposure to chromium compounds in the working environment of seven different industries are summarized in Table I. Physical properties and concentrations of chromium compounds in the airborne particulate are quite different in the various operations examined in the present study. Accordingly, great variations may occur in the urinary excretion of chromium (Table II).

On a group basis, total chromium in the end-of-shift spot samples and its increase above the pre-shift levels were distributed according to the water soluble concentration of chromium(VI) in the air.

Simultaneous monitoring of environmental and urinary concentration of chromium was available in nine subjects. A close relationship was found between water soluble chromium(VI) in the airborne particulate and urinary excretion at the end of the working day (Figure 1). An even better relationship was found when the daily increase in urinary chromium, i.e. when the morning (pre-exposure) values were subtracted from the afternoon ones, was plotted against water soluble chromium(VI) in the air (Figure 2). The subject mostly exposed to chromic sulphate was excluded from the assessment of the relationship, since he showed high pre-exposure values, which were probably due to the slow absorption of chromium(III). It ought also to be noted that our study subjects presumably had heavy body burdens, being for a long time heavily exposed.

TABLE I

Chromium concentrations in the workroom environment of seven different industries

Group	No. of subjects	8-h TWA[a] Airborne chromium ($\mu g\,m^{-3}$) Hexavalent: Water soluble median (range)	Hexavalent: Insoluble median (range)	Total median (range)
Welders				
MMA/SS	36	65 (10–152)	n.a.	94 (12–224)
MIG/SS	12	12 (3–35)	n.a.	62 (15–348)
Chrome-platers				
"Hard"	24	31 (4–146)	n.a.	46 (6–160)
"Bright"	16	5 (0–31)	n.a.	7 (0–39)
Chromate workers				
$K_2Cr_2O_7$	22	43 (8–212)	n.d.	89 (18–312)
$Cr_2(SO_4)_3$	15	6 (2–23)	n.d.	512 (48–1710)
Lead and zinc chromate painters	12	n.a.	990 (450–1450)	1221 (536–1720)

[a]TWA = Time weighted average.
MMA/SS = Manual metal arc/stainless steel.
MIG/SS = Metal inert gas/stainless steel.
n.a. = Not available.
n.d. = Not detectable.

TABLE II

Chromium concentrations in urine of workers exposed to different types of chromium containing aerosols

Group	No. of subjects	Urinary chromium ($\mu g\,g^{-1}$ of creatinine): End-of-shift Mean	End-of-shift (SD)	Daily increase (after pre-exposure) Mean	Daily increase (after pre-exposure) (SD)
Welders					
MMA/SS	36	33.3	(6.9)	8.8	(3.8)
MIG/SS	12	12.1	(4.9)	2.6	(1.3)
Chrome-platers					
"Hard"	24	15.3	(9.5)	6.1	(3.1)
"Bright"	16	5.8	(4.2)	1.9	(1.5)
Chromate workers					
$K_2Cr_2O_7$	22	19.5	(10.1)	8.0	(6.4)
$Cr_2(SO_4)_3$	15	16.7	(12.5)	6.4	(4.8)
Lead and zinc chromate painters	12	13.2	(10.4)	1.3	(1.2)

For abbreviations see Table I.

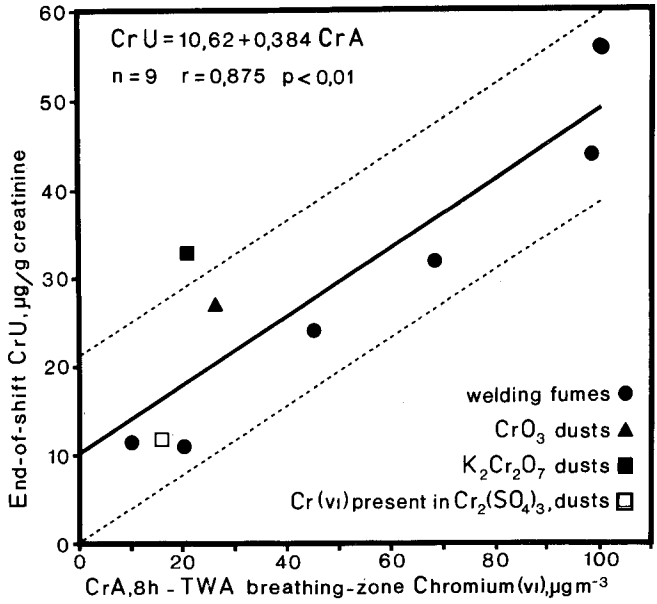

FIGURE 1 Relationship between water soluble chromium (VI) concentration in the air (mean daily exposure) and urinary excretion of chromium (end-of-shift values).

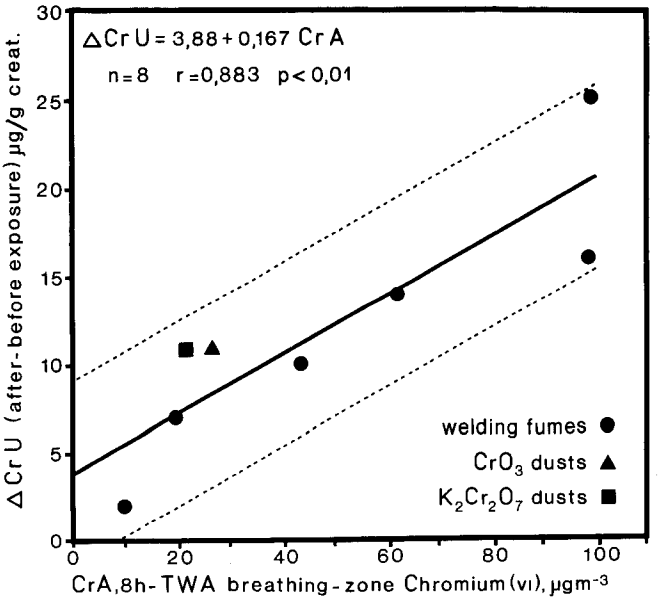

FIGURE 2 Relationship between water soluble chromium (VI) concentration in the workroom environment and daily increase in urinary chromium (pre-exposure values were subtracted from end-of-shift values).

From the regression lines it can be estimated that the end-of-shift values and the daily increase in urinary chromium corresponding to 50 $\mu g\ m^{-3}$ of water soluble chromium(VI) in the air, which is the current TLV in most countries, were 29.8 and 12.2 $\mu g\ g^{-1}$ creatinine. The corresponding lower limit of the 95% confidence interval was 18.5 and 7.1 $\mu g\ g^{-1}$ of creatinine, respectively.

DISCUSSION

The results presented above are consistent with the hypothesis that only water soluble hexavalent chromium compounds are readily absorbed by the inhalation route. Neither water soluble but trivalent chromic sulphate nor hexavalent but water insoluble lead and zinc chromates are absorbed quickly enough to cause a significant increase in the end-of-shift urinary chromium, in spite of the very high exposure levels. The aerodynamic properties of inhaled particles seem to have less importance than valency and solubility in water, at least as far as the biological availability and excretion kinetics are concerned.

In fact, no difference could be detected between workers exposed to welding fumes and chromate workers, as to urinary excretion of chromium at the same exposure level, though the aerodynamic diameter of inhaled particles was much lower for the former. As a result, exposure to water soluble chromates can be monitored following the same criteria recommended for exposure to water soluble chromium(VI) contained in welding fumes and plating mists.[2]

The relationship between water soluble chromium(VI) in the air and urinary chromium found in the present study is in good agreement with previous reports. To our knowledge, only Korallus *et al.*[6] investigated the behaviour of chromium(III) sulphate in humans and reported a two-fold increase in urinary chromium as a consequence of exposure to about 1 $mg\ m^{-3}$ of chromium(III) in the air. We did not find any increase; on the contrary, the end-of-shift urinary excretion of chromium well correlated with the small amount of water soluble chromium(VI) present in the chromium(III) sulphate dust. Thus, urinary chromium cannot be recommended as a reliable biological index of exposure to chromium(III), even for

water soluble compounds. The only exception might be represented by some organic compounds, such as chromium(III) lignosulfonate, for which some evidence has been suggested of exceptional pharmacokinetics in humans.[7]

In addition to some well recognized individual factors, such as pulmonary ventilation and chromium body burden,[5,8] also environmental factors, namely the physical properties of inhaled aerosol should be carefully evaluated when implementing a programme for the biological monitoring of exposure to chromium compounds.

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