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A pilot risk assessment study of strontium chromate among painters in the aeronautical industry

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Strontium chromate; spray-painting; aeronautical industry

Parole chiave
Cromato di stronzio; verniciatura a spruzzo; industria aeronautica

Summary
Objective: *A method for risk assessment of occupational exposure to strontium chromate ($SrCrO_4$) in painters employed in the aeronautical industry is described.* **Methods:** *Assessment was made of 21 male workers of the painting division, potentially exposed to $SrCrO_4$ (exposed), and 20 male workers of the tests and warehouse divisions (controls). All participants completed a questionnaire about work tasks, lifestyle habits, hobbies and diet. Personal active sampling for the determination of Cr and Sr was performed both during paint-spraying and during other operations in the painting division area. On the same day as environmental sampling, urine samples were collected at the beginning and end of the work shift in exposed workers to determine urinary chromium (CrU), and only at the end of the shift in controls. In the second half of the shift, a blood sample was taken in 10 exposed workers and 10 controls, to determine Cr in plasma (CrP) and in red blood cells (CrRBC).* **Results:** *During paint-spraying, Cr concentrations ranged between 1.38 and 17.10 μg/m^3, versus 0.02 to 0.07 μg/m^3 in the painting division area, while the Sr concentration was 22.90 μg/m^3 in the paint-spray booth versus 0.07 μg/m^3 in the painting division area. CrU at the end of the work shift, CrP and CrRBC, did not show significant differences between exposed workers and controls. Moreover, in exposed workers there were no differences between CrU measured at the beginning and at the end of the work shift.* **Conclusions:** *This approach, consisting of simultaneous environmental and biological monitoring, suggested no absorption of chromium in the painters thanks to the efficacy of the technical, organizational and personal protection measures adopted. However, the evident exposure to high levels of $SrCrO_4$ during paint-spraying highlights how absolutely essential it is to ensure strict compliance with all the preventive measures foreseen by the EU and national regulations for occupational exposure to carcinogens.*

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Riassunto

«Studio pilota sulla valutazione del rischio da cromato di stronzio tra i verniciatori dell'industria aeronautica».
Obiettivo: *Illustrare una metodologia per la valutazione del rischio da esposizione occupazionale a cromato di stronzio ($SrCrO_4$) nei verniciatori di un'industria aeronautica.* **Metodi:** *Sono stati esaminati 21 lavoratori maschi che operavano nel reparto verniciatura, potenzialmente esposti a $SrCrO_4$ (esposti), e 20 lavoratori maschi dei reparti collaudo e magazzino (controlli). A tutti i partecipanti è stato somministrato un questionario in diversi momenti del turno lavorativo con domande sull'attività lavorativa svolta, abitudini voluttuarie e hobbistiche e sugli alimenti assunti. Campionamenti attivi personali per la determinazione di Cr e Sr sono stati effettuati sia durante la verniciatura a spruzzo in cabina, sia durante lo svolgimento delle altre attività nel reparto verniciatura. Lo stesso giorno del campionamento ambientale, un campione di urine è stato raccolto ad inizio e fine del turno di lavoro negli esposti e solo a fine turno di lavoro nei controlli per la determinazione del cromo urinario (CrU). Nel secondo emiturno di lavoro, in 10 esposti e 10 controlli è stato prelevato un campione ematico per la determinazione del Cr nel plasma (CrP) e nei globuli rossi (CrRBC).* **Risultati:** *Durante le operazioni di verniciatura a spruzzo in cabina le concentrazioni di Cr erano comprese tra 1.38 e 17.10 $\mu g/m^3$, mentre nell'area di reparto tra 0.02 e 0.07 $\mu g/m^3$, e quelle di Sr di 22.90 $\mu g/m^3$ in cabina di verniciatura e 0.07 $\mu g/m^3$ nell'area di reparto. Le concentrazioni di CrU alla fine del turno di lavoro, CrP e CrRBC non hanno mostrato differenze tra esposti e controlli. Negli esposti, inoltre, le concentrazioni di CrU alla fine del turno di lavoro non hanno mostrato differenze con quelle misurate ad inizio turno di lavoro.* **Conclusioni:** *L'approccio con contemporanea esecuzione di monitoraggio ambientale e biologico indica l'assenza di assorbimento del cromo nei verniciatori per effetto delle misure tecniche, organizzative e protettive personali adottate. Tuttavia, l'evidente esposizione ad alte concentrazioni ambientali di $SrCrO_4$ durante la verniciatura a spruzzo rende comunque necessario adottare tutte le misure preventive indicate dalla legislazione Europea e nazionale per i lavoratori esposti a cancerogeni.*

Introduction

Strontium chromate ($SrCrO_4$) is a slightly soluble compound of hexavalent chromium (Cr^{VI}) that, thanks to its ability to protect metal surfaces from corrosion, is still widely used in paints employed in the aeronautic and space industries, as well as in the coil coating industry for the production of steel and aluminium coils. However, its use is only limited nowadays in the electroplating industry and as a yellow dye in the production of pigments for artistic purposes, fireworks and PVC resins (1, 11). World production of $SrCrO_4$ is estimated at about 9000 tons/year, approximately 4000 of which are produced in the EU (11). Like all the other compounds of Cr^{VI}, $SrCrO_4$ is classified as carcinogenic for humans by the IARC (Group 1) and has recently been included in the list of substances of very high concern (SVHC) by the European Chemical Agency (ECHA) (12, 17).

In accordance with EU regulations for occupational carcinogens, it is compulsory for employers to carry out procedures for health risk assessment in workers with occupational exposure to $SrCrO_4$, and to report the findings in a risk assessment document, when using the carcinogenic substance in an occupational setting, as foreseen in Italy by Law D. Lgs 81/08 and subsequent modifications (14). This is essentially based on assessing exposure to $SrCrO_4$ after having implemented the technical measures aimed at reducing the presence of $SrCrO_4$ in the workplace to the lowest possible concentrations, as well as the obligatory use of adequate personal protective equipment by exposed workers to prevent absorption through all routes of penetration. Such exposure assessment can be achieved by environmental and/or biological monitoring.

The aim of the present study was to illustrate a method for the assessment of exposure to $SrCrO_4$ in painters employed in the aeronautical industry who carry out paint-spraying using paints containing $SrCrO_4$, by applying synergic environmental and biological monitoring techniques so as to achieve a complete assessment of the associated risk.

Materials and methods

Subjects

All 21 male workers employed in the painting division and potentially exposed to $SrCrO_4$ (exposed), including 1 division chief, 1 superintendant and 19 painters, were recruited and compared with 20 male workers (controls) with no occupational exposure to paints and other chemical compounds, randomly selected from among the workers at the tests and warehouse divisions of the same factory. These employees work in a completely separate building located at a distance from the painting division.

All subjects, exposed workers and controls, were administered a questionnaire consisting of two parts. The first part, administered before the start of work, asked both general questions and questions related to hobbies and lifestyle habits, in particular in the last 24 hours, while the second part, administered at the end of the work shift, enquired about the work tasks carried out, as well as active or passive exposure to cigarette smoke, the consumption of alcohol/coffee/water during the work shift, and questions about food eaten over the last 48 hours, with particular attention to foodstuffs with a possible high content of Cr such as canned foods, eggs, fish and seafood, meat, nuts, whole grains, vegetables.

The study was carried out over 24 consecutive hours in conformity with the workers' shifts, starting at the beginning of the second shift on a Thursday (2 pm) and ending at the end of the first shift on the Friday (2 pm) (Figure 1). All participants gave written consent to take part in the study, after being fully informed about the method and aims.

Description of the painting division area and tasks of the operators

The factory selected as the study setting for the method of assessment of exposure to $SrCrO_4$ produces aircraft components for civil and military use. The painting division area is located in a separate building and includes various different sectors where painters carry out specific operations: 1) a closed booth equipped with a downdraft extraction system and air exchange, where the preparation of the aircraft components is carried out, consisting of applying plaster/resins with a spatula, dry or wet

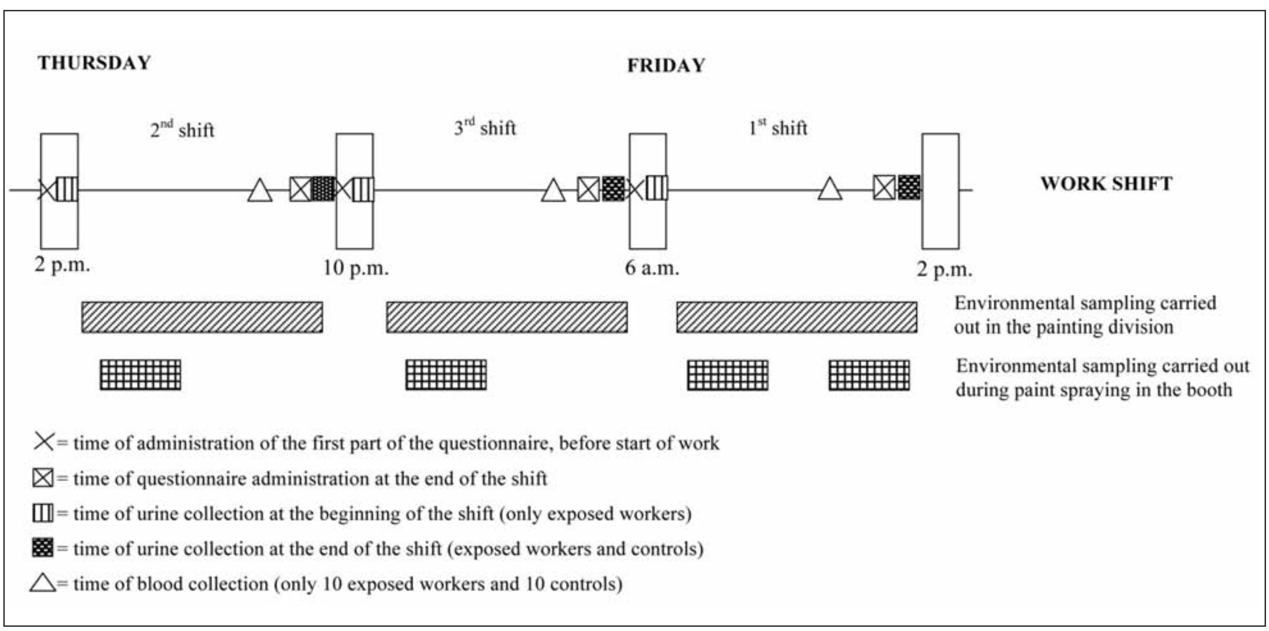

Figure 1 - Temporal sequence of questionnaire administration, environmental sampling and biological sampling throughout the study period

sanding done manually or with an orbital sander, cleaning the pieces with methylethylketone, and masking; 2) a closed paint-spray booth for spray and brush painting, equipped with air exchange and a downdraft air extraction system through the floor grid, with a water film to reduce the paint fumes; 3) inside the paint-spray booth there is a bench with an aspiration hood where the paints are prepared; this takes a few minutes and is done by the painter immediately before application; 4) an oven for drying the painted parts; 5) another booth where sealing operations are carried out by applying glues; this is also equipped with air exchange and a downdraft air extraction system through the floor; 6) a storage area for the products used in the different processing phases. All the equipment in the painting division undergoes regular maintenance including changing the water and air filters periodically.

The work tasks in the painting division are carried out over 3 work shifts that last from Monday to Friday and change weekly; the staff consists of 1 division chief, 1 superintendant and 19 painters. The division chief and superintendant work office hours, and supervise and coordinate the division activities, as well as performing office work. The painters work shifts alternating weekly, and carry out the operations of preparing, drying, finishing, sealing and transporting the components, as well as the actual painting activities done in the booth described above. It is mandatory for all workers to wear personal protective equipment. During painting in the booth, this consists of a half-face elastomeric air purifying negative pressure respirators with organic vapour cartridges and particulate pre-filters which filter out at least 99% of airborne particles, gloves and overalls, while during all the other operations performed in the painting division the operators must wear the filtering face air purifying respirators and gloves. All the workers are trained in the correct use of the personal protective equipment.

For spray or brush painting the paints may contain $SrCrO_4$ in percentages ranging from 10 to 25%, as reported in the safety data sheets compiled in accordance with the EU regulations. Paint-spraying of a single component lasts a maximum of 2 hours and is carried out by a single painter using 3-5 kg of paint. This operation is done exclusively inside the paint-spray booth, using a High Volume Low Pressure (HVLP) hand-held spray gun. The downdraft air flow rate of the spray-booth is 20 m^3/sec and the air exchange rate 200/hour. Painting can be done several times during the day but never by the same operator. Painters can carry out paint-spraying tasks several times a week but never for more than a maximum of 6 hours per week.

The aircraft components to be sprayed are of different sizes ranging between 2 and 6 metres in length, 1-2 metres in height and with a depth of not more than 30 cm. These components are suspended inside the paint-spray booth at a height of about one metre from the ground so that the surfaces to be sprayed, 1 or 2 depending on the type of component, are perpendicular to the booth floor. The worker doing the spraying stands upright and positions the spray-gun at a distance of 15-20 cm from the surface to be sprayed, working from the top downwards. If necessary, a mobile platform is used to attain the right height to carry out the operation safely.

Environmental monitoring

Environmental exposure to $SrCrO_4$ during both paint-spraying and all the other operations performed in the painting division was monitored by sampling the inhalable dust using active personal samplers worn only by the painters. Environmental samplings were taken in the same work shift as the urine sample collection from the workers. Environmental monitoring during the paint-spraying operations in the booth was performed on 4 different painters, who wore the personal samplers one at a time for a duration of 2 hours each, using different paints. During sampling in the paint-spray booth, the air extraction and exchange system efficiency was checked by measuring the air flow speed. The water and air filters of the paint-spray booth were both changed at the beginning of the week when the study was conducted. During the environmental sampling all the workers were using the personal protective equipment specified for the different tasks. In particular, all the workers were given new personal respirator cartridges on the day study started. Environmental monitoring during other operations in all the other areas of the division was performed on 3 painters who wore personal samplers for the entire 8-hour work shift. They did not do any painting inside the paint-spray booth during this shift.

Sampling of the inhalable fraction of the dust was done with the UNI EN 481 method (13). Personal samplers were used (SKC Intermediate), with a constant flow of 2 L/min. Flows were calibrated before and after sampling with a primary precision flow meter (Dry Cal, DC-lite, Bios International Corporation). Airborne matter was collected by filtration, using the IOM (Institute of Occupational Medicine) selector on cellulose ester membranes (diameter 25 mm and porosity 0.8 μm), as indicated in UNICHIM (Italian Association for Unification in the Chemical Industry Sector) method 1998:05 (27).

In the inhalable dust, $SrCrO_4$ was determined as Cr and in two dust samples, one from the 8-hour sampling and the other from the 2-hour paint-spraying operations; Sr was also determined. For analysis, the membranes were dissolved in ultrapure concentrated nitric acid and the solutions obtained were diluted with bidistilled water. For the blank reaction, unused membranes were used with the acid and bidistilled water used for the sample membranes. The calibration curve was built with the external standard method. The solutions obtained were injected into an inductively coupled plasma mass spectrometer (ICP-MS) to determine Sr and an inductively coupled plasma mass spectrometer with dynamic reaction cell (ICP-MS-DRC) to determine Cr. To control the accuracy of the method, certified NIST 1640 material was used. The limit of detection (LOD) for chromium and strontium was 0.0001 μg and the coefficient of variation ranged between 6.5 and 9%. Values were expressed as $\mu g/m^3$.

Biological monitoring

After the administration of the first part of the questionnaire, a urine sample was collected from all the exposed workers at the beginning of the work shift. Another urine sample was collected both at the end of the work shift and after the administration of the second part of the questionnaire. Instead, urine samples were collected from controls only at the end of the work shift. All urine samples were poured into 20 ml test tubes, immediately frozen and preserved at -20°C until required for analytical measurements.

In all the urine samples urinary chromium (CrU) was determined, after diluting the sample with bidistilled water, by the atomic absorption method (4). The LOD was 0.05 μg/L, the range of measurements 0.05-20 μg/L and the CV 4.0%; values were expressed as μg/L.

For adjustment purposes, urinary creatinine was also determined in the urine samples of all the workers, measured by the colorimetric method (16). The LOD was 0.01 mg/dL, the range of measurements 2 - 250 mg/dL and the CV <3%. The values were expressed as g/L and were always within the acceptable range established by the WHO (0.3-3.0 g/L) (28).

In the second half of the work shift on the same day as urine sampling, in 10 painters and 10 controls randomly selected from the respective groups, a 5 ml sample of venous blood was taken, using lithium-heparin test tubes, to determine chromium in plasma (CrP) and red blood cells (CrRBC). Among the exposed workers for this test were the 4 painters who had taken part in the environmental sampling. Immediately after blood withdrawal the whole blood was centrifuged. After removing the plasma, the red cells were washed several times with sterile physiological solution and then centrifuged. The plasma and RBC thus obtained were immediately frozen at -20°C and kept at this temperature until required for analysis.

Measurement of CrP and CrRBC was performed by diluting samples in 0.05% triton-x100 and applying the atomic absorption method for the subsequent analyses (20). The LOD was 0.1 μg/L for CrP and CrRBC, the range of measurements 0.1-20 μg/L for CrP and 0.1-100 μg/L for CrRBC, while the CV was 5.0% for plasma and 5.5% for CrRBC. Values were expressed as μg/L.

All samples of urine, plasma and RBC were code-labelled immediately after collection and analyzed blind within 20 days of collection.

Statistical analysis

Statistical analyses were performed with SPSS (version 14.0, Chicago, IL, USA). Analytical determinations below the LOD of the method were assigned a value of half the respective threshold limit value for data analysis. A normal data distribution of the different variables was checked by the Kolmogorov-Smirnov test. Variables that were not normally distributed were analyzed by non-parametric tests. Significance was set at $p < 0.05$.

Results

There were no differences between the exposed workers and controls in terms of general characteristics, type of residence, lifestyle (table 1) and consumption of food with a high possible content of Cr in the 48 hours before urine collection (data not shown). Neither in exposed workers nor in controls did any subject report the presence of waste dumps or incinerators at a distance of less than 500 m from their homes.

Environmental monitoring in the 2-hour sampling carried out during paint-spraying operations in the booth demonstrated $SrCrO_4$ concentrations, measured as Cr, 2-3 orders of magnitude higher than those measured in the 8-hour sampling done in the painting division area during the performance of operations other than painting (table 2). Also for Sr the concentrations in the booth during paint-spraying were 3 orders of magnitude higher than in the painting division area during other activities.

In table 2 individual results of the different biomarkers for each exposed worker are also showed.

Table 1 - General characteristics and lifestyle in the exposed workers and controls

	Exposed workers (N=21)			Controls (N=20)		
	Mean±SD / N(%)	Median	Range	Mean±SD / N(%)	Median	Range
Age (years)	36.2±11.3	33.0	22-53	39.2±12.9	44.0	21-58
Body mass index (BMI) (Kg/m^2)	26.3±3.6	24.8	20.7-35.5	26.3±3.3	26.7	21.2-34.0
Lenght of working activities (years)	12.5±11.0	4.0	2-29	13.3±11.2	11.0	2-28
Residence						
- Rural	5 (24%)	-	-	7 (35%)	-	-
- Urban	16 (76%)	-	-	13 (65%)	-	-
Alcohol consumption						
- Teetotal	2 (10%)	-	-	3 (15%)	-	-
- Occasional drinker	12 (57%)	-	-	10 (50%)	-	-
- Habitual drinker	7 (33%)	-	-	7 (35%)	-	-
Alcohol units/week*	6.4±10.6	2.0	0-37	5.9±8.0	2.0	0-29
Smoking habits						
- Smoker	5 (24%)	-	-	10 (50%)	-	-
- Non-smoker	12 (57%)	-	-	5 (25%)	-	-
- Ex-smoker	4 (19%)	-	-	5 (25%)	-	-
No. cigarettes/day (only smokers)	13.6±6.3	11.0	8-30	11.4±4.2	12.0	5-15
Pack/years (smokers+ex-smokers)	9.7±7.5	7.0	1-24	11.5±7.4	11.0	2-25

* 1 alcohol unit= 12 g ethanol

Table 2 - Environmental concentrations of $SrCrO_4$ measured as Cr, of Sr and inhalable dust (μg/m^3) found in the paints division, and concentrations of urinary, plasma and RBC chromium, expressed as μg/L, in each exposed worker individually considered

Exposed Workers	Job	2-h sampling during paint-spraying in the booth			8-h sampling during other activitie carried out in the division			Urinary Chromium		Plasma Chromium	RBC Chromium
		Airborne Chromium	Airborne Strontium	Inhalable dust	Airborne Chromium	Airborne Strontium	Inhalable dust	Beginning shift	End shift		
1	Division chief	-	-	-	-	-	-	0.26	0.23	-	-
2	Superintendant	-	-	-	-	-	-	0.16	0.18	-	-
3	Painter	1.38	-	270	-	-	-	0.26	0.10	0.10	1.60
4	Painter	1.62	-	50	-	-	-	0.18	0.49	0.20	1.00
5	Painter	17.10	-	740	-	-	-	0.25	0.16	0.10	1.20
6	Painter	11.20	22.90	1070	-	-	-	0.26	0.29	0.10	1.20
7	Painter	-	-	-	0.07	-	210	0.76	0.06	0.10	0.94
8	Painter	-	-	-	0.02	-	110	0.17	0.31	-	-
9	Painter	-	-	-	0.04	0.07	280	0.28	0.31	0.10	1.60
10	Painter	-	-	-	-	-	-	0.30	0.17	0.30	2.40
11	Painter	-	-	-	-	-	-	0.31	0.09	-	-
12	Painter	-	-	-	-	-	-	0.35	0.19	-	-
13	Painter	-	-	-	-	-	-	<0.05	0.26	-	-
14	Painter	-	-	-	-	-	-	0.29	0.07	-	-
15	Painter	-	-	-	-	-	-	0.22	<0.05	0.10	0.86
16	Painter	-	-	-	-	-	-	0.18	0.16	-	-
17	Painter	-	-	-	-	-	-	0.17	<0.05	-	-
18	Painter	-	-	-	-	-	-	0.39	0.12	-	-
19	Painter	-	-	-	-	-	-	0.25	<0.05	0.10	1.00
20	Painter	-	-	-	-	-	-	0.26	0.23	0.20	1.20
21	Painter	-	-	-	-	-	-	0.09	0.16	-	-

The concentrations of CrU at the end of the shift (ES), expressed as μg/L, showed no significant differences between the exposed workers and controls (table 3) nor, in the exposed workers group, between those carrying out paint-spraying operations in the booth and those carrying out other activities in the painting division area but with no actual contact with paint in the booth (table 2). Similar results were obtained when comparing the CrU concentrations, expressed as μg/g creatinine, in the two groups (data not shown). Indeed, in the exposed workers the median value of CrU ES was lower than at the beginning of the shift (BS), although this difference was not statistically significant (table 3). Moreover, analysis of the differences in CrU between ES and BS showed higher concentrations of CrU at ES only in 7 workers (table 2).

No significant differences in the concentrations of CrP and CrRBC were found between the two groups (table 3), nor, in the exposed workers group, between those who had done paint-spraying in the booth and those who had carried out only other activities in the division (table 2).

Analysis of the correlations between CrU BS, CrU ES, CrP and CrRBC, made by comparing each biomarker with each of the others, considering exposed workers and controls separately and then together, did not reveal any relationship between the different variables. Nor was any correlation observed between these biomarkers and the airborne chromium concentrations in the exposed workers who also underwent environmental sampling procedures. Finally, no correlation emerged when analyzing exposed workers and controls either sepa-

Table 3 - Concentrations of airborne chromium, expressed as μg/m³, and of urinary, plasma and RBC chromium, expressed as μg/L, in exposed workers and controls

	Exposed workers (N=21)			Controls (N=20)		
	Mean±SD	Median	Range	Mean±SD	Median	Range
Airborne chromium (four 2-h samplings)	7.8±7.7	6.4	1.4-17.1		-	
Airborne chromium (three 8-h samplings)	0.04±0.03	0.04	0.02-0.07		-	
Urinary chromium BS	0.26±0.14	0.26	<0.05-0.76		-	
Urinary chromium ES	0.17±0.12	0.16	<0.05-0.49	0.12±0.10	0.10	<0.05-0.34
Plasma chromium*	0.14±0.07	0.10	0.10-0.30	0.30±0.51	0.10	0.10-1.70
RBC chromium*	1.30±0.46	1.20	0.86-2.40	1.29±0.71	1.02	0.70-2.70

*Assayed in 10 exposed workers and 10 controls

rately or together, with any biomarker or with age, length of working activity only in exposed workers, body mass index (BMI), consumption of alcohol, cigarette smoking, or the consumption of foodstuffs with a high possible content of Cr.

Discussion

The method designed to assess occupational exposure to $SrCrO_4$ of painters in the aeronautical industry during paint-spraying operations in a booth, based on an integrated approach consisting of simultaneous environmental and biological monitoring and aimed at achieving a risk assessment of $SrCrO_4$, demonstrated a clear exposure of these workers to $SrCrO_4$ during paint-spraying operations but would also seem to indicate that there was no simultaneous absorption via the different penetration routes.

$SrCrO_4$ is a compound of Cr^{VI}, whose risk for humans has not yet been entirely elucidated. Epidemiologic studies in workers employed in the production of $SrCrO_4$ and other pigments containing chromium did not demonstrate an excess risk for lung cancer or were unable to define what contribution exposure to $SrCrO_4$ might have on the onset of carcinogenic effects caused by other compounds of Cr^{VI} (9, 18). Instead, there is clear experimental evidence of the carcinogenic nature of $SrCrO_4$ at the bronchial level in rats; indeed, a higher carcinogenic potential than that of the other Cr^{VI} compounds was demonstrated (19). On these scientific bases, the EU classified $SrCrO_4$ as carcinogenic (Category 1B), while the ACGIH has differentiated this compound from the other Cr compounds since 1992 and, although it is considered only a suspected carcinogen for humans (Group A2), a TLV-TWA of only 0.5 μg/m³ is recommended, equal to half the TWA set for calcium chromate and 2 orders of magnitude lower than those recommended for the other soluble and insoluble compounds of Cr^{VI}, equal to 50 and 10 μg/m³, respectively (3).

Environmental monitoring in this study demonstrated concentrations of $SrCrO_4$, measured as Cr, ranging between 1.38 and 17.10 μg/m³ during the 2 hours of paint-spraying in the booth, and between 0.02 and 0.07 μg/m³ during all the other operations carried out in the painting division during the 8-hour work shifts. Because no speciation of environmental Cr was performed, it was assumed that the Cr recorded in the paint-spray booth was probably Cr^{VI}. Comparison of the results of environmental monitoring in the paint-spray booth with the TLV-TWA for $SrCrO_4$ of the ACGIH showed that the values were always 2-3 orders of magnitude higher than the recommended limit. However, the concentrations of airborne Cr^{VI} measured during the paint-spraying operations in the booth were always lower than the Permissible Exposure Level (PEL) of 25 μg/m^3 established by the OSHA for painting operations of aircraft or large parts thereof, regardless of the Cr^{VI} compounds contained in the paint (23). This result could be attributable to the fact that the air exchange and downdraft air extraction system with a water film to reduce the paint fumes fitted in the booth of the factory under study was active and efficient. Moreover, exposure to $SrCrO_4$ during paint-spraying was much lower than exposure recorded by other authors in previous research in similar work situations (2, 25). In particular, Carlton studied paint-sprayers in the US Air Force applying paints containing $SrCrO_4$ in a booth, and found mean Cr concentrations of 831.9 μg/m^3 (6). It should be noted that these were referred to measurements made with personal samplers in a variable number of workers ranging from 2 to 8 painters working simultaneously in the booth, so the environmental concentrations of $SrCrO_4$ were affected by the work load of several painters operating simultaneously.

Although the environmental concentrations of Cr measured in the painting division area in the present study were considered to be probably Cr^{III}, they were still, as a precautionary measure, considered as derivatives of $SrCrO_4$ and so compared with the TLV-TWA of this compound. They were always one order of magnitude lower than the TLV-TWA of $SrCrO_4$ and virtually comparable to those found in Europe in urban (0.004-0.070 μg/m^3) and industrial areas (0.005-0.200 μg/m^3) essentially due to Cr^{III} (29). Therefore, the health risk posed by exposure to Cr in the painting division of the aeronautical factory studied appears to be comparable to the risk present in the general population.

In the environmental sampling, Sr showed a similar trend to that of Cr. It was found in concentrations of 22.90 μg/m^3 in sampling carried out during paint-spraying in the booth and 0.07 μg/m^3 during the other activities carried out in the painting division. The presence of high concentrations of Sr in the paint-spray booth, in association with those of Cr, provide indirect confirmation of its origin from $SrCrO_4$.

The biological monitoring carried out by measuring CrU, CrP and CrRBC in the exposed workers and controls did not reveal differences between the two groups. CrU is a biomarker of internal dose, recommended by the ACGIH and DFG for biological monitoring of short-term occupational exposure to soluble compounds of Cr (3, 10). $SrCrO_4$ is, as already pointed out, a slightly soluble compound, for which the ACGIH has proposed a TLW-TWA but not a BEI because knowledge of its toxicokinetics is incomplete and it is not yet clear whether it has a different action in man compared to other, highly soluble compounds. Nevertheless, in the absence of other valid biological indicators of occupational exposure to $SrCrO_4$ in the scientific literature, in this study CrU was used as the BEI for $SrCrO_4$. Also McAughey et al., when monitoring exposure to Cr in workers in two factories producing pigments containing $SrCrO_4$, used CrU and found high concentrations of this biomarker (21).

In the exposed workers, comparison of the CrU values with the BEI of the ACGIH demonstrated that in all the workers they were always 2-3 orders of magnitude lower than the BEI level of 25 μg/L, at the end of the shift and at the end of the work week, and that the difference between the end of the shift and the beginning was much less than 10 μg/L, the BEI for exposure during the work shift. Moreover, in exposed workers and controls, comparison of the CrU results with the reference values in the general Italian population revealed CrU ES concentrations slightly above the upper limit of the range (0.49 vs 0.35 μg/L) only in 1 exposed worker (26). Therefore, our results seem to indicate a comparable exposure to Cr in both groups, and substantially comparable to that in the general population, and therefore no abnormal absorption of Cr during working activities even in those carrying out paint-spraying in the booth, despite the high environmental concentrations of $SrCrO_4$ demonstrated, nor in those carrying out other activities in the painting division. The finding of higher CrU concentrations at the beginning than at the end of the shift in 14 of the 21 exposed workers, albeit with no significant differences, was not found to be attributable to any specific source of pollution.

CrP is considered a biomarker of recent occupational exposure to Cr, like CrU. Goldoni et al. recently observed a significant correlation between CrU and CrP, in 14 workers exposed to soluble compounds of Cr, only in the samples collected at the end of the shift and not at the beginning (15). Instead, our results, even if the blood samples in exposed workers were taken in the second part of the work shift, did not show any correlation between CrP and CrU analyzed at the end of the shift, confirming the absence of any significant absorption of Cr during the first part of the work shift.

CrRBC is a specific biomarker of long term occupational exposure to Cr^{VI} (5, 7, 22). For soluble compounds of Cr, it seems to have the same validity even for exposure to low environmental concentrations, as recently demonstrated by Qu et al. (24). Instead, there are no studies in the literature investigating the behaviour of CrRBC after exposure to $SrCrO_4$, nor any specific Italian reference values for the biomarker. The lack of differences in the concentrations of CrRBC between the exposed workers and controls in our study suggests the absence of an abnormal absorption of Cr during working activities also in the 3 months before the blood samples were taken. The results of biological monitoring, particularly those relating to CrRBC, therefore suggest that the use of new cartridges for the face air-purifying respirators on the day of the start of the study may have contributed minimally to reducing the absorption of Cr in painters compared to what normally occurs under non-test conditions.

The method for assessing occupational exposure to $SrCrO_4$ in painters described in this study seems to be helpful in defining the characteristics of exposure to this carcinogen in paint-sprayers in a booth, the only operation that seems to expose this category of workers to a high risk of $SrCrO_4$. In fact, if only environmental monitoring had been carried out this would certainly have led to an overestimation of the health risk for $SrCrO_4$ in these workers, by indicating high exposure to $SrCrO_4$. Vice versa, only biological monitoring would not have provided any information about the high concentrations of $SrCrO_4$ present in the paint-spray booth, demonstrating only that the workers did not show any Cr absorption. Moreover, no information would have been gained as to the efficacy of the personal protection devices adopted to prevent the absorption of Cr^{VI} during paint-spraying in a booth. Instead, the combined monitoring yielded information on all these factors (8).

The information gained with the method presented here allowed the employer to obtain very useful information for the assessment of occupational exposure to $SrCrO_4$ in painters during the various tasks carried out in the painting division, as well as for evaluating the efficacy of the technical and organizational measures implemented to limit $SrCrO_4$ exposure, and the workers' compliance with the compulsory use of these personal protection devices. Nevertheless, although there did not seem to be any absorption of Cr in the painters, the high levels of airborne Cr^{VI} observed in the paint-spray booth demonstrated the need to implement to the full the requirements recommended by all European and national legislation for workers exposed to carcinogens, such as health surveillance and recording in the register of workers exposed to carcinogens (14). These requirements appear to be foreseen also in US legislation. In fact, although the OSHA considers assessment of exposure to be the main factor on which health safeguards for workers occupationally exposed to carcinogens like Cr^{VI} compounds are based, it identifies a TWA of 0.5 $\mu g/m^3$ for the latter as the minimum level for compliance with the legal requirements and of 2.5 $\mu g/m^3$ as the action level indicating the need to implement further measures including health surveillance (23). This level was exceeded in 2 of the 4 environmental sampling results obtained during the paint-spray operations in the booth.

Conclusion

This study reports the first example of the application of a method involving simultaneous environmental and biological monitoring of occupational exposure to $SrCrO_4$ in paint-sprayers in the aeronautical industry. Although the described methodology needs to be validated in a higher number of workers sampled over a longer period of time, our results suggest that the combined approach is useful in the risk assessment procedure, since it provides information not only on exposure to $SrCrO_4$ in the workplace but also on the absorption of the carcinogen through all routes of penetration, as well as on the efficacy of the technical, organizational and personal protection measures adopted to limit absorption. In any case, occupational exposure to high environmental levels of $SrCrO_4$ highlights how essential it is to ensure strict compliance with all the preventive measures foreseen for safeguarding health in the workplace.

NO POTENTIAL CONFLICT OF INTEREST RELEVANT TO THIS ARTICLE WAS REPORTED

REFERENCES

1. Agency for Toxic Substances and Disease Registry (ATSDR): *Toxicological Profile for Chromium*. Atlanta, GA: ATSDR, 2008
2. Aizenberg V, England E, Grinshpun S, et al: Metal exposure among abrasive blasting workers at four U.S. Air Force facilities. Appl Occup Environ Hyg 2000; *15*: 766-772
3. American Conference of Governmental Industrial Hygienists (ACGIH): *TLVs and BEIs for chemical substances and physical agents*. Cincinnati, OH: ACGIH, 2013
4. Apostoli P, Maranelli G, Duca PG, et al: Reference values of urinary chromium in Italy. Int Arch Occup Environ Health 1997; *70*: 173-179
5. Bova M, Ricciardi Tenore G, Girardi S, et al: Utilizzo del cromo intraeritrocitario quale indicatore di esposizione a cromo esavalente. Folia Medica 2000; *71*: 47-53
6. Carlton GN: Hexavalent chromium exposures during full-aircraft corrosion control. AIHA J (Faifax, VA) 2003; *64*: 668-672
7. Cirla PE, Settimi L, Filipponi A, et al: Attività di galvanica e migliori tecniche disponibili: la direttiva IPPC nella prevenzione dell'esposizione a cromo esavalente. G Ital Med Lav Ergon 2006; *28* (Suppl): 26-27
8. Cirla PE, Nolli F, Galli L, et al: Attività di verniciatura ed agenti chimici cancerogeni: l'esperienza dello Studio PPTP-Verniciatura. G Ital Med Lav Ergon 2009; *31* (Suppl 2): 205-206
9. Davies JM: Lung cancer mortality among workers making lead chromate and zinc chromate pigments at three English factories. Br J Ind Med 1984; *41*: 158-169
10. Deutsche Forschungsgemeinschaft (DFG): *List of MAK and BAT values*. Ochsenfurt-Hohestadt, Germany: DFG, 2012
11. European Chemical Agency (ECHA): Annex XV dossier. Proposal for identification of a substance as a category 1A or 1B CMR, PBT, vPvB or a substance of an equivalent level of concern. Substance Name: Strontium chromate. ECHA, 2012. Available at http://echa.europa.eu/ documents/10162/13640/svhc _axvrep_fr_cmr_srcro4_publ_en.pdf
12. European Chemical Agency (ECHA): SVHC support document for identification of strontium chromate as a substance of very high concern because of its CMR properties. Adopted on 20 May 2011. ECHA, 2011. Available at: http://echa.europa.eu/ documents/10162/13638/svhc_supdoc_msca_strontiumchromate_ec_232-142-6_en.pdf
13. European Committee for Standardization (CEN): Workplace atmospheres – Size fraction definitions for measurement of airborne particles. European Standard EN 481: CEN, 1993
14. European Parliament: Directive 2004/37/EC of the European Parliament and of the Council of 29 April 2004 on the Protection of Workers from the risks related to exposure to carcinogens or mutagens at work. Official Journal of the European Union of 30.04.2004, L158/50
15. Goldoni M, Caglieri A, De Palma G, et al: Chromium in exhaled breath condensate (EBC), erythrocytes, plasma and urine in the biomonitoring of chrome-plating workers exposed to soluble Cr(VI). J Environ Monit 2010; *12*: 442-447
16. Harmoinen AP: Bilirubin and metamizol do not interfere with the randox enzymatic creatinine test. An evaluation of a new enzymatic creatinine determination method. Eur J Clin Chem Clin Biochem 1996; *34*: 975-976
17. International Agency for Research on Cancer (IARC): *Monographs on the Evaluation of Carcinogenic Risks to Humans. A review of human carcinogens. Arsenic, metals, fibres, and dusts*. Volume 100 C. Lyon, France: IARC, 2012
18. Kano K, Horikawa M, Utsunomiya T, et al: Lung cancer mortality among a cohort of male chromate pigment workers in Japan. Int J Epidemiol 1993; *22*: 16-22
19. Levy LS, Martin PA, Bidstrup PL: Investigation of the potential carcinogenicity of a range of chromium containing materials on rat lung. Br J Ind Med 1986; *43*: 243-256
20. Lewalter J, Korallus U, Harzdorf C, Weidemann H: Chromium bond detection in isolated erythrocytes: a new principle of biological monitoring of exposure to hexavalent chromium. Int Arch Occup Environ Health 1985; *55*: 305-318
21. McAughey JJ, Samuel AM, Baxter PJ, Smith NJ: Biological monitoring of occupational exposure in the

chromate pigment production industry. Sci Total Environ 1988; *71*: 317-322

22. Miksche LW, Lewalter J: Health Surveillance and Biological Effect Monitoring for Chromium-Exposed Workers. Regul Toxicol Pharmacol 1997; *26*: S94-S99
23. Occupational Safety and Health Administration (OSHA): Occupational Exposure to Hexavalent Chromium; Final Rule. Federal Register 71, 28 February 2006: 10099-10385
24. Qu Q, Li X, An F, et al: Cr^{VI} exposure and biomarkers: Cr in erythrocytes in relation to exposure and polymorphisms of genes encoding anion transport proteins. Biomarkers 2008; *13*: 467-477
25. Sabty-Daily RA, Harris PA, Hinds WC, Froines JR: Size distribution and speciation of chromium in paint spray aerosol at an aerospace facility. Ann Occup Hyg 2005; *49*: 47-59
26. Società Italiana Valori di Riferimento (SIVR). Terza lista dei valori di riferimento per elementi, composti organici e loro metaboliti. Edizione 2011. Available at http://www.valoridiriferimento.it/
27. UNICHIM: Method UNICHIM 1998:05 Workplaces - Determination of the inhalable fraction – Gravimetric Method. UNICHIM, 2005
28. World Health Organization (WHO): *Biological Monitoring of Chemical Exposure in the Workplace*, vol. 1. Geneva: WHO, 1996.
29. World Health Organization (WHO): *Air quality guidelines for Europe*, 2nd edition. Chromium. Copenhagen: WHO, Regional Office for Europe, 2000

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