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Chromium Concentrations in Iraqi Tanneries

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دراسة تأثير مادة الكروم الثلاثية على عمال معمل الدباغة

الخلاصة:

بهدف دراسة تأثير مادة الكروم الثلاثية (سلفات الكروم القاعدية) المستعملة في معمل دباغة الجلود على العاملين، فقد تم قياس نسبة املاح الكروم الثلاثية في الاماكن المحتمل تعرض العاملين لها حيث قيست في الاجواء المحيطة بالعمال (بيئة العمل) وفي ماء البراميل والمياه الناتجة بعد عصر الجلد وغسله ومياه المجاري، كما ان الدراسة شملت قياس نسبة الكروم في دم وأدرار العاملين في معمل الدباغة ودم وأدرار عمال آخرون غير معرضين لأية مادة كيميائية (مجموعة مقارنة).
لقد بينت الدراسة ان تراكيز الكروم في بيئة العمل اقل من النسب القياسية كما لم نجد قيمة معنوية بين المعرضين للكروم وغير المعرضين عند قياس كميته في الدم والأدرار، إلا ان الدراسة كشفت عن وجود الحساسية التلامسية من هذه المادة لدى العاملين في هذه الصناعة.

SUMMARY

Chromium levels has been detected in the air and different waters of the Iraqi tanneries as well as in the plasma and the urine of the exposed workers. No significant increase in the levels of chromium were observed in the plasma and urine of exposed workers compared to the controls. These levels were correlated with the levels of chromium in the air and waters. The results indicated minimal absorption of chromium through the skin and the lungs of exposed workers.

INTRODUCTION

Chromium has been used for many years in tanning process(1,2). In such process the more toxic hexavalent chromium was replaced by trivalent chromium (3,4). Health effects concerned chromium in tanneries were reported several workers (5,6,7).

In Iraq no scientific and systematic study was done on the hazard of chromium in tanneries. In attempts to study the hazards in such occupation the following study was performed.

MATERIAL AND METHODS

1. Measurements of chromium in water, air and biological fluids.

In this study unicam sp 190 single beam atomic absorption spectro photometer, was used for the determination of chromium in water, and sp 2900 was used for determination of chromium in the biological fluid and air.

a) Water. The method of Miner and Whiteside (8) was used for the determination of chromium in aqueous solution. Some of the samples required only dilution before reading, others required digestion with mixture of nitric and perchloric acids, standard solutions, were prepared from stock chromic nitrate (BDH).*

b) Biological fluids, the method of salvin and Sprague (9) was used for the determination of chromium in plasma and urine of exposed and non-exposed workers (controls).

c) Air: Samples were collected by AFC 123 personal air samples (casella)⁺ fitted with fiber glass filter paper. Collection of samples were performed during the working day (8 hours duration), another samples were collected at

*BDH Chemical Ltd. Poole, England.

+Cassella Ltd. London, England.

night (8 hours duration). Digestion of the filterpaper was done with 8 parts nitric acid and 1 part perchloric acid followed by filtration and dilution (10), chromium concentrations in the samples were then measured by atomic absorption.

2. Collection of Biological samples.

Samples of urine and blood were collected from 25 adult men working at different parts of chromium department, Blood samples (5ml) was collected in heparinized tube and centrifuged. The supernatant was collected in plastic tubes and measured directly by atomic absorption. Similar samples were collected from control workers, working at Iraqi steel industry.

3. Measurement of chromium in basic chromium sulphate powder.

Samples of chromium sulphate powder were taken from 10 different patches, specified weight was dissolved and diluted and subjected to the atomic absorption spectro photometry.

RESULTS

The mean concentration of chromium in basic chromium sulphate powder used in tanning process was 16.94% w/w which represents a theoretical quantity of chromium (table 1). Table 1 also shows the concentrations of chromium in rotating drums. These concentrations represents about 1/32 of the concentration in the powder, which is still high concentration. The concentrations of chromium remained about the same in the water which comes from the pressing of the tanned skin (Table 2). However, during retanning process (washing up the skin followed by the addition of other materials), the concentration of chromium decrease to a significantly low level (0.015% w/v). The concentration of chromium in drainage water of

Table 1. Concentrations of chromium in basic chromium sulphate powder and in rotating drums used for tanning process.

No. of samples	Concentration of chromium	
	%w/w in basic chromium sulphate powder	%w/v in rotating drums
1	17.54	0.477
2	16.9	0.46
3	16.54	0.58
4	17.93	0.576
5	16.6	0.326
6	16.25	0.58
7	17.49	0.566
8	16.42	0.525
9	16.44	0.64
10	17.31	0.326
mean	16.94	0.505
S.E.	± 0.18	± 0.034
S.D.	0.58	0.108

chromium department at different periods of working hours were also measured, the mean values were 0.36, 0.04 and 0.001% w/v at 9-9 Am, 9-12 Am and 12-2 pm respectively (Table 3). Significant differences were found between these values.

Waste water which was collected from all departments of the industry contain an average chromium. 5.82×10^{-3} % w/v which is low level compared with that in Table 3. The concentrations of chromium were significantly decreased ($P < 0.001$) after biological treatment of waste water (Table 4).

Table 2- Concentration of chromium in water
a. after pressing the tanned skin,
b. during retannage process.

No. of samples	Concentration of chromium Is w/v	
	After pressing tanned skin	During retannage process
1	0.42	0.015
2	0.313	0.018
3	0.367	0.0138
4	0.503	0.0166
5	0.543	0.0156
6	0.576	0.0134
7	0.432	0.013
8	0.525	0.017
9	0.356	0.0144
10	0.460	0.0135
mean	0.447	0.015
S.E.	± 0.0277	± 0.0005
S.D.	0.0877	0.0167
t = 15.98		
p 0.001		

The average concentration of the chromium in the air was 0.015 mg/m^3 during the working day hours and 0.047 mg/m^3 /for the night working hours (Table 5).

The difference was highly significant ($p < 0.005$). This could be due to the addition of the powder chromium sulphate to the rotating drums which is done at night. There were no significant differences in the concentration of chromium

Table 3 - Concentrations of chromium in drainage water at different periods during working hours

No. of sample	Chromium concentrations		
	at 7-9 am	at 9-12 am	at 12-2 pm
1	0.318	0.127	0.0015
2	0.336	0.011	0.0016
3	0.344	0.011	0.0005
4	0.388	0.014	0.0006
5	0.440	0.084	
6	0.353	0.035	
7		0.030	
8		0.041	
Mean	0.363	0.044	1.106×10^{-3}
S.E.	± 0.018	± 0.014	$\pm 2.9 \times 10^{-4}$
S.D.	0.044	0.041	5.95×10^{-4}
t		14.1	3.5
p		0.001	0.01

Table 4 - Concentrations of chromium in waste water collected during 24 hours from all departments of the industry before or after biological treatment

No. of samples	Chromium concentrations	
	Before biological treatment $\times 10^{-4}$	After biological treatment $\times 10^{-4}$
1	62.55	0.402
2	10.02	1.125
3	42.9	1.823
4	65.9	0.542
5	115.2	0.462
6	49.75	0.286
7	54.55	0.309
8	83.55	0.339
9	40.45	0.216
10	58	0.2
Mean =	5.828×10^{-3}	$5.70.7 \times 10^{-5}$
S.E.	$\pm 8.7 \times 10^{-4}$	$\pm 1.62 \times 10^{-5}$
S.D.	2.77×10^{-3}	5.15×10^{-5}
t =	7.301	
p	0.001	

Table 5 - Concentrations of chromium in the air of chromium department during day working hours and night working hours

No. of samples	Concentrations of chromium mg/m ³	
	day working hours	night working hours
1	0.007	0.059
2	0.012	0.059
3	0.0089	0.035
4	0.011	0.025
5	0.013	0.059
Mean =	0.0104	0.0474*
S.E. =	± 0.0011	± 0.0072
S.D. =	2.4 x 10 ³	0.01627
t	t = 4.356	
p	0.001	

palsma of exposed workers and controls (Table 6). Similarly the differences in the concentrations of chromium in the urine of the exposed workers and controls were not significant (Table 6).

DISCUSSION

The concentration of chromium in the powder of chromium sulphate was 16.94% w/w, a value similar to that calculated for such compound (Merk Index, No. 7, 1960). Such powder was added to the rotating drums used to soak the skin for the tanning process. The final concentration of chromium in the rotating drums was 0.505% w/v.

Table 6 - Concentrations of chromium in the plasma and urine of workersexposed to chromium and non exposed workers

No. of sample	Chromium concentrations ug/100ml			
	Plasma		Urine	
	exposed workers	nonexposed workers	exposed workers	nonexposed workers
1	0	0	0	0
2	0	0.01	0.015	0
3	0	0	0.003	0
4	0.01	0.015	0.003	0.02
5	0.01	0.01	0.015	0.02
6	0.01	0	0	0
7	0.01	0	0	0.02
8	0.01	0.01	0	0.02
9	0.01	0.015	0	0.015
10	0.01	0	0.02	0.02
11	0.02	0	0.02	0.02
12	0.02	0	0.02	0
13	0.02	0.01	0.02	0
14	0.02	0.015	0.02	0.01
15	0.02	0.02	0.015	0.02
16	0.02	0.015	0.04	0.02
17	0.02	0.02	0.04	0
18	0	0	0.04	0
19	0.01	0.015	0.015	0
20	0	0	0.015	
21	0.02		0.015	
22	0.01		0.015	
23	0.01		0.015	
24	0.01		0.02	
25	0.02		0	
Mean	0.011	0.0078	0.014	0.0088
S.E.	± 0.001	± 0.0017	± 0.0024	± 0.00207
S.D.	7.5×10^{-3}	7.6×10^{-3}	0.012	9.253×10^{-3}

This concentration was relatively high and capable for inducing contact type of hypersensitivity in guinea pigs (11). The concentration of chromium in water after pressing the tanned skin was similar to its concentration in the rotating drum, this similarity could be due to the saturation of the tanned skin with the chromium. In the retannage

process, new washing with water was done and the minute quantities of chromium appeared in the washing (0.015% w/v) represents the unabsorbed chromium.

In the drainage water, the concentrations of chromium measured were depending on the time of collection of the samples.

Addition of chromium sulphate powder done at night to the rotating drums and the skin was left in the drum overnight. In the morning, the drums were empty from their water content and chromium content of this water at this time (7-9 Am) represented the highest quantity; several washings were then done on the tanned skin and the two concentrations at 9-12 Am and 12-2 pm 12-2pm represented the significantly lower concentrations.

Statistical difference was found between the concentrations of chromium in the drainage water before and after biological treatment ($P < 0.001$). This indicated the efficiency of the treatment in removing chromium, since the chromium concentration decreased by about 100. The concentration of chromium in the drainage water of the chromium department. This may be due to the dilution and precipitation occur between different chemicals from the other departments of the tannery.

Statistical difference was found between the concentrations of chromium during the working day hours and night working hours ($P < 0.005$).

This could be due to the chromium sulphate powder which was added to the rotating drums at night, However these concentration were below TLV for chromium (TLV for chromium is 0.5 mg/m^3).

No significant differences in the concentrations of chromium in plasma were found between the exposed workers and controls. This indicated minimal absorption of chromium through the skin and the lung of the workers. Since the skin absorption of the trivalent chromium is very low (12,13) and the concentration of the chromium in the air was within the TLV. Urinary level of chromium in exposed workers was $0.014 \mu\text{g}/100 \text{ ml}$ compared with the control $0.0088 \mu\text{g}/100 \text{ ml}$. These values were statistically insignificant increase in the concentra-

tion of the chromium in the body of the workers, since the urine represents the main route of excretion of chromium (14,15).

In conclusion, the concentration of chromium in the water that might come in contact with the skin of workers is relatively high and might induce a hyperesensitive reaction. However, the concentration was within the TLV in the air. plasma and urinary levels of chromium for exposed workers were within normal values. The work is in progress to define the health hazards of chromium in tanneries.

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