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Urine Chromium as an Estimator of Air Exposure to Stainless Steel Welding Fumes*

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Summary. Welding stainless steel with covered electrodes, also called manual metal arc welding, generates hexavalent airborne chromium. Chromium concentrations in air and post-shift urine samples, collected the same arbitrarily chosen working day, showed a linear relationship. Since post-shift urine samples reflect chromium concentrations of both current and previous stainless steel welding fume exposure, individual urine measurements are suggested as approximate although not exact estimators of current exposure. This study evaluates the practical importance of such measurements by means of confidence limits and tests of validity.

Key words: Chromium - Air - Urine - Stainless steel welding

Introduction

Stainless steel is an alloy which contains mainly iron, but chromium (10-20%) and nickel (0.5-20%) are also present. Welding in stainless steel is usually performed by an electric-arc method using covered electrodes, also known as manual metal arc welding. The electrodes used contain about the same amounts of chromium and nickel as the welded material. The chromium in airborne particles generated from such welding consists of 50-100% hexavalent chromium (Blomquist et al. 1980; Lautner et al. 1978; Thomsen and Stern 1979; Tola et al. 1977). This hexavalent chromium has tentatively been associated with the development of pulmonary tumors (Sjögren 1980), as well as asthma (Keskinen et al. 1980) among stainless steel welders.

Previous studies of stainless steel welders have shown urine chromium concentrations to be related to recent chromium exposure (Gylseth et al. 1977; Tola et al. 1977), as well as to previous exposure (Kalliomäki et al. 1981; Mutti et al. 1979).

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The purpose of this study was to investigate to what extent post-shift urine chromium measurements could predict the current chromium concentration in the air and to calculate sensitivity and specificity for such estimations at given air concentrations.

Subjects

Fifty-three welders participated in the study. All welders were males and worked with rutile as well as basic electrodes in stainless steel. The mean age was 43 years (range 25–64 years) and the mean exposure time was 15 years (range 1–39 years). The number of current smokers in the group was 24. The welders were employed in 14 different companies situated from Lund in the south to Gävle in the north of Sweden. The industries examined manufacture coolers, heat exchangers, turbines, pipe-constructions etc. Local exhaust ventilation was very seldom used.

Methods

The welding fume samples were collected on cellulose ester membrane filters (Millipore Filter AAWP ⌀ 37 mm, mean pore size 0.8 μm) with personal sampling pumps (MSA Monitaire Sampler Pump, Model G). The air flow was checked several times during the sampling period. The filters were placed inside the welding helmet. The sampling time was at least 6 h and all concentrations were calculated as 8-h time weighted averages.

Total chromium concentrations were analyzed with a particle induced X-ray emission (PIXE) technique at the Department of Nuclear Physics, Institute of Technology in Lund. The detection limit was 0.1 $\mu g/m^3$ (Ulfvarson 1981) and the coefficient of variation was 10% (Johansson and Johansson 1976).

At the end of the working day, the welders voided their urine in acid-washed polyethylene bottles. The density of the freshly voided urine was measured with a refractometer. The urine samples were kept frozen at −20°C until further analysis for chromium concentrations.

Chromium concentrations in urine were determined by electrothermal atomic absorption spectrometry. The detection limit of this method was 20 nmol/l (1 $\mu g/l$) and the coefficient of variation was about 10% (Nise and Vesterberg 1979). All these determinations were performed at the Unit of Chemistry at the National Board of Occupational Safety and Health. Urine concentrations were adjusted to standard density, 1,024 (Elkins et al. 1974).

Air and urine concentrations were measured on the same working day. This day was arbitrarily chosen in the working week and should represent normal working conditions.

Linear regression was calculated according to the method of least squares. Tests of equality of regression lines for smokers and non-smokers have been made by covariance analysis (Rao 1965). The p-values refer to two-tailed tests.

Results

The time-weighted mean air chromium concentration was 124 $\mu g/m^3$ (median 103 $\mu g/m^3$) and the mean post-shift chromium concentration in urine was 718 nmol/l (37 $\mu g/l$) and the median was 610 nmol/l (32 $\mu g/l$).

The air concentration of total chromium showed a linear relationship to post-shift urine concentrations among the welders ($r=0.72$, $P<0.001$) (Fig. 1). When urine concentrations were adjusted to standard density (1,024), the coefficient of

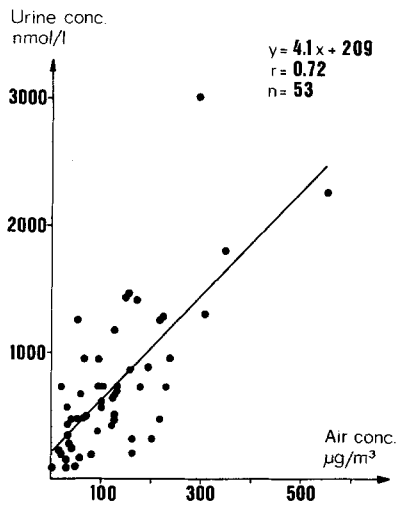

Fig. 1. 8-h TWA air concentrations and unadjusted post-shift urine concentrations of chromium among stainless steel welders

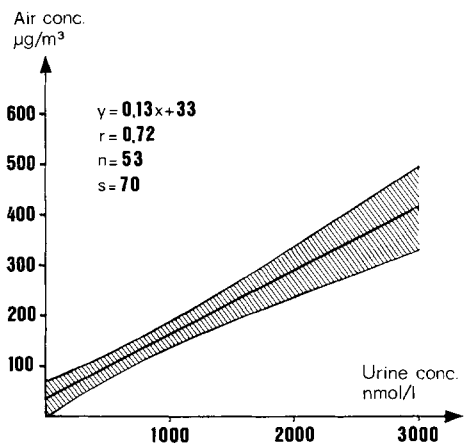

Fig. 2. 95% confidence limits for 8-h TWA mean air exposure of chromium in relation to unadjusted post-shift urine concentrations among stainless steel welders

correlation became somewhat lower ($r=0.68$, $P< 0.001$) while the equation of regression was $y=3.8\ x+273$.

The regression lines for smoking and non-smoking welders did not differ significantly, though there was a tendency for smokers to have higher urine concentrations ($P = 0.08$ for a test of distance between the regression lines).

There was no relationship between exposure time expressed as stainless steel welding years and urine concentrations of chromium. As a linear relationship existed between concentrations of chromium in air and urine, it was possible to use the chromium concentration in urine as an estimator of welding fume chromium exposure. A regression line was calculated with urine concentration

as the independent variable (x) and air concentration as the dependent variable (y). Ninety-five per cent confidence limits for the prediction of mean air concentrations were calculated (Fig. 2).

Discussion

Previous studies and this study have shown a relationship between air and urine chromium concentrations in stainless steel welders. This discussion is focused on the interpretation of such chromium concentrations in urine.

Half-times

Rats inhaling particles from stainless steel welding for 4 weeks increased their content of chromium in several organs. The rate of decrease varied. Blood showed a rapid decrease with a half-time of about 6 days, while lungs showed a slower decrease with a half-time of about 40 days (Kalliomäki et al. 1982).

Welders exposed to stainless steel welding fumes have shown urinary chromium concentration half-times ranging from 15 to 41 h (Tossavainen et al. 1980). Other studies of such welders have shown an accumulation of chromium in the human body (Kalliomäki et al. 1981; Mutti et al. 1979), but the half-time of this slowly excreted fraction is unknown so far.

These studies on animals and humans indicate that chromium excretion follows at least a two-compartment model.

Relations Between Air and Urine Concentrations

Some studies have shown significant correlations between air and post-shift urinary chromium concentrations sampled on the same working day. One study found a linear relationship between the logarithm of total air chromium concentration and the logarithm of urinary chromium concentration (Gylseth et al. 1977). When this regression line is used for predictions, a urinary chromium concentration of about 550 nmol/l (29 μg/l) will correspond to an air concentration of 20 μg/m^3 (the current Occupational Exposure Limit for hexavalent chromium in Sweden). If 50% of the airborne chromium is supposed to be in the hexavalent state, which is regarded as the most hazardous state of chromium, the corresponding urinary chromium concentration will be about 770 nmol/l (40 μg/l).

Another study found a linear relationship between hexavalent chromium in the air and urinary chromium concentration (Tola et al. 1977). When this regression line is used for prediction, a urinary chromium concentration of about 650 nmol/l (34 μg/l) will correspond to a hexavalent chromium air concentration of 20 μg/m^3.

When the regression line of this study (Fig. 1) is used for the same type of predictions, a urinary chromium concentration of about 290 nmol/l (15 μg/l) will correspond to 20 μg/m^3. If 50% of the airborne chromium is supposed to be in the hexavalent state, the corresponding urinary chromium concentration will be about 370 nmol/l (19 μg/l). The discrepancy of the results between this study and

Table 1. Tests of validity for the estimation of air concentrations of chromium above and below 20 $\mu g/m^3$ from post-shift urine concentrations

		Air concentration ($\mu g/m^3$	
		Above 20	Below 20
Urine concentration (nmol/l)	Above 120	48	2
	Below 120	2	1

Sensitivity: $\frac{48}{50}=96\%$

Specificity: $\frac{1}{3}=33\%$

Predictive value: $\frac{48}{50}=96\%$

Table 2. Tests of vailidity for the estimation of air concentrations of chromium above and below 40 $\mu g/m^3$ from post-shift urine concentrations

		Air concentration ($\mu g/m^3$)	
		Above 40	Below 40
Urine Concentration (nmol/l)	Above 250	37	6
	Below 250	4	6

Sensitivity: $\frac{37}{41}=90\%$

Specificity: $\frac{6}{12}=50\%$

Predictive value: $\frac{37}{43}=86\%$

Table 3. Reference values for urinary chromium concentration (nmol/l) (Atomic Absorption Spectrometry) among unexposed persons reported from six countries

Country	Mean	95% confidence limits
FRG (Schaller et al. 1972)	35	0–77
Finland (East) (Punsar et al. 1977)	45	41–48
Finland (West) (Punsar et al. 1977)	41	39–43
Italy (Borghetti et al. 1977)	35	7–62
Japan (Nomiyama et al. 1980)	8	0–22
Sweden (Wrangskogh personal communication 1982)	9	0–20
USA (Guthrie et al. 1978)	10	8–11

the other two studies might to some extent be explained by the very few welders examined in the earlier studies, but also by possible differences in chromium body burden.

However, predictions of air chromium concentrations should not be performed from a regression line where air concentration is the independet variable but rather from a regression line where urine concentration is the independent variable and air concentration is the dependent variable (Fig. 2) (Snedecor and Cochran 1980). This regression line shows that a urine concentration of about 120 nmol/l (6.2 μg/l) corresponds to the lower 95% confidence limit of the mean chromium exposure at 20 $\mu g/m^3$.

Sensitivity and Specificity

The results can be evaluated in terms of sensitivity and specificity. For this purpose 20 $\mu g/m^3$, being the Occupational Exposure Limit for hexavalent chromium in Sweden, was chosen as the air chromium concentration limit and 120 nmol/l, (6.2 μg/l), corresponding to the lower 95% confidence limit for this mean air exposure, was chosen as the urinary chromium concentration limit (Table 1).

If 50% of the airborne chromium is in a hexavalent state, a urine concentration of about 250 nmol/l (13 μg/l) means that with 97.5% probability the mean chromium exposure was above 40 $\mu g/m^3$ according to the regression equation. In this case the sensitivity will be the same but the specificity will increase (Table 2). A urine concentration above 250 nmol/l indicates with high probability (86%) that the current exposure exceeds 20 $\mu g/m^3$, when 50% of the chromium is hexavalent. On the other hand, a urine concentration below 250 nmol/l does not discriminate with respect to this air concentration.

The highest urine concentration in the group exposed to air concentrations below 40 $\mu g/m^3$ was 720 nmol/l (37 μg/l). This means that all urine concentrations above 720 nmol/l are associated with air concentrations above 40 $\mu g/m^3$ (Predictive value 100%, sensitivity 41).

Reference Values and Effects of Smoking

Surveys from six countries indicate that urinary chromium concentrations are most often below 100 nmol/l (5 μg/l) among persons without occupational exposure to chromium (Table 3). It is difficult to explain the discrepancies between the urine concentrations presented from the different countries.

Urinary chromium concentrations have been reported to be somewhat higher in smoking than in non-smoking stainless steel welders (Kalliomäki et al. 1981). This study shows the same tendency, although the difference is not statistically significant.

Conclusion

In view of the present knowledge, it seems as if not only the current exposure to airborne chromium in stainless steel welding fumes, but also previous exposure,

contributes to the urinary chromium concentrations. A single urinary chromium measurement could not be used as an exact estimator of current exposure. However, such urine measurements can be used for approximate estimations of airborne exposure, as has been shown in this and other studies, and therefore can be of some practical value for the monitoring of current exposure among stainless steel welders.

Exposure to other chromium compounds will probably give other relations between chromium in air and urine due to different chemical and physical characteristics of the chromium particles and their different biological behaviour.

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