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Sampling and analysis of hexavalent chromium during exposure to chromic acid mist and welding fumes

by Göran Blomquist, PhD, Carl-Axel Nilsson, PhD, Olle Nygren, BSc¹

BLOMQUIST G, NILSSON C-A, NYGREN O. Sampling and analysis of hexavalent chromium during exposure to chromic acid mist and welding fumes. *Scand j work environ & health* 9 (1983) 489–495. In view of the serious health effects of hexavalent chromium, the problems involved in its sampling and analysis in workroom air have been the subject of much concern. In this paper, the stability problems arising from the reduction of hexavalent to trivalent chromium during sampling, sample storage, and analysis are discussed. Replacement of sulfuric acid by a sodium acetate buffer (pH 4) as a leaching solution prior to analysis with the diphenylcarbazide (DPC) method is suggested and is demonstrated to be necessary in order to avoid reduction. Field samples were taken from two different industrial processes—manual metal arc welding on stainless steel without shield gas and chromium plating. A comparison was made of the DPC method, acidic dissolution with atomic absorption spectrophotometric (AAS) analysis, and the carbonate method. For chromic acid mist, the DPC method and AAS analysis were shown to give the same results. In the analysis of welding fumes, the modified DPC method gave the same results as the laborious and less sensitive carbonate method.

Key terms: atomic absorption spectrophotometry, carbonate, diphenylcarbazide, plating, work environment.

Chromium is widely used in various industrial applications – such as plating, tanning, metallurgy, welding and wood preservation – and gives rise to occupational problems in many work environments. Hexavalent chromium is suggested to be the most toxic form of chromium in view of its ability to penetrate cell membranes and its strong oxidizing effect on biological materials. Known toxic effects are ulcers, perforation of the nasal septa, sinusitis, laryngitis, and asthma. Bronchial carcinogenesis and gastrointestinal diseases have also been reported (6, 7).

Numerous studies on various aspects of chromium are reported in the literature. Recently analytical methods for

the analysis of chromium in water (11), biological material (14), and in the environment and workplace (12) have been reviewed. Specific analytical methods for hexavalent chromium (Cr^{6+}) are, due to its serious health effects, of great interest, especially for samples from work environments.

In the control of occupational exposure, biological monitoring is also a useful tool (10), especially when skin contact is possible (eg, tanning, working with cement).

Analytical methods used for the preparation of air samples from the occupational environment are different extraction procedures with complexing agents like ammonium pyrrolidine dithiocarbamate (APDC) (2) or selective leaching (8, 13). The analysis is then performed with spectrophotometric methods or atomic absorption spectrophotometry (AAS).

The present communication provides a practical and simple approach to some

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of the most frequent types of samples taken from workroom air, ie, chromic acid mist and welding fumes. Other methods discussed in the literature for these types of samples are sulfuric acid extraction followed by diphenylcarbazide (DPC) complexation and spectrophotometric determination (1) and carbonate leaching prior to DPC complexation (8) or AAS (13). These methods are compared and discussed in relation to the modified DPC method proposed in this paper.

Materials and methods

Chemicals

All the chemicals were of analytical grade or higher quality. Water was purified in a Millipore R/Q water purifier. Sodium acetate buffer (0.1 M NaAc buffer, pH 4) was prepared by the addition of 20 ml of 0.1 M acetic acid to 80 ml 0.1 M sodium acetate. The DPC reagent was prepared by the dissolution of 0.5 g of DPC (Merck) in 100 ml of acetone and the addition of water to 200 ml. The DPC reagent can be stored in a dark bottle at 4° C for at least one month. The aqua regia was made by the mixing of two parts of concentrated nitric acid (suprapur, Merck), one part of concentrated hydrochloric acid (suprapur, Merck), and one part of water. Stock solutions of chromium were 1,000 mg/ml of potassium dichromate and

1,000 mg/ml of chromium trioxide (Cr^{6+}) and a commercial atomic absorption standard, 1,000 mg of trivalent chromium (Cr^{3+}) per milliliter (British Drug House Chemicals Ltd) for the analysis of total chromium.

Sampling material and glassware

All glassware was washed with tap water and detergent, soaked in concentrated nitric acid, and then thoroughly rinsed with deionized water. The filters used for the stability tests were Millipore AAWP (cellulose esters, 0.8 μm), Millipore BSWP (polyvinyl chloride, 2.0 μm), Gelman DM 800 (polyvinyl chloride, 0.8 μm) and Whatman GF/A (glass fiber). Millipore BSWP was used for the sampling of workroom air. Air was passed through the filter with the use of a Casella membrane pump with an approximate flow rate of 1 l/min. The exact flow rate was measured with a precision rotameter every 15 min. If the variation in rate exceeded 10 %, the sample was discarded.

Instrumentation

For the spectrophotometric determinations, we used a Pye Unicam SP1700 ultraviolet spectrophotometer operated at 544 nm with a 4-cm cuvette. The AAS determinations were performed with a Pye Unicam SP1900 atomic absorption

Fig 1. Analytical scheme. (DPC = diphenylcarbazide, NaAc = sodium acetate, AAS = atomic absorption spectrophotometry, Cr = chromium, Cr^{6+} = hexavalent chromium, conc = concentrated)

spectrophotometer. Chromium was measured at 357.9 nm in a nitrogen oxide/acetylene flame.

Sampling

Airborne chromic acid was sampled in a chromium-plating plant. Samples were collected above the plating bath and in the breathing zone of the workers. Manual metal arc welding was performed in a workshop under normal ventilation with electrode OK 63.30 (18.5 % chromium, 12.5 % nickel) 4 × 350 mm on stainless steel SIS 2543 (17 % chromium, 11.5 % nickel) on a welding bench in the center of the room.

Analysis

The various methods used for analyzing chromium are summarized in fig 1. A detailed description is given below.

Total amount of chromium. The filters were treated in 10 ml of aqua regia on a water bath (80° C) for 2 h. The samples were filtered and diluted to 15 ml with water. Samples and suitable reference standards (Cr^{3+}) in the same matrix were then analyzed for chromium with AAS.

Hexavalent chromium, modified diphenylcarbazide method. The filters were shaken in 7 ml of NaAc buffer for 3 min and then twice in 3 ml for 1 min. For samples stored for more than one week, the leaching time was extended to 15 min. The volume of the combined extracts was adjusted to 15 ml with the NaAc buffer. (Any undissolved residues were saved for the determination of the total amount of chromium.) Depending on the concentration, 1–10 ml of the samples was further diluted with NaAc buffer to 10 ml. Then 0.5 ml of the DPC reagent was added, and the volume increased to 15 ml with 0.3 M sulfuric acid. Samples and suitable standards (Cr^{6+}), prepared in the same matrix, were allowed to stand for 15 min before the colorimetric determination so that the violet-colored complex could develop. In the remaining NaAc extracts the total amount of chromium was determined by AAS using the Cr^{6+} standard.

Hexavalent chromium, carbonate method. The carbonate method, as described by Thomsen & Stern (13), is based on a fractionated extraction of Cr^{6+} . First, water-soluble chromates (eg, Na^+ or K^+ salts) are extracted with water. Second, chromates that are not readily soluble (eg, Pb^{2+} and Ba^{2+} salts) are dissolved in boiling sodium carbonate solution. Finally, chromium compounds that are the most difficult to dissolve are treated in boiling, concentrated mineral acid or, if necessary, with some kind of incineration (eg, hydrofluoric acid or sodium peroxide). The three fractions are then analyzed for chromium with AAS and compared with suitable standards (Cr^{6+} or Cr^{3+}) in the same matrix. The total amount of chromium is then calculated by the summing of the amount of chromium in each fraction.

Results and discussion

Stability of hexavalent chromium during sampling, sample storage and analysis

For a specific determination of Cr^{6+} any interference which may cause reduction to the trivalent form must be avoided. In the preparation of the sample for analysis by the DPC method, Abell & Carlberg recommend leaching in 0.5 M sulfuric acid (1). This procedure results however in a significant reduction (3, 9) of Cr^{6+} within 10 min. In order to avoid this reduction, the stability of Cr^{6+} in an NaAc buffer was studied and compared with that in sulfuric acid. From the results it is obvious that the NaAc buffer is more suitable for leaching the filters than an acid solution is (fig 2).

A method recently proposed by the US National Institute for Occupational Safety and Health (8) is based on alkaline carbonate leaching of the samples prior to DPC analysis. However, Carelli et al (4) reported that, if sodium carbonate is used for leaching the filters, the absorbance of the sample decreases as a function of time. The average depressive effect was reported to be 26 %. Therefore the stability of the DPC complex in the NaAc buffer was investigated with the use of two different Cr^{6+} compounds – potassium dichromate and chromic acid.

Fig 2. Stability of hexavalent chromium (Cr^{6+}) in various solutions with increasing storage time prior to analysis. (● = sodium acetate buffer, pH4; ▼ = 0.1 M sulfuric acid; ■ = 0.25 M sulfuric acid)

Table 1. Stability of the complex between hexavalent chromium (Cr^{6+}), added as potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) or chromium trioxide (CrO_3), and diphenylcarbazide in sodium acetate buffer at pH 4. Mean value of four determinations. (2 µg chromium sample)

Time	Recovery of Cr^{6+} (%)	
	$\text{K}_2\text{Cr}_2\text{O}_7$	CrO_3
5 min	100	100
15 min	100	100
30 min	100	100
1 h	98	99
1.5 h	97	97
2 h	95	95
24 h	~60	~60

Table 2. Recovery of hexavalent chromium (Cr^{6+}) from various types of filter. (3 µg of hexavalent chromium was added as potassium dichromate to each filter)

Filter	Recovery			
	25 h		1 week	
	%	N	%	N
Millipore BSWP (polyvinyl chloride)	93	5	93	4
Gelman DM 800 (polyvinyl chloride)	95	5	88	4
Millipore AAWP (cellulose esters)	< 50	5	—	—
Whatman GF/A (glass fiber)	95	5	94	4

The results are shown in table 1. The complex was sufficiently stable for 90 min, which should be adequate to accomplish the analysis.

Another important factor to consider for the sampling of Cr^{6+} is possible reduction on the filter. This possibility was pointed out by Dutkiewicz et al (5), who showed that a cellulose acetate filter reduced the Cr^{6+} to Cr^{3+} . Abell & Carlberg (1) reported that the use of polyvinyl chloride filters (Gelman VM-1) eliminated the problem. In this study we determined the recovery of Cr^{6+} from four different types of filter (table 2). As expected, the cellulose ester filters gave a significant reduction of Cr^{6+} . Reduction of Cr^{6+} in samples of welding fumes on cellulose ester filters was not studied. However, to avoid any possibility of reduction due to the filter material, these filters were not used for sampling in workroom air.

No reduction was observed on the polyvinyl chloride or glass fiber filters. If the filters were stored for several days, however, the Cr^{6+} was more difficult to recover from the filters. The leaching time had to be extended to at least 15 min. This effect was especially pronounced for the Gelman DM 800 filters. The glass fiber filter, although no reduction was observed on it, was considered less suitable since disintegration made filtration or centrifugation necessary.

Another factor which might contribute to the reduction of Cr^{6+} is the presence of reducing components in the sample matrix. If organic dust is present in the samples, its influence on the stability of Cr^{6+} in the sample should be investigated for each type of sample matrix. Several other metals frequently occur along with chromium in work environments. Detailed investigations of the reductive effects of different metal ions on Cr^{6+} have been described in the literature (4, 9, 13). Bivalent iron (Fe^{2+}) has been reported to be one of the most severely interfering ions and also a constituent of welding fumes (13). However, Naranjit et al (9) reported that no Fe^{2+} is extracted at levels higher than pH 3. The use of NaAc buffer for leaching the samples thus solves the problem.

In order to demonstrate the stability of Cr^{6+} during the sampling and analysis of welding fumes and to determine the

Cr⁶⁺/total chromium ratio, we collected a number of samples in a small workshop. The welding was performed as manual metal arc welding on stainless steel without shield gas. Cr⁶⁺ was determined by the modified DPC method with NaAc buffer leaching. These results were compared to the level of total chromium obtained by the analysis of the NaAc buffer solution by AAS and also by the analysis of parallel samples with dissolution in aqua regia and AAS analysis. The remaining filters from the NaAc buffer leaching were also dissolved in aqua regia and analyzed by AAS, and the chromium residue was always less than 1 %. The results are shown in table 3. Only a slight reduction could be observed after two weeks' storage. Thomsen & Stern (13) claimed that the reduction they observed in similar samples was due to a matrix reductive effect. They used cellulose filters for sampling, however, which might cause reduction.

Comparison of the diphenylcarbazide method and atomic absorption spectrophotometry in the analysis of chromium in samples from a chromium-plating plant

In the plating process, hydrogen gas is evolved during electrolysis, and, when it leaves the plating bath, a mist of chromic acid is generated. In samples of this type, all chromium should be hexavalent and the analytical method, DPC or AAS, is just a matter of choice. However, flame AAS analysis is less sensitive and requires larger air samples, about 500 l, to obtain a practical detection limit of one-fifth of the Swedish hygienic standard. This amount should be compared to less than 15 l with the proposed DPC method.

In order to verify that all chromium is hexavalent and that no reduction occurs in that type of matrix, we collected 40 samples in a chromium-plating plant. All filters (polyvinyl chloride, Millipore BSWP) were analyzed by the DPC method. The remaining NaAc extracts and acid-digested filter residues were then analyzed for total chromium. The results are presented in fig 3, which shows that only Cr⁶⁺ was present. No reduction occurred, and both methods gave the same result.

Comparison of the modified diphenylcarbazide and carbonate methods

Samples of welding fumes from manual metal arc welding on stainless steel without shield gas were collected on polyvinyl chloride filters. Each filter was cut in half. One-half was analyzed by the modified DPC method, and the other by the carbonate method. The results are shown in table 4. There was no significant difference in the levels of Cr⁶⁺. In the carbonate method, however, DPC analysis of the carbonate fraction is unsuitable since, according to Carelli et al (4), there

Table 3. The effect of storage time on hexavalent chromium in samples of welding fumes collected on polyvinyl chloride filters (Millipore BSWP). The loading on the filters was in the range of 20–40 µg of chromium.

Storage time	Hexavalent chromium: total chromium ratio	Relative standard deviation (%)	N
15 min	1.05	4	17
1 h	1.01	4	17
24 h	1.07	3	18
2 weeks	0.93	6	17

Fig 3. Comparison of the modified diphenylcarbazide (DPC) method with atomic absorption spectrophotometry (AAS) analysis in the case of samples taken on polyvinyl chloride filters in a chromium-plating plant. (Cr⁶⁺ = hexavalent chromium)

Table 4. Comparison of the modified diphenylcarbazide (DPC) and carbonate methods in the analysis of hexavalent chromium (Cr^{6+}) in fumes from manual metal arc welding on stainless steel without shield gas. (Filters divided in two parts before the analysis.) Loading of hexavalent chromium on the filters was in the range of 10–40 μg .

Cr^{6+} (mg/m^3)	Relative standard deviation (%)	N
<i>DPC method</i>		
0.25	8	10
<i>Carbonate method</i>		
0.24	31	10

is a risk of interference from the carbonate. The analysis was thus made by AAS, which makes the method less sensitive. In the carbonate method, about 20 % of the Cr^{6+} was found in the carbonate fraction. All Cr^{6+} was soluble in the NaAc buffer. For these types of samples the modified DPC method thus gives the same result as the more laborious carbonate leaching method (8, 13).

Conclusions

For the sampling and analysis of Cr^{6+} in work environments, the modified DPC method described in this paper has proved to be suitable. A practical detection limit for the method is well below 2 $\mu\text{g}/\text{m}^3$ for a 30-l air sample. As also pointed out by Abell & Carlberg (1), to avoid reduction of the Cr^{6+} , sampling should be performed on polyvinyl chloride filters.

Fumes from welding on stainless steel are a source of occupational exposure to Cr^{6+} . Manual metal arc welding is frequently used, and the samples analyzed in this study showed that all chromium is present in the hexavalent state. The DPC method, based on sampling on polyvinyl chloride filters and NaAc buffer leaching, was demonstrated to give the same results as the more laborious carbonate method (8, 13). For metal inert gas welding on stainless steel, it has been reported that the total chromium content is a maximum of 14 % and that the Cr^{6+} content is 0–0.3 % (13). Hygienic standards in Sweden are 5 mg/m^3 for dust, 0.5 mg/m^3 for chromium, except Cr^{6+} , and 0.02 mg/m^3 for Cr^{6+} . Therefore both the hygienic stan-

dard for dust and chromium are, even in extreme cases, well exceeded before the level of Cr^{6+} reaches 0.02 mg/m^3 . Thus there is no need for a selective analysis of Cr^{6+} in samples from metal inert-gas welding. Simple dissolution in aqua regia and AAS analysis should be sufficient.

For the sampling and analysis of airborne Cr^{6+} in a chromium-plating plant, both the DPC method and the AAS analysis are suitable. The choice depends only on the sampling time and the analytical equipment available.

Because of the disturbance of carbonate already mentioned, the DPC method is less suitable for the analysis of samples containing carbonate, eg, cement dust.

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