

Comparison of three sampling and analytical methods for the determination of airborne hexavalent chromium†

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A field study was conducted with the goal of comparing the performance of three recently developed or modified sampling and analytical methods for the determination of airborne hexavalent chromium (Cr^{VI}). The study was carried out in a hard chrome electroplating facility and in a jet engine manufacturing facility where airborne Cr^{VI} was expected to be present. The analytical methods evaluated included two laboratory-based procedures (OSHA Method ID-215 and NIOSH Method 7605) and a field-portable method (NIOSH Method 7703). These three methods employ an identical sampling methodology: collection of Cr^{VI} -containing aerosol on a polyvinyl chloride (PVC) filter housed in a sampling cassette, which is connected to a personal sampling pump calibrated at an appropriate flow rate. The basis of the analytical methods for all three methods involves extraction of the PVC filter in alkaline buffer solution, chemical isolation of the Cr^{VI} ion, complexation of the Cr^{VI} ion with 1,5-diphenylcarbazide, and spectrometric measurement of the violet chromium–diphenylcarbazone complex at 540 nm. However, there are notable specific differences within the sample preparation procedures used in three methods. To assess the comparability of the three measurement protocols, a total of 20 side-by-side air samples were collected, equally divided between a chromic acid electroplating operation and a spray paint operation where water soluble forms of Cr^{VI} were used. A range of Cr^{VI} concentrations from 0.6 to $960 \mu\text{g m}^{-3}$, with Cr^{VI} mass loadings ranging from 0.4 to $32 \mu\text{g}$, was measured at the two operations. The equivalence of the means of the log-transformed Cr^{VI} concentrations obtained from the different analytical methods was compared. Based on analysis of variance (ANOVA) results, no statistically significant differences were observed between mean values measured using each of the three methods. Small but statistically significant differences were observed between results obtained from performance evaluation samples for the NIOSH field method and the OSHA laboratory method.

Introduction

The carcinogenic properties of hexavalent chromium (Cr^{VI}) are well documented, and workplace exposure to Cr^{VI} remains problematic.^{1,2} As a consequence, the US Occupational Safety and Health Administration (OSHA) anticipates a one hundred-fold reduction in the permissible exposure limit (PEL), to $0.50 \mu\text{g m}^{-3}$ as an 8 h time-weighted average (TWA).³ Because existing sampling and analytical methods for Cr^{VI} were not sufficiently sensitive to quantitatively measure this species at the newly proposed regulatory level, new or modified analytical procedures were needed which offered lower detection limits for Cr^{VI} . Hence OSHA developed laboratory method ID-215,⁴ and the US National Institute for Occupational Safety and Health (NIOSH) modified the NIOSH laboratory methods 7600 and 7604 for hexavalent chromium⁵ (the modification is hereafter referred to as NIOSH Method 7605⁶), in order to provide analytical methods which were able to quantitatively measure Cr^{VI} at much lower levels than the earlier procedures permitted.

An aim of this work was to compare the performance of the new OSHA and NIOSH laboratory methods for the determination of Cr^{VI} (OSHA Method ID-215 and NIOSH Method

7605, respectively). In addition, a sampling and analytical method recently developed for the on-site field analysis of Cr^{VI} air samples (NIOSH Method 7703) was also evaluated.⁷ The availability of these new methods presented an opportunity to compare and evaluate their performance in determining Cr^{VI} concentrations in workplace atmospheres.

Background

Table 1 presents the salient descriptive characteristics of the three Cr^{VI} sampling and analytical methods considered in this work. As shown in Table 1, the two laboratory methods (OSHA ID-215 and NIOSH 7605) are similar procedures with respect to sample collection and analysis, the exception being the extraction solutions employed. Unlike the NIOSH laboratory procedure, the OSHA ID-215 method incorporates Mg^{II} (as magnesium sulfate) in the alkaline buffered extraction solution.⁴ The intended function of added magnesium species in the OSHA procedure is to minimize potential positive bias due to air oxidation of Cr^{III} to Cr^{VI} during hot plate extraction by effecting the precipitation of Cr^{III} .⁸ Although utilizing an alkaline buffered extraction solution, the NIOSH 7605 procedure does not incorporate a precipitation agent during hot plate extraction (since this may cause coprecipitation of Cr^{VI}). Both the OSHA and NIOSH methods rely on ion chromatography^{9,10} to separate Cr^{VI} from Cr^{III} and other metal (and ionic) interferences.

NIOSH method 7703 was developed primarily for assessing Cr^{VI} exposures in occupational environments where sampling

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Table 1 Salient descriptive characteristics of NIOSH and OSHA sampling and analytical methods for hexavalent chromium

Parameter	NIOSH 7605	OSHA ID-215	NIOSH 7703
<i>Sample collection, handling and storage—</i>			
Media:	PVC ^a 37 mm; 5.0 µm Cellulose backup pad	PVC 37 mm; 5.0 µm Cellulose backup pad	PVC, MCE or PTFE 37 mm; 5.0, 0.8, 1.0 µm Cellulose backup pad
Equipment:	Personal sampling pump	Personal sampling pump	Personal sampling pump
Flow rate:	1–4 L min ⁻¹	2 L min ⁻¹	1–4 L min ⁻¹
Sample preparation for shipment to laboratory:	Using Teflon [®] -coated tweezers, transfer filter to 20 mL glass vial with Teflon [®] cap liner	Using Teflon [®] -coated tweezers, transfer filter to 20 mL glass vial with Teflon [®] cap liner	Not applicable if analyzed on-site. Same sample handling as NIOSH 7605 and OSHA ID-215 if analyzed off-site.
Sample refrigeration:	Optional	4 °C	None required
<i>Sample preparation and analysis—</i>			
Extraction solution:	2% NaOH/3% Na ₂ CO ₃ or 0.05 M (NH ₄) ₂ SO ₄ /0.05 M NH ₄ OH (pH 8)	10% Na ₂ CO ₃ /2% NaHCO ₃ /phosphate buffer/Mg II (as MgSO ₄) (pH 8)	0.05 M (NH ₄) ₂ SO ₄ /0.05 M NH ₄ OH (pH 8)
Extraction equipment:	Hot plate	Hot plate	Ultrasonic bath
Cr ^{VI} isolation:	Ion chromatography	Ion chromatography	Strong anion exchange solid phase extraction
Eluent:	0.25 M (NH ₄) ₂ SO ₄ /0.1 M NH ₄ OH	0.25 M (NH ₄) ₂ SO ₄ /0.1 M NH ₄ OH	0.5 M (NH ₄) ₂ SO ₄ /0.1 M NH ₄ OH
Post-column reagent: (derivatization)	2 mM 1,5 diphenylcarbazide/ 10% methanol/1 M H ₂ SO ₄	2 mM 1,5 diphenylcarbazide/ 10% methanol/1 M H ₂ SO ₄	1,5 diphenylcarbazide/acetonitrile solution added to eluent acidified with 1 M HCl
Analyte:	Cr–DPC complex ^b	Cr–DPC complex	Cr–DPC complex
Detection:	UV-Vis: ^c 540 nm	UV-Vis: 540 nm	UV-Vis: 540 nm
LOD/LOQ ^d /µg:	0.02/0.06	0.01/0.03	0.09/0.27
Accuracy:	± 16.5%	± 12.9%	± 16.8%

^aPVC: polyvinylchloride; MCE: mixed cellulose ester; PTFE: polytetrafluoroethylene. ^bDPC: diphenylcarbazide/diphenylcarbazone. ^cUV-Vis: ultraviolet-visible. ^dLOD/LOQ: limit of detection/limit of quantitation.

results are needed within a short time period (*i.e.*, less than two hours after sampling). This method has been shown to be a simple, fast, practical and economical alternative to the laboratory methods, with an analytical detection limit slightly higher than the fixed-site laboratory methods.^{7,11} The NIOSH 7703 procedure employs a portable, battery-powered spectrophotometer and other portable laboratory equipment, which underscores the utility of this method for field analysis. Additionally, the field method allows for the use of other sampling media besides PVC filters, if desired.¹² Furthermore, this method can be used by employers with in-house analytical capabilities who require valid sampling results in less time than it takes for contract laboratory analysis. It is also noted that ultrasonic extraction is used for the field-portable method instead of hot plate extraction, and solid-phase extraction is employed rather than ion chromatography in order to effect the isolation of Cr^{VI}.^{7,11–14} These sample preparation procedures were chosen because of their ease for on-site use and demonstrated performance attributes.^{11,12}

Experimental

Collection of field samples

Workplace air samples were collected during electroplating operations at a hard chrome electroplating facility and during spray painting operations at an aircraft engine manufacturing facility. Both facilities utilized water-soluble forms of Cr^{VI}; in the former operation no other sources of chromium were apparent, whereas in the latter operation Cr^{III} was also a known (minor) constituent in the paint. The sampling strategy involved collection of ten sample clusters per operation, for a total of twenty sample clusters (as recommended for field testing of analytical methods).¹⁵ Each sampling cluster was composed of four 37 mm diameter filter cassettes positioned in a side-by-side configuration. Three of the four cassettes in each cluster contained 5.0 µm pore size polyvinyl chloride (PVC) membrane filters for subsequent Cr^{VI} analysis. The remaining cassette contained a mixed cellulose ester (MCE) filter intended

for subsequent total chromium analysis by NIOSH Method 7300.¹⁶ Overall, the sampling strategy involved the collection of 80 filter samples, *i.e.*, 20 filter samples for each of the three Cr^{VI} methods and 20 filter samples for the total chromium method. Pre-loaded filter cassettes containing either PVC or MCE filters were obtained from SKC, Inc. (Eighty-Four, PA, USA).

Each filter cassette was connected to a Universal XR personal sampling pump (SKC) calibrated at an air flow rate of 2 ± 0.1 L min⁻¹. The sampling clusters were positioned above open surface chromic acid tanks or downstream of a paint sprayer in a ventilated, walk-in paint spray booth. Variable particulate (*i.e.*, Cr^{VI}) loadings were achieved on each of the clusters by adjusting sampling times, location of clusters from the source and/or duration of operation. Sampling durations ranged from 5 to 356 min. Following sampling, the PVC filters were removed from the cassettes and placed into appropriately labeled 20 mL glass vials with a Teflon[®] lined caps (Fisher Scientific, Pittsburgh, PA, USA). (The NIOSH 7600 and 7604 procedures, *i.e.*, measurement of Cr^{VI} by visible absorption spectrophotometry or by ion chromatography with conductivity detection, respectively, recommend this transfer in order to prevent the reduction of Cr^{VI} collected on the filters. However, this step is probably unnecessary for PVC filters). The MCE filters were not removed from the cassettes until analysis (by NIOSH 7300). The vials and cassettes were stored in a cooler or refrigerator at 4 °C until prepared for analysis.

Analysis

The three PVC filter samples within each sampling cluster of four filters were analyzed for Cr^{VI}: one by OSHA ID-215,⁴ one by NIOSH 7605,⁶ and one by NIOSH 7703⁷ (see Table 1). The NIOSH 7605 procedure⁶ combines the hot plate extraction and ion chromatographic sample preparation steps of NIOSH 7604 with the spectrophotometric detection technique of NIOSH 7600.⁵ The MCE filter sample within each sampling cluster was analyzed for total chromium by hot plate extraction and inductively coupled plasma atomic emission spectrometry (ICP-AES), per NIOSH 7300.¹⁶

Quality assurance/quality control

To estimate recoveries of the Cr^{VI} methods, two types of quality assurance/quality control (QA/QC) samples were utilized: spiked samples and certified reference material (CRM) samples. The spiked QA/QC samples contained known concentrations of Cr^{VI}, prepared from potassium chromate (obtained from Aldrich, Milwaukee, WI, USA) aqueous solution, which were quantitatively added to PVC filters and MCE filters within previously unopened filter cassettes. The PVC filters were subsequently analyzed for Cr^{VI} by each of the three Cr^{VI} analytical methods, and the MCE filters were subsequently analyzed for total chromium by NIOSH 7300. The CRM samples (CRM 545) consisted of welding dust loaded onto glass fiber filters, and were obtained from the Institute for Reference Materials and Measurements (IRMM, European Commission, Brussels, Belgium); each CRM contained approximately 100 µg of Cr^{VI} in welding dust loaded onto the filter.¹⁷ All QA/QC samples (both CRMs and spikes) were prepared and measured at least in triplicate by NIOSH 7605, OSHA ID-215, NIOSH 7300 and NIOSH 7703. QA/QC spike samples were prepared blind to the analyst, with Cr^{VI} mass loadings ranging from 0.24 to 124 µg per filter. All QA/QC samples were labeled in the same way as were the field samples, incorporated with the field samples during shipment to the respective laboratories, and subjected to the same extraction and analysis procedures as the field samples.

Statistical treatment

The chromium concentrations in field samples were found to follow a lognormal distribution, so all statistical tests on field samples were performed using logarithmically transformed data. A two-way analysis of variance (ANOVA) was used to test the equivalence of the mean values obtained from each method.¹⁸ The ANOVA model took the form:

$$y_{ij} = \log(x_{ij}) = \mu + M_i + G_j + e_{ij} \quad (i = 1, 2, 3; j = 1, 2, \dots, 20),$$

where y_{ij} is the logarithm of the measurement result x_{ij} from the i th analytical method for the j th sample cluster, μ is the overall mean value, M_i represents the effect of method i , G_j represents the effect of cluster j , and e_{ij} is an error term. Sample results obtained using each method were also compared using paired t -tests and bivariate plots of the experimental data. In the bivariate plots, best-fit lines through the data were estimated

Table 2 Hexavalent and total chromium concentrations (µg m⁻³) measured in field samples (by sample cluster)

Cluster	NIOSH 7605 ^a	OSHA ID-215 ^a	NIOSH 7703 ^a	NIOSH 7300 ^b
1	2.38	1.90	0.61	6.07
2	5.16	4.01	3.23	9.33
3	26.3	19.4	15.0	28.8
4	57.3	38.9	33.7	65.1
5	70.0	41.9	87.2	73.7
6	160	159	151	206
7	160	147	206	251
8	212	252	247	284
9	170	174	221	299
10	285	216	259	311
11	261	211	352	320
12	199	217	— ^c	324
13	250	254	270	347
14	289	334	421	510
15	429	304	482	521
16	259	280	360	588
17	686	485	519	653
18	438	377	379	659
19	648	764	812	980
20	689	675	960	1061

^aMethods for hexavalent chromium. ^bMethod for total chromium. ^cSample lost.

using least squares linear regression, and the resulting slopes were tested to see whether they were significantly different from unity.

Results

Analysis of field samples

All filter samples (with the exception of one filter sample meant for analysis by NIOSH Method 7703, which was lost) yielded detectable levels of Cr^{VI} or total chromium. Table 2 presents Cr^{VI} and total chromium concentrations for each of the 20 clusters, arranged in order from lowest to highest total chromium concentration. A wide range of Cr^{VI} concentrations, ranging from 0.6 to 960 µg m⁻³, with mass loadings ranging from 0.4 to 32 µg per filter, was measured. Although spanning three orders of magnitude, the measured Cr^{VI} concentrations were all greater than the OSHA proposed PEL (8 h time-weighted average) of 0.5 µg m⁻³, with 75% of the values exceeding 100 µg m⁻³, which is the current OSHA PEL (ceiling).

To evaluate the comparability of the measured Cr^{VI} concentrations for the 20 sample clusters, the equivalence of the means for the three Cr^{VI} sampling and analysis methods was tested using analysis of variance (ANOVA) on the log-transformed Cr^{VI} concentrations.¹⁹ The ANOVA results for the field samples showed no statistically significant differences ($p > 0.05$) among the mean Cr^{VI} concentrations measured by each of the three methods. Pairwise comparisons between methods using paired t -tests gave identical results.

Analytical results for total chromium were generally greater than corresponding results for the speciation analysis of Cr^{VI} (from samples within the same sample cluster). When comparing Cr^{VI} concentrations for the three methods to total chromium concentrations, Cr^{VI} concentrations typically averaged between 60 and 80% of total chromium concentrations (Table 2), and these differences were statistically significant ($p < 0.05$).

Additional statistical tests of the analytical results obtained by the three different Cr^{VI} methods were carried out to assess whether or not the methods performed equivalently. Specifically, comparisons of Cr^{VI} concentrations measured for each of the three Cr^{VI} methods were made by determining whether a statistically significant difference (at the $\alpha = 0.05$ significance level) existed between the slope of the line of best fit and a slope of unity. (A slope of exactly unity would indicate that each method measured identical concentration values.)

Plots of the following three possible combinations of Cr^{VI} sampling and analytical methods, namely NIOSH 7605 vs.

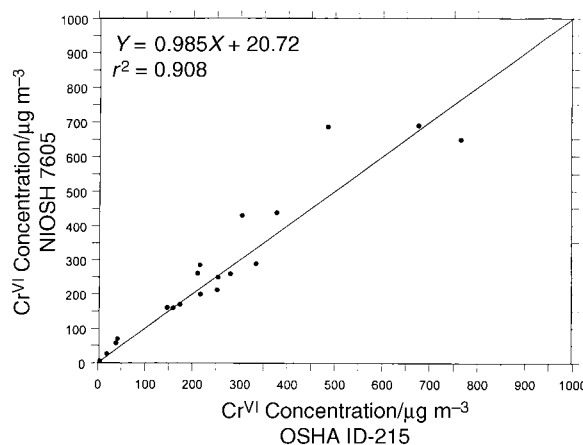


Fig. 1 Comparison of hexavalent chromium concentrations measured in field samples: NIOSH Method 7605 vs. OSHA Method ID-215. The line through the plot indicates unity slope and zero intercept, and does not represent the equation of the best fit line indicated on the figure.

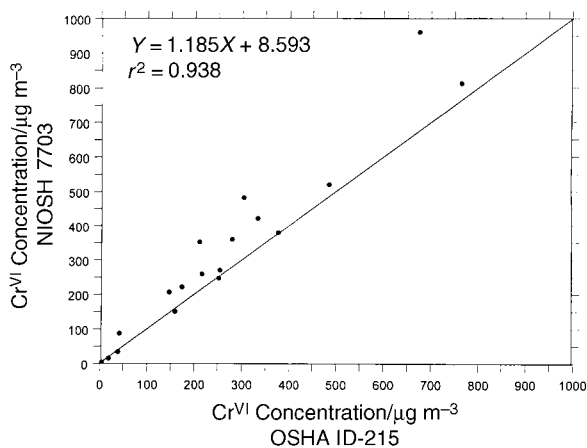


Fig. 2 Comparison of hexavalent chromium concentrations measured in field samples: NIOSH Method 7703 vs. OSHA Method ID-215. The line through the plot indicates unity slope and zero intercept, and does not represent the equation of the best fit line indicated on the figure.

OSHA ID-215, NIOSH 7703 vs. OSHA ID-215, and NIOSH 7703 vs. NIOSH 7605, are presented in Fig. 1, 2 and 3, respectively. (Also shown in the figures are lines of slope unity for comparison purposes.) It is noted that in each case the intercept for each line was not found to be significantly different from zero. There were no statistically significant differences observed between a line of slope 1.0 and the slope of the line defined by Cr^{VI} concentrations measured by OSHA ID-215 and NIOSH 7605, nor for those measured by NIOSH 7605 and NIOSH 7703. Cr^{VI} concentrations measured by NIOSH 7703, however, were (slightly) statistically significantly higher than those measured by OSHA ID-215, as evidenced by a slope close to but nonetheless significantly greater than unity (Fig. 2). Correlations of $r^2 \approx 0.9$ were observed for all three method comparisons (see Fig. 1, 2 and 3).

Quality assurance/quality control samples

Mean recoveries for QA/QC samples, which consisted of spiked samples and CRMs, were found to be quantitative (*i.e.*, 100% ± 20%) for all three Cr^{VI} methods, as well as for the total chromium analysis by NIOSH Method 7300 (Table 3). Recoveries of Cr^{VI} are lowest by the OSHA ID-215 procedure, intermediate for the NIOSH 7605 method, and highest for the NIOSH 7703 protocol. However, differences in recoveries from QA/QC samples are statistically significant only between NIOSH 7703 and OSHA ID-215 (as determined using two-way ANOVA,¹⁸ $p < 0.05$, as well as pairwise *t*-tests¹⁹). Relative standard deviations (RSDs) are less than 10% in all but one instance (Table 3).

Discussion

The ANOVA results described above for Cr^{VI} measurement in field samples (see Table 2) showed no statistically significant difference ($p > 0.05$) among the means obtained by each of the three methods. This analysis indicates that the three analytical methods investigated performed equivalently in terms of the

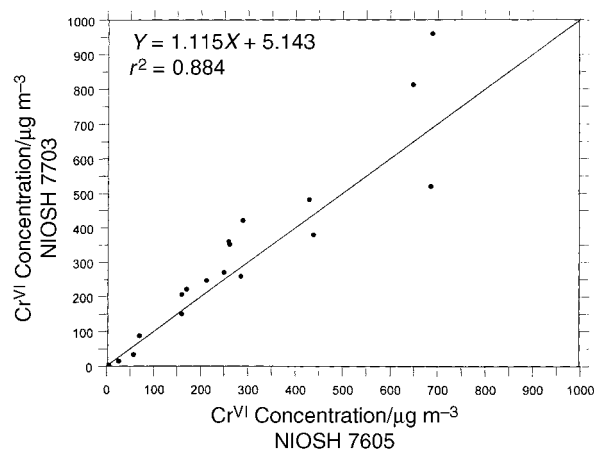


Fig. 3 Comparison of hexavalent chromium concentrations measured in field samples: NIOSH Method 7703 vs. NIOSH Method 7605. The line through the plot indicates unity slope and zero intercept, and does not represent the equation of the best fit line indicated on the figure.

mean airborne concentrations of Cr^{VI} in each sample cluster measured by each method.

Analytical results for total chromium are generally greater than results for Cr^{VI} (Table 2), since apparently not all of the sampled chromium is in the hexavalent form; evidently some trivalent and/or metallic chromium, Cr⁰, is also present.²⁰ Some reduction of Cr^{VI} to Cr^{III} may occur during sampling,^{21,22} and this is a limitation of the sampling method which the analytical procedure cannot alleviate. If such a reduction is suspected, Cr^{III} can be measured (if desired) by various means, *e.g.*, ion chromatography,^{4,23} voltammetry,²⁰ or other techniques.²⁴

Recoveries greater than 75% are recommended by NIOSH for acceptable air sampling and analytical methods, and RSDs of 15% or less are generally recommended for QA/QC samples of the kind analyzed here.¹⁵ The QA/QC recovery and precision data (Table 3) indicate that the three methods evaluated here are acceptable for the quantitative measurement of airborne Cr^{VI} in the workplaces investigated.

Slightly lower recoveries of Cr^{VI} were obtained by using the OSHA ID-215 method vs. the two NIOSH procedures (Tables 2 and 3). Some co-precipitation of Cr^{VI} could occur in concert with precipitation of Cr^{III} when using the OSHA hot plate extraction procedure (which employs Mg^{II} as a precipitation agent for Cr^{III}; see Table 1). Co-precipitation of Cr^{VI} may be responsible for the slightly lower recoveries obtained when using the OSHA ID-215 procedure.

The NIOSH 7703 field procedure has shown no evidence of Cr^{VI} reduction nor Cr^{III} oxidation,¹¹ which suggests that ultrasonic extraction in ammonium sulfate buffer serves to stabilize both chromium species during the extraction procedure. Indeed, confirmation of this contention by other workers has recently demonstrated the stabilization of Cr^{III} and Cr^{VI} during ultrasonic extraction in ammonium buffer.²⁵ Thus ultrasonic extraction in this buffer may offer advantages to hot plate extraction in other buffer systems for the purpose of chromium speciation. Such extractions may be used in the fixed-site laboratory as well as in the field by on-site analysis.¹³

In conclusion, a field comparison of three recently developed or modified Cr^{VI} sampling and analytical methods showed no

Table 3 Hexavalent and total chromium recoveries (%) from QA/QC samples

Analytical method	<i>n</i> spikes; CRMs	Mean recovery ± RSD ^a (%) for spikes; CRMs
OSHA ID-215	13; 3	90.4 ± 8.2; 84.3 ± 1.9
NIOSH 7605	13; 3	94.9 ± 6.4; 94.2 ± 9.9
NIOSH 7703	11; 6	96.0 ± 12.9; 98.4 ± 6.7 ^b
NIOSH 7300	7; 5	107.4 ± 7.4; 111.3 ± 6.8

^aRelative standard deviation. ^bExcludes one statistical outlier (Dixon's *Q*-test¹⁹).

statistically significant differences among the means of the three methods based on statistical analysis of variance. The overall performance of the three Cr^{VI} methods was comparable in electroplating and spray painting operations where soluble Cr^{VI} was present. Although the findings reported herein are representative of workplace operations utilizing soluble forms of Cr^{VI}, these analytical methods (using identical sample preparation procedures) also have been shown to quantitatively measure insoluble forms of Cr^{VI} in other occupational settings.¹¹⁻¹⁴ There were no significant differences observed among Cr^{VI} concentrations measured by NIOSH 7605 and OSHA ID-215. By using regression analysis to compare methods, Cr^{VI} concentrations measured by NIOSH 7703 were found to be statistically significantly higher than those measured by OSHA ID-215, and higher (but not with statistical significance) than those measured by NIOSH 7605. Mean recoveries from QA/QC samples were found to be quantitative (100% ± 20%) for all three methods. The precision of the three Cr^{VI} methods (as measured by RSDs from analysis of QA/QC samples) ranged from ~2 to ~13%

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