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Chromium speciation by anion-exchange high-performance liquid chromatography with both inductively coupled plasma atomic emission spectroscopic and inductively coupled plasma mass spectrometric detection ☆

Francine A. Byrdy, Lisa K. Olson, Nohora P. Vela, Joseph A. Caruso*

Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172, USA

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Abstract

Development of a new method for the determination of Cr(III) and Cr(VI) is described. Anion-exchange high-performance liquid chromatography (HPLC) was used to separate Cr(III) and Cr(VI) with on-line detection by inductively coupled plasma atomic emission spectroscopy (ICP-AES) at 2766 Å in preliminary studies, and inductively coupled plasma mass spectrometry (ICP-MS) with single-ion monitoring at m/z 52 and m/z 53 for final work. A mobile phase consisting of ammonium sulfate and ammonium hydroxide was used, and a simple chelation procedure with EDTA was followed to stabilize the Cr(III) species in standard solutions. ICP-MS results indicated the feasibility of using chromium isotope m/z 53 instead of the more abundant m/z 52 isotope due to a high mobile-phase background most significantly from the SO^+ polyatomic interference. The absolute detection limits based on peak-height calculations were 40 pg for Cr(III) and 100 pg for Cr(VI) in aqueous media by HPLC–ICP-MS. The linear dynamic range extended from 5 ppb (ng/ml) to 1 ppm (μg/ml) for both species. By HPLC–ICP-AES, detection limits were 100 ng for Cr(III) and 200 ng for Cr(VI). Cr(III) was detected in NIST-SRM 1643c (National Institute of Standards and Technology-Standard Reference Material, Trace Elements in Water) by HPLC–ICP-MS at the 20 ppb level.

1. Introduction

In May 1988, a symposium was held entitled "The Chromium Paradox in Modern Life [1]". The symposium title not only illustrates the current interest in chromium, but aptly describes the element as a "paradox" as well. Chromium is naturally-occurring, commonly found in rocks and minerals, and is used in numerous industrial processes including steel alloying and textile production. Known to exist in all oxidation states from 0 to VI, Cr(III) and Cr(VI) are the forms most commonly found [2]. There are a number of predominant chromium species which may exist depending on solution pH [2–4].

Chromium is a "paradox" since it is classified as both biologically important and also as a toxic industrial hazard depending upon its oxidation state. Cr(III) is known to be an essential trace nutrient involved in the mechanism of the action

* Corresponding author.

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of the pancreatic hormone insulin and/or glucose metabolism [5]. No minimum daily requirement of chromium has yet been established, but 50–200 μg per day is considered adequate. Cr(III) is found in fruits, vegetables, meats, cereals and various other foods. A deficiency of this nutrient may lead to glucose intolerance [6]. Conversely, Cr(VI) is known to be carcinogenic and mutagenic. Unlike Cr(III), Cr(VI) may cross cellular membranes by way of non-specific anion carriers [7], causing skin ulcerations, nasal perforations, and lung cancer [2]. The subsequent reduction of Cr(VI) to intermediates such as Cr(IV) and Cr(V) is thought to play a role in its toxicity [7].

It is obvious that speciation (the determination and quantitation of different chemical forms) is necessary to obtain an adequate toxicological sample assessment for chromium. As a result, several methods for inorganic chromium speciation have been described. Non-chromatographic methods are generally labor and time-intensive. In general, flow-injection and HPLC procedures appear to be simpler and more rapid. A summary of some of these methods with UV, FAAS (flame atomic absorption spectroscopy), ETAAS (electrothermal atomic absorption spectroscopy), DCP (direct current plasma)-AES, and ICP-AES detection may be found in Ref. [8]. Often, Cr(III) is calculated by subtraction of Cr(VI) from total chromium. This type of calculation may involve some uncertainty. Simultaneous determination would not only be less time-consuming, but would pose less risk of calculation errors [9]. In some studies, a conversion step with Ce(IV) was necessary, but this may introduce contaminants [10,11]. Preconcentration is commonly done on-column to improve detection limits. However, poor sensitivity, low sampling frequency [12,13], and incomplete recovery [12] may result anyway. In another study spectral interferences from low selectivity posed a problem [14].

There are only a few HPLC techniques which have employed ICP-AES or DCP-AES detection for the speciation of chromium [15–21]. Various advantages may be obtained using ICP-MS detection over these optical techniques. ICP-MS provides excellent sensitivity, selectivity, and the potential for isotope determinations. Plasma-MS detection limits are generally two to three orders of magnitude lower than those attainable using AES, and new advances in software programs allow the user to acquire data simultaneously for several elements over time. In addition, elemental MS spectra are relatively simple compared to optical spectra.

Roehl and Alforque [22] have compared colorimetric with ICP-MS detection for the determination of Cr(VI) by ion chromatography (IC). Detection limits for both methods were in the 1–2 ppb range for Cr(VI). Total chromium was determined without IC and Cr(III) may be calculated from the difference. As stated earlier, this type of calculation is unfavorable. Arar et al. [23] have reported the off-line determination of Cr(VI) in sludge incinerator emissions using an ion chromatographic method from Ref. [3]. A preconcentration scheme and post-column reaction were used, followed by the collection, acidification, and dilution of samples prior to ICP-MS detection. On-line detection of both Cr(III) and Cr(VI) in one step would be less time-consuming. Jakubowski et al. [24] have speciated chromium using ion-pair chromatography and hydraulic high-pressure nebulization with ICP-MS detection. Since the eluent contained 25% methanol, polyatomic interferences from carbon were a problem.

As indicated in the previous paragraph, problems may be encountered when an HPLC method is developed for ICP-MS detection. The coupling of HPLC with plasma MS is not always straightforward. Restrictions are placed on the types of mobile phases which may be employed in order to achieve overall simplicity of the interface. Particular areas of concern include the salt and organic content of the mobile phase. Clogging of the torch tip and orifices of the ICP-MS may result from salt deposition when mobile phases with total dissolved salt concentrations greater than 0.2% are used. Clogging can lead to decreased sensitivity and unsatisfactory detection limits. Organic mobile phases tend to cause plasma instability as well as carbon deposition on the sampler and skimmer cones which can lead to decreased sensitivity. Additionally, the polyatomic ion $^{40}Ar^{12}C^{+}$ may form when organic mobile phases such as those com-

monly employed in reversed-phase or ion-pairing techniques are used, and interference problems may ensue.

The method chosen was adapted from a Technical Note by Dionex Corporation [3]. This anion-exchange method was described for the determination of Cr(VI) in water, wastewater, and solid waste extracts employing a post-column reaction scheme using diphenylcarbohydrazide (DPC) in an acidic medium with visible detection at 520 nm. Bulk sample analysis may be done using DPC. There are, however, potential interferences from other colored species such as Fe(III) or Cu(II) complexes. Additionally, V, Mo, and Hg may form colored reaction products with DPC and interfere with the detection of Cr [8]. This technical note has been modified and extended to the determination of both Cr(III) and Cr(VI) by utilizing a very simple chelation procedure to stabilize the former species [9]. No post-column reaction was necessary with either ICP-AES or ICP-MS detection. The accuracy of the final method was assessed by analyzing a certified reference material, and the experimental results were compared with the certified reference value.

2. Experimental

2.1. Instrumentation

A Dionex metal-free HPLC system (Model DX-300, Sunnyvale, CA, USA) consisting of an advanced gradient pump with an eluent degas module was used. A Rheodyne (Cotati, CA, USA) Model 9125 metal-free injector was employed with a 100-μl injection loop. The temperature of the analytical column was controlled at 25°C with an Alltech water jacket (Alltech Associates, Deerfield, IL, USA). The outlet of the analytical column was connected directly to a type C1 concentric nebulizer (Precision Glassblowing of Colorado, Parker, CO, USA) by means of Teflon tubing of 0.012 mm I.D. and 68 cm in length. A double-pass spray chamber was used.

For preliminary work, the ICP-AES instrument used was a Plasma-Therm HFS-2500D (Kreeson, NJ, USA). All gas flow-rates were regulated with a needle valve flowmeter which was calibrated before experiments were begun. A 1.26 m Czerny-Turner Model 1269 (Spex Industries, Metuchen, NJ, USA) monochromator with a 2400 lines/mm grating was used. A potential of 750 V was applied for detection with the photomultiplier tube. The data acquisition was done with a Datamate microcomputer (Spex Industries) and spectra were plotted using a Houston Instrument's HI Plotter. Operating conditions for the ICP-AES set-up are given in Table 1.

The ICP-MS instrument was a VG PlasmaQuad PQII + Turbo equipped with a high-performance interface (VG Instruments, Winsford, Cheshire, UK). A nickel sampler and skimmer, each with a 1.0-mm orifice, were used. Adjustment of the sampling position and ion lenses for the optimum chromium signal at m/z 52 and m/z 53 was done using solution nebulization of a 10 ppb standard of both chromium species in distilled, deionized water. Operating conditions for the ICP-MS set-up are given in Table 1.

2.2. Reagents

The mobile phase was prepared from 99.999% ammonium sulfate (Aldrich, Milwaukee, WI, USA), double distilled ammonium hydroxide (Aldrich), and distilled, deionized 18 MΩ water (Barnstead, Boston, MA, USA). The mobile

Table 1
Typical ICP-AES and ICP-MS operating conditions

Conditions	ICP-AES	ICP-MS
Rf power		
Forward	1.35 kW	1.45 kW
Reflected	<5 W	<5 W
Gas flow-rates		
Auxiliary	1 l/min	1.2 l/min
Coolant	16 l/min	12 l/min
Nebuliser	1 l/min	1 l/min
Spray chamber	double-pass	double-pass
Nebuliser	concentric	concentric

phase was degassed prior to use and an in-line filter was employed. For ICP-AES work, Cr(III) stock solutions (1000 ppm) were made from $CrCl_3 \cdot 6H_20$ (Fisher Scientific, Fair Lawn, NJ, USA) in 5% (v/v) redistilled nitric acid (GFS Chemicals, Columbus, OH, USA) (in distilled, deionized 18 MΩ water). For the ICP-MS method, a chelation procedure was followed as given below.

For both ICP-AES and ICP-MS work, a Cr(VI) stock solution (1000 ppm) was prepared after drying $K_2Cr_2O_7$ (99.95–100.05%, Aldrich) in a 90°C oven for 2 h. Distilled, deionized 18 MΩ water was used for dilutions. All working solutions were prepared fresh daily from stock solutions filtered through sterile 0.2-μm hydrophilic nylon membranes (Alltech Associates). Standards ranging in concentration from 1 ppm to 100 ppm were employed in the ICP-AES study. With ICP-MS detection, standards ranged from 1 ppb to 1 ppm. Stock solutions were made separately and then mixtures of Cr(III) and Cr(VI) were prepared fresh on the day of analysis. The mixtures were naturally at a pH of 5.

2.3. Chelation procedure

To stabilize the Cr(III) species and guard against the potential oxidation of Cr(III) to Cr(VI), a chelation procedure found in the literature was employed in the ICP-MS method only [9]. For the stock standard (600 ppm), Cr(III) as $CrCl_3 \cdot 6H_2O$ was dissolved in distilled, deionized 18 MΩ water, and the disodium salt of EDTA (Fisher Scientific) was added to the 600 ppm Cr(III) stock standard. The mixture was heated for 1 h at 50°C and the pH of the solution was adjusted to 4.0 with NH_4OH. A blank solution was prepared with an amount of EDTA corresponding to that present in a mixture of chelated Cr(III) and Cr(VI) at a concentration of "1 ppm" which was the highest standard concentration employed.

2.4. Chromatography

For this study, a 250 × 4 mm I.D. IonPac AS7 10 μm column (Dionex Corp.) was used. In addition, an IonPac AG7 guard column (50 × 4 mm I.D.) was employed in the ICP-AES method, and an IonPac NG1 guard column (35 × 4 mm I.D.) in the ICP-MS method. Both guard columns were purchased from Dionex. The IonPac NG1 is a polymeric reversed-phase column, while the IonPac AS7 and IonPac AG7 are mixed-mode columns. This means that although the AS7 and AG7 columns are primarily used as anion-exchangers, they do have some cation-exchange sites.

Two mobile phase conditions were studied. The chromatography for the ICP-AES method was taken from Ref. 3 with a few modifications: (1) the corresponding guard column to the AS7, the AG7, was used instead of the NG1 as proposed in the publication; (2) no post-column reaction scheme was employed; and (3) standards were made in doubly distilled 5% HNO_3 since this matrix was found to be optimal for the study. The ICP-MS method utilized a weaker mobile phase, the NG1 guard column, and a flow-rate of 2.0 ml/min to reduce the analysis time by 1/3. A comparison of the method conditions is given in Table 2. Prior to use, both the analytical and guard columns (Dionex AS7 and AG7 or NG1) were conditioned by pumping the mobile phase through the columns at a flow-rate of 2 ml/min for at least 1 h.

Chromatography data were collected at 2677.16 Å for ICP-AES detection and using single-ion monitoring at m/z 52 and m/z 53 with a 1.3-s integration time for ICP-MS detection. Data were transferred to an in-house program so that results could be easily imported into a spreadsheet.

3. Results and discussion

In anion-exchange chromatography, the column contains cationic sites to which solute anions are attracted. In the simplest case, an anion should be retained on an anion-exchange column, while a cationic species should be unretained and elute with the void volume or the solvent front. At acidic pH, Cr(III) exists pri-

Table 2
HPLC method conditions for ICP-AES and ICP-MS detection

Conditions	ICP-AES Method	ICP-MS Method
Eluent	250 m*M* $(NH_4)_2SO_4$ 100 m*M* NH_4OH pH 9.2	35 m*M* $(NH_4)_2SO_4$ pH 9.2 with NH_4OH
Column	Dionex IonPac AS7 Dionex IonPac AG7	Dionex IonPac AS7 Dionex NG1
Dimensions	250 × 4 mm 10 μm particle size	250 × 4 mm 10 μm particle size
Injection loop	100 μl	100 μl
Flow-rate	1.5 ml/min	2.0 ml/min
Detector	ICP-AES 2677.16 Å ICP-MS *m/z* 52 and 53	ICP-MS *m/z* 52 and 53

marily as a cation, while Cr(VI) exists as an anion from pH 2 and beyond pH 6. Since the AG7 column has some cation-exchange sites, the elution of both species proved to be more complicated than originally expected.

3.1. ICP-AES method

Fig. 1 shows a chromatogram obtained from a mixture injection of 5 μg of each chromium species with ICP-AES detection using the sulfate

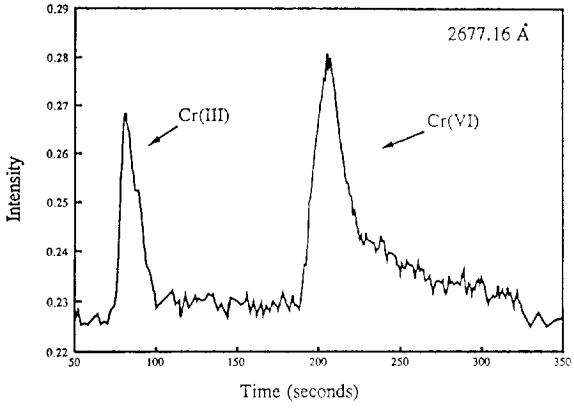

Fig. 1. Chromatogram of a 5- μg injection of a chromium mixture at 2677 Å using the HPLC–ICP-AES conditions outlined in Table 2.

mobile phase. Tailing was evident on the Cr(VI) peak, and the retention time of the Cr(VI) species was slightly longer than that found in Ref. [3]. Table 3 gives the analytical figures of merit obtained utilizing this method with the emission system. Absolute detection limits were 100 ng for Cr(III) and 200 ng for Cr(VI). From the %R.S.D. (>10%), however, it became clear that Cr(III) was not eluting reproducibly from the column. Most likely, Cr(III) was strongly attracted to the cation-exchange sites on the column.

Table 3
Analytical figures of merit for HPLC–ICP-AES data

Figures of merit	Cr(III)	Cr(VI)
R^2 (cal. curve)	0.9987	0.9996
Slope of log–log curve	1.205 (10–50 ppm)	0.9131 (25–100 ppm)
Linear dynamic range	0.5	1
Relative detection limit	1 ppm	2 ppm
Absolute detection limit	0.1 μg	0.2 μg

3.2. ICP-MS method

The ICP-AES method was next applied to the ICP-MS system. A chromatogram showing the injection of 0.1 μg of each chromium species at m/z 53 is given in Fig. 2. As seen in the figure, tailing was now evident on the Cr(III) peak. The retention of Cr(III) was the same as that observed in the ICP-AES study, but Cr(VI) had shifted to a slightly longer retention time. Ultimately, the method as developed for AES detection was not suitable for MS detection due to the behavior of Cr(III) as well as the high mobile phase concentration which led to salt deposition and high background signals.

Additionally, it was discovered that the NG1 column used in Ref. [3] was employed to remove non-ionic organic compounds from the sample matrix which appear to complicate chromate analyses with the AS7 column. In order to adapt the method to ICP-MS detection, a new AS7 column and an NG1 guard column were used. To stabilize the Cr(III) species, a chelation procedure was followed. Finally, the concentration of ammonium sulfate in the mobile phase was decreased.

Using the new columns, the first parameter evaluated was the mass to use for single-ion monitoring. At m/z 52, chromium is 83.76% abundant, while at m/z 53 it is 9.55% abundant.

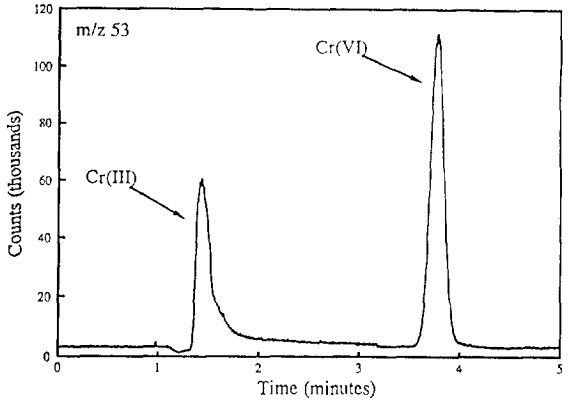

Fig. 2. Chromatogram of a 0.1-μg injection of a chromium mixture at m/z 53 using the HPLC–ICP-AES conditions outlined in Table 2.

Preliminary studies at m/z 52 showed a substantially high background (> 100 000 counts) from the 250 mM mobile phase alone. The background increased at both m/z values as the ammonium sulfate concentration was increased; presumably as a result of the formation of $^{36}S^{16}O^{+}$ and $^{36}S^{16}O^{1}H^{+}$ at m/z 52 and m/z 53, respectively. The effect was more pronounced at the former m/z value. Although ^{36}S only has a relative abundance of 0.02%, it can be present in a concentration equivalent to roughly 2 ppm in the 250 mM mobile phase. This is a substantial quantity for the very sensitive ICP-MS instrument. Roehl and Alforque [22] stated that the formation of this interference would "probably preclude the use of ^{52}Cr for the determination of chromium by ICP-MS" using a sulfate-containing mobile phase. Neither m/z 50 nor m/z 54 were used since the polyatomic interferences from argon and sulfate at these m/z values would be more abundant (i.e. $^{34}S^{16}O^{+}$ and $^{36}Ar^{14}N^{+}$ at m/z 50, and $^{38}Ar^{16}O^{+}$ at m/z 54).

As a result of the extremely high background at m/z 52, signal-to-background ratios were degraded. A comparison of the chromatograms in Fig. 3 shows improved ratios at m/z 53. Hence, this m/z value was chosen for the remainder of the studies. The abundance advantage at m/z 52 is largely offset by the high background signal.

Fig. 4 shows the effect of the mobile phase concentration on the retention of both Cr(III) and Cr(VI) at m/z 53. Since values for capacity factors between 2 and 10 are considered optimal for a given separation, it is immediately obvious from the figure that mobile phase concentrations below 35 mM are not ideal for the elution of Cr(VI). The capacity factor was calculated using a dip in the baseline at 78 s (corresponding to the solvent front) as the t_0 value. Ordinarily, one does not see the void volume using ICP-MS since one is detecting by mass. Sometimes, however, a baseline disturbance may be observed if the solvent plug briefly alters the plasma conditions.

Mobile phases containing high salt concentrations and the resulting clogging of parts of the ICP-MS system generally lead to decreased sensitivity. To circumvent this complication, the

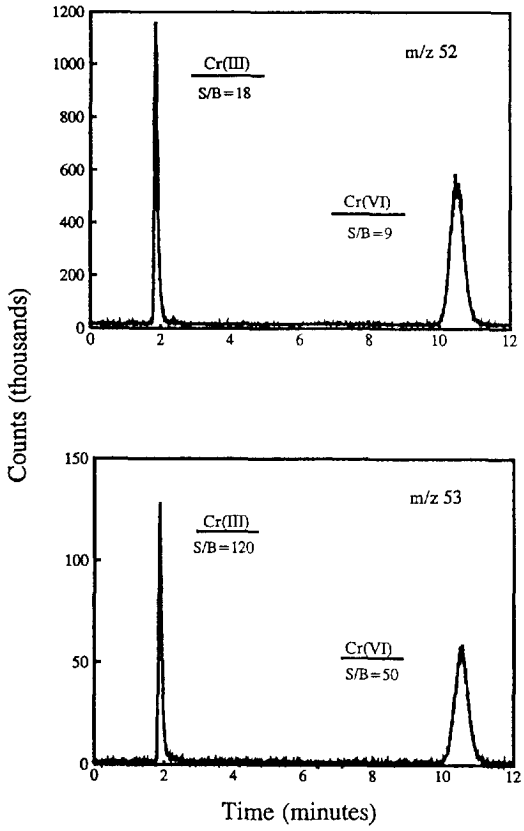

Fig. 3. Chromatograms of a mixture of Cr(III) (60 ng) and Cr(VI) (100 ng) with single-ion monitoring at *m/z* 52 and *m/z* 53 showing improved signal-to-background ratio at the latter *m/z* value. Conditions: pH 9.2, flow-rate 2 ml/min, 35 m*M* $(NH_4)_2SO_4$.

forward Rf power was initially increased to 1450 W and a nitric acid wash was employed when using the 250 m*M* mobile phase (containing 3.3% total dissolved salt). Both helped slightly, but because the background was very unstable at high concentrations, lowering the buffer concentration had the most significant effect. The best compromise between *k'* values for both chromium species and the mobile phase concentration was found using 35 m*M* $(NH_4)_2SO_4$ (containing 0.5% total dissolved salt).

Next, the effect of the mobile phase pH on the retention of both Cr(III) and Cr(VI) was evaluated using 35 m*M* ammonium sulfate and a flow-rate of 1.5 ml/min. No significant change was noted between pH 8.6 and 9.8. As a result, pH

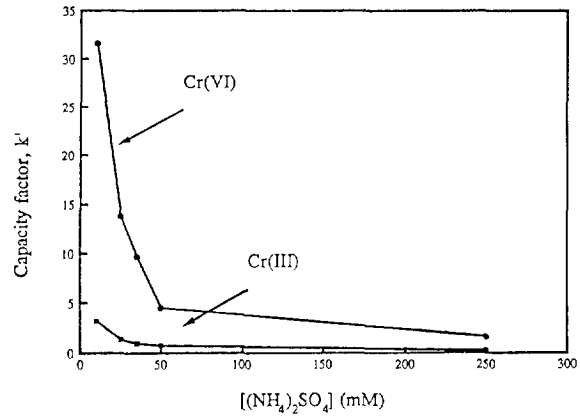

Fig. 4. Effect of mobile phase concentration on the retention of Cr(III) (6 ng) and Cr(VI) (10 ng) based on injection of a mixture at a flow-rate of 1.5 ml/min, mobile phase pH 9.2, and single-ion monitoring at *m/z* 53.

9.2 was chosen, corresponding to the pH used in the initial work [3].

Interconversion between the Cr(III) and Cr(VI) species was not observed in fresh solutions. No peaks corresponding to the elution of Cr(VI) or Cr(III) were observed in chromatograms when solutions of Cr(III) or Cr(VI), respectively, were injected onto the column. Some researchers have expressed concern that Cr(VI) could be converted to Cr(III) at low pH values [25], and that interconversion may also occur under other conditions [26]. The pH value and chelation procedure used here, however, did not facilitate Cr(VI) to Cr(III) conversion, thus indicating the stability of the chromium species under these conditions. Gjerde et al. have observed the same [18].

Analytical figures of merit for the ICP-MS method are given in Table 4. The method was linear over 2.5 orders of magnitude and the %R.S.D. values were found to be less than 5% for 7 replicate injections of a 50 ppb mixture. A significant improvement in the linear dynamic range is found when ICP-MS results are compared with ICP-AES data. This is more likely a result of initial problems with the chromatography rather than differences between the detection schemes. As expected, an improvement in detection limits of over 3 orders of magnitude from ICP-AES to ICP-MS detection was ob-

Table 4
Analytical figures of merit for HPLC–ICP-MS data

Figures of merit	Peak area		Peak height	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
R^2 (cal. curve)	0.9998	0.9990	0.9999	0.9990
Slope of log–log curve	1.081 (3–600 ppb)	0.9320 (5–1000 ppb)	1.072 (3–600 ppb)	0.9346 (5–1000 ppb)
Linear dynamic range	2.5	2.5	2.5	2.5
%R.S.D.	4	3	4	4
Relative detection limit	3 ppb	3 ppb	0.4 ppb	1 ppb
Absolute detection limit	0.3 ng	0.3 ng	0.04 ng	0.1 ng

served. Detection limits were calculated using 3 times the standard deviation of the blank divided by the slope of the calibration curve. Peak-height values for absolute detection limits were improved over peak-area values as a result of the way in which they were calculated. Since 12 blank values were used in the calculations for peak height as opposed to 6 blank values for the peak-area calculations, standard deviations were lower for the peak-height calculations and hence, detection limits were better. These limits are slightly lower than those found by Jakubowski et al. [24]. Additionally, the method presented here does not require a complex nebulization system.

3.3. Reference material

Since the method proposed in Ref. [3] is used for the analysis of chromium in water, wastewater, and solid waste extracts, a NIST-SRM 1643c (Trace Elements in Water) was chosen to assess the applicability of this method. The certified value for total chromium in the SRM is 19.0 ± 0.6 ppb. A standard curve was prepared using direct nebulization of the standards without chromatography, and a value of 21.0 ± 1.0 ppb was obtained for total chromium in the SRM. Only one peak corresponding to Cr(III) was found in the SRM (a chromatogram of unchelated SRM 1643c is given in Fig. 5). This is in agreement with the results obtained by others for this standard reference material [8,17]. A peak-area calculation for the single peak (18.5 ± 2.2 ppb) falls within the range for the certified value.

SRM 1643c was chelated with the disodium salt of EDTA. The complex was only slightly retained on the column, and a large baseline disturbance was observed after the peak. There is likely some carbon in the sample from excess free EDTA which gives rise to a rather broad

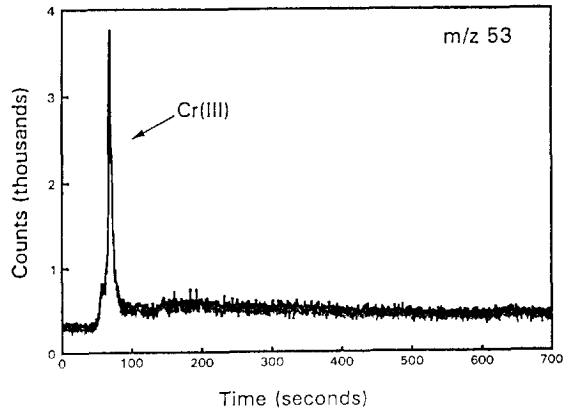

Fig. 5. Injection of 100 μl of NIST-SRM 1643c (Trace Elements in Water) using the HPLC–ICP-MS conditions outlined in Table 2 with single-ion monitoring at *m/z* 53.

peak as the EDTA elutes from the column. This is evident in chromatograms from the formation of ArC^+ in the plasma. Future work will include an investigation of alternative chelation procedures.

Unfortunately, at this time there are no commercially available standard reference materials for chromium which are certified to contain certain amounts of different species. Admittedly, developing these types of standards is a challenge since maintaining the integrity of the individual species may be difficult in certain matrices. Until a way is found to reliably produce these samples, researchers will have to continue to look at spiked samples, total elemental concentration standards, and interlaboratory results to assess the viability of a method.

4. Conclusions

In summary, it was concluded that chromium isotope m/z 53 will provide lower detection limits than the use of m/z 52 due to a high SO^+ mobile phase background. However, if one wishes to, the analysis may be performed successfully at m/z 52 in order to avoid a possible chlorine interference at m/z 53. Chlorine polyatomic interferences which may occur at m/z 53 include $^{37}Cl^{16}O^+$ and $^{35}Cl^{18}O^+$. Additionally, a "quick and dirty" sample analysis may be done at m/z 53 using a concentration of 50 mM $(NH_4)_2SO_4$ in the mobile phase to reduce the analysis time. Long analyses at this condition are poor due to salt deposition on the ICP-MS glassware over time.

One future possibility which could be explored is the use of a concentration gradient which could lead to a reduction in the analysis time. The method presented here, with absolute detection limits at the picogram level, should prove to be a viable alternative to other speciation techniques for chromium. Ultra-trace level detection by ICP-MS will be advantageous to various researchers. The use of this method for the evaluation of the purity of chromium in dietary supplements [27], the speciation of chromium in a urine standard reference material [28], and the determination of chromium in dyes has been presented elsewhere [29].

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