Chromium Speciation Analysis by Ion Chromatography Coupled with Inductively Coupled Plasma – Optical Emission Spectroscopy

Paul P. Coetzee*, Johann L. Fischer and Samantha Jansen van Vuuren

Department of Chemistry and Biochemistry, Rand Afrikaans University, P.O. Box 524, Auckland Park, 2006 South Africa.

Received 25 June 2003; revised 21 September 2003; accepted 19 January 2004.

ABSTRACT

Two methods coupling ion chromatography with inductively coupled plasma – optical emission spectroscopy (ICP-OES) were developed for the simultaneous separation and determination of Cr(III) and Cr(VI) species. In the first method, anion chromatography with sodium bicarbonate/carbonate solution as the eluent was utilized. Cr(III) species were protected from precipitation by complexation with ethylenediaminetetra-acetic acid (EDTA) prior to analysis. The detection limits were determined experimentally as 0.05 mg L^{-1} for both species. Most of the common cations were found to interfere with the accurate determination of Cr(III) when present in excess of 50 mg L^{-1}. In the second method using cation chromatography, a guard column was employed in conjunction with a stepwise elution programme to elute the chromium species. The detection limits were experimentally determined as 0.1 mg L^{-1} for both species.

KEYWORDS

Ion chromatography, ICP-OES, chromium speciation.

1. Introduction

Chromium has many industrial applications such as in the metallurgical (steel), chemical (electroplating, tanning) and refractory industries. It is due to its wide use in industry that chromium compounds find their way into the environment as liquid, solid and gaseous wastes. These wastes can have adverse effects on the environment. Only trivalent and hexavalent chromium are stable enough to occur in the environment. These two species are drastically different in their physicochemical properties as well as in their chemical and biochemical reactivity. Chromium(III) is regarded as an essential trace element in the human body and its roles include the control of glucose and lipid metabolism.[1,2] Chromium (VI), however, is found to be carcinogenic.[3] Hexavalent compounds are highly soluble and mobile whereas Cr(III) species are only sparingly soluble.

In the last decade various analytical techniques have been developed and employed to separate and determine chromium species in various samples. Often methods are based on prior separation before detection. Separation is mainly carried out by high performance liquid chromatography[4–13] and flow injection analysis.[14–19] Detection techniques include atomic absorption spectrometry, [20–23] inductively coupled plasma – optical emission spectroscopy (ICP-OES),[4,5,24] inductively coupled plasma – mass spectrometry,[5,10,25–28] chemiluminescence[9,11,29] and UV-VIS.[7,25,30]

The purpose of the current work was to develop a simple, fast and cost-effective method for the simultaneous determination of Cr(III) and Cr(VI) in routine analysis. This was achieved by developing two hyphenated techniques using ion chromatography and ICP-OES. In the first method separation was preceded by the complexation of Cr(III) with EDTA to form a stable anion. The chromium species were subsequently separated using anion chromatography. A second method using cation chromatography was also developed as it allowed for the use of an acidic eluent. Thus the metals did not require prior stabilization through complexation as the acidic medium prevents precipitation of the metals.

* To whom correspondence should be addressed: E-mail: ppc@na.rau.ac.za

2. Experimental

2.1. Instrumentation

2.1.1. Ion Chromatography

A Dionex Gradient Pump equipped with a Rheodyne Model 9126 Injection Valve (50 μL sample loop) was coupled to Dionex Ionpac AG 9 and AS 9 columns for the anion method and a Dionex Ionpac CG 12A (4 × 50 mm) column for the cation method. The flow rate was 2 mL min^{-1} for both methods.

A stepwise elution programme (Table 1) was developed for the cation chromatography method.

2.1.2. Inductively Coupled Plasma – Optical Emission Spectroscopy

The chromatographic columns were coupled with a Varian Liberty 110 ICP Emission Spectrometer via a V-groove nebulizer. Data capturing and peak analyses were performed with the use of Star Chromatography Software.[31] The optimized ICP-OES conditions are summarized in Table 2.

Table 1 Stepwise elution programme for the cation chromatography method.

Time (min)	% NH_4NO_3	% HNO_3
0.0	100	0
1.0	100	0
1.1	0	100
4.0	0	100
4.1	100	0

Table 2 The operating parameters for the ICP-OES.

Parameter	Value
Cr emission wavelength	283.563 nm
Plasma viewing height	5 mm
Peak search window	0.03 nm
Plasma power	1.3 kW
Plasma gas flow rate	15.0 L min^{-1}
Auxiliary gas flow rate	1.50 L min^{-1}
Nebulizer pressure	150 kPa

2.2. Reagents

All reagents were of AR grade and all solutions were prepared from high quality deionized water (18 MΩ). Samples and eluents were filtered through 0.22 μm membrane filters.

Separate stock solutions containing 1000 mg L^{-1} of Cr(III) and Cr(VI) were prepared by dissolving $Cr(NO_3)_3.9H_2O$ (SAARCHEM (Pty) Ltd., Halfway House, South Africa) and K_2CrO_4 (Protea Lab Services (Pty) Ltd.) in deionized water. A series of standards and synthetic sample mixtures with varying ratios of Cr(III) and Cr(VI) were prepared by appropriate dilution of the stock solutions with deionized water for the cation chromatography method and with a 14 mM EDTA matrix [0.423 g Na_2CO_3 (BDH Chemical Ltd, Poole, England) dissolved in 140 mL 0.1 M EDTA stock solution [as Na_2EDTA, SMM Chemical (Pty) Ltd, Booysens, South Africa and diluted to 1000 mL] in the case of the anion chromatography method.

The eluent for the anion method was made up from stock solutions of CO_3^{2-} (as Na_2CO_3, BDH Chemicals Ltd, Poole, England), HCO_3^- (as $NaHCO_3^-$, SAARCHEM (Pty) Ltd, Halfway House, South Africa) and EDTA. The eluents for the cation method were HNO_3 (Merck Chemical (Pty) Ltd, Halfway House, South Africa) and NH_4NO_3 (N.T. Laboratory Supplies (Pty) Ltd, Midrand, South Africa).

3. Results and Discussion

3.1. Anion Chromatography Method

3.1.1. Stabilization of Cr(III)

Owing to the alkaline conditions used in this method it was necessary to protect the Cr(III) species from precipitation by complexation with EDTA. EDTA formed a monovalent Cr(III)-EDTA anion [$Cr(EDTA)^-$] with Cr(III), which was separated from the divalent chromate anion [CrO_4^{2-}]. Cr(III) was stabilized in solution by addition of a prepared 14 mM EDTA matrix, as determined by de Beer[32], to a sample. This concentration of EDTA was sufficient to ensure complete complexation of Cr(III) at high levels and it was found to be low enough to prevent overloading of the column. The complex formed between Cr(III) and EDTA was experimentally determined to be very stable over five months. The complex has a stability constant of log K = 23.[33]

3.1.2. Eluent Optimization and Column Selection

A Dionex AG 14 guard column was selected for the separation of the chromium species, as it would allow the analysis time to remain short. A sodium bicarbonate/carbonate solution containing EDTA was optimized for this column. EDTA is added to ensure that the Cr(III)-EDTA complex and all other metal-EDTA complexes remain stable during the chromatographic process so that no precipitation occurs. The addition of EDTA was also found to decrease the retention times as well as the half peak

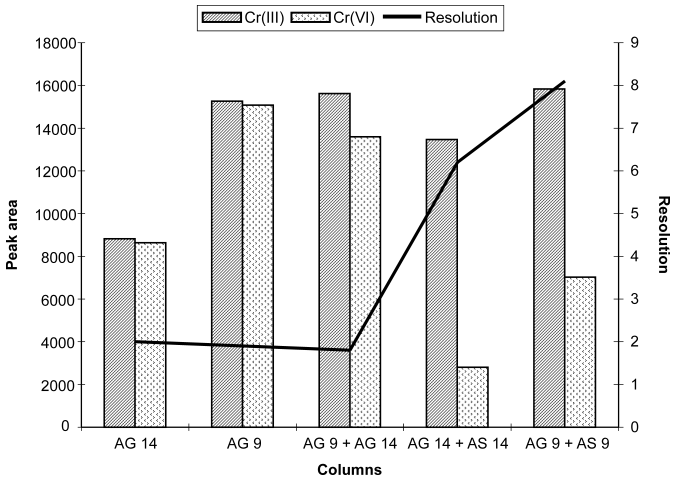

Figure 1 Comparison of the sensitivity and resolution obtained by various anion chromatographic systems (sample: 20 mg L^{-1} Cr(III) and 20 mg L^{-1} Cr(VI)).

widths of the species. The optimum eluent for the AG 14 column was determined as 1 mM HCO_3^-, 3 mM CO_3^{2-} and 20 mM EDTA. After testing of the AG 14 column using synthetic samples it was found that the results obtained were not always accurate as complete baseline separation of the species had not been achieved and it was thus not possible to accurately integrate the peaks.

Therefore various columns (all from Dionex) and column combinations were evaluated to see which provided the best chromatographic separation but still maintained relatively short retention times (Fig. 1).

Although guard columns (AG 9 and AG 14) provided the lowest retention times, the resolution obtained with these columns was not sufficient when analysing various ratios of chromium species. Guard columns are thus not able to provide baseline separation of the chromium species and so the separation columns were used in conjunction with their respective guard columns.

The AG 9 / AS 9 and AG 14 / AS 14 column combinations were able to provide baseline separation of the chromium peaks. The AG 9 / AS 9 columns when compared to the AG 14 / AS 14 columns were found to give better sensitivity for both species as well as a shorter analysis time and were thus used for further experimental work.

Although baseline separation was achieved with the AG 9 and AS 9 the chromatogram shows multiple peak for Cr(III) and peak tailing in the case of the Cr(VI) peak (Fig. 2). Thus the eluent had to be re-optimized for the new column system.

The optimum eluent was determined as 3 mM HCO_3^-, 9 mM CO_3^{2-} and 20 mM EDTA. This solved the problem of peak tailing of Cr(VI); however, the multiple peaks observed for Cr(III) were still evident. The eluent strength could not be further optimized in order to resolve this problem, thus the pH of the eluent was investigated. The pH of the 3 mM HCO_3^-, 9 mM CO_3^{2-} and 20 mM EDTA eluent was measured experimentally as 7.05. The addition of EDTA to the eluent thus caused a lowering of the pH which resulted in a decrease in the eluant strength because the carbonate/bicarbonate ratio was also decreased. Eluents with constant concentrations of 3 mM HCO_3^- and 9 mM CO_3^{2-} but with different concentrations of EDTA were prepared and tested. The results show that a decrease in EDTA concentration caused an increase in pH as expected and a single peak was observed for Cr(III) at 5 mM EDTA (pH 9.55) (Fig. 3). The sensitivity of both chromium species was also found to increase.

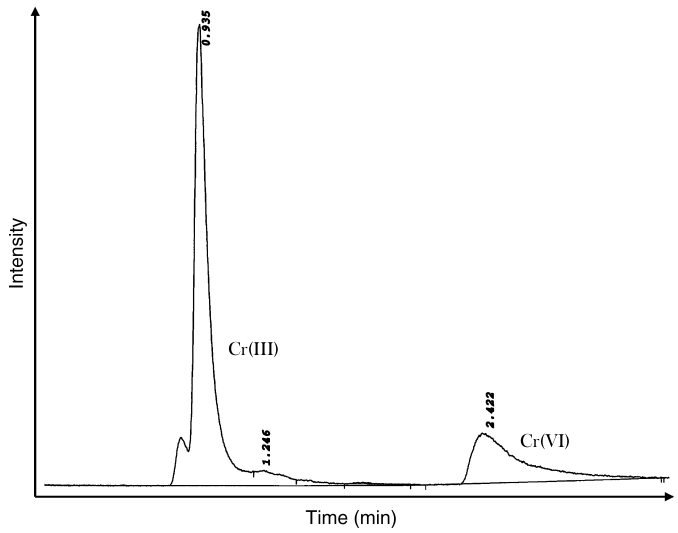

Figure 2 Typical chromatogram achieved with AG 9 and AS 9 columns (sample: 20 mg L^{-1} Cr(III) and 20 mg L^{-1} Cr(VI)).

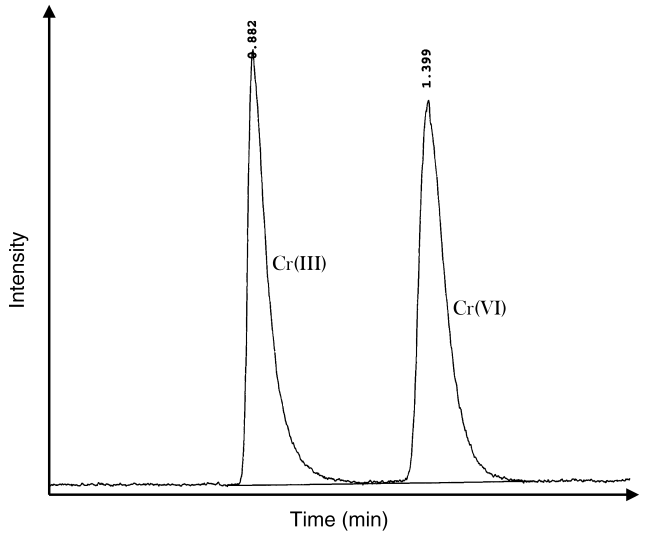

Figure 3 Typical chromatogram achieved using the 3 mM HCO_3^-, 9 mM CO_3^{2-} and 5 mM EDTA eluent (sample: 20 mg L^{-1} Cr(III) and 20 mg L^{-1} Cr(VI)).

The above hypothesis that the pH causes the multiplicity of the Cr(III) peaks was tested by preparing a 3 mM HCO_3^-, 9 mM CO_3^{2-} and 20 mM EDTA eluent with pH adjusted to 9.55 with NaOH. Multiple peaks were not observed for the Cr(III) peak when the 20 mM EDTA-containing eluent with adjusted pH was used. Therefore for optimum results a pH of 9.55 and above should be maintained. Either eluent may be used for this method but the 3 mM HCO_3^-, 9 mM CO_3^{2-} and 5 mM EDTA eluent was used for further experimental work.

3.1.3. Flow Rate Optimization

From the Van-Deemter Theory[34] it is known that in anion chromatography the analysis time can be decreased by increasing the flow rate and that the resolution is not significantly affected by this action. The results obtained for the measurement of a sample containing 20 mg L^{-1} Cr(III) and 20 mg L^{-1} Cr(VI) in 14 mM EDTA at various eluent flow rates is shown in Table 3 and is in line with this theory.

At high flow rates the retention time was decreased significantly although the sensitivities were found to be poor. The lower flow rates had a definite increase in analysis time; however, the sensitivity was found to be better. A compromise between analysis time and sensitivity was made and an intermediate flow rate of 2 mL min^{-1} was used.

3.1.4. Evaluation of the Method

Interference Study of Other Cations. The influence of each of the following metals zinc, manganese(II), cobalt, nickel, iron(III), Cu, potassium and vanadium on the separation and detection of Cr(III) and Cr(VI) was studied.

Interferences were observed for Cr(III) when in the presence of other metals (Table 4). It was thus assumed that Cr(III) may be unstable when other metals are present as the available EDTA in the sample matrix may not be sufficient to complex both Cr(III) and the metals. Cr(III), however, reacts in a 1:1 relationship with EDTA, thus for 100 mg L^{-1} of Cr(III), 1.9 mM of EDTA is required. The 14 mM EDTA sample matrix is therefore available in large excess and the decrease in Cr(III) was not caused by stabilization problems due to a lack of EDTA.

The decrease in Cr(III) was also not due to a spectral interference as the chromium wavelength used, is far from neighbouring interferent lines.

Destabilization of the Cr(III)-EDTA complex due to the presence of other metals is also not likely as, excluding iron ($\log K_f = 25.1$), the Cr(III)-EDTA complex is very stable ($\log K_f = 23.0$) when compared to the other metal-EDTA complexes, with $\log K_f$ values of: 18.8 (Cu), 14.04 (Mn(II)), 18.6 (Ni), 16.5 (Zn), 16.3 (Co), 1.7 (K) and 12.7 (V). Decomposition of the Cr(III)-EDTA complex is only probable in the presence of very large concentrations of iron where the concentration of EDTA is insufficient to complex all the metal species.

Further investigation is required to determine why a decrease in Cr(III) is observed when in the presence of high concentrations of these metals. From the data in Table 4 it is clear that Cr(III) can thus only be analysed accurately in the presence of up to 50 mg L^{-1} of zinc, nickel, iron, copper, potassium and vanadium and up to 100 mg L^{-1} of manganese and cobalt.

A decrease in Cr(VI) concentration was observed (Table 4) when metals were present in the sample but this was not a true interference as metal chromates are generally insoluble. Thus the Cr(VI) precipitates out and a lower concentration was measured as samples are filtered prior to analysis. A real sample containing metals with chromate would already contain precipitated metal chromates but this is not considered as an interference as this method extends only to the analysis of chromium in solution and not that of solids.

Table 3 The effect of varying flow rates on the chromatographic factors.

Flow rate (mL min^{-1})	Retention time (min)		Peak area		Resolution
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
1.0	1.774	3.328	19 978	22 601	6.69
2.0	0.956	1.748	15 886	17 625	6.56
3.0	0.664	1.182	12 325	13 508	6.56

Table 4 Results of the metal interference study.

Metal	Salts used	Metal concentration (mg L^{-1})	Measured concentration of Cr(III) (mg L^{-1})	Measured concentration of Cr(VI) (mg L^{-1})
Zn	$ZnCl_2$	100	3.1 ± 0.2	13.3 ± 0.4
		50	20.2 ± 1.0	20.2 ± 1.1
Mn(II)	$MnSO_4\ H_2O$	100	22.0 ± 0.6	18.7 ± 0.4
Co	$CoSO_4\ 7H_2O$	100	21.4 ± 0.5	17.1 ± 0.2
Ni	$NiCl_26H_2O$	100	2.2 ± 0.07	17.2 ± 0.6
		50	18.8 ± 0.8	18.4 ± 1.0
Fe(III)	$Fe(NO_3)_3\ 9H_2O$	100	6.2 ± 0.3	10.8 ± 0.3
		50	22.1 ± 0.4	9.2 ± 0.5
Cu	$CuCl_2\ 2H_2O$	100	6.9 ± 0.3	10.5 ± 0.2
		50	23.0 ± 1.0	21.6 ± 1.2
K	KCl	100	2.7 ± 0.2	17.5 ± 0.4
		50	18.6 ± 0.1	17.3 ± 0.2
V	Saarchem	100	18.1 ± 0.6	13.8 ± 0.3
	1000 ppm V solution	50	20.1 ± 0.6	17.8 ± 0.7

[a] The samples contain 20 mg L^{-1} Cr(III) and 20 mg L^{-1} Cr(VI).

Table 5 Results obtained for samples with varying pH values.

Sample	pH	Measured concentration of Cr(III) (mg L^{-1})	Measured concentration of Cr(VI) (mg L^{-1})
1	2.01	Precipitate	Precipitate
2	3.03	18.3 ± 1.4	13.8 ± 0.6
3	3.94	22.7 ± 0.5	20.2 ± 0.4
4	6.26	22.6 ± 0.7	21.3 ± 1.2
5	8.06	22.4 ± 0.9	19.4 ± 0.7
6	10.00	21.5 ± 1.0	19.7 ± 0.5

Effect of Sample pH. Industrial samples are expected to have a large pH range, thus the effect of sample pH on analytical results was explored. Four synthetic samples with different pH values but with the same concentrations (20 mg L^{-1} Cr(III) and 20 mg L^{-1} Cr(VI)) were prepared with 14 mM EDTA. A fifth sample (sample 4) was prepared without a change in pH as a control measure. The results are shown in Table 6.

A white precipitate occurred in the sample at a pH of 2 and below as EDTA occurs in the fully protonated state.[35] At a pH of 3, both Cr(III) and Cr(VI) concentrations are lower than expected. The useful pH range is therefore between a pH of 4 and 10.

A change in pH of the sample is found to be negligible when compared to that of the eluent as only 50 μL of the sample is injected into a large volume of eluent. Thus multiple peaks did not occur, as was the case with a change in pH of the eluent.

Analytical Merits. Detection limits could not be calculated by using the standard deviation of several blank measurements because in chromatography a blank sample results in no peak and thus cannot be integrated. The qualitative detection limit for chromium was determined as the lowest concentration at which a peak could be distinguished from the background. This was found to be 0.05 mg L^{-1} for both species. The quantitative detection limit was established as the lowest concentration of chromium needed to produce a peak that could be integrated and produce a linear calibration curve. The quantitative detection limits were 0.5 mg L^{-1} for both Cr(III) and Cr(VI). The analytical working range for both chromium species was determined as 0.5–100 mg L^{-1}.

Table 6 Results of the analysis of synthetic samples.

Sample	Cr(III)		Cr(VI)	
	Known concentration (mg L^{-1})	Measured concentration (mg L^{-1})	Known concentration (mg L^{-1})	Measured concentration (mg L^{-1})
1	2	2.0 ± 0.05	2	2.2 ± 0.1
2	10	10.0 ± 0.4	10	9.6 ± 1.4
3	20	19.6 ± 4.9	20	19.9 ± 0.7
4	40	41.5 ± 2.4	40	40.7 ± 3.7
5	10	10.9 ± 0.6	5	5.0 ± 0.1
6	10	10.8 ± 0.7	30	28.7 ± 3.2
7	10	10.8 ± 2.8	50	49.6 ± 4.4
8	2	2.1 ± 0.3	20	19.6 ± 1.3

Table 7 Influence of varying concentrations of NH_4NO_3 and HNO_3 on the chromatographic factors.

HNO_3 concentration (mM)	NH_4NO_3 concentration (mM)	Retention time (min)		Peak area		Resolution
		Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	
40	40	0.348	3.819	17 453	15 808	20.3
60	40	0.338	3.536	17 661	16 630	22.4
100	40	0.342	3.116	15 819	15 602	23.6
60	20	0.372	3.330	18 159	14 488	21.4
60	40	0.338	3.536	17 661	16 630	22.4
60	100	0.359	3.623	15 039	12 686	21.5

3.1.5. Applications of the Method

A range of synthetic samples with known concentrations of Cr(III) and Cr(VI) were analysed and the results are summarized in Table 6. The confidence intervals are based on three replicate measurements with a confidence level of 95%. The measured concentrations are shown to be in good agreement with the known concentrations.

The method was also applied to an industrial chromium plating bath solution. A quantitative ICP-OES analysis of the sample was done (total chromium = 24.0 ± 0.5 mg L^{-1}) and was found to compare favourably with the sum of the individual species (Cr(III) = 1.9 ± 0.2 mg L^{-1} and Cr(VI) = 20.7 ± 1.0 mg L^{-1}) as determined by the anion chromatography method.

3.2. Cation Chromatography Method

3.2.1. Eluent Optimization

First, a 60 mM nitric acid solution, which is the standard eluent for a Dionex CG 12A column, was used as the eluent. Cr(III) was found to elute first followed by a broad peak of Cr(VI). To improve the peak shape for Cr(VI) a 40 mM ammonium nitrate solution was tried as the eluent. This eluent resulted in the rapid elution of Cr(VI); however, Cr(III) was not detected within 15 minutes of injection. It was thus retained on the column and was only successfully eluted with 60 mM nitric acid.

Cr(VI) is an anion and was not expected to interact with the cation column and was thus supposed to elute with the void volume. Separations using ion-exchange columns, however, cannot be explained by the basic principles of ionic equilibria alone. This occurs, as most packing materials are able to interact with the analyte ions via some secondary mechanism of adsorption, partition or hydrogen bonding effects. The mechanism of ion exchange is further complicated by the selectivity introduced by the charge and radius of the ions competing for the ion-exchange sites. A hybrid mechanism thus governs the elution of Cr(VI) and makes the elution behaviour difficult to predict.

Cr(III) was eluted with nitric acid and Cr(VI) was eluted with ammonium nitrate, thus varying ratios of the ammonium nitrate and nitric acid eluents were used in conjunction to see if both species could be eluted efficiently. This did not prove successful in separating the species and eluting Cr(VI) as a narrow peak.

A stepwise elution programme (Table 1) was then opted for to elute the species using both eluents. Ammonium nitrate was first used to elute Cr(VI) and then the eluent was switched to nitric acid to elute the Cr(III) species. This proved to be a more successful approach as both species were separated and a relatively narrower Cr(VI) peak was achieved.

The ammonium nitrate and nitric acid concentrations were optimized to observe the effect on the chromatographic factors (retention times, sensitivity and resolution) and to see if Cr(VI) could be eluted more effectively (Table 7). The retention time of Cr(III) was found to decrease and the resolution increased as the nitric acid concentration increased. However, the sensitivity of the chromium peaks was very poor at high concentrations of nitric acid, thus 60 mM nitric acid was chosen as the optimum concentration. No general trends were observed for changes in the ammonium nitrate concentrations but the best sensitivity for Cr(III) and the best resolution occurred at 40 mM ammonium nitrate.

The peak shape for Cr(VI), however, was still found to be a bit broad using stepwise elution unlike the peak obtained for Cr(VI) when only ammonium nitrate was used. When ammonium nitrate was first tested as a possible eluent it was run through the column for half an hour to equilibrate it. The Cr(VI) peak obtained after this was narrow and sharp. A test was thus undertaken to see the influence of the time that ammonium nitrate is run through the column prior to analysis on the Cr(VI) peak shape (Table 8). Both the sensitivity for Cr(VI) as well as the resolution increases with increasing equilibration time.

The time needed for a column to equilibrate to a new eluent is dependent on the selectivity coefficient for the competing ion in the new eluent over that of the previous eluent as well as the concentration of the competing ion in the new eluent. A CG 12A column was used in this method and according to the manufacturers the 'stationary phase is functionalized with relatively weak phosphonic and carboxylic acids having a high selectivity for the hydronium ion'.[36] Thus the 30-minute equilibration is needed when nitric acid is switched to ammonium nitrate as the resin has a higher selectivity for the hydronium ion.

The ammonium nitrate concentration was significantly increased to see if a higher concentration of the competing ion would lead to faster equilibration of the chromatographic

Table 8 Influence of ammonium nitrate equilibration time on the chromatographic factors.

Equilibration time (min)	Peak area		Half peak width (sec)		Resolution
	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	
0	14 821	13 203	38.2	8.0	4.5
10	16 670	12 755	16.2	5.2	15.6
20	16 723	12 899	13.3	5.6	18.8
30	17 216	13 133	12.1	6.0	20.4

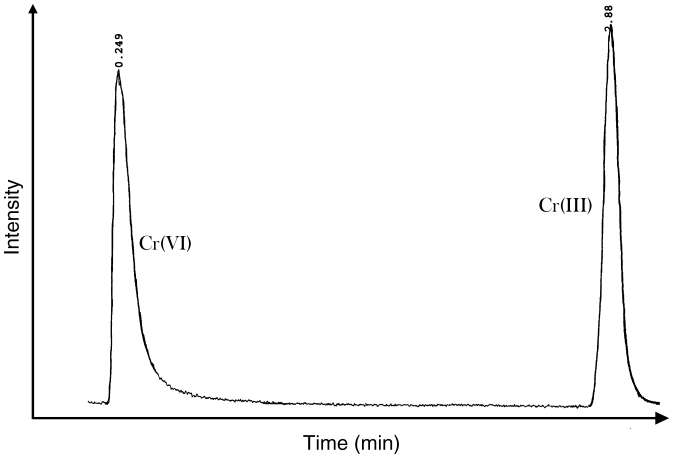

Figure 4 Typical chromatogram achieved using the CG 12 A column with a 30 minute equilibration time before analysis (sample: 20 mg L^{-1} Cr(III) and 20 mg L^{-1} Cr(VI)).

column. The results indicate that greater sensitivity was achieved when using the stronger eluent; however, it impacted negatively on the Cr(III) peak, which decreased in sensitivity.

Other eluents such as ammonium chloride, ammonium sulphate, sodium nitrate and potassium nitrate were tested to see if the 30-minute equilibration time could be overcome. When no equilibration time was allowed between analyses ammonium nitrate was still able to provide the best sensitivity for Cr(VI) and the peak width was relatively narrow. The Cr(III) peak was not found to be significantly affected by the different eluents.

As no better alternative could be found the ammonium nitrate eluent was run through the chromatographic column for 30 minutes prior to each analysis and produced a useful chromatogram as depicted in Fig. 4.

3.2.2. Flow Rate Optimization

The Van-Deemter Theory[35] states that the column efficiency is dependant on the flow rate in a cation column and so a compromise between resolution and analysis time has to be made. The results obtained from the measurement of a sample containing 20 mg L^{-1} Cr(III) and 20 mg L^{-1} Cr(VI) at different eluent flow rates is shown in Table 9.

A flow rate of 1 mL min^{-1} caused the species to be retained too long such that the program used to record the chromatogram ran out of time. High flow rates were found to reduce retention times but lower sensitivities were also observed. Lower flow rates were found to increase retention times but sensitivities were improved.

Contrary to the Van-Deemter Theory, the resolution is not significantly affected by the change in flow rate. This may be attributed to the fact that the retention time of Cr(III) is controlled by the stepwise elution programme and so a limit was placed on the degree to which the retention time could be influenced.

Thus a compromise between efficiency at lower flow rates and a shorter analysis time at higher flow rates was made and an intermediate flow rate of 2 mL min^{-1} was used.

3.2.3. Evaluation of the Method

Interference Study of Other Cations. Zinc, iron(III) and nickel as well as the anions, chloride and sulphate were studied to determine their influence on the successful analysis of the chromium species. Only iron has an influence on the determination of the chromate species in a sample. Metal chromates are generally insoluble, thus a decline in recovery is observed when iron is present in a sample as the precipitate has been removed by filtration prior to analysis. As mentioned above, this is not considered to be an interference.

Effect of Sample pH. The determination of the influence of the pH of a sample on the method was studied (Table 10). Four synthetic samples with different pH values but with the same concentrations (20 mg L^{-1} Cr(III) and 20 mg L^{-1} Cr(VI)) were prepared. A fifth sample (sample 2) was prepared without changing the pH and was used as a control.

The results show that Cr(III) was not observed from pH 6–10. This can be explained by the hydrolysis behaviour of trivalent chromium which forms $Cr(OH)_3$ (s) at a pH above 5.5. Thus Cr(III) precipitates out and as the sample is filtered prior to analysis, Cr(III) is not observed in the chromatogram.

Relatively constant concentrations were observed for the chromate species at different pH values, which showed that chromate, is not affected by a change in pH in this method.

Table 9 The effect of flow rate on the retention times and sensitivities of Cr species.

Flow rate (mL min^{-1})	Retention time (min)		Peak area		Resolution
	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	
1.0	[a]	[a]	[a]	[a]	[a]
2.0	0.358	3.223	27 205	19 439	24.9
2.5	0.284	2.837	28 381	18 758	27.0
3.0	0.271	2.599	22 664	16 082	29.2

[a] The flow rate is too slow for both species to be eluted within five minutes.

Table 10 Results obtained for samples with varying pH values.

Sample	pH	Measured concentration of Cr(VI) (mg L^{-1})	Measured concentration of Cr(III) (mg L^{-1})
1	2.42	24.2 ± 1.4	27.3 ± 1.0
2	4.00	20.8 ± 1.3	22.2 ± 0.9
3	6.00	20.2 ± 1.0	Precipitate
4	8.01	22.0 ± 0.4	Precipitate
5	10.09	23.7 ± 1.7	Precipitate

Table 11 Results of the analysis of synthetic samples.

Sample	Cr(VI)		Cr(III)	
	Known concentration (mg L^{-1})	Measured concentration (mg L^{-1})	Known concentration (mg L^{-1})	Measured concentration (mg L^{-1})
1	10	9.9 ± 0.4	10	10.1 ± 0.8
2	15	15.6 ± 0.4	15	15.7 ± 0.8
3	20	20.7 ± 1.2	20	22.1 ± 2.0
4	50	49.6 ± 1.5	50	49.1 ± 1.2
5	30	31.6 ± 3.1	40	45.8 ± 2.9
6	10	9.5 ± 0.1	5	4.7 ± 0.7
7	5	4.3 ± 0.3	40	47.8 ± 1.9
8	15	14.2 ± 1.4	30	32.8 ± 2.6

Analytical Merits. The analytical merits were determined in a similar fashion to that used for the anion chromatography method. The qualitative detection limits were found to be 0.1 mg L^{-1} for both species. The quantitative detection limits were established as 0.4 mg L^{-1} for both Cr(III) and Cr(VI). The dynamic linear range for both species was determined as 0.4–150 mg L^{-1}.

3.2.4. Applications of the Method

The same industrial plating bath solution was analysed using the developed cation chromatography method. The results (Cr(III) = 1.9 ± 0.1 mg L^{-1} and Cr(VI) = 22.9 ± 0.3 mg L^{-1}) were found to correlate well with both the total chromium content (24.0 ± 0.5 mg L^{-1}) as well as the results obtained by the anion method.

A range of samples with known concentrations of Cr(III) and Cr(VI) were prepared and analysed (Table 11). The confidence intervals are based on three replicate measurements with a confidence level of 95%. The measured concentrations are shown to coincide with the known concentrations.

4. Comparison of the Two Methods

Two methods were developed for the speciation analysis of chromium, based on a hyphenated system where ion chromatography is coupled with ICP-OES.

The method to be used in a given situation depends on the sample to be analysed. If a sample with low concentrations of other metals, e.g. water sample, is to be analysed, the anion chromatographic method should be used as it has a shorter analysis time and does not require a 30-minute equilibration time as in the case of the cation method. If a sample contains high concentrations of other metals it is advisable to use the cation method as the anion method is subject to interference effects.

Both the anion and the cation chromatography methods are simple with no complicated sample preparation or instrumental setup. Baseline separation is achieved in both, thus a limit on the ratio of the chromium species is avoided. The analytical merits observed for the anion and the cation methods are similar.

Acknowledgements

Financial support from the National Research Foundation and Rand Afrikaans University is greatly appreciated.

References

1 R.A. Anderson, *Sci. Tot. Environ.,* 1989, **86**, 75.
2 J. Barrett, P. O'Brien and J.P. De Jesus, *Polyhedron,* 1985, **4**, 1.
3 Daugherty M.L., *Toxicity Summary for Chromium,* 1992, http://risk.1sd.ornl.gov/tox/profiles/chromium.shtml.
4 S.B. Roychowdhury and J.A. Koropchak, *Anal. Chem.,* 1990, **62**, 484.
5 F.A. Byrdy, L.K. Olson, N.P. Vela and J.A. Caruso, *J. Chromatogr. A,* 1995, **712**, 311.
6 H. de Beer and P.P. Coetzee, *S. Afr. J. Chem.*, 1988, **41**, 152.
7 H. de Beer and P.P. Coetzee, *S. Afr. J. Chem.*, 1991, **44**, 105.
8 B. Gammelgaard, O. Jøns and B. Nielsen, *Analyst,* 1992, **117**, 637.
9 B. Gammelgaard, Y. Liao and O. Jøns, *Anal. Chim. Acta,* 1997, **354**, 107.
10 M. Pantsar-Kallio and P.K.G. Manninen, *J. Chromatogr. A,* 1996, **750**, 89.
11 M. Derbyshire, A. Lamberty and P.H.E. Gardiner, *Anal. Chem.,* 1999, **71**, 4203.
12 P.M. Paquet, J. Gravel, P. Nobert and D. Boudreau, *Spectrochim. Acta B,* 1998, **53**, 1907.
13 M. Šikovec, M. Novič, V. Hudnik and M. Franko, *J. Chromatogr. A,* 1995, **706**, 121.
14 R.M. Céspon-Romero, M.C. Yebra-Biurrun and M.P. Bermejo-Barrera, *Anal. Chim. Acta,* 1996, **327**, 37.
15 S. Hirata, Y. Umezaki and M. Ikeda, *Anal. Chem.,* 1986, **58**, 2602.
16 P.A. Sule and J.D. Ingle, *Anal. Chim. Acta,* 1996, **326**, 85.
17 M. Sperling, S. Xu and B. Welz, *Anal. Chem.,* 1992, **64**, 3101.
18 J.L. Manzoori, M.H. Sorouraddin and F. Shemirani, *Talanta,* 1995, **42**, 1151.
19 J. Prokisch, S.A. Katz, B. Kovács and Z. Györi, *J. Chromatogr. A,* 1997, **774**, 363.
20 M.J. Marqués, A.E. Morales-Rubio, A. Salvador and M. de la Guardia, *Talanta,* 2001, **53**, 1229.
21 B.C. Mondal, D. Das and A.K. Das, *Talanta,* 2002, **56**, 145.
22 H. Bağ, A.R. Türker, M. Lale and A. Tunceli, *Talanta,* 2000, **51**, 895.
23 Ş. Tokalioğlu, Ş. Kartal and L. Elçi, *Anal. Chim. Acta,* 2000, **413**, 33.
24 S. Nam, M. Kim, S. Oh, J.H. Lee and Y. Pak, *Amer. Lab.,* 2001, 40.
25 C.M. Andrle, N. Jakubowski and J.A.C. Broekaert, *Spectrochim. Acta B,* 1997, **52**, 189.
26 Y. Inoue, T. Sakai and H. Kumagai, *J. Chromatogr. A,* 1995, **706**, 127.
27 F. Vanhaecke, S. Saverwyns, G. De Wannemacker, L. Moens and R. Dams, *Anal. Chim. Acta,* 2000, **419**, 55.
28 M.K. Donais, R. Henry and T. Rettberg, *Talanta,* 1999, **49**, 1045.
29 H.G. Beere and P. Jones, *Anal. Chim. Acta,* 1994, **293**, 237.
30 M. Bittner and J.A.C. Broekaert, *Anal. Chim. Acta,* 1998, **364**,
31 Star Chromatography Software, version 4.01, 1995, Varian Associates Inc., Australia
32 H. de Beer, *Metal speciation by high performance liquid chromatography,* Ph.D. thesis, Rand Afrikaans University, Johannesburg, South Africa, 1993
33 J. Inczédy, *Analytical Applications of Complex Equilibria,* Ellis Horwood, England, 1976.
34 J. Weiss, *Handbook of Ion Chromatography,* (L. Edward, ed.), DIONEX Corporation, California, USA, 1986
35 D.A. Skoog, D.M. West and F.J. Holler, *Fundamentals of Analytical Chemistry,* 7th edn, Saunders College Publishing, New York, United States of America, 1996.
36 DIONEX Corporation, *Installation Instructions and Troubleshooting Guide for the Ionpac® CG 12A Guard Column Ionpac® CS 12A Analytical Column,* document no. 031132, 2000.