An Evolved GFAAS Method for Trace and Ultratrace Determination of Cr(III) and Cr(VI) in Water and Wastewater: Speciation of Chromium

Raghbendra Thakur^a, P.K. Tarafder^{a,*}, and Raj Ranjan Jha^b

^a Chemical Laboratory, Regional Centre for Exploration and Research, AMD, Department of Atomic Energy, P.O. Tatanagar, Jamshedpur 831002, India

^b Department of Chemistry, Ranchi University, Ranchi 834001, India

ABSTRACT

A highly evolved method for the determination of Cr(III) and Cr(VI) at the ppm to ppb level in water and wastewater samples has been developed. For the ppm level determination of chromium, Cr(III) is separated from Cr(VI) by its R_2O_3 precipitation along with $Fe(OH)_3$, then both Cr(III) and Cr(VI) are separately determined by GFAAS in a smaller aliquot of sample solution after removal of associated interfering elements by a novel solvent extraction system involving 2,3-dihydroxynaphthalene as an extractant. However, for ppb level determination of Cr(III) and Cr(VI), a pre-concentration technique needs to be combined with a solvent extraction system. Here, Cr(III) is separated and pre-concentrated by R_2O_3 precipitation as above, however, from a large volume of water sample, i.e., about 400-500 mL. The analyte Cr(III) is further separated from iron and other interfering elements by selective solvent extraction using the same extractant (2,3-dihydroxynaphthalene) and was then determined selectively by GFAAS. Total chromium [Cr(III)+Cr(VI)] from a 400-500 mL

separate water sample is pre-concentrated as R_2O_3 ppt of Cr(III) [after reducing Cr(VI) with Fe(II)] along with R_2O_3 ppt of Fe(III) generated *in situ* by way of oxidation of residual Fe(II) by HNO_3 . Iron and other interfering elements are similarly removed by solvent extraction using the same extractant (2,3- H_2ND) as in the determination of Cr(III), and total Cr as Cr(III) is similarly determined by GFAAS. The content of Cr(VI) was deduced by subtracting the value of Cr(III) from the content of total chromium determined as Cr(III). The method developed is highly effective and reliable. While the detection limit (3σ) and %RSD of the method for ppm level chromium (without further pre-concentration) was $0.4 \mu g L^{-1}$ and 5-10%, respectively, at the $4.0 \mu g L^{-1}$ level, the corresponding values of the method for ppb to ppt level chromium determination were $0.01 \mu g L^{-1}$ and 3 to 5%, respectively, at the $0.1 \mu g L^{-1}$ level. The pre-concentration factor of this system was ~40-50. The method was applied to a range of real samples and the results obtained have been successfully validated by standard methods.

ways, primarily due to industrial activities involving electroplating, the leather and tanning industries, sheet works, smelters, dyeing and leaching from sanitary landfills (5-7). Corrosion inhibitors used in water pipes and water cleaning materials can also increase the content of Cr(VI) in potable waters (6). Stream and river waters become enriched in Cr(VI) if these pass through ophiolite mineral belts (8) due to catalytic leaching.

Although a number of methods are known for the separation and determination of chromium species, very few sensitive and selective analytical techniques are known which could be directly applied to water samples for trace and ultratrace determination of Cr(III) and Cr(VI). Even for graphite furnace atomic absorption spectrometry (GFAAS) analysis, which is considered to be a highly sensitive tool for instrumental analysis, preliminary separation and pre-concentration is required (9). Precision of analytical results for chromium determination by GFAAS at ultratrace level is usually poor.

Analytical methods for speciation of chromium are primarily based on solvent extraction (9-11), solid phase extraction (12), co-precipitation (13), ion-exchange separation (14-15), electrochemical methods (16), high performance liquid chromatography (17-18), ion chromatography (19), and capillary electrophoresis (20-21). Most extraction methods (22-24) and a few ion-exchange resin methods (25) for the speciation of chromium species use Cr(VI) complexes of dithiocarbamate (26), ammonium-pyrolidinedithiocarbamate (APDC)

INTRODUCTION

In nature, the two stable chromium species are known as Cr(III) and Cr(VI). Their biological activity, chemical behavior, and influence on the environment are different. While Cr(III) is essential for the

metabolism of glucose, lipids, and proteins in living organisms, Cr(VI) is highly toxic and can affect lungs, liver, and kidneys, and is also carcinogenic (1-3). Because of its strong oxidation potential and easy permeation through biological membranes, the hexavalent chromium damages the macromolecules, proteins, and DNA (4). Cr(VI) finds its way into the environment, particularly the water-

Corresponding author.
E-mail: pktarafder1954@gmail.com
Tel: +91 9234885532

(11) extracted into isobutylmethyl ketone (IBMK), and 1,5-diphenyl-carbazone complex loaded on amberlite XAD-16 (27).

Methods on speciation of chromium species based on extraction or ion-exchange separation are not well known and most of these use complexation of Cr(VI). The drawbacks/shortcomings associated with systems involving Cr(VI) complexation are: (i) The reductants present in the system, particularly introduced through reagents, can reduce a significant amount of Cr(VI) at the ultratrace concentration level and introduce bias in the results (28-30). This is particularly important for the preparation of standard solutions and for the recovery tests of Cr(VI). It seems that the poor recoveries reported by some authors may result from reduction of small amounts of Cr(VI) in their experiments. (ii) The preconcentration factors and detection limits are extremely low, i.e., for extraction involving Cr(VI), in most cases, there is no preconcentration, and in extreme cases, the preconcentration factor is 5 or so for Cr(VI) when the ratio of aqueous to organic solvent is 5:1. Under no circumstances, is the preconcentration factor for certain systems above 20, such as those involving ion-exchange separation of Cr(VI). (iii) There is least possibility of further preconcentration of the analytes, because no other preconcentration technique can be combined with the system involving the extraction of Cr(VI).

However, the above drawbacks/shortcomings with the existing extractive/other preconcentration or separation techniques hitherto adopted can be overcome or done away with if the strategy were reversed. Instead of analyzing chromium as Cr(VI), as with most extraction-based procedures/systems for the speciation of chromium, if Cr(III) or, for that matter,

total chromium [after reducing Cr(VI) to Cr(III)] is extracted or separated and then determined by sensitive tools like GFAAS, the above-mentioned shortcomings associated with the extraction of Cr(VI) can be overcome. The advantages of Cr(III) extraction over that of Cr(VI) are (i) the probability of Cr(VI) getting reduced to Cr(III) by oxidants and reductants creeping into the system is altogether avoided, thereby eliminating the scope of obtaining wrong results; (ii) the preconcentration factor (PCF), which is very poor for systems involving solvent extraction of chromium in the form of Cr(VI), can be enhanced many-fold (PCF may be enhanced to 50 or more) by preceding/combining the solvent extraction steps with other preconcentration steps, particularly co-precipitation of Cr(III) with hydrated iron or titanium oxides, etc. [unlike Cr(VI) which cannot be precipitated as R_2O_3].

Some authors have proposed procedures based on the separation and determination of Cr(III) and total chromium (31-33) but these are not useful for water analysis at trace and ultra-trace levels (30). Only very few papers (11, 34, 35) have been published describing speciation of chromium based on the extraction of Cr(III). The methods involving cloud point extraction of Cr(III) (34, 35) are cumbersome, and the results obtained are affected by variables such as Critical Micellar Concentration (CMC) of the surfactant used, volume ratio of immiscible solvents and temperature, etc. Although speciation of chromium is possible by the method reported by Subramanian et al. (11), it cannot yield precise results for the ultratrace determination of chromium by GFAAS due to the limited pre-concentration factor (5 or so).

In view of the above, a robust method recommending two dynamic ranges for the estimation

of Cr (one for ppm level determination and the other for ppb level determination) in a wide variety of water samples has been developed and applied to different water samples with varied chromium concentration ranges.

In the first case involving the determination of chromium species at ppm level in chromium-rich water samples, Cr(III) is selectively separated from Cr(VI) as R_2O_3 precipitate along with hydrated Fe(III) oxide which facilitates co-precipitating traces of Cr(III) species and leaves Cr(VI) intact in the aqueous solution. The separated Cr(III) and Cr(VI) are then determined by GFAAS after their further extractive separation from the interfering ions/salts including iron which is expected to contribute towards background absorption. Or, the Cr(III) concentration determined in a separate aliquot by GFAAS (as discussed above) is subtracted from total chromium [(Cr(III) and Cr(VI)] determined by GFAAS in a separate aliquot after their solvent extraction together. This procedure fails when applied to certain water samples such as river and stream waters where the concentrations of the chromium species are very low, i.e., at ppb level.

For such samples, preconcentration of the chromium species needs to be carried out in order to determine Cr(III) and Cr(VI) precisely and accurately at ultratrace level. Cr(III) is separated from a large volume (400-500 mL) of water sample by co-precipitating it along with hydrated Fe(III) oxide. The added iron is removed by solvent extraction using the reagent 2,3- H_2ND at pH 4-5. The separated Cr(III) is then determined by GFAAS after its selective solvent extraction using 2,3- H_2ND at pH 11-12 in order to eliminate other interfering ions. Total chromium from another portion of the sample solution (400-500 mL) is determined by

GFAAS after reducing Cr(VI) to Cr(III) with added Fe(II), co-precipitating total Cr(III) together with Fe(III) generated *in situ* by oxidizing Fe(II) with HNO₃, thus eliminating Fe(III) as above, followed by selective solvent extraction of total chromium as Cr(III) at pH 11-12. The content of Cr(VI) is deduced by subtracting the content of Cr(III) determined separately from the content of total chromium determined as Cr(III).

The method thus developed has been successfully applied to a number of water samples of different origin, and the results obtained have been validated by those obtained from the application of the standard methods.

The present paper describes the systematic studies on the variables affecting the optimization of parameters involved in the development of a suitable method for the determination of Cr(III) and Cr(VI) at trace to ultratrace levels.

EXPERIMENTAL

Instrumentation

A model ZeeNit-700 GFAAS (Analytikjena, Germany) was used. The instrumental operating conditions are listed in Table I.

Reagents and Standard Solutions

All reagents used were of analytical reagent grade. Stock Cr(III) solution (1 mg/mL) was prepared by placing 0.7693 g Cr(NO₃)₃ · 9H₂O into a 100-mL calibrated volumetric flask, dissolving the salt with 50 mL distilled water, followed by adding 1 mL concentrated HCl, and then diluting the solution to 100 mL with distilled water. A working standard solution (100 µg/mL) was made up by transferring 10 mL of the stock solution into a 100-mL volumetric flask, followed by the addition of 5 mL concentrated sulfuric acid, then diluting the solu-

tion to 100 mL with distilled water. Further dilution of this solution will give the desired concentration of 20 µg/mL.

Stock Cr(VI) solution (1 mg/mL) was prepared by placing 0.2827 g K₂Cr₂O₇ into a 100-mL calibrated volumetric flask, dissolving the salt with 50 mL distilled water, followed by adding 2 mL (1:1) sulfuric acid, and then diluting the solution to 100 mL with distilled water. A working standard solution (100 µg/mL) was made up by transferring 10 mL of the stock solution into a 100-mL volumetric flask, followed by the addition of 2 mL (1:1) sulfuric acid, then diluting the solution to 100 mL with distilled water. Further dilution of this solution will give the desired concentration of 20 µg/mL.

Reagents used were 2,3-dihydroxy-naphthalene (Merck, Germany) of 98% purity, sulfuric acid, hydrofluoric acid, cetyltrimethylammonium bromide, ferrous and ferric ammoniumsulphate, and solvents like ethylacetate. All reagents used were of AR/GR grade.

PROCEDURES

Determination of Total Chromium

A 10-mL filtered water sample was taken into a 125-mL separating funnel and 10 mL of 0.5% (m/v) 2,3-H₂ND in ethylacetate added, mixed well, then 5 mL of 0.5% aqueous CTAB solution was added. The pH was raised to about 11-12 by using 5 mL of 10% KOH solution, shaken well for 2-3 minutes and allowing for phase separation. The aqueous layer was drained out. The extracted chromium from the organic layer was stripped off by adding 5 mL distilled water containing 1.0 mL concentrated sulfuric acid, and shaking the mixture contained in the separating funnel for 1-2 minutes. The aqueous layer containing the stripped off chromium was drained out and transferred into a 10-mL volumetric flask, and made up to volume with fresh distilled water.

Determination of Cr(III)

Another 10-mL aliquot was placed into a 100-mL beaker, about 1.0 g of NH₄Cl and 10 mg of Fe(III) as ferric ammonium sulphate and ~50 mL distilled water were added.

TABLE I
Instrumental Operating Conditions

Parameters	
Instrumentation	ZeeNit-700 GFAAS
Autosampler	MPE-60
Wavelength	357.9 nm
HCL Current	8 mA
Graphite Furnace	
Dry Temperature	110 °C (Ramp 1 s, Hold 30 s) 130 °C (Ramp 15 s, Hold 30 s)
Ashing Temperature	1500 °C (Ramp 10 s, Hold 20 s)
Atomization Temperature	2300 °C (Ramp 0 s, Hold 5 s)
Cleaning Temperature	2450 °C (Ramp 1 s, Hold 3 s)
Flow Rate (Ar)	-250 cm ³ min ⁻¹
Sample Volume	-20-30 µL
pH meter for Reaction Solutions	ELICO (LI-120) pH meter

While agitating and mixing the solution with a glass rod, the Fe(III) precipitated with NH_4OH . The precipitate $[\text{Fe}(\text{OH})_3 + \text{Cr}(\text{OH})_3]$ was warmed in a waterbath at about 100°C for 10–15 minutes. Traces of Cr(III) thus co-precipitated along with the hydrated Fe(III) oxide. The solution was filtered through a Whatman-540 filter paper. The precipitate on the filter paper was dissolved in a minimum amount of 1:1 H_2SO_4 , and 0.1 g of 2,3- H_2ND added, and mixed well. Then 10 mL of 10% (m/v) aqueous sodium acetate solution was added and the pH adjusted to 4–5. The solution was transferred back into the 125-mL separating funnel, 15 mL of ethylacetate was added, and mixed well. The solution was shaken for 2–3 minutes in order to extract out iron as a bluish-violet Fe^{3+} -2,3- H_2ND neutral complex. The organic layer was discarded. The aqueous layer was taken into the same separating funnel and 10 mL of 0.5% 2,3- H_2ND in ethylacetate was added and mixed well. To this solution, 5 mL of 0.5% aqueous CTAB solution was added, the pH raised to about 11–12 by using 5 mL of 10% KOH solution, then shaken well for 2–3 minutes to allow for phase separation, and the aqueous layer was removed. Cr(III) was stripped off from the organic layer (ethylacetate) by adding 5 mL distilled water, followed by adding about 1.0 mL of H_2SO_4 , shaking the mixture contained in the separating funnel for 1–2 minutes, then allowing phase separation for 1–2 minutes, and draining the aqueous layer into a 10-mL volumetric flask. The stripped off solution was made up to 10-mL volume with distilled water, and Cr(III) was determined by GFAAS. The concentration of Cr(VI) is found by subtracting the concentration of Cr(III) from the concentration of total chromium.

Preconcentration, Separation, and Determination of Total Chromium

A 400–500 mL filtered water sample was taken into a 600-mL beaker and 20 mg of Fe^{2+} of ferrous ammonium sulphate added, mixed well, and heated at about 90 – 100°C for 5–10 minutes in order to completely reduce Cr^{6+} into Cr^{3+} by ferrous ion. Then cooled and 1.0 mL of concentrated nitric acid was added to oxidize the residual ferrous ion into ferric ion. The residual HNO_3 was destroyed by adding a pinch of sulphamic acid. Then about 2 g NH_4Cl was added and total chromium as Cr^{3+} precipitated with ammonia. During this precipitation, the ferric ion present in excess is precipitated as ferric hydroxide $[\text{Fe}(\text{OH})_3]$ which helps in co-precipitating traces of total chromium as Cr(III). The precipitate was digested in a waterbath at around 100°C for 10–15 minutes, cooled, and then filtered through Whatman 540 filter paper. The filtrate was discarded. The residue was dissolved in diluted H_2SO_4 and the solution transferred back into the 125-mL separating funnel to which 0.1 g solid 2,3- H_2ND was added, and mixed well. Then 10 mL of 10% (m/v) aqueous sodium-acetate solution was added, the pH adjusted to 4–5, 20 mL of ethylacetate added, and mixed well. The solution was shaken for 2–3 minutes in order to extract the iron out as a bluish-violet neutral chelate of Fe^{3+} -2,3- H_2ND . The organic layer was discarded. The aqueous layer was taken in the same separating funnel and to it was added 10 mL of 0.5% 2,3- H_2ND in ethylacetate and mixed well. Then, 5 mL of 0.5% aqueous CTAB solution was added. The pH was raised to about 11–12 by using 5 mL of 10% KOH solution, shaken well for 2–3 minutes, and allowed for phase separation. The aqueous layer was removed. Chromium was stripped off from the organic layer (ethylacetate) by adding 5 mL dis-

tilled water, followed by adding 1.0 mL (1:1) H_2SO_4 , and shaking the mixture contained in the separating funnel for 1–2 minutes. The stripped off solution was drained out into a 10-mL volumetric flask, made up to volume with distilled water, and total chromium determined by GFAAS.

Preconcentration, Separation, and Determination of Cr(III)

Another 400–500 mL of filtered water sample was taken into a 600-mL beaker and 20 mg of Fe^{3+} in the form of ammonium ferric sulphate was added, mixed well, and about 2 g of NH_4Cl added. The added iron and Cr^{3+} present in the sample solution was precipitated by adding ammonia dropwise. The precipitate was agitated and digested in a waterbath for 10–15 minutes, then cooled, and the slurry filtered using Whatman 540 filter paper. The filtrate was discarded and the residue dissolved in diluted H_2SO_4 . Iron was removed and Cr(III) extracted, then determined by GFAAS (as mentioned in a section above), resulting in the value of Cr(III). The difference of this value from the value of total chromium determined gives the value of Cr(VI).

RESULTS AND DISCUSSION

GFAAS is most commonly used for the trace analysis of chromium in water samples because of its high sensitivity. For speciation studies on chromium, separation of Cr(III) from Cr(VI) is needed. This is achieved by solvent extraction prior to the determination of the metal ions by GFAAS.

Separation of these two ions [Cr(III) and Cr(VI)] from each other is brought about by selectively extracting either of the two forms of chromium. There are a number of extractants known for the Cr(VI) species. However, very few reagents are known for the selec-

tive extraction of Cr(III). APDC and diphenylcarbazide are the well tested extractants for Cr(VI). As mentioned earlier in this paper, separation of Cr(III) from Cr(VI) by way of selectively extracting Cr(VI), although more common, has very serious drawbacks, i.e., Cr(VI) is easily reduced to Cr(III) by reductants present in the water samples as well as by some of the reagents used in the separation and determination of chromium. This definitely introduces error in the determination of the chromium species. On the contrary, owing to the very high oxidation potential of Cr(VI), very drastic conditions are required to oxidize Cr(III) into Cr(VI). In general, the oxidants present in natural water are not capable of oxidizing Cr(III). Besides, the reagents used in the separation and determination of chromium cannot easily oxidize Cr(III) present in waters and is thus comparatively more stable in natural water. Accordingly, it is desirable to separate Cr(III) from Cr(VI) by extracting total chromium as Cr(III) rather than extracting out total chromium in the form of Cr(VI). In this study, an effective solvent extraction system was searched where total chromium could be extracted as Cr(III).

In this endeavour, a novel reagent system for the extraction of both Cr(III) as well as Cr(VI) was found where the reversal of the prevalent system of carrying out solvent extraction of total chromium as Cr(VI) is effected. Instead of oxidizing Cr(III) into Cr(VI) quantitatively by certain strong oxidants, in the proposed system total chromium as Cr(III) is extracted after easily reducing Cr(VI) with excess Fe(II) ion. In this way, the shortcomings associated with the earlier system of extracting total chromium as Cr(VI) where, as mentioned above, error is inadvertently introduced due to the reduction of Cr(VI) into Cr(III)

by the reductants present in natural waters or by reagents used in the separation and determination of chromium, are eliminated.

In this work, one additional substantial improvement was brought about while determining chromium at ultratrace level (ppb to ppt level). As is well known, precision of GFAAS determination of many elements including chromium is usually poor compared to using flame AAS. At ultratrace level, the precision of the determination becomes so poor that many elements including chromium in water samples cannot be determined satisfactorily. This problem has been eliminated and precision improved by preconcentrating the chromium content in water by way of co-precipitating Cr(III) and total chromium in the form of Cr(III) after reducing Cr(VI) with added Fe(II) ion, along with hydrated Fe(III) oxide.

Thus, the method has been made more robust by combining a preconcentration step along with an effective and novel solvent extraction step. Following are the details of the systematic studies on the variables affecting the reduction of Cr(VI), preconcentration of chromium [Cr(III) and Cr(VI)] by co-precipitating it along with hydrated Fe(III) oxide, and the performance evaluation of the novel and effective solvent extraction procedure developed.

Effect of Variables on the Reduction of Cr(VI) by Fe(II) in the Determination of Total Chromium

In order to determine total chromium without preconcentration, there is no need for the reduction of Cr(VI) into Cr(III) because both species can be extracted together and determined by GFAAS. However, when preconcentration of chromium by R_2O_3 [$R = Fe(III)$ or Cr(III)] precipitation is needed

and total chromium is to be extracted and determined in the form of Cr(III), reduction of Cr(VI) into Cr(III) is required.

Fe(II) is an effective reductant for converting Cr(VI) into Cr(III). Determination of total iron in diverse samples based on the Pratt's redox titration of $K_2Cr_2O_7$ by Fe(II) ion using Na/Ba diphenylamine sulphonate is well established. This very reaction for the reduction of Cr(VI) by Fe(II) ion has been optimized and the effects of variables like pH, temperature and time, etc., needed for complete reduction have been studied.

Effect of pH on the Reduction of Cr(VI) With Fe(II)

The suitable pH for optimum reduction of Cr(VI) with Fe(II) in the form of ferrous ammonium sulphate has been found to be 2–5. Among the acids that facilitate reduction, HCl or H_2SO_4 has been found to be the most suitable. HNO_3 should not be used as it seriously hinders the reduction process because, on the contrary, Fe(II) instantaneously gets oxidized to Fe(III).

Effect of Concentration of Fe(II) on the Reduction of Cr(VI)

The effect of concentration of Fe(II) on the complete reduction of Cr(VI) was studied by varying the Fe(II) concentration from 100 μg to 100 mg in the form of ferrous ammonium sulphate. At microgram level of Fe(II) concentration, no reduction of Cr(VI) was observed. However, reduction starts above the 1-mg level. Up to 5 mg of Fe(II), the reduction was never complete, i.e., it is about 70–85%. At a concentration of 10 mg Fe(II), the reduction was found to be practically complete at $\sim 100^\circ C$. The reduction remains constant, i.e., $\sim 100\%$, even up to 50 mg Fe(II). However, to be safe, 20 mg Fe(II) was used for complete reduction of Cr(VI) to Cr(III).

Fig. 1. Effect of pH on percentage extraction of Cr(III) [Plot (1a)] and Cr(VI) [Plot (1b)].

Fig. 2. Effect of 2,3-dihydroxynaphthalene concentration on extraction of Cr(III) [Plot (2a)] and Cr(VI) [Plot (2b)].

Fig. 3. Effect of Cetyltrimethylammonium bromide concentration on extraction of Cr(III) [Plot (3a)] and Cr(VI) [Plot (3b)].

Effect of Temperature and Time on Reduction of Cr(VI) to Cr(III)

A temperature of 90–100 °C was found to be the most suitable range for almost complete reduction of Cr(VI) to Cr(III). At this temperature, the reduction was found to be completed within 10 minutes. However, heating for longer periods, i.e., more than 15 minutes, affects the results of Cr determination by GFAAS, probably due to the onset of oxidation of Fe(II). At still higher temperature, the rate of reduction of Cr(VI) into Cr(III) decreases, probably because the dissolved oxygen in water might be slowly oxidizing the Fe(II) ion into the Fe(III) ion.

Effect of Variables in the Pre-concentration of Chromium [Cr(III) and Cr(VI)] by Co-precipitating Total Chromium into Cr(III) With Hydrated Fe(III) Oxide

In a usual case (determination of chromium at ppm level) where further preconcentration of chromium is not needed, Cr(III) from Cr(VI) in the sample solution is separated by R_2O_3 precipitation along with hydrated Fe(III) oxide. Here, Fe(III) in the form of ferric ammonium sulphate is extraneously added.

In the system requiring preconcentration of Cr(III) as well as Cr(VI), Cr(III) is as usual preconcentrated as mentioned above but Cr(VI) is preconcentrated in the form of Cr(III) after reduction of Cr(VI) with added Fe(II) in the form of ferrous ammonium sulphate, followed by its [Cr(III)] co-precipitation with Fe(III) ion generated *in situ* by oxidizing residual Fe(II) ion with concentrated HNO_3 and destroying the excess of the same by sulphamic acid.

It has been observed that traces of Cr(III) [ppb to ppt level] cannot be precipitated unless they are co-

precipitated along with requisite amounts of Fe(III) ion. Cr(III) at ppb and ppt level can be satisfactorily precipitated along with Fe(III) added/generated *in situ*. The suitable concentration of Fe(III) ion required for co-precipitating ultra-trace level of chromium [0.1 to 1000 ppb] is about 10 mg of Fe(III) added/generated. To be safe, 20 mg of Fe(III) was used for better recovery of chromium owing to a substantial amount of Fe(OH)₃ formed at pH 8–10 by adding ammonia in the presence of NH₄Cl, which helps in co-precipitating Cr(III) and carrying it along with Fe(OH)₃.

Effect of Variables in the Extraction and Separation of Cr(III) and Cr(VI)

Similar to U, Mn, and Fe, chromium too [both Cr(III) and Cr(VI)] forms ion-pair complexes with 2,3-dihydroxynaphthalene and cetyltrimethylammonium cation, which are easily extracted into an organic solvent like ethylacetate. Here, cetyltrimethylammonium bromide, the cationic surfactant provides a micellar medium for easy extraction of both Cr species and, at the same time, also acts as a counter cation in the neutralization of the anionic species formed of both Cr(III) and Cr(VI) with the reagent 2,3-dihydroxynaphthalene, while extracting these species in the organic solvent.

In what follows are the accounts of systematic studies on the variables affecting the formation of the complex and their subsequent extraction into an organic solvent, followed by their determination by GFAAS.

Effect of pH on the Extraction of Cr(VI) and Cr(III)

The pH of the extraction was varied from 0 to 14 for the extraction of both chromium species [Cr(III) and Cr(VI)]. It was found that the ion-pair complex of both species is best extracted in the pH

range of 11–12 brought about by KOH. The efficacy of this extraction system, i.e., the degree of extraction, which is best expressed in terms of distribution coefficient, was ascertained by stripping the extracted metal into water and determining it by flame AAS. The plot of pH vs. % extraction for Cr(III) and Cr(VI) is given in Figures 1(a) and 1(b).

Effect of 2,3-dihydroxynaphthalene Concentration on the Extraction of Chromium

Under the optimized condition of pH and other reagents, the effect of the reagent 2,3-H₂ND (the complexing agent) was studied over a wide range, i.e., from 0.01 to 2% solution (m/v) in ethylacetate. The maximum extraction (near 100%) was found with 10 mL of 0.2% of the reagent. However, in order to allow for reagent impurity, 10 mL of 0.5% (m/v) solution in ethylacetate was recommended. Figures 2(a) and 2(b) show the plots of % extraction of Cr(III) and Cr(VI) vs. the concentration of 2,3-H₂ND.

Effect of Cetyltrimethylammonium Bromide on the Extraction of Chromium

The concentration of the surfactant required in the extraction of the anionic species [Cr(III)/Cr(VI)-2,3-H₂ND] was also found by varying the concentration of CTAB over the range 0.05 to 5% (m/v) aqueous solution. The plots [Figures 3(a) and 3(b)] for the % extraction of Cr(III)/Cr(VI) vs. the concentration of CTAB show that 5 mL of 0.2% (m/v) aqueous solution of the reagent was sufficient for near 100% extraction of both chromium species [Cr(III) and Cr(VI)].

However, similarly as done in the case of the optimization of 2,3-H₂ND, here too, 5 mL of 0.5% (m/v) aqueous solution was recommended in order to allow for reagent impurity.

Choice of Solvents

Extraction of the ion-pair species into various organic solvents was tried. These include ethylacetate, butylacetate, MIBK, hexane, toluene, benzene, chloroform, carbon tetrachloride, 2,3-dichlorobenzene, etc. However, the best extraction in terms of maximum distribution coefficient of the metal extracted, equilibrium time, etc., was found to be with ethylacetate.

Effect of Equilibrium Time, Electrolyte, Temperature, and Volume Ratio of Solvents on the Extraction of Cr(III) and Cr(VI)

No electrolyte was required for the extraction of the metal ions, although a number of electrolytes were added separately and the extraction properties studied. Similarly, the equilibrium time for the extraction of both species was found to be less than two minutes. The extraction of both species was found to be independent of temperature in the range 20–40 °C. Satisfactory extraction (>98%) of Cr(III) as well as Cr(VI) is possible with a volume ratio up to 5:1 (aqueous to organic). However, extraction (~99.0%) takes place at the 1:1 volume ratio (aqueous to organic solvent).

Effect of Diverse Ions on Extraction

The effect of various metal ions, including iron which was used in large quantity for the co-precipitation of Cr(III), was studied. Ions like Fe(III), Cu(II), Ni(II), Co(II), Zn(II), Mn(II), Pb(II), Rb, Na, K, Ca(II), Mg(II), Al(III), etc., at different concentration levels were added individually to the spiked solution [500 mL water containing 25 µg L⁻¹ each of Cr(III) and Cr(VI)], and the general procedure was applied. Recoveries of Cr(III) and Cr(VI) were quantitative when the ratio of the ions to Cr(III) or Cr(VI) was 20 for Fe(III); 25 for Al(III), Cu(II), Co(II), and Mn(II); 50 for

Pb(II), Zn(II), Ni(II), Na, K, Ca, and Mg.

Elements such as Fe, which is used in excess for co-precipitation of Cr(III), interferes by contributing towards background absorption in GFAAS. Hence, this element [Fe(III)], in particular along with Cu, Al, and Mn to some extent, is removed by a prior solvent extraction at the pH 4–5 using the same extractant (2,3-dihydroxynaphthalene).

The main advantage of solvent extraction of Fe(III), Cr(III), and Cr(VI) is to completely eliminate the salt content of the analyte solution, which otherwise contributes seriously towards background absorption in GFAAS and seriously affects the results of Cr determination.

Tentative Extraction Equilibria and Probable Composition of the Complexes

Composition of the complexes of both species [Cr(III) and Cr(VI)] was found by the Curve-fitting method (38), i.e., plotting % extraction vs. logarithmic concentration of 2,3-H₂ND and CTAB, respectively. It was found that in case of Cr(III), a slope of near 2 was obtained for the plot of % E vs. logarithmic concentration of 2,3-H₂ND and a slope of near 1 was obtained for the plot of % E vs. logarithmic concentration of CTAB. This shows the composition of the complex [Metal: 2,3-H₂ND : CTA is 1:2:1]. Similarly, a slope of 3 and 2 was obtained for the plot of % E vs. logarithmic concentration of 2,3-H₂ND and CTAB, respectively, in case of Cr(VI), indicating that the composition of the complex is 1:3:2. The tentative formulae of the extracted species are given as (CTA)₂[Cr^(III)(ND)₂] and (CTA)₂[Cr^(VI)O(ND)₃].

Extraction Equilibria for Cr(VI)

(Eq. 1)

where, H₂ND stands for 2,3-dihydroxynaphthalene and CTA⁺ stands for cetyltrimethylammonium ion.

The equilibrium constant K of the reaction can be written as,

(Eq. 2)

$$K_{\text{ex}(w,x)} = \frac{[\text{CTA}^+]^x [\{\text{CrO}(\text{ND})_w\}_o^{(1-w)}] [\text{H}^+]^{(2w)} [\text{Br}^-]^x}{[\text{Cr}^{6+}] [(\text{H}_2\text{ND})_o]^w [\text{CTABr}]^x}$$

or, (Eq. 3)

$$K_{\text{ex}(w,x)} = D [\text{H}^+]^{(3+w)} [\text{Br}^-]^x / [\text{H}_2\text{ND}]_o^w [\text{CTABr}]^x$$

where,

$$D = \frac{[\text{CTA}^+]^x [\{\text{CrO}(\text{ND})_w\}_o^{(1-w)}]}{[\text{Cr}^{6+}]}$$

Equation (3) can be re-written as:

(Eq. 4)

$$\log K_{\text{ex}(w,x)} = \log D - (2w)\text{pH} - w \log [\text{H}_2\text{ND}]_o - x \log [\text{CTABr}] + x \log [\text{Br}^-]$$

Analyzing the experimental values of the distribution ratio (D) as a function of equilibrium pH and extractant concentration at constant values of the other parameters, allows the estimation of the number of extractant molecules associated with the extracted metal. In order to clarify the distribution behavior of Cr(VI), slope analysis was used by plotting the logarithm of the distribution ratio of Cr(VI) vs. experimental variables (curve fitting method). The plot of log D value vs. the logarithm of concentration of 2,3-dihydroxynaphthalene (H₂ND) in the organic phase at a constant CTA⁺Br⁻ concentration gives a slope of near 3. It showed that three molecules of 2,3-H₂ND were used in the extraction process. The number of CTA cations used to extract the chelate

into the organic phase at a constant 2,3-H₂ND concentration indicates that 2 CTA⁺ ions take part in the extraction. Thus, the stoichiometry of the Cr(VI) complex is 1:3:2 [Cr(VI) : 2,3-H₂ND : CTA⁺].

Extraction Equilibria for Cr(III)

K_(w,x) = (Eq. 1)

Assuming no side reaction, the equilibrium constant K of the reaction can be written as

(Eq. 2)

$$K_{\text{ex}(w,x)} = \frac{[\text{CTA}^+]^x [\{\text{Cr}(\text{ND})_w\}_o^{(1-w)}] [\text{H}^+]^{(2w)} [\text{Br}^-]^x}{[\text{Cr}^{3+}] [(\text{H}_2\text{ND})_o]^w [\text{CTABr}]^x}$$

or (Eq. 3)

$$K_{\text{ex}(w,x)} = D [\text{H}^+]^{(2w)} [\text{Br}^-]^x / [(\text{H}_2\text{ND})_o]^w [\text{CTABr}]^x$$

$$\text{where, } D = \frac{[\text{CTA}^+]^x [\{\text{Cr}(\text{ND})_w\}_o^{(1-w)}]}{[\text{Cr}^{3+}]}$$

Equation (3) can be re-written as:

(Eq. 4)

$$\log K_{\text{ex}(w,x)} = \log D - (2w)\text{pH} - w \log [\text{H}_2\text{ND}]_o - x \log [\text{CTABr}] + x \log [\text{Br}^-]$$

A slope of near 2 is obtained for the plot of log D value vs. log of 2,3-H₂ND, attesting to the fact that two molecules of 2,3-H₂ND were required for the extraction of Cr(III) complex. Similarly, a slope of near 1 is obtained for the plot of log D vs. log [CTAB]. It demonstrates that one molecule of CTAB is required for the extraction of the Cr(III) complex. Thus the stoichiometry of the Cr(III) complex is 1:2:1 [Cr(III) : 2,3-H₂ND : CTA⁺].

From the above study, it can be stated that the tentative composition of Cr(VI) and Cr(III) ion-pair complexes are (CTA⁺)₂[CrO(ND)₃] and (CTA⁺) [Cr(ND)₂], respectively.

TENTATIVE REACTION SCHEME

Preconcentration Factor, Detection Limits, and Precision of Method

The preconcentration of Cr(III) and Cr(VI) by way of co-precipitation of Cr(III) as well as total chromium as Cr(III) with hydrated Fe(III) oxide is brought about to a great extent. The preconcentration factor was about 40 (400 mL water is finally brought down to 10 mL).

As a consequence, the detection limit (3σ) for $0.1 \mu\text{g L}^{-1}$ level of chromium determination was $0.01 \mu\text{g L}^{-1}$. The precision of the method in terms of relative standard deviation (RSD) was of the order of 3–5%.

Analytical Applications

In water samples, chromium is usually present at ppb levels. At this level, ICP-AES determination of chromium in water samples failed due to instrumental sensitivity constraints. Although GFAAS determination of chromium is quite sensitive, at ultratrace (ppb to ppt) level the precision of determination is so poor that determination of chromium is not reliable. Hence, speciation of chromium based on the direct determination (without preconcentration) is usually not satisfactory. In order to make the determination more reliable in terms of improved precision and detection, preconcentration of both Cr^{3+} and Cr^{6+} is resorted to. The methodology involves reduction of Cr^{6+} present in about

400–500 mL water using an excess of Fe^{2+} , and then oxidizing residual Fe^{2+} into Fe^{3+} with concentrated HNO_3 , followed by co-precipitation of total Cr^{3+} [Cr^{3+} present in water] + [Cr^{3+} obtained by reduction of Cr^{6+}] along with hydrated iron oxide [$\text{Fe}(\text{OH})_3$] using NH_4OH . Although HNO_3 used for oxidizing Fe(II) to Fe(III) does not interfere in the system, it (residual HNO_3) is destroyed with a pinch of sulphamic acid. Total chromium as Cr^{3+} was separated from iron (Fe^{3+}) by filtering the precipitate, re-dissolving the same in diluted H_2SO_4 and then extracting Fe^{3+} as Fe^{3+} -2,3- H_2ND neutral complex at pH 4–5 (otherwise Fe contributes towards high background absorption in GFAAS). This way, total chromium is determined as per the procedure prescribed. For the preconcentration and determination of

Cr^{3+} present in water samples, Cr^{3+} , in the same volume of water sample, was co-precipitated along with added Fe^{3+} , and processed similarly as discussed above for total chromium. The difference of the two is the measure of Cr^{6+} . In order to validate the method developed, it was applied to (i) synthetic mixture of Cr^{3+} and Cr^{6+} , (ii) effluent samples, and (iii) natural water samples. The results are shown in Tables II, III, IV, respectively. The results obtained were validated by those obtained by the method reported by Subramanian et al. (11).

CONCLUSION

The proposed method for the speciation of chromium [Cr(III) and Cr(VI)] in natural as well polluted water was found to be more effective and reliable because unlike earlier reported methods, here the chromium species [Cr(III) and Cr(VI)] were determined at ultratrace level with improved precision after preconcentration. The limit of determination of chromium by GFAAS was improved still further (40-fold) by co-precipitating ultratrace level of chromium along with Fe(III) prior to their determination. The method is recommended for routine GFAAS determination of Cr(III) and Cr(VI) in different water samples. The most striking feature

TABLE II
Determination of Cr(VI) and Cr(III) in Synthetic Mixture
by GFAAS (n = 5)

Sl. No.	Composition of Mixture*	Cr(VI) Found ^a (μg)	Cr(III) Found ^a (μg)	Cr(VI) Recovery ^b (%)	Cr(III) Recovery ^b (%)
1.	5 μg Cr(VI) + 5 μg Cr(III)	4.90	5.10	98.0 $\pm$ 4.2	102.0 $\pm$ 4.0
2.	5 μg Cr(VI) + 10 μg Cr(III)	4.87	9.77	97.4 $\pm$ 3.6	97.7 $\pm$ 2.9
3.	5 μg Cr(VI) + 15 μg Cr(III)	5.17	14.95	103.4 $\pm$ 3.0	99.6 $\pm$ 2.8
4.	10 μg Cr(VI) + 5 μg Cr(III)	9.92	4.88	99.2 $\pm$ 2.9	97.6 $\pm$ 3.4
5.	15 μg Cr(VI) + 5 μg Cr(III)	15.27	4.96	101.8 $\pm$ 4.0	99.2 $\pm$ 3.9

*Added in 25 mL of distilled water.

^a Mean of 5 determinations.

^b Mean and SD of 5 determinations.

TABLE III
Determination of Cr in Effluents and Wastewater by GFAAS (n =5)

Sl. No.	Sample No.	Proposed Method			Reported Method (Ref. 11)		
		Total Cr (ppm)	Cr(VI) (ppm)	Cr(III) (ppm)	Total Cr (ppm)	Cr(VI) (ppm)	Cr(III) (ppm)
1.	Effluent-1	0.91±0.06	0.41±0.03	0.50±0.04	0.89±0.09	0.39±0.04	0.50±0.06
2.	Effluent-2	0.62±0.05	0.27±0.02	0.35±0.04	0.67±0.08	0.25±0.03	0.42±0.05
3.	Effluent-3	0.29±0.02	0.16±0.01	0.13±0.01	0.32±0.04	0.15±0.02	0.17±0.02
4.	Effluent-4	0.12±0.01	0.05±0.004	0.07±0.008	0.10±0.01	0.05±0.007	0.05±0.008
5.	Wastewater-1	0.09±0.007	0.03±0.003	0.06±0.005	0.08±0.009	0.04±0.006	0.04±0.006
6.	Wastewater-2	0.04±0.005	0.015±0.001	0.025±0.003	0.05±0.006	0.017±0.002	0.033±0.004

n.d. = not detected.

^a Mean of 5 determinations.

^b Mean and SD of 5 determinations

TABLE IV
Determination of Cr in Natural Water Samples by GFAAS (n = 5)

Sl. No.	Sample No.	Proposed Method			Reported Method (Ref.11)		
		Cr[III+VI]* (ppb)	Cr[VI]* (ppb)	Cr[III]* (ppb)	Cr[III+VI]* (ppb)	Cr[VI]* (ppb)	Cr[III]* (ppb)
1	Stream water-1	24.24±1.2	17.53±0.89	6.71±0.39	24.80±2.7	18.40±2.1	6.40±1.1
2	Stream water-2	14.69±0.70	9.96±0.58	4.73±0.26	15.12±1.9	10.22±1.8	4.90±0.87
3	Bore well water	3.7±0.17	0.89±0.06	2.81±0.20	3.5±0.47	0.96±0.12	2.54±0.12
4	Tap water	0.21±0.02	0.09±0.01	0.15±0.02	nd	nd	nd
5	Rain water	1.9±0.20	0.79±0.09	1.11±0.08	nd	nd	nd

* Mean± Standard Deviation.

nd= not detected.

Chemical Analysis of Stream Water Samples for the Determination of Chromium (n = 3)

Sl. No.	Sample No.	(mg/L)									
		Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	CO ₃ ²⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻	F ⁻
1.	Stream water-1	33	11	48	17	nil	261	36	<5	<1	<1
2.	Stream water-1	56	22	71	34	nil	208	25	<5	<1	<1

of the proposed method is that hardly any solvent extraction method is known which is capable of extracting both species of chromium [Cr(III) and Cr(VI)] together at the same pH and the same concentration of reagent (2,3-dihydroxynaphthalene).

ACKNOWLEDGMENT

The authors are grateful to Director, Additional Director, Regional Director (Eastern Region), and Head Chemistry Group, AMD, for giving constant encouragement and

inspiration as well as for providing facilities to carry out the research work. The authors are also thankful to Director, AMD, for giving permission to publish this work.

Received August 8, 2017.

Revision received March 13, 2018.

REFERENCES

1. T. M. Florence, Talanta 29, 345 (1982).
2. P.C. Grevatt, Toxicological Review for chromium(VI); CAS No. 18540-

29-9, U.S. EPA (Aug. 1998), www.epa.gov/iris/toxreviews/0144-fr.pdf.

3. E. Berman, Toxic Metals and Their Analysis, Heyden and Sons, London, U.K. (1980).
4. A. Zhitkovich, Chem. Res. Toxicol. 18, 3 (2005).
5. A.V.Padarauskas and L.G.Kazlauskienė, Talanta 40, 827 (1993).
6. M. Sperling, S. Xu, and B. Welz, Anal. Chem. 64, 3101 (1992).
7. M. Sperling and A. Townshend (Eds.), Encyclopedia of Analytical

- Sciences, Vol.2, Academic Press, London, U.K., 729 (1995).
8. E. Kaprara, N. Kazakis, K. Simeonidis, S. Coles, A.I. Zouboulis, and P. Samaras, *J. Hazard. Materials* 281, 2 (2015).
  9. C.M. Wai, L.M. Tsay, and J.C. Yu, *Microchim. Acta* 11, 73 (1987).
  10. V. Andruch, M. Telepcakova, J. Balogh, and N. Urbanova, *Microchim. Acta* 142, 109 (2003).
  11. K.S. Subramanian, *Anal. Chem.* 60, 11 (1988).
  12. D.M. Adria-Cerezo, M. Lobat-Estelles, and A.R. Mauri-Aucejo, *Talanta* 51 (3), 531 (2000).
  13. L. Wang, B. Hu, Z. Jiang, and Z. Li, *Int. J. Environ. Anal. Chem.* 82, 387 (2002).
  14. E. Menendez-Alonso, S.J. Hill, M.F. Foukes, and J.S. Crighton, *J. Anal. At. Spectrom.* 14, 187 (1999).
  15. J. Wang, K. Ashley, D. Marlow, E.C. England, and G. Carlton, *Anal. Chem.* 71 (5), 1027 (1999).
  16. L. Jin and L. Yang, *Chin. J. Anal. Chem.* 16, 410 (1998).
  17. Y. Martinez-Bravo, A.F. Roig-Navarrow, F.J. Lopez, and F. Hernandez, *J. Chromatogr. A* 926, 265 (2001).
  18. J. Posta, A. Gaspar, R. Toth, and L. Ombodi, *Microchem. J.* 54, 195 (1996).
  19. M. Derbyshire, A. Lamberty, and P.H.E. Gardiner, *Anal. Chem.* 71, 19 (1999).
  20. Y.Y. Chan and W.T. Chan, *J. Chromatogr. A* 853 (1-2), 141 (1999).
  21. I.I. Stewart and J.W. Olesik, *J. Chromatogr. A* 872 (1-2), 227 (2000).
  22. M. Gardner and S. Comber, *Analyst* 127, 153 (2002).
  23. D. Baralkiewicz and J. Siepak, *Chem. Anal. (Warsaw)* 44, 879 (1999).
  24. G.J. de Jong and U.A.Th. Brinkman, *Anal. Chim. Acta* 98, 243 (1978).
  25. A.G. Coedo, T. Dorato, I. Padilla, and F.I. Alguacil, *J. Anal. At. Spectrom.* 51, 1564 (2000).
  26. T. Tande, J.E. Patterson, and T. Torgimson, *Chromatographia* 13, 607 (1980).
  27. A. Tunceli and A. Rehber Turker, *Talanta* 57, 1199 (2002).
  28. A. Beni, R. Karosi, and J. Posta, *Microchem. J.* 85, 103 (2007).
  29. C.D. Palmer and P.R. Wittbrodt, *Environ. Health Perspect.* 92, 25 (1991).
  30. J. Chwastowska, W. Skwara, E. Sterlinska, and L. Pszonicki, *Talanta* 66, 1345 (2005).
  31. H. Filik, *Microchim. Acta* 140, 205 (2002).
  32. Zhi-Hua Wang, Ming Song, Quan-Li Ma, Hui Min Ma, and Shu-Chuan Liang, *Microchim. Acta* 134, 95 (2000).
  33. F. Shemirani and M. Rajabi, *Fres. J. Anal. Chem.* 371(7), 1037 (2001).
  34. E.K. Paleologos, C.D. Stalikas, and M.I. Karayanni, *Anal. Chim. Acta* 49, 436 (2001).
  35. E.K. Paleologos, C.D. Stalikas, S.M. Tzouwarakaryanni, G.A. Pilidis, and M.I. Karayannis, *J. Anal. At. Spectrom.* 15, 287 (2000).
  36. S.E. Fendorf and G. Li, *Environ. Sci. Technol.* 30 (5), 1614 (1996).
  37. D.L. Sedlak and P.G. Chan, *Geochimica et Cosmochimica Acta* 61(11), 2185 (1997).
  38. L.G. Sillen, *Acta Chem. Scand.* 10, 186 (1956).