

ORIGINAL PAPER

Speciation of Chromium in Ground Water samples by Ion Exchange Chromatography after pre-column oxidation using Potassium Permanganate solution

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ABSTRACT

Chromium exists in its two stable oxidation states including chromium (III) and chromium (VI) in natural waters. The presence and ratio between these two forms is dependent on chemical and photochemical redox transformation, precipitation /dissolution and adsorption/desorption reactions. Chromium is an essential micronutrient in the trivalent form, however the hexavalent form of chromium is considered to be a carcinogen. There are a number of methods available for chromium determination. Speciation of chromium is essential to know the exact composition of chromium. Ion exchange chromatography is one of the technique used to determine chromium (VI). The proposed method can be used to perform the speciation of chromium (III) and chromium (VI). It is a two-step process, first chromium (VI) is determined, followed by total Chromium determination by treating the sample with potassium permanganate solution to oxidize the Chromium (III) present in the sample to chromium (VI) and determining it as chromium (VI). Addition of potassium permanganate solution to the ground water samples for oxidizing the chromium (III) to chromium (VI) is the newly adopted sample preparation technique and further determining it by ion exchange chromatography with conductivity detection. This method can be used for chromium speciation in river water and ground water samples.

Key words: Ion exchange chromatography, speciation, chromium (III), chromium (VI), suppressed conductivity detection, pre-column oxidation.

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INTRODUCTION

It has long been recognized that chromium can exist in at least two different ionic forms, viz., chromic ion (+3), Cr⁺³, Cr (III), and chromium (VI) ion (+6), Cr⁺⁶, Cr (VI), CrO₄²⁻. It is also well known that each of these forms has very different biological, medical, and toxicological properties, and the problem of chromium toxicity is currently one considerable interest and concern. Trivalent chromium (III) is an essential element in mammalian systems, whereas hexavalent chromium (VI) is considered to be a moderate to severe industrial hazard. Epidemiologic studies have suggested that chromium (VI) anion, is a carcinogen. Quite obviously, possible health hazards associated with the presence of chromium in foods or beverages for human consumption will depend on which particular oxidation state of chromium is present. Thus the safety of drinking water supplies, environmental watersheds, beverages, foods, and industrial environments, can only be determined, at least as regards chromium metal, once a correct determination has been made as to the specific forms or species present. For about the past decades, a large number of toxicological studies have been reported related to chromium and its various ionic species, but most of these have omitted a valid analytical determination of the particular and actual species of chromium present in particular samples. Later on, EPA (METHOD 7199) has proposed a method for the determination of hexavalent chromium in drinking water, ground water and industrial waste water effluents by ion exchange chromatography. This method provides procedures for the determination of hexavalent chromium in drinking water, groundwater, and industrial wastewater effluents. But this method provides only the information on the concentration of hexavalent chromium present in the samples. The other spectrophotometric methods available like atomic absorption spectroscopy (AAS) and inductive coupled plasma atomic emission spectroscopy (ICP-AES) provides the information of the total chromium present in the samples.

The determination of toxic properties for any metal or nonmetal cannot be accurately or reliably made in the absence of appropriate and reliable analytical speciation determinations. There have been a large number of reports over the past years with regard to specific analytical methods for the speciation of chromium ions. Most of these methods have used ion exchange resins for pre-concentration and separation prior to atomic absorption or atomic emission spectroscopy, while still others have used ion exchange separations with precolumn derivatisation with suitable complexing agents like Pyridine-2,6-dicarboxylic acid (PDCA) followed by post column derivatisation with 1,5-diphenylcarbohydrazide and the with UV-Visible detection. But these methods are tedious and time consuming. Moreover if the complexation is not done properly there is always a chance of low precision and less accuracy.

Ion exchange chromatographic method with conductivity detection is suitable for the determination of hexavalent chromium. The same method can be employed for determining the trivalent chromium by additional sample preparation. This will be a two step process. In the first step the water sample is directly injected into the ion exchange chromatographic system after filtering it through 0.45 μm filter, this injection will provide the hexavalent chromium content. The second step will be oxidizing the same water sample using potassium permanganate solution to oxidise the trivalent chromium, if any present, in the sample to hexavalent chromium and determining the total chromium present in the water sample. By this we will get the results for hexavalent chromium in the first step and total chromium in the second step. The difference between these two results will provide the concentration of trivalent chromium present in the water samples.

In this study, the analytical parameters for speciating Chromium (III) and Chromium (VI), like eluent type, sample preparation, sample volume also the matrix influence were investigated and optimized to get a suitable chromatographic method for chromium speciation. The established method was applied to three ground water samples and spike tests were also performed to check the suitability of the method for ground water samples.

MATERIALS AND METHODS

2.1 Apparatus: A 940 Professional Ion Chromatography instrument from Metrohm (Herisau, Switzerland), together with 858 Professional IC Sample Processor with built-in injector and peristaltic pump was used. The instruments were controlled and data acquisition was done through the MagIC Net 3.0 software. Metrosep A Supp 5 – 150, which is based on a polyvinyl alcohol Polymer with quaternary ammonium groups as functional group is used for the separation of chromium (VI) ions and other common anions.

2.2 Chemicals and reagents: All solutions were prepared using deionized water (> 18 M Ω) purified by an Elga Purelab Flex 1 system (Elga Veolia, UK). Sodium carbonate puriss, sodium bicarbonate puriss ACS Reg. Ph Eur, potassium permanganate and suprapure sulfuric acid, were purchased from Sigma Aldrich (Missouri, USA).

Sodium carbonate (12.8 mmol/L) and sodium hydrogen bicarbonate (4 mmol/L) was used as eluent. Sulphuric acid (100 mmol/L) and ultra-pure water were used as the suppressor regenerants. Chromium (VI) standard stock solution of 1000 $\mu\text{g}/\text{mL}$ was prepared from the potassium dichromate salt and chromium (III) standard stock solution of 1000 $\mu\text{g}/\text{mL}$ was prepared from chromium nitrate salt. Potassium permanganate stock solution of 1000 $\mu\text{g}/\text{mL}$ was prepared from potassium permanganate salt. Lower concentrations were prepared freshly from this stock solution.

2.3 Sample preparation: The sample has to be injected twice, first for determination of chromium (VI) and the second time for the determination of total chromium. For chromium (VI) determination the sample can be transferred into the sample tube and placed in the autosampler. Since the autosampler is equipped with ultra filtration setup, the water sample will be filtered through the ultrafiltration cell with 0.45 μm membrane filter and injected into the ion chromatograph system automatically. For total chromium content, 100 μL of 1000 $\mu\text{g}/\text{L}$ potassium permanganate stock solution is added to a 10 mL volumetric flask and diluted to the mark with the water sample. This sample solution is shaken well and transferred to a sample tube and placed in the autosampler for sample injection. The concentration of potassium permanganate in the sample solution is 10 $\mu\text{g}/\text{mL}$. The concentration of potassium permanganate solution can be varied based on the concentration of oxidisable components present in the samples.

RESULTS AND DISCUSSION

3.1 Inline sample filtration: Inline sample filtration cell with 0.45 μm membrane filter, is fixed to the 858 Professional Sample Processor through which the standards and the sample solutions were injected into the ion chromatography system automatically. Figure 1. shows the instrument setup used for the analysis.

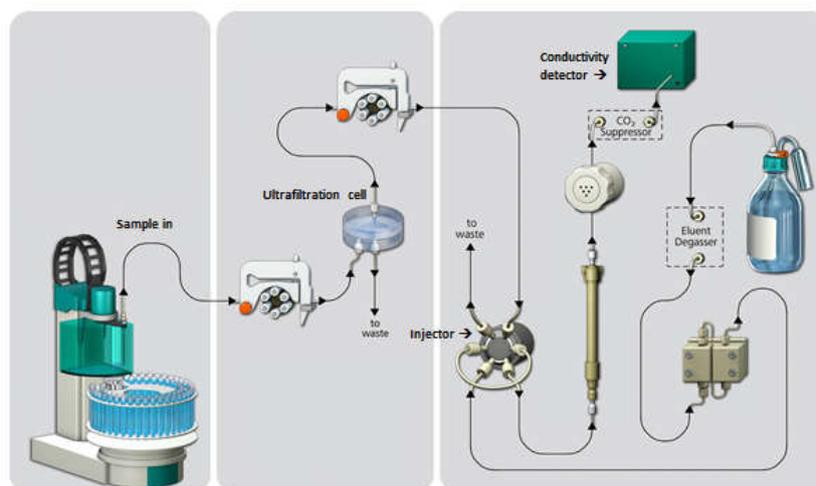


Figure 1: Instrument setup

3.2 Method Specificity: Blank solution, mixed anion standards with fluoride, chloride, bromide, nitrate, phosphate, sulphate and chromium (VI) were injected to check the specificity. Relative retention times for the anions fluoride, chloride, bromide, nitrate, phosphate and sulphate are 0.40, 0.53, 0.60, 0.69, 0.72 and 0.80 respectively. RRT values prove good separation of chromium (VI) from common anions in the sample matrix, and hence, it is suitable for the determination of chromium (VI) in water samples. The separation of chromium (VI) from common anion is shown in Figure 2 with the chromatographic conditions.

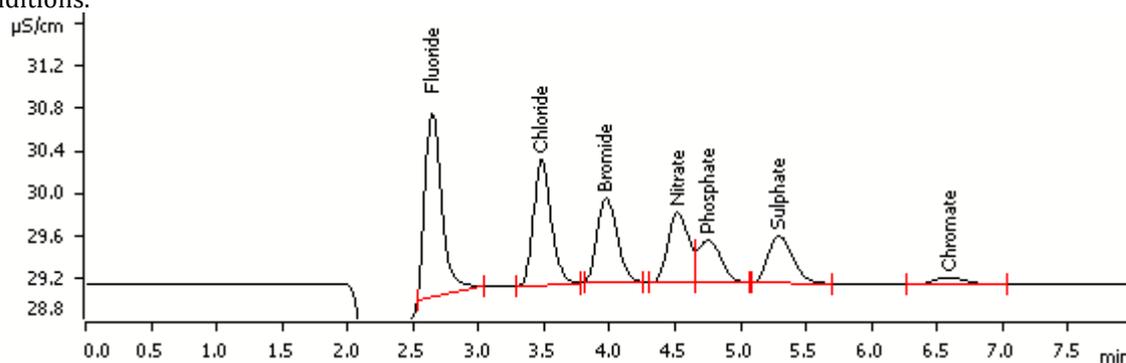


Figure 2: Specificity of chromium (VI) from common anions. Column: Metrosep A Supp 5–150; eluent: 12.8 mmol/L sodium carbonate + 4 mmol/L sodium bicarbonate; flow: 0.7 mL/min; detection: suppressed conductivity

3.3 System precision: System precision was calculated from the relative standard deviation (RSD) value obtained for area and retention time (RT) for the six consecutive injections of 10 ng/mL chromium (VI) standard. The RSD values for area and RT were 1.27% and 0.18%, respectively. The RSD for peak area obtained was well within the acceptance criteria of ICH guidelines.

Table 1: Chromium (VI) 10 ng/mL standard injection for system precision checking.

Injection No.	Area in ($\mu\text{S}/\text{cm}$) x min	Retention time in min.
1	0.00166	6.51
2	0.00166	6.52
3	0.00164	6.52
4	0.00168	6.54
5	0.00162	6.51
6	0.00164	6.53
Average	0.00165	6.52
RSD	1.27	0.18

3.4 Linearity: Chromium (VI) standard concentrations of 10, 50, 100, 250, 500, and 1000 ng/mL were prepared by diluting 1 $\mu\text{g}/\text{mL}$ stock chromium (VI) standard with ultra-pure water. The prepared low-level concentrations were injected in duplicate to check the precision and linearity aspects.

A regression line was obtained by plotting peak area ($\mu\text{S}/\text{cm} \times \text{min}$) of the chromium (VI) using the least square method. The relationship between peak response and concentration was found to be linear between the ranges of 10 to 1000 ng/mL of chromium (VI), with the coefficient of determination (r^2) of 0.9999. The RSD of the response factor was 0.668%.

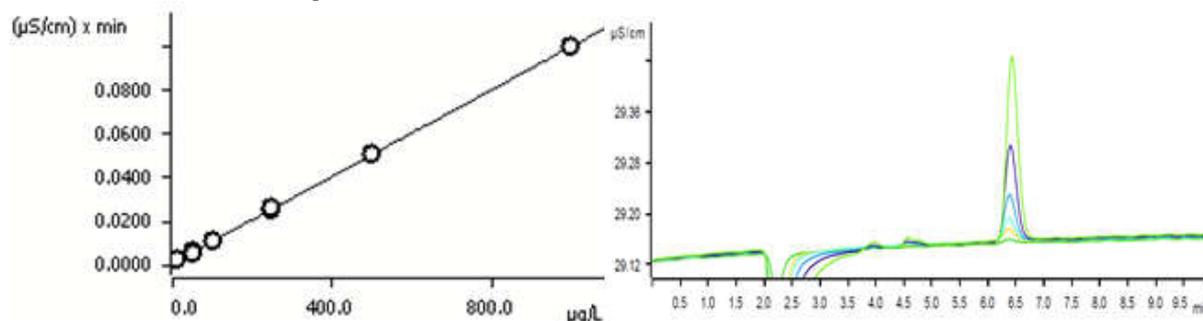


Figure 3: Linearity curve and chromatogram for chromium (VI) standards

3.5 Limits of detection and quantification: Based on the linearity of calibrations and the response of the chromium (VI) ion for the given chromatographic conditions the limit of detection is calculated as 2 ng/mL and the limit of quantification is calculated as 10 ng/mL.

3.6 Accuracy and precision: Conversion of chromium (III) to chromium (VI) was achieved by addition of potassium permanganate solution. The concentration of potassium permanganate was optimized to 10 $\mu\text{g}/\text{mL}$, since the concentration of chromium analysed in water samples are in ng/mL level the optimized concentration of potassium permanganate is sufficient for the oxidation. To check the efficiency of oxidation, multi-level chromium (III) standard of 10, 25, 50, 100, 200 and 400 ng/mL was injected with addition of potassium permanganate solution. The relationship between peak response and concentration was found to be linear between the ranges of 10 to 400 ng/mL of chromium (VI), with the coefficient of determination (r^2) of 0.9997. The RSD of the response factor was 2.719%. The peak area for the chromium (III) standards which were oxidized to chromium (VI) was compared with the standards of chromium (VI) ion standards and was found to be matching. This shows that there is 100% oxidation of chromium (III) to chromium (VI) on addition of potassium permanganate solution.

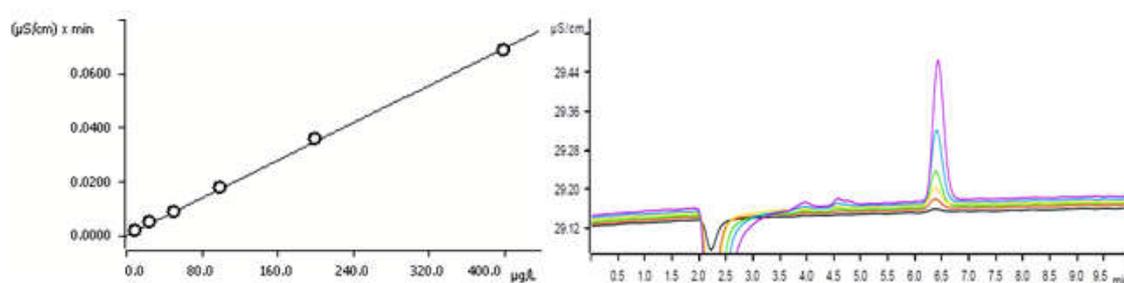


Figure 4: Linearity curve and chromatogram for chromium (III) standards after oxidation with Potassium permanganate solution

Three ground water samples collected from the localities were injected to check the presence of chromium species. Since chromium species were below the limit of detection, the samples were spiked with 5 ng/mL each of chromium (III) and chromium (VI) from the stock standards to the water samples. Spiked samples were analysed and the recovery ranging from 95% to 105% was obtained. This shows that the proposed method is suitable for quantifying and speciation of chromium (III) and chromium (VI) in ground water samples.

CONCLUSION

A simple and rapid method has been optimized for the speciation of chromium in ground water samples by short anion exchange column and conductivity detection. Determination of chromium (VI) by direct injection, followed by addition of potassium permanganate solution to the water sample for the oxidation of chromium (III) to chromium (VI) and subsequent determination of total chromium as chromium (VI) is much more simpler method compared to the speciation methods that are available currently. Since we have taken a shorter column of 150 mm, the analysis time is also within 10 minutes. This method can be

used for water samples with moderate TDS values where the concentrations of the other anions are not more than 300 to 400 µg/mL. The samples with higher ionic concentration may load the analytical column. In such cases the same method can be used, but instead of conductivity detection UV-Visible detection can be used along with 1,5-diphenylcarbohydrazide as post column reagent. This method has distinctive advantages over the conventional methods available for speciation, with respect to the short sample preparation time and free from toxic organic chemicals.

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