



Determination of Hexavalent Chromium using Bifunctional Ion Exchanger by Ion Chromatography

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Abstract

A new method was developed for determination of hexavalent chromium using bifunctional ion exchanger by ion chromatography with UV detection. The method was optimized against the eluent pH, concentration and flow rate using certified soil sample (NCS DC 73325). The detection limit achieved was about 0.01 mgL^{-1} with relative standard deviation of 0.048%. The developed method has been applied for the determination of Cr(VI) in three geological materials. However, this paper presented simple determination of Cr(VI) in various materials without prior technological methodologies of separation of the ion concentrate which plays an important role in high accuracy sample determinations.

Keywords: separation, determination, hexavalent chromium, bifunctional ion exchanger, ion chromatography

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1. Introduction

Chromium happens normally in the earth and has both advantageous and probable human hazards. Cr(III) and Cr(VI) represents the main oxidation states than others in the environment [1]. Hexavalent chromium (Cr(VI)) is considered as a strong oxidizing agent as well as one of the most poisonous and cancer-causing species [2], along these lines it is viewed as destructive to organic frameworks, the fact which necessitates its guideline in the environment. On the other hand, Cr(VI) is utilized in different enterprises including calfskin tanning, electroplating, painting, and metallurgy businesses [3].

Chromium was used as a coating matter because of its phenomenal erosion opposition, high liquefying point, great quality, high hardness, and great wear obstruction [4]. Attributable to its mechanical and thermal possessions, chromium has a robustly defensive conduct, permitting it to be compatible with Zr-based alloys, as CrN-coated Zr-1% Nb [4-6]. Hence, chromium and chromium nitride covered cladding are basic for nuclear fuel reactors. Besides, working involvement in chromium inside reactor cores since control bars in some Light Water Reactors (LWRs) were plated with chromium for accident-tolerant fuel cladding so as to build wear opposition [7].

The improvement of analytical techniques for chromium determination starts from across the board modern utilization of this element. The analytical determination of metal ions at low concentration levels has gotten impressive consideration over the most recent couple of years [8]. The determination of chromium has conventionally been performed by means of atomic absorption spectrometry (AAS) [9] or inductively coupled plasma (ICP) [10]. In spite of the fact that these instrumental techniques are accurate and sensitive however permit determination of total chromium only where the concentration of Cr(VI) is assessed from the

difference of total chromium content and Cr(III), the strategy which achieves erroneous decided concentrations. From that point onward, a few techniques have been progressed for the determination of Cr(VI) in various natural samples, for example; co-precipitation [11], spectrophotometric [12], solvent extraction [13], ion-exchange [14] and differential pulse polarography [15].

As noticed from literature reviews, most of the chromatography techniques were considered as vigorous fundamental analytical methods accessible for analyzing hexavalent chromium [16]. From among these methods, the frequently applied is ion chromatography, where a method using UV detection and post-column derivatization with diphenylcarbazide at 520 nm was published by Dionex [17]. Another update was achieved by Dionex concerned with the sensitive estimation of Cr(VI) in drinking water using visible detection only [18]. Hyphenated techniques are very sensitive and permit determination of chromium species [19-21].

The main target of this research is to provide an analytical method for the selective determination of hexavalent chromium in geological materials using bifunctional ion exchanger by ion chromatography technique. To achieve such objective, the method was optimized against the eluent's pH, concentration and flow rate using certified soil sample (NCS DC 73325). Furthermore the advanced chromatographic conditions was applied for the determination of Cr(VI) in three geological materials.

2. Experimental Procedures

2.1 Instrumentation

Ion chromatographic separation was carried out on Dionex DX-500 ion chromatograph system (Sunnyvale, CA, USA) which includes; gradient pump (GP40), UV-Vis detector (AD20), rear-loading Rheodyne injection

valve and Chromeleon Workstation. Ion-exchange columns from Dionex IonPac CG5A (guard column) and IonPac CS5A (analytical column) containing bifunctional anion and cation beds with sulfonic acid and alkanol quaternary ammonium functional groups were used [22], thus ionic species can be separated using either anion- or cation-exchange chromatography.

The pH measurements were made on a digital Jenway pH meter (UK).

2.2 Reagents

Standard solutions of Cr(VI) have been prepared by diluting stock solutions of $1000 \mu\text{g mL}^{-1}$ as chromate (CrO_4) (GFS, USA). Pyridine-2,6-dicarboxylic acid (PDCA) (Merck, Germany) was used as a mobile phase in NH_4OH (Merck, Germany) buffer solution. pH adjustment was done using formic acid and ammonia solution (Merck, Germany). All reagents used for sample digestion (nitric, hydrofluoric, perchloric acids and hydrogen peroxide) are of analytical grade (Sigma Aldrich, USA). Detection of the separated Cr(VI) ion was measured at 365nm with UV detection. PDCA eluent was degassed with a nitrogen gas. All solutions were prepared using nanopure water ($18.2 \text{ M}\Omega\text{-cm}$) obtained from a Thermo Scientific "Barnstead" lab water system (Thermo Fisher Scientific Inc., USA).

2.3 Chromatographic Conditions

The analysis has been performed with PDCA eluent using isocratic elution conditions. The worked eluent was prepared in selected ammonia buffer solution. After a preliminary optimization, the mobile phase flow rate was set at 0.8 mL min^{-1} .

2.4 Sampling and Sample Preparation

2.4.1 Location and geology of the study samples

After optimization of the working procedure using certified soil sample (NCS DC 73325) approved by China National Analysis Center of Iron and Steel, (Beijung, China), the optimized developed method was applied for the analysis of three Cr samples of different contents and locality. These include two granite samples from Gabal El Sela-Qash Amer and Gabal Gattar areas while the other sample was phosphate rock from Abu Tartur deposit.

Gabal El Sela-Qash Amer area is located in the South Eastern Desert of Egypt, between Latitudes $22^\circ 17' 44''$ - $22^\circ 18' 10''$ N and Longitudes $36^\circ 13' 28''$ - $36^\circ 14' 27''$ E. at a distance of about 50 km South Western of Abu Ramad city close to the Sudanese border [23]. Gabal Qash Amer has a higher relief than Gabal El-Sela in the area. The Qash Amer granites are medium to coarse-grained, whitish to pink. They intrude ultramafic rocks and schistosed metavolcanics. Qash Amer is a muscovite garnet leucogranite where Zinnwaldite may occur in the core of muscovite crystals [24]. Columbo-tantalite and uraninite represent the accessory minerals. The nature of the micas and accessory minerals are characteristic of highly fractionated Rare-metal granites (RMG).

Gabal Gattar region, as a section of the north Eastern Desert of Egypt, is a piece of the Arabian-Nubian shield. It is situated within the north Eastern Desert of Egypt between Latitudes $26^\circ 52'$ & $27^\circ 08'$ N and Longitudes $33^\circ 13'$ & $33^\circ 25'$ E [25]. This region is predominantly covered with Pan-African rocks, chiefly Younger Granites

of late Proterozoic age. The Gattarian granite mass structures a prolonged colossal granite batholith orienting by its long dimension (40 km) in an exceedingly NS direction.

Abu Tartur deposit is situated in Eastern Sahara, in the "New Valley" area of the Western Desert of Egypt, 50 km^2 west of El-Kharga [26]. The deposit prolongs over 100 km^2 at the south-eastern corner of Abu Tartur plateau. Its middle is at $25^\circ 26'$ N and $30^\circ 02'$ E. The highest of the plateau lies somewhere in the range 550 and 560 m above mean sea level. The lowlands and scattered hills of the depression south of the Abu Tartur plateau have a height of around 200-300 m above mean sea level [27]. The phosphate formation is formed of lower and upper phosphorite beds isolated by shales, glauconitic sandstone, carbonate rocks and sandstones.

To guarantee appropriate preparation of the study samples, they were properly grinded and exposed to an ashing step before digestion.

2.4.2 Sample Digestion

In the wake of ashing, the four study samples were appropriately dissolved utilizing acid digestion procedure. Subsequently to 2 g of every of the three applied geological samples and to 5 g of the certified soil sample weights, a blend of concentrated nitric, hydrofluoric, and perchloric acids was included in an exceedingly 120 mL TFM container. The solution was then heated on a hot plate till dryness then followed by adding (1:1) HNO_3 acid solution to dissolve the dried sample. After complete dissolution, hydrogen peroxide was added so as to oxidize all the Cr(III) ions found in each sample solution to Cr(VI). The resulting solution was then neutralized to pH range of (9-9.5) with 10 M sodium hydroxide, left to settle then filtered and made up to 50 mL mark with nanopure deionized water.

2.4.3 Geological and certified soil samples preparation for analysis

In order to achieve certain elution of Cr(VI) and therefore facilitates its determination from the three study geological and the certified soil samples, the following steps have to be tracked [17]:

Take 5mL of each of the previously 50 mL digested sample solution in 100 mL beaker. Spike the three study geological samples only with 12.5 mL of 1000 mg L^{-1} Cr(VI) stock standard solution then add 15 mL eluent stock (PDCA) to each beaker. Mix thoroughly each of the spiked and the unspiked certified soil sample then check/adjust the solution pH (9-9.5), where at this pH range Cr exists as CrO_4^{2-} species [3, 28, 29]. Put the beaker of each sample in a water bath at 70°C for 1 hour. Cool the solution then transfer to a 50 mL volumetric flask. Complete to the mark volume by nanopure water. The solution was ready for injection.

2.4.4 Preliminary calibration curve preparation

Preliminary calibration curve for Cr(VI) was prepared by diluting 1000 mg L^{-1} Cr(VI) stock standard solution with different volumes according to the required concentrations. Add about 4 mL nanopure water to each standard solution volume then mix with 5 mL PDCA eluent in 10 mL volumetric flask. Check/adjust the

solution pH at 9-9.5. Each flask was then placed in a water bath of 70°C for 1 hour. Cool the solution then complete to the mark volume by nanopure water.

2.4.5 Method calibration curve preparation

Cr(VI) calibration curve for the study developed method was prepared using the certified soil sample. Standards were set up by diluting the firstly prepared certified soil sample (50 mL digested sample) with different volumes according to the required concentrations (1-6 ppm) in 10 mL volumetric flask. Add 5 mL PDCA eluent then check/adjust solution pH at 9-9.5. Each volumetric flask was then placed in a water bath of 70°C for 1 hour. Cool the solution then complete to the mark volume by nanopure water.

The experiments were carried out under the following requirements:

1- Samples that contain no measurable amounts of Cr(VI) are spiked with known quantities of Cr(VI) standard to feasible its determination [3, 17].

2- At pH values below 6, chromate can convert to dichromate, which can be harmful to the column and reduce the measurable Cr(VI)[17].

3- 70°C was chosen since the complexation was complete after an hour for both low and high concentrations of Cr(VI) to determine the stability of the species during derivatization [30].

3 Results and Discussion

In a previous paper, a method was developed to investigate the determination of trace levels of chromium (VI) in water by ion chromatography method [16]. Based on this study, an optimal conditions were taken as a starting point for the ion chromatographic determination of hexavalent chromium in nitric acid medium namely; 10 mM PDCA / 148 mM NH₄OH mobile phase with pH of 9.8, bifunctional ion exchanger column viz. Ionpac CS5A, eluent flow rate of 0.8 mL min⁻¹, injection volume of 100 µL and 365 nm wavelength for UV detection. Undergoing a preliminary calibration using these conditions and checking the analysis of Cr(VI) using the certified soil sample (which attained 410 ppm) for validation, resulting in low Cr(VI) value of 330 ppm. So, it was decided to optimize the conditions under consideration using the worked certified soil sample as a validator.

3.1 Optimization of the separation and determination factors

3.1.1 Influence of eluent pH variation

The influence of eluent pH variation on the determination of the separated Cr(VI) ion, from the certified soil sample, by the ion chromatograph system (IC) was performed at different PDCA pH ranging from 6-10.5. The other parameters such as eluent concentration and flow rate were kept constant at 10 mM and 0.8 mL min⁻¹ respectively. The resulted data presented in Figure (1) shows that increasing the PDCA eluent pH from 9.8-10.5 was accompanied by decreasing the value of the determined Cr(VI). On the other hand, going in the opposite direction of decreasing the pH value than 9.8 resulting in raising the determined Cr(VI) value to 375 and 370 ppm. Accordingly, it can be mentioned that the pH

range of 6-8 can be considered to be the optimum, so the chosen value is actually 7.5 for PDCA eluent.

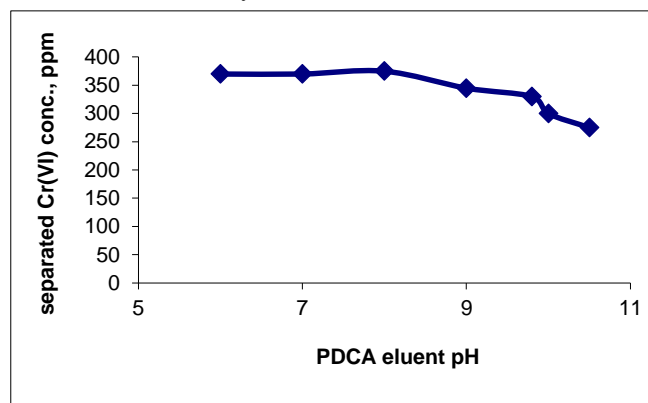


Fig (1): Influence of PDCA eluent pH on the separation of Cr(VI)

3.1.2 Influence of eluent concentration variation

Figure (2) shows the influence of PDCA eluent concentration variation on the separation and determination of Cr(VI) in the certified soil sample. To achieve maximum separation and determination of Cr(VI), six series of runs were carried out where the concentration of PDCA was varied from 9-11.5 mM whereas the other components namely; PDCA pH of 7.5 and 0.8 mL min⁻¹ eluent flow rate remain constant. Apparently, it was found from Figure (2) that the variation in the PDCA mobile phase concentration has affected on the elution process of the Cr(VI) ion in the certified soil sample nitrate medium. Decreasing PDCA eluent concentration from 10-9 mM resulted in low Cr(VI) values than the certified value, so, going through increasing PDCA concentration from 10-11.5 indicated steady increase in Cr(VI) elution till reaching constant plateau. PDCA eluent concentration of 11 mM was chosen as the optimum value where it achieved a good value (400 ppm) close to that of the certified soil sample (410 ppm).

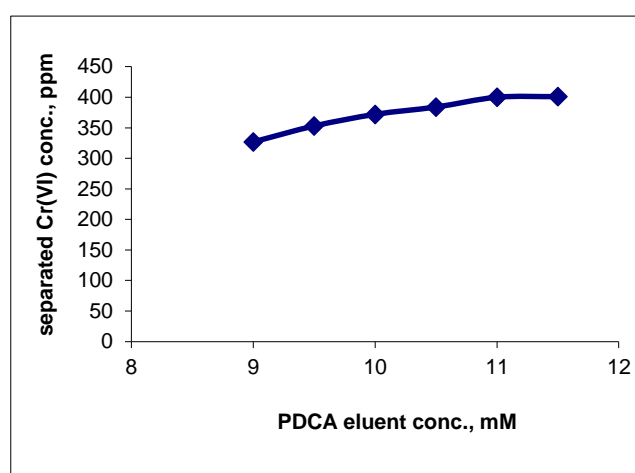


Fig (2): Influence of PDCA eluent concentration on the separation of Cr(VI)

3.1.3 Influence of eluent flow rate variation

The influence of the eluent flow rate variation on the Cr(VI) separation was performed at different PDCA eluent flow rates ranging from 0.6 to 1 mL min⁻¹. 11 mM eluent

concentration and 7.5 pH were kept constant. As shown in Figure (3), it is evident that the best flow rate for Cr(VI) separation was at 0.7 mL min⁻¹ at which the determined Cr(VI) of the certified soil sample (408 ppm) became compatible with the value (410 ppm) approved by China National Analysis Center of Iron and Steel.

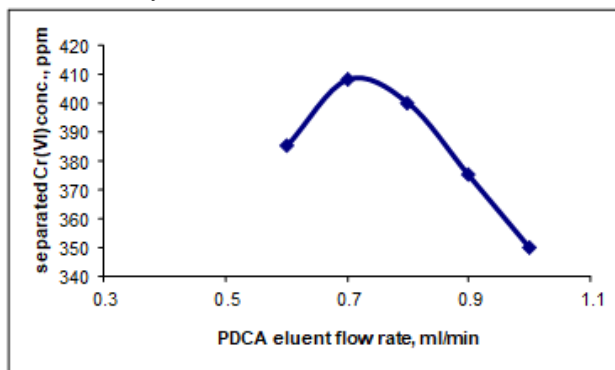


Fig (3): Influence of PDCA eluent flow rate on the separation of Cr(VI)

3.1.4 Influence of interfering ions

As observed from all the trials done in the present work, no other elements than Cr(VI) were eluted in the chromatograms this is due to the pretreatment step occurred to the study certified soil sample during the sample preparation as described in the experimental section. Although PDCA eluent has the ability to elute heavy metals [31-33] and other trace elements [34], the sample pretreatment step allowing the precipitation of such elements by sample pH adjustment to 9-9.5. So, hexavalent chromium could be eluted easily from the column with good separation and resolution without any interference.

On the basis of the above chromatographic results, the worked bifunctional ion exchanger (CS5A) afforded a reliable and accurate analysis of the validator certified soil sample. Therefore, the final run isocratic program for determination of Cr(VI) in nitric acid medium included PDCA eluent concentration of 11mM with pH of 7.5 and flow rate of 0.7 mL min⁻¹. The isocratic run program is expressed in Table (1) and the typical separation chromatogram resulted is represented in Figure (4) for the applied certified sample.

Table 1 Isocratic run program of the optimized method for Cr(VI) separation from the worked certified soil sample

Time (min.)	PDCA (11mM, 7.5 pH) (%)
0.7 mL/min. flow rate	
Initial	100
0.0	100
10	100

Table (2): RSD percentage for the worked certified soil sample

Reported value from optimization experiments (ppm)	No. of injections	Mean Value (ppm)	RSD (%)
408	5	407.8	± 0.048

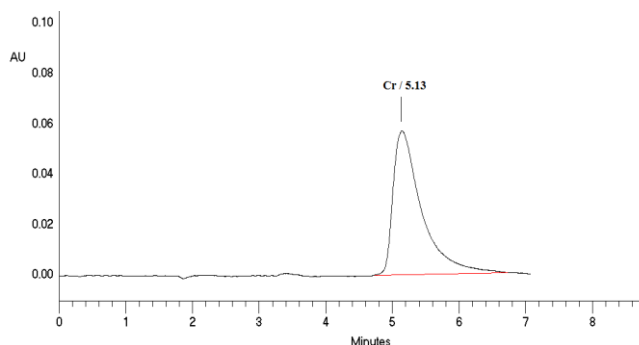


Fig (4): Typical separation chromatogram resulted from injection of the certified soil sample. Optimum conditions; IonPac CS5A separating column, 100µL injection volume, 11mM PDCA eluent of 7.5 pH with 0.7 mL/min flow rate and 365 nm wavelength for UV detection.

3.2 Calibration plot of the optimized separation procedure

After adjusting the optimum conditions for separation and determination of Cr(VI) in the certified soil sample (nitrate medium), chromatographic calibration plot of the studied ion was carried out using different concentrations of the certified soil sample assaying from 1 to 6 ppm. With respect to the calibration curve shown in Figure (5), Cr(VI) showed a good linear correlation with regression coefficient of about 0.999.

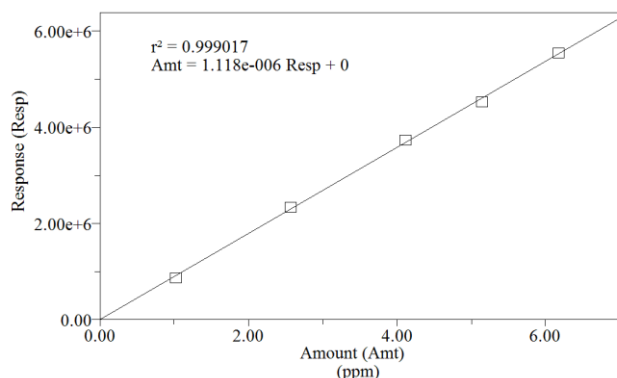


Fig (5): Calibration plot of the certified oil sample covering the range of 1 - 6 ppm

3.3 Performance of the optimized separation procedure

The advanced developed method performance was established by estimating the relative standard deviation (RSD) of Cr(VI) for the worked certified soil sample. The latter sample was injected 5 times in five independent runs after which the RSD was mathematically calculated and represented by 0.048 % (Table 2). Detection limit reported for hexavalent chromium was about 0.01 ppm for 100µL injection volume.

3.4 Application of the developed ion chromatographic procedure

Application of the currently developed ion chromatographic method on three geological rock samples has been occurred. These analyzed samples have certainly been gathered from three different localities; two of which were granite samples from of Gabal El Sela-Qash Amer area (South Eastern Desert of Egypt) and Gabal Gattar

area (North Eastern Desert of Egypt) while the third was phosphate rock sample from Abu Tartour deposits (Western Desert of Egypt). The analytical results of the study applied samples were represented in Table (3). RSD of the current method was calculated for Cr(VI) in the latter samples (Table 3) taken in consideration the number of sample injections, ion mean values and ion standard deviation values.

Table (3): Analytical results of the hexavalent chromium in both Gabal El Sela-Qash Amer and Gabal Gattar granite samples, and Abu Tartur phosphate rock sample using the currently developed IC procedure

Element	Gabal El Sela-Qash Amer Granite Sample, (ppm)	Gabal Gattar Granite Sample, (ppm)	Abu Tartur Phosphate Rock Sample, (ppm)
Cr(VI)	37.17	23.92	54.70
RSD*, (%)	± 0.027	± 0.043	± 0.032

where *: Employing 5 injections in 5 independent runs

4. Conclusion

A simple and accurate ion chromatographic procedure had been developed for separation and determination of hexavalent chromium using bifunctional ion exchanger by ion chromatography with UV detection. The results obtained under optimum eluent conditions using the certified soil sample, provided an excellent separation

behavior without prior sample preconcentration method. Finally, the developed method is actually considered promising for its adaptation in the routine quality control analysis of hexavalent chromium in geological rock samples.

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