Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2023.29927

308 (2023) 211–216
October

Flow injection spectrophotometric determination of chromium(VI) after preconcentration on potassium-benzoic acid hydrazide dithiocarbamate

Rabia Shabir[a,†], Shabnam Shahida[b,†,*], Tahseen Ghous[c], Muhammad Imran Khan[d,*], Lubna Ghani[e], Saiqa Yousaf[e], Ashfaq Ahmed Khan[e], Mumtaz Khan[f], Ajaya Bhattarai[g], Abdallah Shanableh[d]

[a]*Department of Chemistry, University of Azad Jammu & Kashmir Muzaffarabad, Pakistan, email: Rabi.shabir@gmail.com*
[b]*Department of Chemistry, University of Poonch, Rawalakot AJK, Pakistan, email: shabnamshahida01@gmail.com*
[c]*Department of Chemistry, Mirpur University of Science and Technology (MUST), Mirpur, Pakistan, email: tahseen.ghous@gmail.com*
[d]*Research Institute of Sciences and Engineering (RISE), University of Sharjah, Sharjah 27272, United Arab Emirates, emails: raoimranishaq@gmail.com (M.I. Khan), Shanableh@sharjah.ac.ae (A. Shanableh)*
[e]*Department of Chemistry, Women University of Azad Jammu & Kashmir Bagh, Pakistan, emails: lubnaghani41@gmail.com (L. Ghani), saiqa.yousaf@yahoo.com (S. Yousaf), ashfaqahmad1564@gmail.com (A.A. Khan)*
[f]*Pakistan Institute of Nuclear Science and Technology, Nilore, Pakistan, email: mumtazk36@gmail.com*
[g]*Department of Chemistry, Mahendra Morang Adarsh Multiple Campus, Tribhuvan University, Biratnagar 56613, Nepal, email: bkajaya@yahoo.com*

Received 15 April 2023; Accepted 27 August 2023

ABSTRACT

In this study a sensitive, easy to operate, robust and reproducible column preconcentration method was developed for the determination of Cr(VI) by flow injection system coupled with spectrophotometer. The proposed method is based on the retention of the analyte in a column containing potassium-benzoic acid hydrazide dithiocarbamate from buffered solution of pH 4.0 at a flow rate of 15 $mL\cdot min^{-1}$, and then its elution from the column with 7.0 $mol\cdot dm^{-3}$ nitric acid solution. The eluted Cr(VI) solution was then mixed with 0.25% solution of 1,5-diphenylcarbazide (DPC) and purple-red Cr(VI)-DPC complex was determined spectrophotometrically at 545 nm in acidic medium. The parameters studied include volume, pH, flow rate and concentration of the sample solution, different eluents and their concentration. The proposed method has a linear calibration range from 3–15 $mg\cdot L^{-1}$ of Cr(VI) with the regression $y = 0.0467C + 0.0013$, $R^2 = 0.9984$. The 3δ detection limit of Cr(VI) is 1 $\mu g\cdot L^{-1}$ with enrichment factor of 4, sampling frequency of 6 $samples\cdot h^{-1}$ and relative standard deviation of 1.82% at 10 $mg\cdot L^{-1}$. The adsorbent used has a good adsorption potential as well as appreciable recovery. The column had a constant performance during all experiments except 2%–3% loss during flow rate optimization. The developed method was effectively employed for the determination of Cr(VI) from standard reference material (CRM Cu1/3 Cu alloy).

Keywords: Cr(VI); Potassium-benzoic acid hydrazide dithiocarbamate; Column; Preconcentration; Spectrophotometry; 1,5-diphenylcarbazide

1. Introduction

The pollution caused by heavy metals is of great environmental concern. The release of metals continuously from natural and artificial sources such as industrial effluents, atmospheric emission, fossil fuels, waste stream and urban habitation into the environment makes the life more complicated as the higher concentration of these metals in

---

* Corresponding authors.
† Both the author's contributed equally to this work.

living species results in mutagenic, carcinogenic and other toxic effects [1]. Chromium is a heavy metal, that is being introduced into the ecosystem by various industries such as steel, alloys, tannery of hides, galvano plasty, treatment of wood and the dying industry [2] etc. Cr mostly exists as Cr(III) and Cr(VI) in the aquatic environment as its stable forms. Cr(III) in trace amounts is considered as a nutritionally essential trace element for carbohydrate and fat metabolism. Cr(III) is less toxic compared to Cr(VI). However, some diseases like eczematous dermatitis are caused as a result of Cr(III) exposure [3,4]. Cr(VI) poses a serious threat to human health and the environment because of its bio accumulation in living tissues, toxicity and potential carcinogenic nature [5]. The maximum acceptable concentration values for Cr are reported to be 50 $\mu g \cdot L^{-1}$ [6,7]. Short-term exposure to Cr(VI) causes skin and stomach irritation or ulceration however, long-term exposure cause dermatitis, liver damage, kidney failure, nerve tissue damage, and cancer [8,9]. Therefore, the discharge control of Cr(VI) and its removal from the aquatic environment is a matter of great importance and has drawn tremendous attention over the years. Various techniques have been studied for the efficient removal of Cr(VI) ions from solutions such as ion exchange [10], chemical precipitation [11], coagulation–flocculation [12], adsorption [13], reverse osmosis [14] and electrochemical technologies [15].

Although the development of these techniques has enabled progress in many aspects of analytical chemistry, the detection techniques available do not present sufficient sensitivity for low concentration of chromium. It is sometimes necessary to carry out preconcentration in a preliminary fashion to quantify the metal from different matrices to resolve this limitation [16–18]. The batch and manual methods suggested for preconcentration of chromium needs greater time manipulation. Therefore, the online preconcentration methods were used using flow injection analyzer that has additional advantages of high sample throughput, better repeatability, low consumption of reagent and samples, no chance of contamination during analysis, highly sensitive as well as comparatively low cost of instrumentation [19]. Several flow injection online preconcentration methods have been developed for the determination of chromium(VI) by using column packed with stationary phases like activated carbon [20], activated alumina [21], granular activated carbon [7], cellulose sorbent cellexT [22], magnetic polythiophene nanoparticle [23], Amberlite XAD-16 loaded with salicylic acid [24] and triazole derivative [25] etc.

Potassium-benzoic acid hydrazide dithiocarbamate is a derivative of dithiocarbamate (DTCs) that is completely insoluble in water at room temperature and stable in acidic/basic medium [23]. Due to its insolubility and stability it can be used in column of flow injection analyzer. In continuous to our previous work [26–32], another effort was made to develop a fast, sensitive, selective and low cost preconcentration method for Cr(VI) by using the potassium-benzoic acid hydrazide dithiocarbamate in a column of flow injection analyzer. The 1,5-diphenylcarbazide solution was used as the chromogenic reagent for the spectrophotometric determination of Cr(VI) due to its fast complex formation kinetics with Cr(IV) [30]. Various parameters affecting the online preconcentration and determination of Cr(IV) were optimized. Then the developed method was also applied on standard reference material (CRM Cu I/III) for the determination of Cr(IV).

2. Experimental setup

2.1. Chemicals and reagents

All chemicals used were of analytical reagent grade. For the preparation of standard and sample solutions distilled deionized water (DDW) and high purity reagents were used. The Cr(VI) stock solution (500 $mg \cdot L^{-1}$) was prepared by dissolving 0.05 g of dried K_2CrO_4 (E. Merck, Darmstadt, Germany, ≥99% purity) in 100 mL of DDW. The working Cr(VI) solutions were prepared in the range of 10–60 $mg \cdot L^{-1}$ immediately before use by stepwise dilution of Cr(VI) stock solution. All the dilutions were made with pH 4 buffer solution prepared by mixing an appropriate volume of equimolar (0.1 $mol \cdot L^{-1}$) solution of acetic acid (E. Merck, Darmstadt, Germany) and sodium acetate (E. Merck, Darmstadt, Germany). A 1,5-diphenylcarbazide (DPC) solution (0.25%) was prepared by first dissolving 250 mg of DPC in 10 mL of ethanol by thorough stirring and then dilution with sulfuric acid (0.2 $mol \cdot L^{-1}$) upto 100 mL. The 0.2 $mol \cdot L^{-1}$ sulphuric acid solution was prepared from 98% sulphuric acid (10.88 $mol \cdot L^{-1}$) which is used as a carrier. Different eluents were prepared for the desorption of Cr(VI) from the column. Hydrochloric acid solutions (1–7 $mol \cdot dm^{-3}$) were prepared from concentrated (37%) HCl (E. Merck, Darmstadt, Germany) by its dilution in DDW. Similarly nitric acid solutions (1–7 $mol \cdot dm^{-3}$) were prepared from concentrated (37%) nitric acid (E. Merck, Darmstadt, Germany) by dilution with DDW. 2 $mol \cdot dm^{-3}$ ammonium nitrate (16.01 g/100 mL) was also tried as an eluent (E).

2.2. Instruments and apparatus

A spectrophotometer (Model Shimadzu UV-1800 UV, Japan) equipped with flow through cell (30 μL volume and 10 mm path length) was used for absorbance measurement. A flow injection system (Ismatec Reglo, USA) consists of one peristaltic pump (Rheodyne RH 5020, Luton, Bedfordshire, UK) and six channel multifunctional valve was used. For the propulsion of sample through the column with the peristaltic pump, acid resistant tubes (Tygon) of 1.02 mm (i.e.), whereas for chromogenic reagent (CR) solution Teflon tubes were used. All the connections were made from Teflon tubing. The volume of injection loops was 100 μL. A pH meter model Hanna 211 (microprocess pH meter) was used. Magnetic stirrer and electric hot plate (Griffin & George, USA) was used for dissolution of various salts and reagents during the formation of solution. A column (5 cm length, 1.5 cm i.d.) made of glass was used. Then the column was packed with potassium-benzoic acid hydrazide dithiocarbamate (50 mg) that was soaked in DDW. Glass wool was used on both side of column to prevent the loss of adsorbent from the column.

2.3. Methodology

The complete cycle of determination of Cr(VI) after online preconcentration in the column containing potassium-benzoic acid hydrazide dithiocarbamate by flow injection-spectrophotometry using DPC as a chromogenic reagent consists of three steps, that is, preconcentration, washing and elution. During preconcentration, the Cr(VI) solution of pH 4.0 (15 mL) was passed through the column using peristaltic pump at a flow rate of 2 mL·min^{-1} for 7.5 min. In this step, Cr(VI) ions were retained in the column by forming Cr(VI)–potassium-benzoic acid hydrazide dithiocarbamate complex. In order to remove the un-adsorbed chromium from the column and that retained in the tubes, 2 min washing was done with buffer solution of pH 4.0. After washing step 7.0 mol·dm^{-3} HNO_3 was used as eluent to desorb Cr(VI) from the column. Then DPC was injected and mixed with eluent solution containing desorbed Cr(VI). DPC form the purple red colored complex with Cr(VI) while flowing through the flow through cell of spectrophotometer. Then the absorbance of complex was recorded spectrophotometrically at 545 nm. The complex was formed as a result of reduction of Cr(VI) to Cr(III) and oxidation of 1,5-diphenylcarbazide into 1,5-diphenylcarbazone as shown in Eq. (1).

$$CrO_4^{-2} + 3H_4L + 8H^+ \leftrightarrow \left[Cr\left(H_2L\right)_2\right]^+ + Cr_3^+ + H_2L + 8H_2O \quad (1)$$

where H_4L: 1,5-diphenylcarbazide and H_2L: diphenylcarbazone.

2.4. Pretreatment of certified reference material (CRM Cu1/3 Cu alloy)

For the analysis of chromium in real samples, a portion (0.04 g) of the certified reference material (CRM Cu1/3 Cu alloy from China) was weighed into a 50 mL beaker and added 0.5 mL of concentrated nitric acid into it. The beaker was covered with a watch-glass and the mixture was evaporated to near dryness on a hot plate. The solution was then cooled and diluted to 10 mL with DDW. Finally, the preconcentration procedure given above was applied to the final diluted solution. The same procedure was applied to the blank solution.

3. Results and discussion

3.1. Optimization of parameters

The FI on-line preconcentration system was optimized in order to establish the best chemical and flow conditions for the determination of hexavalent chromium with good sensitivity and precision. The parameters studied include volume, pH, flow rate and sample concentration, different eluents and eluent concentration.

3.1.1. Effect of pH

The pH value of the sample solution is important as it controls the adsorption of specific metal ions onto the adsorbent surface. In order to explore the pH effect on the preconcentration of Cr(VI) on potassium-benzoic acid hydrazide dithiocarbamate, 15 mL of 10 mg·L^{-1} of Cr(VI) solutions in the pH range of 2–6 were passed through the column for 7 min and absorbance of DPC-Cr(VI) complex was recorded at 545 nm. The obtained results are recorded in Fig. 1. The results showed that absorbance increases with increasing pH from 2–4 after that there is a sharp decrease at pH 5.0 and 6.0. Better adsorption was achieved at pH 4.0 which may be attributed to the strong binding of the metal ion upon the surface of potassium-benzoic acid hydrazide in acidic conditions [7]. So, pH 4.0 was selected for further studies.

3.1.2. Effect of sample flow rate

The sample flow rate is the variable that controls the amount of material that passes through the column. Therefore, the influence of the sample flow rate was investigated in order to allow the maximum mass transfer from the liquid to solid phase. The effect of the sample flow rate was studied from 2–10 mL·min^{-1} and the results are shown in Fig. 2. The results showed that peak absorbance was maximum at slower flow rate because dispersion increases with increase in flow rate resulting in decreased peak absorbance. At higher flow rate, back pressure also increased that caused leakage at connection points. Therefore, flow rate of 2 mL·min^{-1} was selected for sample loading in further experimental work.

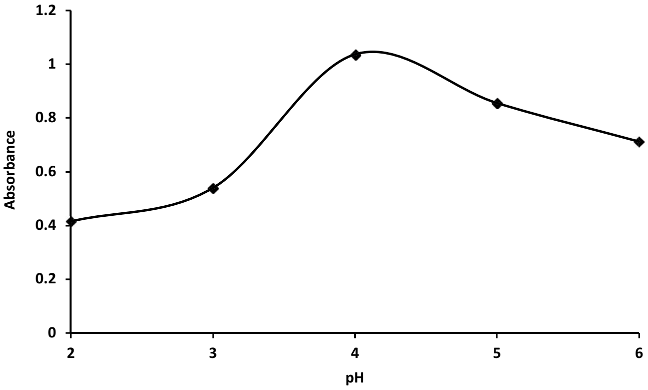

Fig. 1. Plot of sample pH vs. peak absorbance. Cr(VI) = 10 mg·L^{-1}, pH = 4.0, sample flow rate = 2 mL·min^{-1}, *E* = 7.0 mol·dm^{-3} HNO_3, CR = 0.25% DPC, preconcentration time = 7.5 min.

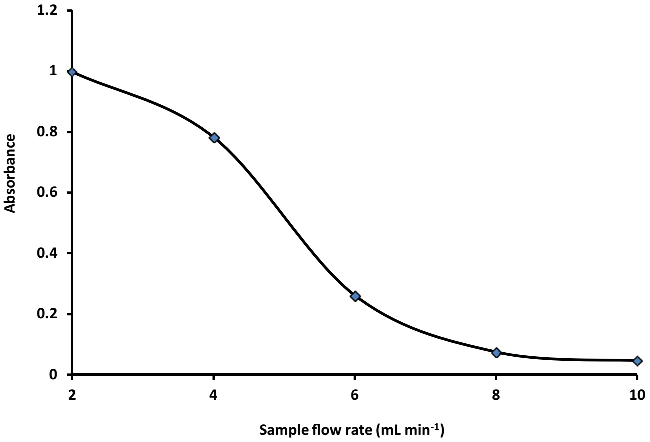

Fig. 2. Plot of sample flow rate vs. peak absorbance. Cr(VI) = 10 mg·L^{-1}, pH = 4.0, *E* = 7.0 mol·dm^{-3} HNO_3, CR = 0.25% DPC, preconcentration time = 7.5 min.

3.1.3. Effect of different eluents

During all these experiments Cr(VI) solution (10 mg·L^{-1}) was allowed to pass through the column for 7.5 min at flow rate of 2.0 mL·min^{-1}, eluted with different eluents of varying concentrations (0.5–3.0 mol·dm^{-3}) and absorbance was recorded. As is clear from Fig. 3 that peak absorbance (0.133) was observed when ammonium nitrate (2 mol·L^{-1}) was used as an eluent. A small increase in absorbance (0.162) was observed when NaOH (0.5 mol·L^{-1}) was used as an eluent. Again, small increase in absorbance was observed by using equi-molar mixture (2 mol·L^{-1}) of HNO_3 and NH_4NO_3 (1:1). Using HNO_3 (7.0 mol·L^{-1}) as an eluent a significant increase in the absorbance (0.8) was observed. Therefore, 7.0 mol·L^{-1} HNO_3 was selected for further studies.

3.1.4. Effect of selected eluent concentration

Since too low eluent concentration would elute Cr(VI) incompletely from the column while too high eluent concentration would waste the reagent so optimum eluent concentration was needed. In the study 2.0–7.0 mol·L^{-1} of HNO_3 were tried to elute the Cr(VI) that was adsorbed on a column and the results are given in Fig. 4. The results showed that absorbance increased with the increasing eluent molarity and maximum absorbance was achieved for 7.0 mol·L^{-1} HNO_3. This may be due to the reason that stronger Cr(VI)-DTC complex is formed at pH 4.0, so a highly acidic solution (7 mol·L^{-1}) was required to break this complex. Therefore, 7 mol·L^{-1} of HNO_3 was selected for further studies.

3.1.5. Effect of sample volume

The effectiveness of the preconcentration of the analyte in the column depends on the sample volume. The effect of sample volume on peak absorbance was examined by changing 10 mg·L^{-1} sample (pH 4.0) volume from 10 to 30 mL. Peak absorbance increased with increasing sample volume as shown in Fig. 5. The initial increase in absorbance is due to the fact that free adsorbent sites are available for adsorption of Cr(VI). The slow increase in absorbance for greater sample volume may be due to the partially available sites of DTC for adsorption of chromium. At 25 mL loading the curve becomes linear because the adsorbent is completely saturated and no more sites are available for the sample. Since there is no significant increase in absorbance after 15 mL sample, so 15 mL sample volume was selected for further studies.

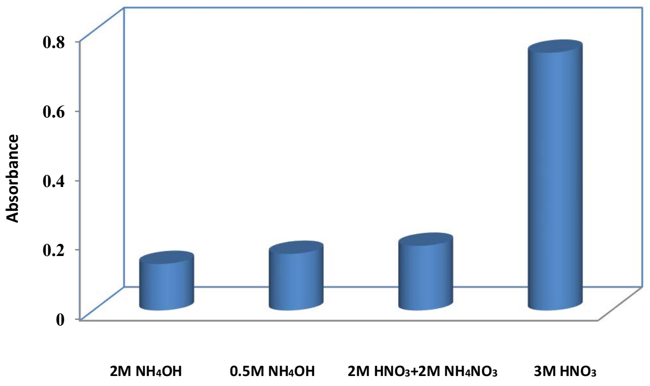

Fig. 3. Effect of different eluents on elution of Cr(VI) (10 mg·L^{-1}). pH = 4.0, sample flow rate = 2 mL·min^{-1}, E = 7.0 mol·dm^{-3} HNO_3, CR = 0.25% DPC, preconcentration time = 7.5 min.

3.2. Features of the method

Under the above optimized condition of preconcentration and elution, calibration curves were constructed with and without preconcentration. The calibration curve of Cr(VI) without preconcentration was constructed by varying the concentration of Cr(VI) from 10 and 60 mg·L^{-1} that resulted in Eq. (2).

$$A = 0.0116C + 0.0007 \qquad R^2 = 0.9958 \qquad n = 18 \tag{2}$$

where "A" is peak absorbance, "C" is concentration of Cr(VI) in mg·L^{-1}, "R" is correlation coefficient and 'n' is the number of readings including triplicate.

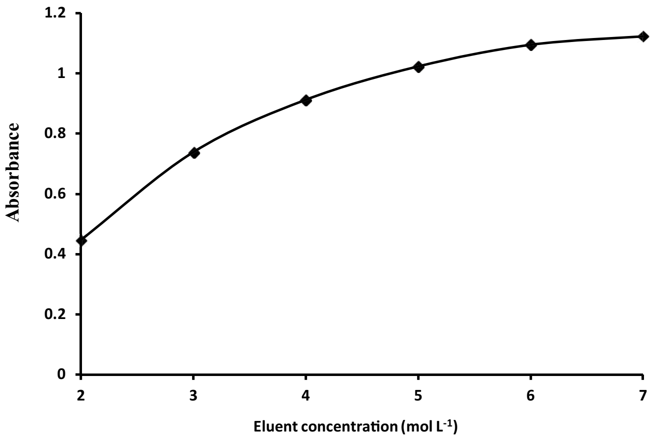

Fig. 4. Effect of concentration of eluent on peak absorbance. Cr(VI) = 10 mg·L^{-1}, pH = 4.0, sample flow rate = 2 mL·min^{-1}, E = 7.0 mol·dm^{-3} HNO_3, CR = 0.25% DPC, preconcentration time = 7.5 min.

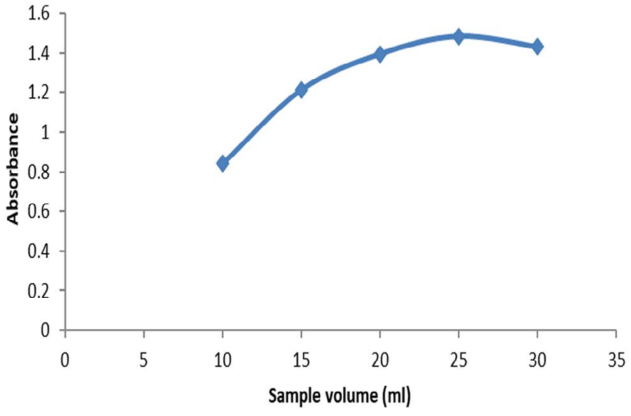

Fig. 5. Plot of sample volume vs. peak absorbance. Cr(VI) = 10 mg·L^{-1}, pH = 4.0, sample flow rate = 2 mL·min^{-1}, E = 7.0 mol·dm^{-3} HNO_3, CR = 0.25% DPC, preconcentration time = 7.5 min.

For 7.5 min preconcentration time, 15 mL sample was used. Under this condition, the system showed linearity for concentration of Cr(VI) between 3–15 mg·L^{-1} and resulted in Eq. (2).

$$A = 0.0467C + 0.0013 \qquad R^2 = 0.9984 \qquad n = 15 \tag{3}$$

The enrichment factor was calculated by using the following formula:

Enrichment factor (EF) = slope of the calibration curve with preconcentration/slope of the calibration curve without preconcentration [33].

The enrichment factor was calculated by using the above relation and was found to be 4 indicates that the adsorbent has a good adsorption potential for Cr(VI).

At optimized flow injection system, the performance of flow injection spectrophotometer for the preconcentration of Cr(VI) is shown in Table 1. For 7.5 min preconcentration time 15 mL sample volume was used. The detection limit corresponding to 3ð of the blank was found to be 1 µg·L^{-1}. The relative standard deviation was calculated by taking ten measurements of 10 mg·L^{-1} solution of Cr(VI) and was found to be 1.82%. The sample throughput achieved under the optimized experimental condition was 6 samples·h^{-1}.

To evaluate the potassium-benzoic acid hydrazide dithiocarbamate loaded column stability, several loading and elution column operations were carried out. The sorption capacity of the column was reproducible after many preconcentration-elution cycles except 2%–3% loss during flow rate optimization. This showed an excellent stability of column. The reason may be the insolubility of the potassium-benzoic acid hydrazide dithiocarbamate in aqueous solutions [34].

3.3. Application of the method to real sample

The accuracy of the developed method was examined by the determination of total chromium in certified copper sample (CRM Cu I/III alloy from China) and the results are given in Table 2. The results showed that the determined value is in good agreement with the reported value.

Table 1
Performance of flow injection spectrophotometric system for online preconcentration and determination of Cr(VI)

Performance parameters	Determined value
Detection limit (µg·L^{-1})	1
Precision (n = 10, % RSD)	1.82
Enrichment factor	4.0
Sample throughput (f, h^{-1})	6
Sample consumption (mL)	15
Calibration equation (n = 18)	$A = 0.0467C + 0.0013$ $R^2 = 0.994$

Table 2
Determination of Cr from standard reference materials (CRM Cu I/III)

Elements	Concentration (w/w) %	
	Certified value	Determined value
Cr	2.20×10^{-2}	$(2.12 \pm 0.01) \times 10^{-2}$

3.4. Possible mechanism of reaction

In order to determine the binding of Cr(VI) with DTCs IR studies of DTCs have been taken before and after preconcentration From the results the following two types of mechanisms have been proposed.

Mechanism 1:

The most possible mechanism is shown in Fig. 6.

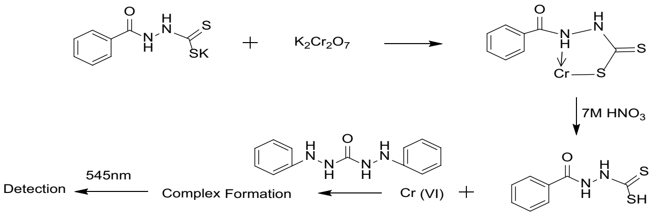

Fig. 6. Possible mechanism of the reaction.

Mechanism 2:

Another possible mechanism is shown in Fig. 7.

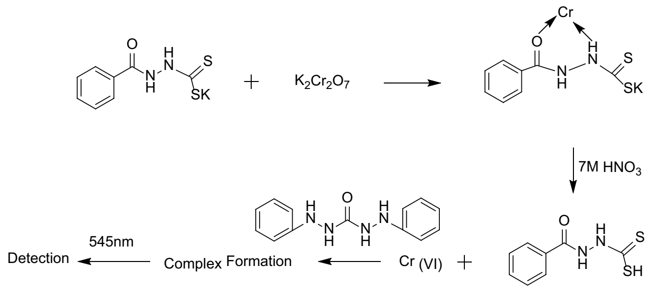

Fig. 7. Possible mechanism of the reaction.

4. Conclusions

This paper is the first report on the use of potassium-benzoic acid hydrazide dithiocarbamate filled column for the preconcentration of Cr(VI) in continuous flow system. High accuracy, high precision (1.82%) and low-detection limit (1 µg·L^{-1}) and fully automated analysis were some of the advantages of the proposed method. The proposed method was applicable to the determination of Cr(VI) in samples having complex matrix like CRM Cu I/II alloy. This showed that developed method can be applied on real samples with good accuracy.

Declaration of competing interest

There are no conflicts of interest to declare.

Acknowledgements

The authors are highly thankful to Higher Education Commission (HEC), Islamabad, Pakistan, for financial support.

References

[1] K.H. Shah, S. Ali, M. Waseem, F. Shah, M. Fahad, S. Shahida, A.M. Khan, A.R. Khan, Native and magnetic oxide nanoparticles (Fe_3O_4) impregnated bentonite clays as economic adsorbents for Cr(III) removal, J. Solution Chem., 48 (2019) 1640–1656.

[2] E.A. de Oliveira Farias, M.C. dos Santos, N. de Araujo Dionísio, P.V. Quelemes, J.R. de Souza Almeida Leite, P. Eaton, D.A. da Silva, C. Eiras, Layer-by-layer films based on biopolymers extracted from red seaweeds and polyaniline for applications in electrochemical sensors of chromium(VI), Mater. Sci. Eng., B, 200 (2015) 9–21.

[3] S. Pooja, P.S. Surendra, K.P. Sheetal, W.T. Yen, Health hazards of hexavalent chromium (Cr(VI)) and its microbial reduction, Bioengineered, 13 (2022) 4923–4938.

[4] N.I. Sex, Sax's Dangerous Properties of Industrial Materials, Van Nostrand Reinhold Co., New York, 1984.

[5] W. Jin, K. Yan, Recent advances in electrochemical detection of toxic Cr(VI), RSC Adv., 5 (2015) 37440–37450.

[6] M.-N. Georgaki, M. Charalambous, Toxic chromium in water and the effects on the human body: a systematic review, J. Water Health, 21 (2023) 205–223.

[7] D. Satapathy, G.S. Natarajan, S.J. Patil, Adsorption characteristics of chromium(VI) on granular activated carbon, J. Chin. Chem. Soc., 52 (2005) 35–44.

[8] A.E. Martell, Chemistry of carcinogenic metals, Environ. Health Perspect., 40 (1981) 207–226.

[9] R. Wani, K.M. Kodam, K.R. Gawai, P.K. Dhakephalkar, Chromate reduction by *Burkholderia cepacia* MCMB-821, isolated from the pristine habitat of alkaline crater lake, Appl. Microbiol. Biotechnol., 75 (2007) 627–632.

[10] P. Meshram, A. Ghosh, Y. Ramamurthy, B.D.P. Abhilash, M.L. Torem, Removal of hexavalent chromium from mine effluents by ion exchange resins-comparative study of Amberlite IRA 400 and IRA 900, Russ. J. Non-Ferrous Met., 59 (2018) 533–542.

[11] H. Peng, J. Guo, Removal of chromium from wastewater by membrane filtration, chemical precipitation, ion exchange, adsorption electrocoagulation, electrochemical reduction, electrodialysis, electrodeionization, photocatalysis and nanotechnology: a review, Environ. Chem. Lett., 18 (2020) 2055–2068.

[12] G. Qin, M.J. McGuire, N.K. Blute, C. Seidel, L. Fong, Hexavalent chromium removal by reduction with ferrous sulfate, coagulation, and filtration: a pilot-scale study, Environ. Sci. Technol., 39 (2005) 6321–6327.

[13] V.E. Pakade, N.T. Tavengwa, L.M. Madikizela, Recent advances in hexavalent chromium removal from aqueous solutions by adsorptive methods, RSC Adv., 9 (2019) 26142–26164.

[14] A. Çimen, Removal of chromium from wastewater by reverse osmosis, Russ. J. Phys. Chem., A, 89 (2015) 1238–1243.

[15] Md. Nur-E-Alam, Md. Abu Sayid Mia, F. Ahmad, Md. Mafizur Rahman, An overview of chromium removal techniques from tannery effluent, Appl. Water Sci., 10 (2020) 205–210.

[16] N.F. Fahim, B.N. Barsoum, A.E. Eid, M.S. Khalil, Removal of chromium(III) from tannery wastewater using activated carbon from sugar industrial waste, J. Hazard. Mater., 136 (2006) 303–309.

[17] A. Sarı, M. Tuzen, M. Soylak, Adsorption of Pb(II) and Cr(III) from aqueous solution on Celtek clay, J. Hazard. Mater., 144 (2007) 41–46.

[18] G. Tiravanti, D. Petruzzelli, R. Passino, Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery, Water Sci. Technol., 36 (1997) 197–207.

[19] L.H. Marcolino-Júnior, M.F. Bergamini, M.F.S. Teixeira, É.T.G. Cavalheiro, O. Fatibello-Filho, Flow injection amperometric determination of dipyrone in pharmaceutical formulations using a carbon paste electrode, Il Farmaco, 58 (2003) 999–1004.

[20] T. Prasada Rao, S. Karthikeyan, B. Vijayalekshmy, C.S.P. Iyer, Speciative determination of chromium(VI) and chromium(III) using flow-injection on-line preconcentration and flame atomic-absorption spectrometric detection, Anal. Chim. Acta, 369 (1998) 69–77.

[21] M. Sperling, S. Xu, B. Welz, Determination of chromium(III) and chromium(VI) in water using flow injection on-line preconcentration with selective adsorption on activated alumina and flame atomic absorption spectrometric detection, Anal. Chem., 64 (1992) 3101–3108.

[22] A.M. Naghmush, K. Pyrzyńska, M. Trojanowicz, Determination of chromium in different oxidation states by selective on-line preconcentration on cellulose sorbents and flow-injection flame atomic absorption spectrometry, Anal. Chim. Acta, 288 (1994) 247–257.

[23] N.E. Sodan, S.G. Elci, A.A. Kartal, A. Hol, L. Elci, Speciation and preconcentration of chromium in real samples by magnetic polythiophene nanoparticle solid-phase extraction (SPE) coupled with microsampling injection – flame atomic absorption spectrometry (FAAS), Instrum. Sci. Technol., 49 (2021) 585–603.

[24] S. Tiwari, N. Sharma, R. Saxena, Online preconcentration procedure for chromium speciation and determination in industrial water samples using flame atomic absorption spectrometry, Anal. Sci., 32 (2016) 1321–1325.

[25] Z. Bahadır, V.N. Bulut, D. Ozdes, C. Duran, H. Bektas, M. Soylak, Separation and preconcentration of lead, chromium and copper by using with the combination coprecipitation-flame atomic absorption spectrometric determination, J. Ind. Eng. Chem., 20 (2014) 1030–1034.

[26] S. Shahida, A. Ali, M.H. Khan, M.M. Saeed, Flow injection on-line determination of uranium after preconcentration on XAD-4 resin impregnated with dibenzoylmethane, J. Radioanal. Nucl. Chem., 289 (2011) 929–938.

[27] A. Ali, S. Shahida, M.H. Khan, M.M. Saeed, Online thorium determination after preconcentration in a minicolumn having XAD-4 resin impregnated with *N*-benzoylphenylhydroxylamine by FI-spectrophotometry, J. Radioanal. Nucl. Chem., 288 (2011) 735–743.

[28] S. Shahida, A. Ali, M.H. Khan, M.M. Saeed, Flow injection on-line spectrophotometric determination of uranium after preconcentration on XAD-4 resin impregnated with nalidixic acid, Environ. Monit. Assess., 185 (2013) 1613–1626.

[29] S. Shahida, A. Ali, M.H. Khan, On-line spectrophotometric determination of scandium after preconcentration on XAD-4 resin impregnated with nalidixic acid, J. Iran. Chem. Soc., 10 (2013) 461–470.

[30] S. Shahida, A. Ali, M.H. Khan, Flow injection on-line spectrophotometric determination of thorium(IV) after preconcentration on XAD-4 resin impregnated with oxytetracycline, J. Iran. Chem. Soc., 11 (2014) 1–8.

[31] S. Shahida, A. Ali, Determination of europium(III) in environmental samples using a flow injection analysis system with on-line preconcentration and spectrophotometric detection, J. Radioanal. Nucl. Chem., 300 (2014) 423–429.

[32] S. Shahida, M.I. Khan, S. Zafar, K.H. Shahd, U. Farooq, M. Hafeez, N. Elboughdiri, A. Shanableh, A. Abdelfattah, XAD-4 resin impregnated with oxytetracycline for the online preconcentration of zirconium(IV) from environmental and geological samples, Inorg. Nano-Metal Chem., (2022), doi: 10.1080/24701556.2023.2165678 (in Press).

[33] M. Hafeez, S.A. Abbasi, M. Rafique, R. Hayder, M. Sajid, J. Iqbal, N. Ahmad, S. Shahida, Calibration-free laser-induced breakdown spectroscopic analysis of copper-rich mineral collected from the Gilgit-Baltistan region of Pakistan, Appl. Opt., 59 (2020) 68–76.

[34] K. Mumtaz, S. Iqbal, S. Shahida, M.A. Shafique, M. Wasim, B. Ahmad, Synthesis and performance evaluation of diphenylcarbazide functionalized mesoporous silica for selective removal of Cr(VI), Microporous Mesoporous Mater., 326 (2021) 111361, doi: 10.1016/j.micromeso.2021.111361.