Down-scaling sample preparation using polyurethane foam and colorimetric technique for the chromium assay in accessories

Chonnipa Yeerum,* Piyanat Issarangkura Na Ayutthaya,* Kullapon Kesonkan,* Apidech Chaiyakhan* and Monnapat Vongboot*†

*Department of Chemistry, Faculty of Sciences, King Mongkut's University of Technology Thonburi, Bangkok, 10140, Thailand

†To whom correspondence should be addressed.

E-mail: sumalee.tan@kmutt.ac.th
Abstract

A simple alternative colorimetric assay of chromium in accessories is proposed. A miniature part of a sample was dissolved by acid digestion. With dithiooxamide (DTO) complexes, metal interferences retain in polyurethane foam synthesized in the lab while chromium ions present in the eluate. A 100 µL of the eluate was measured for the absorbance using a handy spectrometer. The proposed method was successful for chromium assay and the results obtained agreed with the reference (FAAS) method. The amounts of chromium in accessories were found in the range of 100 to 390 mg g⁻¹.

Keywords: Down-scaling, Chromium, Accessory, Polyurethane foam, Dithiooxamide, Colorimetry.
Introduction

Nowadays, most cheap accessories will be added by chromium to increase some properties such as luster, strength and rust resistance\textsuperscript{1,2}. Nonetheless, the patching or piercing these ornaments to skin in a long-time can lead to derma diseases. For this reason, National Institute for Occupational Safety and Health (NIOSH) suggests the maximum concentration of chromium (III) and chromium (VI) for patching within 8 hours per day should be up to 5 ppm and 2 ppb, respectively\textsuperscript{3}.

Some conventional instruments for the determination of chromium are such as inductively coupled plasma mass spectrometer (ICP-MS)\textsuperscript{4,5} and UV-Visible spectrometer\textsuperscript{6-8}. Although, the results obtained of these methods are highly precise, unfortunately, some drawbacks are inevitable like an expensive cost for maintenance, immense apparatus, and profuse reagents.

Recently, the down-scaling method as the micro-scale operation has been introduced for minimizing in several dimensions, there are sample size, the volume of reagents, sample volume and powered energy of detector accordingly, and this method is miniature part of the samples and can be inexpensive, reducing of wastes and clean. Additionally, this method can properly approach to green analytical chemistry\textsuperscript{9,10} owing to an environmentally friendly method.

Interestingly, using polyurethane foam (PUF) as a mini-column was performed in our prior work for the determination of nickel in the pierced ring by FIA-UV/visible spectrophotometer \textsuperscript{11}. Although the results obtained were fulfilling expectations, there were some disadvantages, namely, milliliter level of reagent-consuming, profuse wastes, high cost and non-on-site.

This work aims to optimize the down-scaling method for simple, green and fast assay of chromium in accessories based on employing PUF as a mini-column to eliminate the metal ion
interferences. Dithiooxamide was applied as a chelating agent in which it can chelate with various metal ions such as Ni(II), Pd(II), Cu(II), Fe(III), Cr(III) and so on. Besides, in the mixture solution at pH 1, the formation of [Cr(DTO)$_n$] complexes will not achieve\textsuperscript{12,13}. The interferences complexes would sorb on the PUF surface to be removed. The blue-colored eluate containing merely chromium was collected and further measured by PiCOEXPLORER via the red channel. Furthermore, the method validation has been investigated by flame atomic absorption spectrometer (FAAS).

**Experimental**

**Reagents**

All reagents used in this work are of analytical grade. Deionized water was used throughout the work. A 0.05 g of dithiooxamide (Sigma Aldrich, USA) in 20 mL of 1 mol L$^{-1}$ NaOH, and finally diluted to 100 mL with water. The concentration of Cr(III) working solutions were prepared by dilution of 1 g L$^{-1}$ Cr(III) solution (Chromium(III) nitrate, Honeywell Fluka, German) with a 1 mmol L$^{-1}$ of nitric acid.

**Apparatus**

A handy spectrometer (PiCOEXPLORER, Ushio, Japan) was used for the measurement of the RGB values combining with PAS-110 application on a smartphone and/or a tablet for the Cr(III) color processing. The synthesized PUF was packed in a polyethylene small syringe. The method validations were performed by using FAAS (PerkinElmer, USA) with Cr wavelength at 357 nm.
**PUF syringe**

Following the preparation procedure of PUF from our previous work\textsuperscript{11,14}, briefly, methylene diphenyl diisocyanate (MDI; IRPC, Thailand) and polyol (polyether; IRPC, Thailand) were mixed in a ratio of 1:2 at room temperature. After the polymerization process was taking place for approximately 5 minutes, then, PUF obtained was directly blended and sieved through 180-600 µm meshes before being packed in a polyethylene small syringe (0.5 cm i.d. × 7 cm length).

**Sample preparation**

Cheap accessory samples (S1-S3) were weighted in the closest to 400 mg and digested in a mixture of 2 mL concentrated nitric acid and 2 mL concentrated hydrochloric acid by heating at least 30 minutes. In the treated solution, chromium will present and be literally stable in the form of Cr(III) as the half-cell reduction of Cr(III)/Cr(0) is -0.71 V, Cr(III) cannot be oxidized to Cr(VI) as the half-cell reduction in acid condition of Cr(VI)/Cr(III) is 1.33 V. Finally, the treated samples were made up to 5 mL with deionized water.

The proposed method was performed by the utilization of a PUF syringe to get rid of the interference-DTO complexes. Firstly, 200 µL of each sample solution was mixed with the DTO and adjusted to pH 1. After that, the mixture solutions were passed into the PUF syringe. 100 µL of the eluate was collected and measured the absorbance using a handy spectrometer connecting with smartphone processing, as shown in Fig. 1. The FAAS method: The 50 µL of each digested sample was treated with 2 mol L\(^{-1}\) nitric acid in 100 mL volumetric flasks for FAAS.
Results and Discussion

Metal-DTO complexes

A mixture solution at pH 1 consisting of 0.5 g L\(^{-1}\) each of metal ion and 1.0 g L\(^{-1}\) DTO solution was checked complexes formation. The results have summarized in Table 1 and Fig. S1-S4.

Color channel of Cr(III)

The optimum color RGB channel (Red, Green and Blue) for Cr(III) measurement has been investigated. The absorbance of Cr(III) in a range concentration from 0.2 to 1.0 g L\(^{-1}\) was measured by a handy spectrometer. As displayed in Fig. 2, it indicates that the red channel is the most proper channel for the measurement of Cr(III) absorbance due to the highest R\(^2\) and slope from the linear equation. For this reason, the red channel would be chosen for further experiments.

Volume fraction from PUF syringe

The mixture solution at pH 1 containing Cr(III), [Cu(DTO)]
\(^m\), [Ni(DTO)]
\(^n\) and [Fe(DTO)]
\(^n\) was percolated into PUF syringe. Ten fractions were collected at 0.50 mL of each fraction. After the 4\(^{th}\) fraction (≥2.0 mL), the metal-DTO complexes were completely removal owing to the absorbance observed remained constant as shown in Fig. 3. It would be clarified that at the initial state, the PUF surface is probably a non-positive charge, for this reason, the removal of the interference metal-DTO complexes was not effective. It could be decided that after the 4\(^{th}\) fraction would be appropriate for further work.
Removal check of interferences

The Cr(III) solution of accessory samples possibly gave blue color containing the metal ion interferences such as Cu(II), Fe(III) and Ni(II), thus the elimination step should be necessary. On the metal-DTO complexes study, at pH 1, only Cr (III) does not form a complex with DTO, but other metals formed. However, the confirmation of no sorption of Cr(III) on the PUF surface was carried out. As shown in Fig. 4a, the absorbance of the Cr(III) solution before (red line) and after (black line) percolating into PUF small syringe was no significantly different. Apparently, the interaction between Cr(III) and the PUF surface does not occur.

Similarly, the performance of sorption of the metal-DTO complexes on PUF surface was also operated as the complexes of Cu(II), Ni(II) and Fe(III) with DTO in the ratio of 1:2 were proposed as \([\text{Cu(DTO)}_x]^n\), \([\text{Ni(DTO)}_x]^n\) and \([\text{Fe(DTO)}_x]^n\), respectively. From Fig. 4b, it presents the analytical results obtained of three series: the Cr(III) standard solutions (black line), the Cr(III) standard solutions with 0.5 g L\(^{-1}\) DTO (green line) and the Cr(III), Fe(III), Cu(II) and Ni(II) standard solutions with 0.5 g L\(^{-1}\) DTO (blue line) were passed into PUF syringe and measured the absorbance of each series. No significant difference in the absorbance from each series was observed. This result authentically indicates that the interferences were completely removed.

Analytical features

Under the optimum condition of the proposed method, the calibration graph was obtained: absorbance = 0.055[Cr(III), g L\(^{-1}\)] - 0.0022 (R\(^2\)=0.9928) with the 0.07 g L\(^{-1}\) of the limit of detection. The relative standard deviation was less than 3.0%, and the analytical results were found that the average percent recovery (S1-S3) is 89.9 ± 3.4 %.
Analysis samples

Following the procedure for sample preparation, the proposed and the reference (FAAS) methods for the analysis of chromium in accessories were subjected to statistical treatment (student’s t and F tests) at 95% confidence with no significant difference, which indicates the precision and accuracy of the proposed assay. An amount of chromium in three samples was reported as shown in Table 2.

Conclusions

The proposed colorimetric down-scaling method provided the high performance for chromium assay in different accessory samples and good agreement with the reference method. The preparation of samples in microliter levels was successfully allowed owing to the robustness of the PUF small syringe coupling with the specific chelating agent for the elimination of the metal ion interferences. For this reason, several dimensions of the advantage can be done, namely, the alternative method, microscale detection, less reagents consuming, reduced wastes, simple, fast, green and inexpensive cost. Moreover, its uncomplicated application for operation and being portable, it could be suitable to offer for the on-site assay especially in the remote areas.

Acknowledgements

The authors are thankful to Department of Chemistry, Faculty of Science, King Mongkut's University of Technology Thonburi. This work was supported by Petchra Pra Jom Klao Ph.D. Research Scholarship from King Mongkut’s University of Technology Thonburi and Achievement Scholarship of Thailand (SAST), Thai Unique Co., Ltd. and USHIO for
PiCOEXPLORER support.

**Supporting Information**

Preliminary study of metal-DTO complexes. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

**References**

1. L. E. Finch, M. M. Hillyer, and M. C. Leopold, *J. Chem. Educ.*, 2015, 92, 849.

2. S. Liu, H.-Z. Cui, Y.-L. Li, A.-L. Yang, J.-F. Zhang, R. Zhong, Q. Zhou, M. Lin, and X.-F. Hou, *Microchem. J.*, 2017, 131, 130.

3. Centers for Disease Control and Prevention, “*Niosh Pocket Guide to Chemical Hazards*”, 2007, third ed., U.S. Government Printing Office Internet, United States, 347.

4. M. Jabłońska-Czapła, S. Szopa, K. Grygojć, A. Łyko, and R. Michalski, *Talanta*, 2014, 120, 475.

5. M. K. Donais, R. Henry, and T. Rettberg, *Talanta*, 1999, 49, 1045.

6. A. R. Borges, L. L. François, E. M. Becker, M. G. R. Vale, and B. Welz, *Microchem. J.*, 2015, 119, 169.

7. M. S. El-Shahawi, S. S. M. Hassan, A. M. Othman, M. A. Zyada, and M. A. El-Sonbati, *Anal. Chim. Acta.*, 2005, 534, 319.

8. D. G. Themelis, F. S. Kika, and A. Economou, *Talanta*, 2006, 69, 615.

9. W. R. Melchert, B. F. Reis, and F. R. P. Rocha, *Anal. Chim. Acta.*, 2012, 714, 8.

10. A. Gałuszka, Z. Migaszewski, and J. Namieśnik, *Trends Anal. Chem.*, 2013, 50, 78.

11. M. Vongboot, and M. Suesoonthon, *Talanta*, 2015, 131, 325–329.

12. M. Ghaedi, F. Ahmadi, and M. Soylak, *J. Hazard Mater.*, 2007, 147, 226.

13. B. R. J. Muhyedeen, and A. A-A. Drea, *J. Multi. Funct. Mater. Photosci.*, 2014, 5(1), 1.

14. C. Yeerum, W. Wongwilai, K. Grudpan, and M. Vongboot, *Talanta*, 2018, 190, 85.
Table 1 Preliminary check of metal-DTO complexes.

| Metal ions | Complexes          | pH of complexes | The changing of solutions |
|------------|--------------------|-----------------|---------------------------|
| Cr(III)    | [Cr(DTO)ₙ]ⁿ⁺       | 1               | No changing               |
| Cu(II)     | [Cu(DTO)ₙ]ⁿ⁺       | 1               | Brown precipitate         |
| Ni(II)     | [Ni(DTO)ₙ]ⁿ⁺       | 1               | Clear purple solution     |
| Fe(III)    | [Fe(DTO)ₙ]ⁿ⁺       | 1               | Turbid yellow solution    |

Table 2 Amount of chromium in accessory samples.

| Samples | Amount of chromium, mg g⁻¹, mean (n = 3, ±SD) |
|---------|-----------------------------------------------|
|         | Proposed method | FAAS            |
| S1      | 390 ± 12        | 379 ± 0         |
| S2      | 100 ± 4         | 99 ± 0          |
| S3      | 199 ± 3         | 200 ± 1         |
Figure Captions

Fig. 1 Illustration of a PUF small syringe for metal removal and a handy spectrometer with a smartphone display.

Fig. 2 Absorbance of Cr(III) based on the RGB channel.

Fig. 3 A 0.50 mL of each fraction of the mixture solution (Cr(III) and interference metal-DTO complexes) after passing PUF small syringe.

Fig. 4 (a) Interaction check of Cr(III) with PUF and (b) Removal check of metal interferences by PUF small syringe.
Fig. 1 Illustration of a PUF small syringe for metal removal and a handy spectrometer with a smartphone display.
Fig. 2 Absorbance of Cr(III) based on the RGB channel.

The absorbance data for Cr(III) in the RGB channels is shown in the graph. The equations for each channel are as follows:

- **Red channel**: $y = 0.055x - 0.0022$, $R^2 = 0.9928$
- **Green channel**: $y = 0.0495x - 0.0023$, $R^2 = 0.9829$
- **Blue channel**: $y = 0.033x - 0.0038$, $R^2 = 0.9855$
Fig. 3 A 0.50 mL of each fraction of the mixture solution (Cr(III) and interference metal-DTO complexes) after passing PUF small syringe.
Fig. 4 (a) Interaction check of Cr(III) with PUF and (b) Removal check of metal interferences by PUF small syringe.
Polyurethane foam was packed in a small syringe for the removal of metal interferences via dithiooxamide (DTO) complexes. A handy spectrometer (PiCOEXPLORER) connecting with a smartphone was used for absorbance measurement and display.