EXTRACTION AND SPECIATION OF CHROMIUM(VI) AND CHROMIUM(III) AS ION-ASSOCIATION COMPLEXES OF TETRAMETHYLAMMONIUM-CHROMATE

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ABSTRACT

A specific, selective and simple method for speciation of chromium(VI) and chromium(III) has been developed. This method is based on the quantitative extraction of chromium(VI) and chromium(III) as an ion association of tetramethylammonium-chromate in methyl isobutyl ketone (MIBK), followed by back extraction and preconcentration with an acidic diphenylcarbazide (DPC) solution. Back extraction was applied to achieve further preconcentration by a final factor of 20. The chromium(VI)-DPC complex was determined by a UV-Visible spectrophotometer. The optimum conditions of this method are as follows, optimum wavelength at 545 nm, MIBK as organic solvent, 7.5 mL of nitric acid (65%) for each 100 mL sample, mole ratio of TMAC to Cr(VI) of 2x104:1, 5 min shaking time, mole ratio of DPC to chromium(VI) of 8:1, and immediate UV-Vis measurement after obtaining of back-extract. The calibration curve was linear in the concentration range 0.00-0.40 μg.mL^{-1} of chromium(VI) with a regression equation of Abs=0.0038+1.7427x, in which x was the chromium species concentration (μg.mL^{-1}). The correlation coefficient (r) for the curve was 0.9991 and the detection limit was found to be 0.946 ng.mL^{-1}. The result of analysis and speciation of chromium in water samples from a river near a leather processing plant in Yogyakarta area showed that the total content of chromium was in the range of 0.04 - 0.05 μg.mL^{-1} consisting of 0.03 - 0.04 μg.mL^{-1} of chromium(VI) and 0.002 - 0.01 μg.mL^{-1} of chromium(III). This result indicates that the concentration of chromium in the river is still below the safety limit.

Keywords: *extraction, speciation, chromium, preconcentration, ion-association, tetramethylammonium.*

INTRODUCTION

The presence of heavy metals in the environment is one of the major concerns because of their toxicity to many life forms. According to the World Health Organization (WHO), the metals that need special concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury, and lead [1].

Chromium and its compounds are widely use in industry as plating or alloying agents, pigments, preservatives or tanning agents [2,3]. Chromium(VI) compounds have higher toxicity than chromium(III) because of its solubility in water which readily cross cell membranes and have deleterious effect to certain organs such as lung, liver, and kidney [4]. In contrast, chromium(III) is found to be essential for human, where it is involved in glucose, lipid, and protein metabolism [4,5]. Determination of the total chromium content in water does not provide sufficient information about chromium pollution to the environment and living organism. For lower levels of chromium concentration, detection, speciation, and analysis of chromium require a sensitive method; therefore the sensitivity of chromium identification and speciation methods need a continuous development. An alternative in improving this method is prior treatment to the sample through chromium preconcentration process such as solvent extraction [3, 6-8]

Several extraction and preconcentration methods have been reported for the determination and speciation of low levels of chromium. Among these was extraction-spectrophotometric of chromium as tetrabutylammonium-chromate into methyl isobutyl ketone (MIBK), and its preconcentration by back-extraction using an acidic diphenylcarbazid (DPC) solution [8].

The present paper shows the procedure for the extraction and speciation of chromium(VI) and chromium(III) as ion-association complex of tetramethylammonium-chromate into organic solvent, and pre-concentration of this ion association by back-extraction into an acidic diphenylcarbazide (DPC) solution which is then determined by a UV-Visible spectrophotometer. The chromium(III) concentration can be measured indirectly by first oxidizing chromium(III) to chromium(VI) using cerium(IV) solution [8,9] and then determine its content using the mentioned procedure.

EXPERIMENTAL SECTION

Reagents

All reagents were of analytical grade and the solutions were prepared using deionized water. A stock

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solution of 0.1 g.L^{-1} chromium(VI) was prepared by dissolving 0.3735 g of potassium chromate (Merck) in 1 L of water. A chromium(III) solution was prepared by dissolving 0.5125 g of $CrCl_3(H_2O)_6$ (Merck) in 1 L of water to obtain 0.1 g.L^{-1} chromium(III) solution. A 100 mL portion of TMAC 0.1 M was prepared by dissolving 1.096 g of tetramethylammonium chloride (Merck) in 100 mL of water. A 50 mL portion of 9.5x10^{-4} M DPC was prepared daily by dissolving 0.0115 g of diphenylcarbazide (Merck) in 15 mL of ethanol (Meck), added with 10 mL of 2.5 M HNO_3 solution, and diluting to 50 mL with water. A solution of 0.4% m/V Ce^{IV} was prepared by dissolving 0.4 g $Ce(SO_4)_2$ in 0.5 M HNO_3. HNO_3 solutions were made from concentrate HNO_3 (Merck), and methyl isobutyl ketone (MIBK, Merck) was used.

Apparatus

A Perkin Elmer Lambda-20 UV-Vis spectrophotometer with a 1.0 cm optical path quartz cell was used for all spectrophotometric measurements.

Procedures

A 100 mL standard solution of chromium(VI) and chromium(III) were pipetted into separatory funnels and added with 5 mL of HNO_3 (65%) and 10 mL of TMAC solution and shaken for 5 min; then, 10 mL of MIBK was added and continued shaken for 5 min. The organic phase was separated and transferred into a new separatory funnels and 5 mL of an acidic DPC solution was added and shaken for another 5 min. The ion-pair compound was back-extracted from MIBK into an acidic DPC solution, which was used for a spectrophotometric measurement of chromium(VI).

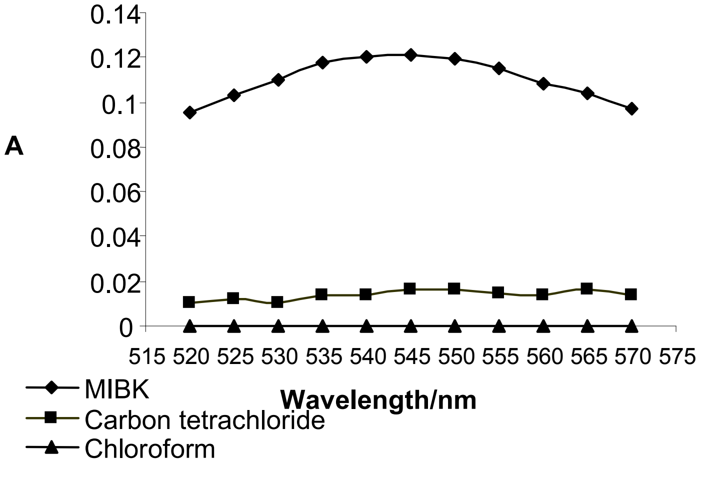

Fig 1. Effect of organic solvents on ion association complex extraction, $[(TMA^+)_2{\cdot}CrO_4^{2-}]$.

The determination of chromium(III) was done by adding 10 mL of cerium(IV) solution to oxidize chromium(III) to chromium(VI) and then heated and mixed with magnetic stirrer for 5 min. The solution was then treated as for the determination of chromium(VI).

RESULT AND DISCUSSION

Optimization of extraction conditions

Tetraalkylammonium as a counter ion reacts with oxyanions, such as chromate (CrO_4^{2-}) to form tetraalkylammonium-chromate [8]. The addition of tetramethylammonium chloride into chromate solution produces an ion association complex that could be extracted into an organic solvent. The equilibrium is as follows:

$$2TMA^+ + CrO_4^{2-}{}_{(aq)} \rightleftharpoons [CrO_4^{2-}{\cdot}(TMA^+)_2]_{(org)}$$

Chloroform, carbon tetrachloride, and MIBK have been tested as organic/extracting solvents. The results are shown in Fig. 1. Chloroform is unable to extract the ion-pair at all, while the ion-pair extraction using carbon tetrachloride is not quantitative. Therefore, MIBK is recommended as a convenient solvent because the absorbance of the back-extract solution is the highest one and gives a quantitative result. In other words, the extraction of the ion-association complex of tetramethylammonium-chromate from aqueous phase with MIBK gives a maximum result.

The $[CrO_4^{2-}{\cdot}(TMA^+)_2]$ ion-pair, after being extracted into MIBK and separated from aqueous solution, is back-extracted into an acidic DPC solution. The reaction between chromium(VI) and DPC produceds a soluble red-violet color of chromium(VI)-DPC complex [10-12], which is finally determined by UV-Vis spectrophotometer at 545 nm.

The equilibrium of the ion-pair formation in solution is influenced by the acidity of solution. The effect of the acidity on the efficiency of ion-pair formation and extraction has been investigated by determining the absorbance of chromium(VI)-DPC complexes in various additions of nitric acid (65%) volumes to a 100 mL volume of 0.5 μg.mL^{-1} chromium samples. The results are shown in Fig. 2. By increasing the volume of added nitric acid, the efficiency of the extraction (determined by absorbance parameter) is increased up to the addition of 7.5 mL HNO_3 and after that the absorbance of the solution decreases. Thus, the optimum volume of nitric acid addition for the formation and extraction of $[CrO_4^{2-}{\cdot}(TMA^+)_2]$ is found to be 7.5 mL.

Since the formation of TMA-chromate complex involves equilibrium reaction, the effect of various concentrations of TMAC on the absorbance of the extract solution has been studied to determine the minimum concentration of TMAC required to

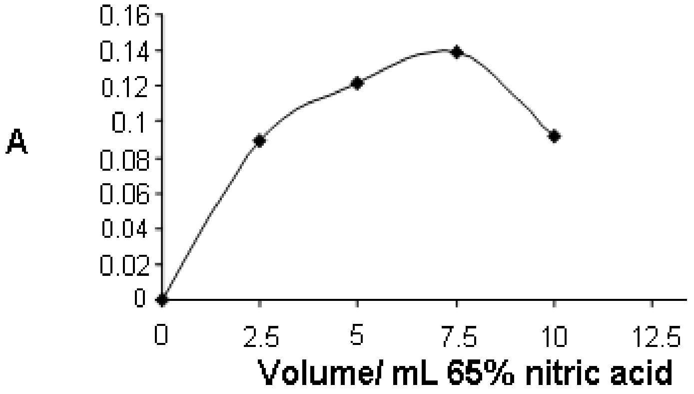

Fig 2. Effect of acidity on ion association complex extraction $[(TMA^+)_2 \cdot CrO_4^{2-}]$ in MIBK of [Cr(VI)]=0.5 μg.mL^{-1} by [TMAC]=0.1 M; shaking time=5 min; [DPC]=9.5x10^{-4}M

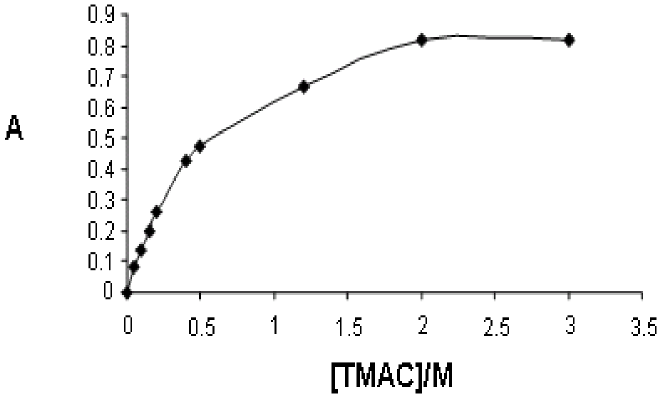

Fig 3. Effect of TMAC concentration on ion association complex extraction $[(TMA^+)_2.CrO_4^{2-}]$ into MIBK of [Cr(VI)]=0.5 μg.mL^{-1}; volume HNO_3 65%=7.5 mL; shaking time= 5 min; [DPC]=9.5x10^{-4} M

completely complex chromate ions in solution in order to have an effective extraction. Fig 3 shows that for fixed amount of chromium (0.5 μg.mL^{-1}), the concentration of TMAC in the solution should be not less than 2 M TMAC, e.g. the mole ratio of TMAC to chromium(VI) in the solution is 2x10^4.

The formation and distribution of ion association complexes in extraction process are also influenced by the distribution time of the complexes from aqueous phase into organic phase. The effect of extraction time on the efficiency of extraction process has been studied by varying shaking time of ion-pair extraction between 1 to 10 min. The minimum shaking time required for a quantitative extraction has been found to be 3 min (Fig. 4). In this work, the shaking time of 5 min has been selected for further experiments to make sure that all of the ion-association complexes formed is already quantitatively transferred into organic phase.

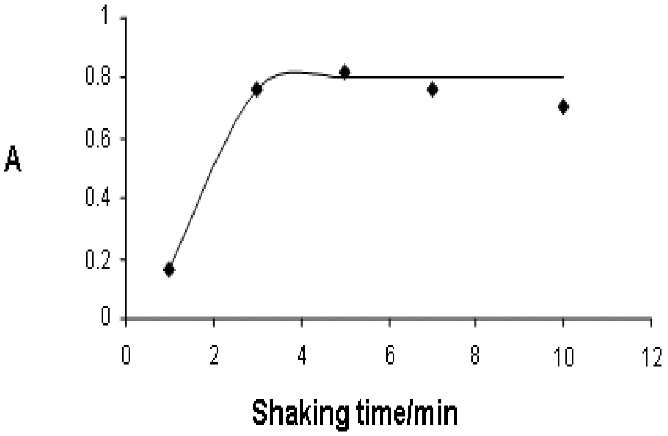

Fig 4. Effect of shaking time on ion association complex extraction $[(TMA^+)_2.CrO_4^{2-}]$ into MIBK of [Cr(VI)]=0.5 μg.mL^{-1}; volume HNO_3 65%=7.5 mL; [TMAC]=2 M; [DPC]=9.5x10^{-4} M

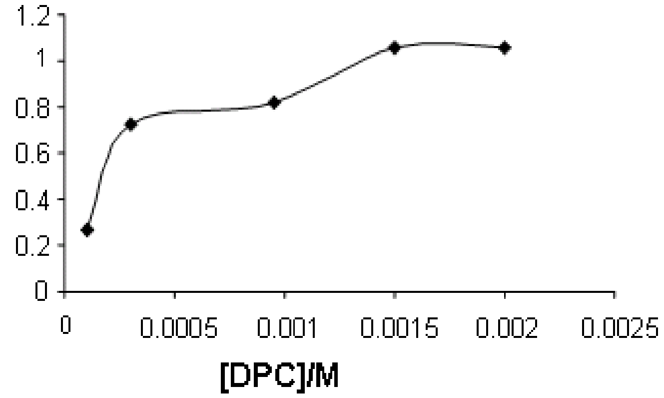

Fig 5. Effect of DPC concentration on ion association complex extraction $[(TMA^+)_2.CrO_4^{2-}]$ into MIBK of [Cr(VI)]=0.5 μg.mL^{-1}; volume HNO_3 65%=7.5 mL; [TMAC]=2 M; shaking time = 5 min.

The DPC concentration has also been optimized to achieve maximum extraction of ion-pair by adding various concentration of DPC in the concentration range of 1x10^{-4} M - 2x10^{-3} M. Fig 5 shows that optimum concentration of DPC for back-extracting the chromium(VI) from MIBK is 1.5x10^{-3} M or 7.5x10^{-6} mole of DPC for 9.61x10^{-7} mole of chromium(VI), which is equal to mole ratio of DPC to chromium(VI) ≈ 8:1.

Determination of analytical performance on the extraction and speciation method

The calibration curve for this method has been constructed using various standard concentration of chromium(VI) under optimized conditions of 7.5 mL of nitric acid (65%), mole ratio of TMAC to chromium(VI) of 2x10^4, 5 minutes of shaking time, and mole ratio of DPC : chromium(VI) of 8:1. The calibration curve is linear in the concentration range 0.00-0.40 μg.mL^{-1} of chromium(VI) with a regression equation of Abs=0.0038+1.7427X, in which X was the chromium species concentration (μg.mL^{-1}). The correlation coefficient (r) for the curve was 0.9991 and the detection limit (evaluated as three times the standard deviation divided with slope of calibration curve [13]) was 0.946 ppb. Based on these results, it can be concluded that the proposed method is quite sensitive and may be used for the speciation and analysis of Cr at the level of ppb.

Application

The application of this method for the speciation and quantitative analysis of chromium was tested by analyzing synthetic samples of chromium(VI) and chromium(III) and real samples from a river near a leather processing plant. The analytical results for the synthetic samples are given in Table 1. The solutions of chromium(VI) and chromium(III) at a concentration of 0.2 μg.mL^{-1}were analyzed with the proposed method. A same type solution contain of chromium(III) was also analyzed with the same method, but before ion association formation, the chromium(III) was oxidized first to chromium(VI) by using a cerium(IV) solution. The absorbance of a sample of MIBK (without TMAC) contacted with a chromium(VI) solution and back extracted into an acidic DPC solution and the absorbance of the blank solution (acidic DPC solution) are also given in Table 1. As shown in Table 1, the extraction of chromium(VI) with the proposed method can be quantitative, and the presence of chromium(III) in solutions does not give any interferences. It is also emerged from the table that the extraction and determination of chromium(III) was possible as long as the prior oxidation of chromium(III) to chromium(VI) with cerium(IV) was completely done.

The application of the proposed method to the analysis and speciation of chromium in real samples was done by determining the chromium content in water samples from Gadjah Wong River which were suspected to contain chromium from liquid waste of leather processing plant in Yogyakarta. The samples were collected in certain distance from the nearest to the leather plant with grapping method. The samples were filtered, acidifying at the sampling place by adding 1 mL of nitric acid (65%) for each 100 mL samples, and determined by the proposed method. The results of analysis and speciation of chromium in those samples are given in Table 2. It is clearly shown that the total content of chromium was found to be 0.04-0.05 μg ml^{-1} comprising 0.03-0.04 μg.mL^{-1} of chromium(VI) and 0.002-0.01 μg.mL^{-1} of chromium(III). This indicates that the concentration of chromium is still bellow the safety limit.

Table 1. Measured absorbances of synthetic sample solutions containing Cr(VI) dan Cr(III) after extracted with TMA and back-extracted with DPC solution under different conditions

Samples	Absorbance
Cr(VI) solution (0.2 μg.mL^{-1})	0.344
Cr(III) solution (0.2 μg.mL^{-1})	0.000
Blank solution (DPC solution)	0.000
Cr(III) solution (0.2 μg mL^{-1}) after oxidation to Cr(VI) by Ce(IV)	0.340 (98.8%)
MIBK without TMAC which is contacted with Cr(VI) solution	0.000
A solution containing both Cr^{VI} and Cr^{III} (0.2 μg.mL^{-1} each) without oxidation	0.339
A solution containing Cr^{VI} and Cr^{III} (0.2 μg.mL^{-1} each) with oxidation	0.680 (99.7%)

Table 2. Analysis and speciation results of chromium in river water samples with the proposed method

Samples [a]	Concentration of chromium/ μg.mL^{-1}		
	Cr(VI)	Cr(III)	Cr total
A	0,043	0,011	0,054
B	0,037	0,010	0,047
C	0,037	0.002	0,039

[a] Based on the sampling distance from the nearest to industry location (A) and the farthest (C); the samples were taken in August 2005.

CONCLUSION

The sensitivity and applicability in the speciation of chromium by using TMAC as a counter ion in ion association extraction have been demonstrated. The solvent extraction and back-extraction which was followed by a spectrophotometric determination was applicable to the separation and preconcentration of the chromium species in real samples.

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