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Yogyakarta, 31 October 2012

To:

Aman Sentosa Panggabean
Department of Chemistry FMIPA-University of Mulawarman, Samarinda-75119

Dear Sir,

This is to acknowledge and inform you that the paper entitles:

Preconcentration of Chromium(VI) at Trace Levels using Acid Alumina Resin with Column Method

written by:

Aman Sentosa Panggabean, Subur P. Pasaribu, Bohari Yusuf, and Nurhasanah

has been reviewed and could be published in Indo. J. Chem. after major revision. The author should make some correction as follows:

1. The main weakness of this manuscript is there many paper on the usage of alumina its modified form as the adsorbent for preconcentration of Cr(VI) that were not cited and discussed. The published papers were much more advanced that the work reported in this manuscript. Here are some important examples for such publication:
   a) Michael Sperling, Shukun Xu, Bernhard Welz, 1992, Determination of chromium(III) and chromium(VI) in water using flow injection online preconcentration with selective adsorption spectrometric detection, *Anal. Chem.*, 64, 24, 3101-3108, DOI: 10.1021/ac00048a007.
   b) Mohamed E. Mahmouda, Amr A. Yakout, Somia B. Ahmed, Maher M. Osman, 2008, Speciation, selective extraction and preconcentration of chromium ions via alumina-functionalized-isatin-thiosemicarbazone, *J. Hazard. Mater.*, 158, 2-3, 541-548.
   c) Abbas Afkhami, Mohammad Saber-Tehrani, Hasan Bagheri, Tayyebeh Madrakian, 2011, Flame atomic adsorption spectrometric determination of trace amounts of Pb(II) and Cr(III) in biological, food and environmental samples after preconcentration by modified nano-alumina, *Microchim. Acta*, 172, 1-2, 125-136.
   d) Sabermahani F, Taher, MA, 2011, Polyacrylic acid-modified alumina for solid-phase extraction and preconcentration of trace iron and chromium from plant samples, *J. AOAC Int.*, 94, 6, 1918-1924.
2. The English language used in this manuscript is poor in the usage of appropriate vocabularies and grammar.
3. Outcome data were not given an adequate explanation. Scientific explanation of any data/research is adequate and appropriate given.

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4. **If the authors revised the manuscript so that this work would not seem too simple compared to the previously reported by other authors and revised the English used; it is still have a chance to be published in this journal. The originality of this work should be emphasized in comparation to the other reports.**

Please kindly send your revised manuscript by 14 November 2012, so that the article could be published in the upcoming Indo. J. Chem. Also **kindly send your response to the reviewers' comments in a separate letter**. Thank you for your submission and we are waiting for the other articles from you and your colleagues.

Sincerely yours,

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PRECONCENTRATION OF CHROMIUM(VI) AT TRACE LEVELS USING ACID ALUMINA RESIN WITH COLUMN METHOD

ABSTRAK

Analisis runut ion Kromium(VI) menggunakan alumina asam sebagai resin pengisi kolom dalam tahapan prakonsentrasi telah dilakukan. Metode prakonsentrasi dilakukan dengan menggunakan kolom yang berisikan alumina asam yang diaktivasi dengan H_2SO_4 pada pH 1. Kondisi Optimum untuk kinerja analitik yang paling baik dalam tahapan prakonsentrasi ini adalah volume sampel sebanyak 10 mL yang dapat dielusi secara kuantitatif dengan eluen NH_4OH 1M dengan volume 3 mL. Hasil penelitian menunjukkan kapasitas retensi alumina asam sebesar 3,955 mg Cr(VI)/g resin. Kinerja analitik pengukuran metode ini sangat baik, ditunjukkan dengan pengukuran nilai batas deteksinya adalah 3,648 µg/L. Kebolehulangan yang dinyatakan sebagai persentase koefisien variansi adalah 2,06%. Penggunaan alumina asam sebagai resin pengisi kolom dapat meningkatkan signal sebesar 15,36 kali dalam pengukuran ion Cr(VI). Metode ini memiliki akurasi cukup baik dengan menggunakan teknik *spike* memberikan nilai persen perolehan kembali > 95%, menunjukkan bahwa matriks sampel air tidak mempengaruhi hasil pengukuran dan dapat digunakan untuk analisis Cr(VI) dalam sampel air pada tingkat runut.

Kata Kunci : Kromium(VI), Analisis runut, Prakonsentrasi, Alumina asam, Resin.

ABSTRACT

Trace analysis of Chromium(VI) ions using acid alumina resin as filler column in preconcentration system has been carried out. The preconcentration method was performed using a column filled with acid alumina was activated with H_2SO_4 at pH 1. The optimal conditions for the best analytical performed in preconcentration steps were 10 mL injection volume of waters samples, can by eluting for quantitative with eluent 1M NH_4OH and the volume was 3 mL. This research showed retention capacity was 3.955 mg Cr(VI)/g resin. The analytical performance this method is good, showed with the limit of detection values was 3.648 µg/L. The reproducibility of this method shown as percentage of coefficient variance was 2.06 %. Acid alumina used as resin filler column can to increase signal up 15.36 times for measured Cr(VI) ions. This method had a good accuracy used spike technique with according to recovery percentage > 95%, showed the matrices of water samples didn't effect the results of measurements and can be used to analyze Cr(VI) in water samples at trace levels.

Keywords : Chromium(VI), Trace analysis, Preconcentration, Acid alumina, Resin.

INTRODUCTION

Chromium is a generally abundant element in the earths crust. It occurs in oxidation states ranging from Cr(II) to Cr(VI) but only Cr(III) (trivalent) and Cr(VI) (hexavalent) forms are biological significance. It has been proved that trace amounts of Cr(III) are necessary for mammalian health in order to maintain glucose, lipid and to perform protein metabolism. On the other hand, Cr(VI) can be toxic for biological systems, and water soluble Cr(VI) is extremely irritating and toxic to human body tissue owing to its high oxidizing potential and easy permeation of biological membranes [1]. Accumulation and inhalation of hexavalent chromium bearing substances lead to bronchitis, pneumonitis, asthma, nasal septum and inflammation of the larynx and liver and increased incidence of bronchogenic carcinoma. Mean-while, direct contact with these materials may cause dermatitis, dermal necrosis, skin allergies and dermal corrosion [2,3]. Cr(VI) and Cr(III) enter the environment in discharges from the steel, electroplating, leather tanning and wood-preservative industries. They may also enter the tap water supply from the corrosian inhibitors used in water pipes and containers. It is therefore important to determine the Cr(VI) quantity in environmental samples. However, Cr(VI) is normally present at very low concentrations, such as those found in natural water and seawater, where typical concentrations are in the 0.1–0.5 μg L^{-1} range [4,5]

In the analysis of trace metal ions present in various samples such as natural and waste water, biological and alloy samples, the direct determination with various instrumental methods is not possible owing to matrix effect and low concentration of metal ions in a sample. In trace analysis, therefore, a preconcentration and separation of trace elements from the matrix is frequently necessary to improve the detection limit and selectivity. The direct determination of chromium in water may not be possible with sufficient sensitivity by also expensive analytical methods such as inductively coupled plasma atomic emission spectrometry (ICP-AES) or electrothermal atomic absorption spectrometry (ETAAS) because of low concentrations and matrix interferences [6,7].

Preconcentration technique tools provide a solution to the limitations of the instrument in the determination of heavy metals at very low concentrations. Preconcentration steps by sorption technique not only increases the concentration of the analyte but also can eliminate the matrix effects that can interfere with the process of analysis [8]. Preconcentration technique using cation exchange resins have advantages than other preconcentration, because of the loss of analytes can be minimized, the amount of resin used slightly (0.1 to 0.5 g), and can be regenerated so

that they can be used repeatedly for the same analysis [9,10]. Preconcentration is usually the preparation of an analysis and aims to raise the concentration of the analyte to enter the analytical measurement range.

Several studies have been conducted to determine Cr(VI) with the preconcentration technique using specific resin as filler mini column based flow injection analysis with FAAS detector are 1.5-diphenylcarbazone complex on amberlite XAD-16 resin [6], melamine based polymeric sequestering succinic acid resin [11], and Si-C_{18} [12]. In this research, the preconcentration technique done using a column method (off-line system), has not been reported previously. This method is expected to be done in a simple laboratory because it requires only spectrophotometer visible as detector and can detect the presence of metal ions Cr(VI) at trace levels.

In this research have been studied a several of conditions that affect the success of preconcentration Cr (VI) in a sample, which includes activation of pH alumina resin, retention capacity, analytical performance this method including reproducibility, linearity, limit of detection and % recovery. The study was based on techniques that preconcentration system Cr (VI) on acid alumina column which then complexes with a 1.5-diphenylcarbazide (DPC) to form a red–violet complex in the detection using a spectrophotometer visible.

METHODOLOGY

Instrumentation and Reagents

Instrumentation. Equipment used in the columns, glass equipment (E 'Merck), pH meter Orion model 420A, to determine the the absorbance Cr(VI) used spectrophotometer visible (Rayleigh Vis-7220G).

Reagents. The materials used in this research were Al_2O_3, $K_2Cr_2O_7$, $CrCl_3$. $6H_2O$, 1.5-diphenylcarbazide, H_2SO_4, HNO_3, HCl, H_3PO_4, CH_3COOH, NH_4OH, acetone, all reagents were of analytical-reagen grade (E'Merck) and aquabidest.

Effect of pH activation alumina resin

0.1 g of Al_2O_3 (alumina) immersed into the H_2SO_4 with variations of pH 1 - 4, and visible allowed to stand for 24 hours, filtered and dried. 10 mL of Cr (VI) 0.5 mg/L is inserted into a beaker glass containing acid alumina and stirred slowly. Soaked for 2 hours and then filtered, measured by using a spectrophotometer visible.

To determine the absorbance of Cr (VI), into the sample solution was added drops of 2 N H_2SO_4 and H_3PO_4 to pH close to 1. Add with 1 mL of 0.1% 1.5

diphenylcarbazide. Allowed to stand for 10 minutes and the absorbance of sample were measured with a spectrophotometer visible at 540 nm.

Retention capacity

The batch method was used at this stage, 0.1 g of acid alumina resin soaked into 10 mL standard solution of Cr (VI) with variation in concentration of 1 - 10 mg/L at pH optimum conditions. Soaking carried out for 1 hour and measured the absorbance of Cr(VI) by using a spectrophotometer visible.

Optimization Preconcentration

Effect of eluent concentration

1 mL of Cr(VI) 1 mg/L inserted into the column containing acid alumina resin. Cr(VI) ions retented were eluted with 2 mL of NH_4OH with various concentrations of 0.1 – 4.0 M. absorbance of the eluate was measured by visible spectrophotometer visible. From the measurement results will be obtained optimum concentration of NH_4OH as the eluent.

Effect of eluent volume

1 mL of Cr(VI) 1 mg/L inserted into the column containing acid alumina resin. Cr(VI) retented was eluted with 2 mL of NH_4OH with variety of volumes 0.5 - 5 mL and absorbance of the eluate was measured by spectrophotometer visible.

Effect of Volume Cr(VI)

Into a column containing acid alumina, inserted a standard solution of Cr(VI) 1 mg/L with a variety of volumes 1 - 10 mL. Cr(VI) retention was eluted with 2 mL NH_4OH at optimum concentrations obtained and the absorbance was measured with spectrophotometer visible.

Analytical performance

Reproducibility

absorbance of the 25 µg/L Cr(VI) was measured as many times (n = 7) with the optimum conditions with the same procedure above.

Liniearity

absorbance of Cr(VI) in the range of variation of 10 - 300 µg/L was measured with the

optimum conditions and the same procedure as above. Regression line equation was obtained by plotting absorbance vs concentration of Cr(VI).

Limit of Detection (LOD)

In this study the LOD was determined by measuring the absorbance of the concentration of Cr(VI) is the smallest that can be determined and distinguished from the blank absorbance measurements at several times. Detection limit is expressed as the ratio of the absorbance of the standard (S) against the blank (N) or (S/N) = 3.

Effect of species Cr (III)

To determine the effect of species of Cr(III) to the measurement of Cr(VI), made measurements of a solution containing Cr(III) and Cr(VI) with a ratio of 1 : 1 the concentration of Cr(VI) is made permanent 1 mg/L and Cr(III) is made different from the variation of 1 - 5 mg/L. Mixture of species Cr(III) and Cr(VI) is passed into the column, Cr(VI) retented at column eluted with NH_4OH and the absorbance of eluats was measured using a spectrophotometer visible.

Determination of Samples

To determine the influence of matrix on the determination of Cr(VI) ions in water samples from nature, done by the spike method. In this method a certain amount of volumes of Cr(VI) pipette and diluted with the samples. The treatment is then performed with the optimum conditions and the absorbance was measured using a spectrophotometer visible.

RESULTS AND DISCUSSION

The determination of chromium is frequently achieved by spectrophotometry after derivatisation with a reagent such as DPC. The reaction of DPC is very selective for Cr(VI) so it can be performed directly without a separation step. The chromate oxidizes DPC to diphenylcarbazone (DPCO) to form a soluble strongly red–violet compound with Cr(III) (Cr(III)-$DPCO^{(3-n)+}$). A large excess of DPC is essential as compounds present in the sample may consume the reagent [5].

Effect of pH activation alumina resin

Alumina is amphoteric resin, it must be activated in acidic conditions in order to more specifically bind to the Cr(VI) ion. Determination of optimum pH was aimed to obtain optimum conditions for the formation of chelates reaction. It is expected to absorb resin ion Cr(VI) is optimal. The result of measurements are shown in Figure 1.

The measurement results show the pH above 3, less than the maximum absorb Cr(VI) because the resin has not been activated alumina perfectly into acidic alumina. Alumina resin can completely absorb Cr(VI) at pH 1 and 2.

Retention Capacity

One of the important fundamental value of which must be owned by resin is retention capacity to certain metal ion. Retention capacity is the amount of acid alumina resin ability to absorb ions of Cr(VI). Determination of retention capacity of Cr(VI) to alumina resin done at optimum absorption pH with contact time during 1 hours.

Figure 2, that retention capacity obtained are 3.955 mg Cr(VI)/ g alumina resin, means that for every 1 g of alumina resin can absorb optimally 3.955 mg Cr(VI) ions. This retention capacities values would hardly determines how method preconcentration based on column method must be done if it is applied this alumina resin as filler material of column to preconcentration technique for determination of trace chromium in samples.

Optimization Preconcentration

Effect of Eluent Concentration

Eluent is one important part in this research. Eluent used to remove the bound analyte on the resin. Effectiveness of the elution is determined by the type and concentration of eluent was used. NH_4OH was used as an eluent with a consideration of the elution process is expected that there is no damage resin in the column.

Figure 3. obtained, the following elution using smaller than 0.5 M NH_4OH concentration showed that the ion Cr (VI) retented in the column are not eluted completely. Cr(VI) ions were eluted all at concentrations above 1 M. The concentration of 1 M NH_4OH was used in the optimum concentration for further work.

Effect of Eluent Volume

Influence on the measurement of the amount of NH_4OH eluent volume, measured concentrations of Cr(VI) ion by varying the volume of NH_4OH eluent used to elution of Cr(VI) ion in the resin column

Figure 4. the greater the volume of eluent used to elution of the Cr(VI) ion retented in the resin, the greater the ion Cr(VI) is eluted. Elution using eluent volume over 3 mL shows the measurement results are not significantly different, this means that the

volume of 3 mL eluent, Cr(VI) ions was completely eluted. The optimum volume of 1 M NH_4OH eluent obtained was 3 mL to be used for further work.

Effect of Cr(VI) Volume

In the determination of the influence of the volume of Cr(VI), the absorbance of Cr(VI) ion measured by varying the amount of volume ion Cr(VI) to the column containing the alumina resin with the made same of the concentration Cr(VI) ion.

Figure 5. for a amount of 2 g of alumina resin, the optimum volume of the ion Cr(VI) 1 mg/L was 10 mL. In the above conditions the amount of volume, the resin has been maximum point in the capture of Cr (VI) ion is passed into the column.

Analytical Performance

Reproducibility

The reproducibility of the method was examined under the optimum experimental conditions described above by using the model solution. Reproducibility level as shown as a percentage of the coefficient of variation (CV) obtained from the seven measurement results, determine as the relative standard deviation in standar solutions containing 25 µg/L Cr(VI), was 2.06 % . These results are quite good considering the % CV is still ≤ 5% [13,14].

Linearity

Calibration curve prepared by plotting concentration of Cr(VI) standard series with absorbance value. Absorbance data used in the made of this calibration curve is the absorbance of standard solutions of Cr(VI) on preconcentration system using alumina resin. Based on the measurement results obtained by the linear range at a concentration of 0.01 – 0.3 mg/L. Equation of the regression linear are y = 0.276x + 0.030 with correlation coefficient values (R) are quite good that is equal to 0.996.

Limit of Detection (LOD)

Detection limit is the concentration or mass minimum analyte that was detected with a high level of confidence. Detection limit is expressed as the ratio between the standard signal (S) of the blank signal (N) or S / N = 3. The results showed that preconcentration systems developed to give good results with the detection limit are 3.648 µg/L. Preconcentration system can provide minimum mass measurements in the µg. L^{-1} (ng) levels.

Enrichment Factor (EF)

Enrichment factor, or often called the sensitivity of increase is done by comparing the absorbance of the ion Cr(VI) measured before and after preconcentration done. The determination of EF values is very important because it illustrates the magnitude of the increase in signal measurement method was developed. Based on the results of calculations with known value of EF are 15.36 times. Mean that through the use of alumina resin as filler at column in the technique of preconcentration Cr(VI) ion can increase the absorbance value as much as 15.36 times. The increase shows the Cr(VI) ion at trace concentrations can be detected using this method.

Effect of species Cr (III)

To determine the effect of species Cr(III) to the measurement of Cr(VI), conducted the analysis of a solution containing Cr(III) and Cr(VI) with various comparisons. Table 1. shows the measurement results show that Cr(III) does not affect the measurement of Cr(VI). Cr(III) ion directly out of the column with the carrier. Species of Cr(VI) was eluted with NH_4OH shows stable results and did not change significantly, it's mean species Cr (III) did not retented in the column and the column of acid alumina species selective for Cr (VI).

Application to River Water Samples

The alumina acid resin has been employed for the preconcentration and analysis of Cr(VI) ion in river water samples. For that purpose, the procedure given was applied. The result, which are shown in Table 2, have been calculated on the assumption of >95 % recovery od Cr(VI) ions. These data indicate that the accuracy of the method developed is very good and the water sample matrix does not effect on the measurement results [15].

CONCLUSION

Technique of preconcentration using acid alumina resin as a filler column for analysis of Cr(VI) ion at trace levels obtained at the optimum condition of concentration of eluent was 1 M NH_4OH, volume eluent of NH_4OH was 3 ml, sample volume 10 mL and the retention capacity was 3.955 mg Cr(VI)/g acid alumina resin. Analytical performance obtained is very well shown with the reproducibility as percentages of coefficient variance are 2.06 %, limit of detection was 3.648 mg/L and the enrichment factor of resin was 15.36 times. Technique of preconcentration developed can be applied to

determine the concentration of Cr(VI) in water samples, shown by the percentage recovery are >95%.

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Table 1. Effect of interfere Cr(III) ion

Comparisons of Cr(VI) and Cr(III) (1 mg/L)	Absorbance
1 : 1	0.296
1 : 2	0.294
1 : 3	0.294
1 : 4	0.292
1 : 5	0.291

Tabel 2. Result of determination of Cr(VI) ions in water samples

Sampel	Cr(VI), µg L^{-1}		Recovery %
	Added	Found	
R-01	0	75.36 ± 6.57	-
	100	182.24 ± 5.72	96.22 ± 0.67
R-02	0	36.44 ± 3.52	-
	25	62.18 ± 4.15	98.80 ± 0.52

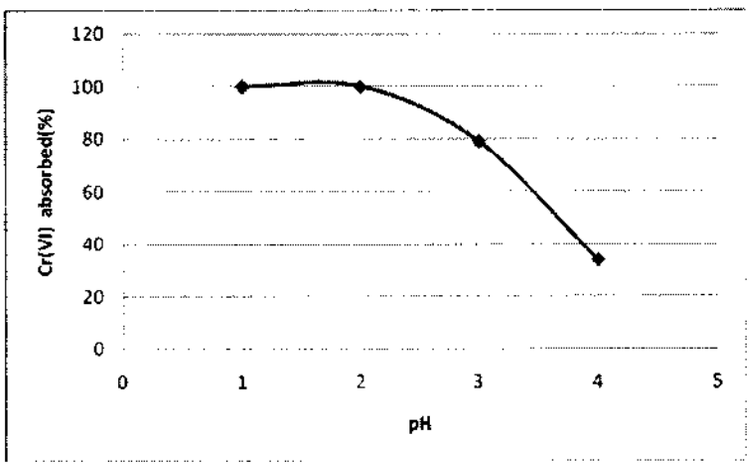


Figure 1. Effect of pH activation with Cr(VI) absorbed

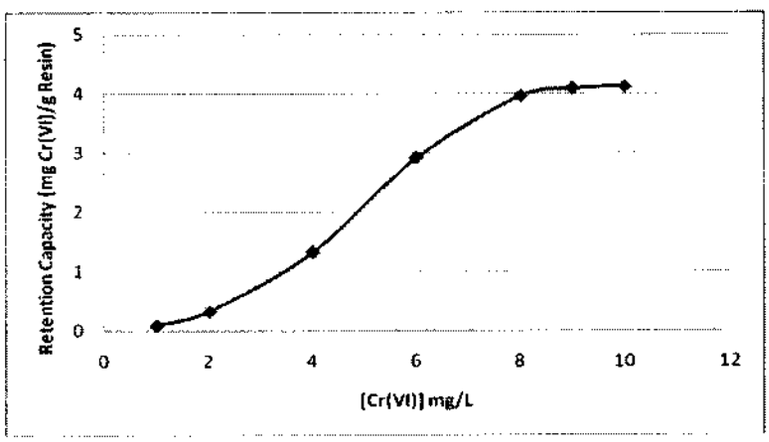


Figure 2. Retention capacity of acid alumina resin

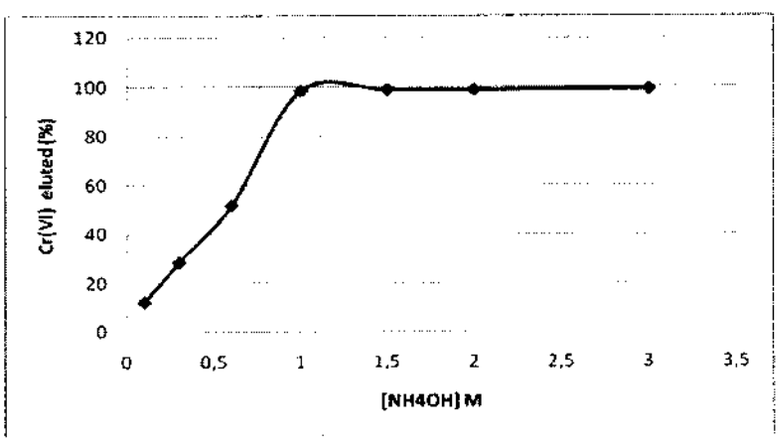


Figure 3. Effect of eluent concentration

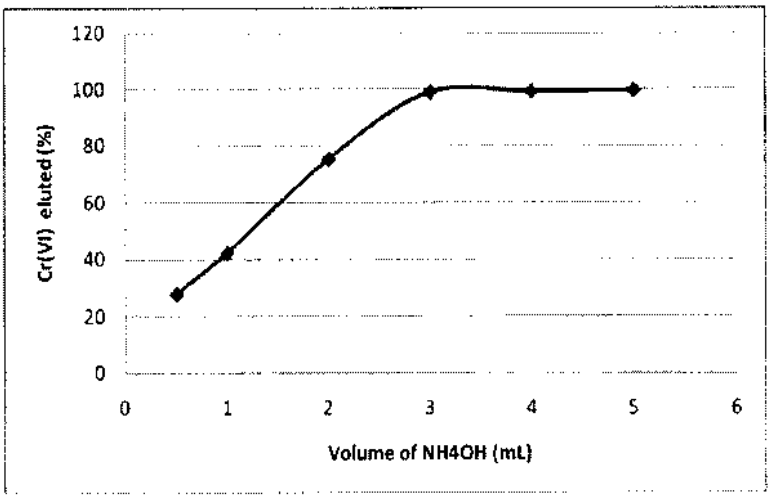
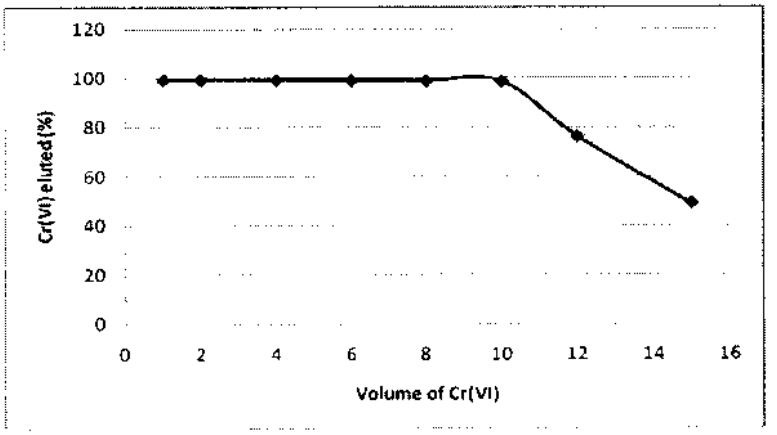


Figure 4. Effect of eluent volume



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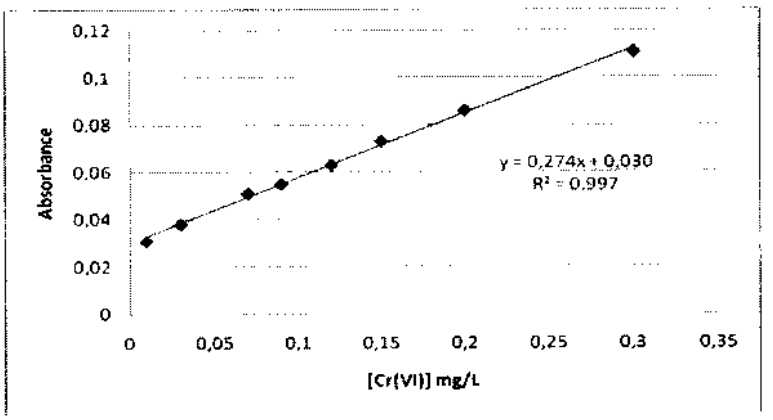

Figure 6. Calibration curve of Cr(VI)

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ABSTRAK

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Kata Kunci : Kromium(VI), Analisis runut, Prakonsentrasi, Alumina asam, Resin.

ABSTRACT

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Keywords : Chromium(VI), Trace analysis, Preconcentration, Acid alumina, Resin.

INTRODUCTION

Chromium is a generally abundant element in the earths crust. It occurs in oxidation states ranging from Cr(II) to Cr(VI) but only Cr(III) (trivalent) and Cr(VI) (hexavalent) forms are biological significance. It has been proved that trace amounts of Cr(III) are necessary for mammalian health in order to maintain glucose, lipid and to perform protein metabolism. On the other hand, Cr(VI) can be toxic for biological systems, and water soluble Cr(VI) is extremely irritating and toxic to human body tissue owing to its high oxidizing potential and easy permeation of biological membranes [1]. Accumulation and inhalation of hexavalent chromium bearing substances lead to bronchitis, pneumonitis, asthma, nasal septum and inflammation of the larynx and liver and increased incidence of bronchogenic carcinoma. Mean-while, direct contact with these materials may cause dermatitis, dermal necrosis, skin allergies and dermal corrosion [2,3]. Cr(VI) and Cr(III) enter the environment in discharges from the steel, electroplating, leather tanning and wood-preservative industries. They may also enter the tap water supply from the corrosian inhibitors used in water pipes and containers. It is therefore important to determine the Cr(VI) quantity in environmental samples. However, Cr(VI) is normally present at very low concentrations, such as those found in natural water and seawater, where typical concentrations are in the 0.1–0.5 μg L^{-1} range [4,5]

In the analysis of trace metal ions present in various samples such as natural and waste water, biological and alloy samples, the direct determination with various instrumental methods is not possible owing to matrix effect and low concentration of metal ions in a sample. In trace analysis, therefore, a preconcentration and separation of trace elements from the matrix is frequently necessary to improve the detection limit and selectivity. The direct determination of chromium in water may not be possible with sufficient sensitivity by also expensive analytical methods such as inductively coupled plasma atomic emission spectrometry (ICP-AES) or electrothermal atomic absorption spectrometry (ETAAS) because of low concentrations and matrix interferences [6,7].

Preconcentration technique tools provide a solution to the limitations of the instrument in the determination of heavy metals at very low concentrations. Preconcentration steps by sorption technique not only increases the concentration of the analyte but also can eliminate the matrix effects that can interfere with the process of analysis [8]. Preconcentration technique using cation exchange resins have advantages than other preconcentration, because of the loss of analytes can be minimized, the amount of resin used slightly (0.1 to 0.5 g), and can be regenerated so

that they can be used repeatedly for the same analysis [9,10]. Preconcentration is usually the preparation of an analysis and aims to raise the concentration of the analyte to enter the analytical measurement range.

Several studies have been conducted to determine Cr(VI) with the preconcentration technique using specific resin as filler mini column based flow injection analysis with FAAS detector are 1.5-diphenylcarbazone complex on amberlite XAD-16 resin [6], melamine based polymeric sequestering succinic acid resin [11], and Si-C_{18} [12]. In this research, the preconcentration technique done using a column method (off-line system), has not been reported previously. This method is expected to be done in a simple laboratory because it requires only spectrophotometer visible as detector and can detect the presence of metal ions Cr(VI) at trace levels.

In this research have been studied a several of conditions that affect the success of preconcentration Cr (VI) in a sample, which includes activation of pH alumina resin, retention capacity, analytical performance this method including reproducibility, linearity, limit of detection and % recovery. The study was based on techniques that preconcentration system Cr (VI) on acid alumina column which then complexes with a 1,5-diphenylcarbazide (DPC) to form a red–violet complex in the detection using a spectrophotometer visible.

METHODOLOGY

Instrumentation and Reagents

Instrumentation. Equipment used in the columns, glass equipment (E 'Merck), pH meter Orion model 420A, to determine the the absorbance Cr(VI) used spectrophotometer visible (Rayleigh Vis-7220G).

Reagents. The materials used in this research were Al_2O_3, $K_2Cr_2O_7$, $CrCl_3.6H_2O$, 1.5-diphenylcarbazide, H_2SO_4, HNO_3, HCl, H_3PO_4, CH_3COOH, NH_4OH, acetone, all reagents were of analytical-reagen grade (E'Merck) and aquabidest.

Effect of pH activation alumina resin

0.1 g of Al_2O_3 (alumina) immersed into the H_2SO_4 with variations of pH 1 - 4, and visible allowed to stand for 24 hours, filtered and dried. 10 mL of Cr (VI) 0.5 mg/L is inserted into a beaker glass containing acid alumina and stirred slowly. Soaked for 2 hours and then filtered, measured by using a spectrophotometer visible.

To determine the absorbance of Cr (VI) into the sample solution was added drops of 2 N H_2SO_4 and H_3PO_4 to pH close to 1. Add with 1 mL of 0.1% 1.5

diphenylcarbazide. Allowed to stand for 10 minutes and the absorbance of sample were measured with a spectrophotometer visible at 540 nm.

Retention capacity

The batch method was used at this stage, 0.1 g of acid alumina resin soaked into 10 mL standard solution of Cr (VI) with variation in concentration of 1 - 10 mg/L at pH optimum conditions. Soaking carried out for 1 hour and measured the absorbance of Cr(VI) by using a spectrophotometer visible.

Optimization Preconcentration

Effect of eluent concentration

1 mL of Cr(VI) 1 mg/L inserted into the column containing acid alumina resin. Cr(VI) ions retented were eluted with 2 mL of NH_4OH with various concentrations of 0.1 – 4.0 M. absorbance of the eluate was measured by visible spectrophotometer visible. From the measurement results will be obtained optimum concentration of NH_4OH as the eluent.

Effect of eluent volume

1 mL of Cr(VI) 1 mg/L inserted into the column containing acid alumina resin. Cr(VI) retented was eluted with 2 mL of NH_4OH with variety of volumes 0.5 - 5 mL and absorbance of the eluate was measured by spectrophotometer visible.

Effect of Volume Cr(VI)

Into a column containing acid alumina, inserted a standard solution of Cr(VI) 1 mg/L with a variety of volumes 1 - 10 mL. Cr(VI) retention was eluted with 2 mL NH_4OH at optimum concentrations obtained and the absorbance was measured with spectrophotometer visible.

Analytical performance

Reproducibility

absorbance of the 25 µg/L Cr(VI) was measured as many times (n = 7) with the optimum conditions with the same procedure above.

Liniearity

absorbance of Cr(VI) in the range of variation of 10 - 300 µg/L was measured with the

optimum conditions and the same procedure as above. Regression line equation was obtained by plotting absorbance vs concentration of Cr(VI).

Limit of Detection (LOD)

In this study the LOD was determined by measuring the absorbance of the concentration of Cr(VI) is the smallest that can be determined and distinguished from the blank absorbance measurements at several times. Detection limit is expressed as the ratio of the absorbance of the standard (S) against the blank (N) or (S/N) = 3.

Effect of species Cr (III)

To determine the effect of species of Cr(III) to the measurement of Cr(VI), made measurements of a solution containing Cr(III) and Cr(VI) with a ratio of 1 : 1 the concentration of Cr(VI) is made permanent 1 mg/L and Cr(III) is made different from the variation of 1 - 5 mg/L. Mixture of species Cr(III) and Cr(VI) is passed into the column, Cr(VI) retented at column eluted with NH_4OH and the absorbance of eluats was measured using a spectrophotometer visible.

Determination of Samples

To determine the influence of matrix on the determination of Cr(VI) ions in water samples from nature, done by the spike method. In this method a certain amount of volumes of Cr(VI) pipette and diluted with the samples. The treatment is then performed with the optimum conditions and the absorbance was measured using a spectrophotometer visible.

RESULTS AND DISCUSSION

The determination of chromium is frequently achieved by spectrophotometry after derivatisation with a reagent such as DPC. The reaction of DPC is very selective for Cr(VI) so it can be performed directly without a separation step. The chromate oxidizes DPC to diphenylcarbazone (DPCO) to form a soluble strongly red–violet compound with Cr(III) (Cr(III)-$DPCO^{(3-n)+}$). A large excess of DPC is essential as compounds present in the sample may consume the reagent [5].

No Correlation

Effect of pH activation alumina resin

Alumina is amphoteric resin, it must be activated in acidic conditions in order to more specifically bind to the Cr(VI) ion. Determination of optimum pH was aimed to obtain optimum conditions for the formation of chelates reaction. It is expected to absorb resin ion Cr(VI) is optimal. The result of measurements are shown in Figure 1.

The measurement results show the pH above 3, less than the maximum absorb Cr(VI) because the resin has not been activated alumina perfectly into acidic alumina. Alumina resin can completely absorb Cr(VI) at pH 1 and 2.

Retention Capacity

One of the important fundamental value of which must be owned by resin is retention capacity to certain metal ion. Retention capacity is the amount of acid alumina resin ability to absorb ions of Cr(VI). Determination of retention capacity of Cr(VI) to alumina resin done at optimum absorption pH with contact time during 1 hours.

Figure 2, that retention capacity obtained are 3.955 mg Cr(VI)/ g alumina resin, means that for every 1 g of alumina resin can absorb optimally 3.955 mg Cr(VI) ions. This retention capacities values would hardly determines how method preconcentration based on column method must be done if it is applied this alumina resin as filler material of column to preconcentration technique for determination of trace chromium in samples.

Optimization Preconcentration

Effect of Eluent Concentration

Eluent is one important part in this research. Eluent used to remove the bound analyte on the resin. Effectiveness of the elution is determined by the type and concentration of eluent was used. NH_4OH was used as an eluent with a consideration of the elution process is expected that there is no damage resin in the column.

Figure 3. obtained, the following elution using smaller than 0.5 M NH_4OH concentration showed that the ion Cr (VI) retented in the column are not eluted completely. Cr(VI) ions were eluted all at concentrations above 1 M. The concentration of 1 M NH_4OH was used in the optimum concentration for further work.

Effect of Eluent Volume

Influence on the measurement of the amount of NH_4OH eluent volume, measured concentrations of Cr(VI) ion by varying the volume of NH_4OH eluent used to elution of Cr(VI) ion in the resin column

Figure 4. the greater the volume of eluent used to elution of the Cr(VI) ion retented in the resin, the greater the ion Cr(VI) is eluted. Elution using eluent volume over 3 mL shows the measurement results are not significantly different, this means that the

volume of 3 mL eluent, Cr(VI) ions was completely eluted. The optimum volume of 1 M NH_4OH eluent obtained was 3 mL to be used for further work.

Effect of Cr(VI) Volume ⟶ The amount of Cr(VI)

In the determination of the influence of the volume of Cr(VI), the absorbance of Cr(VI) ion measured by varying the amount of volume ion Cr(VI) to the column containing the alumina resin with the made same of the concentration Cr(VI) ion.

Figure 5. for a amount of 2 g of alumina resin, the optimum volume of the ion Cr(VI) 1 mg/L was 10 mL. In the above conditions the amount of volume, the resin has been maximum point in the capture of Cr (VI) ion is passed into the column.

Analytical Performance

Reproducibility

The reproducibility of the method was examined under the optimum experimental conditions described above by using the model solution. Reproducibility level as shown as a percentage of the coefficient of variation (CV) obtained from the seven measurement results, determine as the relative standard deviation in standar solutions containing 25 µg/L Cr(VI), was 2.06 % . These results are quite good considering the % CV is still ≤ 5% [13,14].

Linearity

Calibration curve prepared by plotting concentration of Cr(VI) standard series with absorbance value. Absorbance data used in the made of this calibration curve is the absorbance of standard solutions of Cr(VI) on preconcentration system using alumina resin. Based on the measurement results obtained by the linear range at a concentration of 0.01 – 0.3 mg/L. Equation of the regression linear are y = 0.276x + 0.030 with correlation coefficient values (R) are quite good that is equal to 0.996.

Limit of Detection (LOD)

Detection limit is the concentration or mass minimum analyte that was detected with a high level of confidence. Detection limit is expressed as the ratio between the standard signal (S) of the blank signal (N) or S / N = 3. The results showed that preconcentration systems developed to give good results with the detection limit are 3.648 µg/L. Preconcentration system can provide minimum mass measurements in the µg. L^{-1} (ng) levels.

Enrichment Factor (EF)

Enrichment factor, or often called the sensitivity of increase is done by comparing the absorbance of the ion Cr(VI) measured before and after preconcentration done. The determination of EF values is very important because it illustrates the magnitude of the increase in signal measurement method was developed. Based on the results of calculations with known value of EF are 15.36 times. Mean that through the use of alumina resin as filler at column in the technique of preconcentration Cr(VI) ion can increase the absorbance value as much as 15.36 times. The increase shows the Cr(VI) ion at trace concentrations can be detected using this method.

Effect of species Cr (III)

To determine the effect of species Cr(III) to the measurement of Cr(VI), conducted the analysis of a solution containing Cr(III) and Cr(VI) with various comparisons. Table 1. shows the measurement results show that Cr(III) does not affect the measurement of Cr(VI). Cr(III) ion directly out of the column with the carrier. Species of Cr(VI) was eluted with NH_4OH shows stable results and did not change significantly, it's mean species Cr (III) did not retented in the column and the column of acid alumina species selective for Cr (VI).

Application to River Water Samples

The alumina acid resin has been employed for the preconcentration and analysis of Cr(VI) ion in river water samples. For that purpose, the procedure given was applied. The result, which are shown in Table 2, have been calculated on the assumption of >95 % recovery od Cr(VI) ions. These data indicate that the accuracy of the method developed is very good and the water sample matrix does not effect on the measurement results [15].

CONCLUSION

Technique of preconcentration using acid alumina resin as a filler column for analysis of Cr(VI) ion at trace levels obtained at the optimum condition of concentration of eluent was 1 M NH_4OH, volume eluent of NH_4OH was 3 ml, sample volume 10 mL and the retention capacity was 3.955 mg Cr(VI)/g acid alumina resin. Analytical performance obtained is very well shown with the reproducibility as percentages of coefficient variance are 2.06 %, limit of detection was 3.648 mg/L and the enrichment factor of resin was 15.36 times. Technique of preconcentration developed can be applied to

determine the concentration of Cr(VI) in water samples, shown by the percentage recovery are >95%.

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Table 1. Effect of interfere Cr(III) ion

Comparisons of Cr(VI) and Cr(III) (1 mg/L)	Absorbance
1 : 1	0.296
1 : 2	0.294
1 : 3	0.294
1 : 4	0.292
1 : 5	0.291

Tabel 2. Result of determination of Cr(VI) ions in water samples

Sampel	Cr(VI), µg L^{-1}		Recovery %
	Added	Found	
R-01	0	75.36 ± 6.57	-
	100	182.24 ± 5.72	96.22 ± 0.67
R-02	0	36.44 ± 3.52	-
	25	62.18 ± 4.15	98.80 ± 0.52

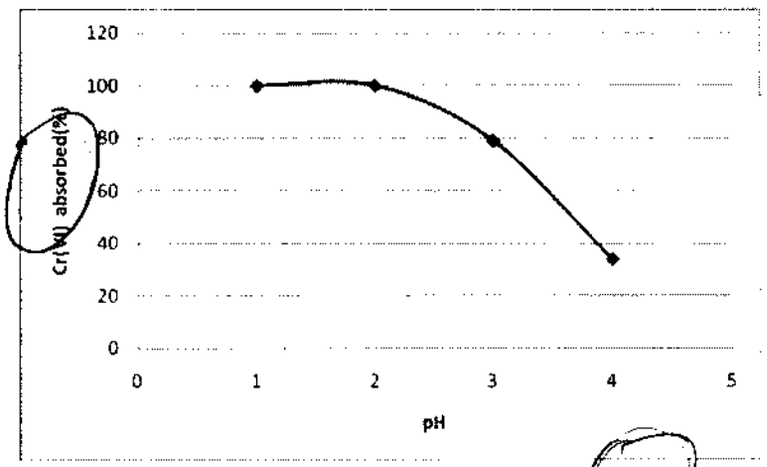

Figure 1. Effect of pH activation with Cr(VI) absorbed

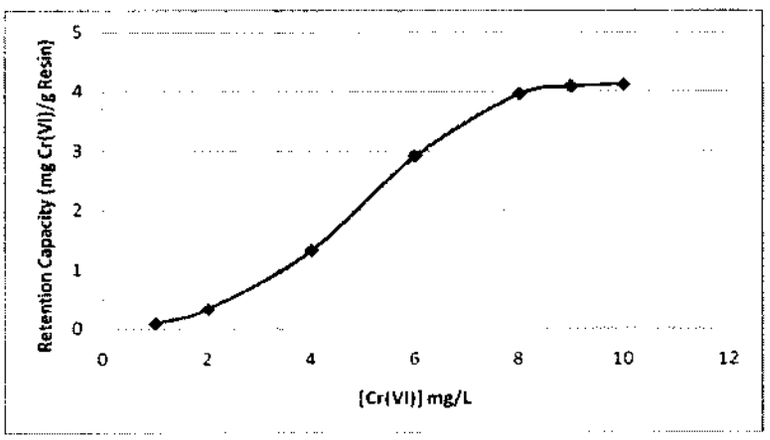

Figure 2. Retention capacity of acid alumina resin

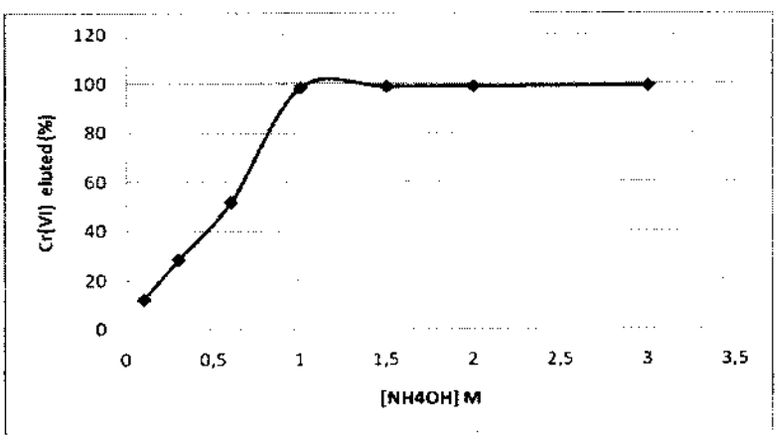

Figure 3. Effect of eluent concentration

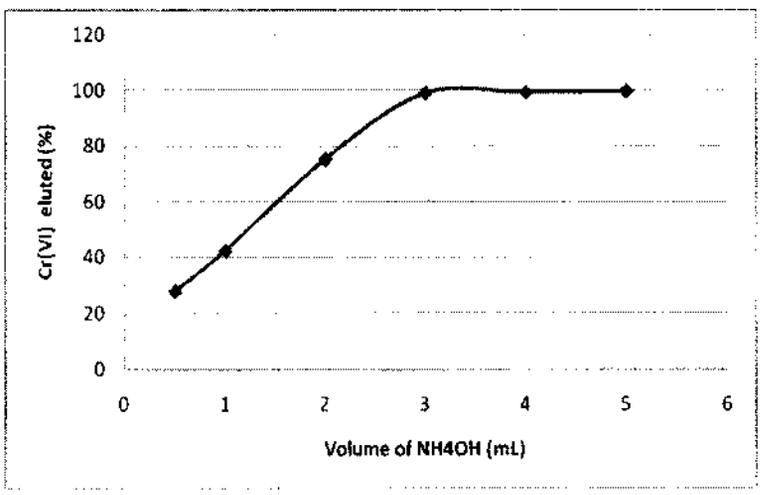

Figure 4. Effect of eluent volume

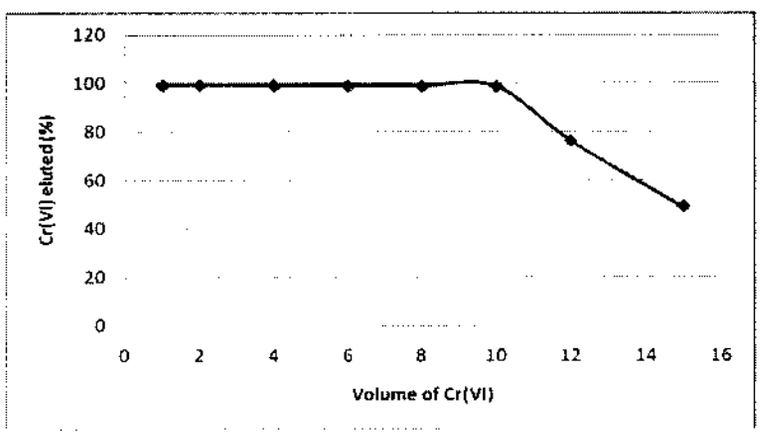

Figure 5. Effect of Cr(VI) volume

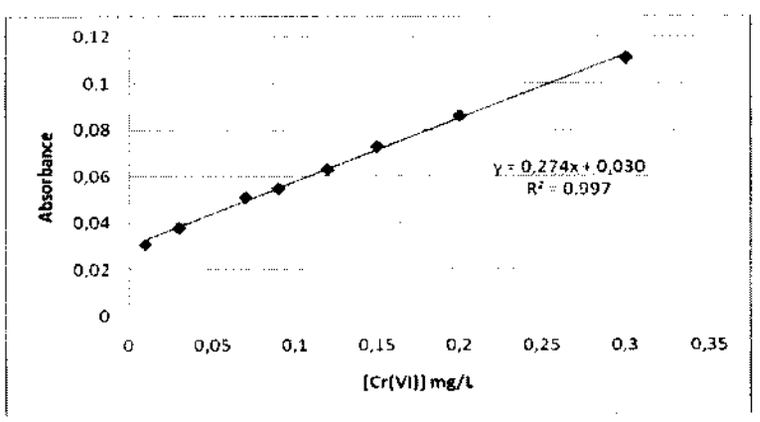

Figure 6. Calibration curve of Cr(VI)

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Yogyakarta, 21 January 2013

To:

Aman Sentosa Panggabean
Department of Chemistry FMIPA-University of Mulawarman, Samarinda-75119

Dear Sir,

This is to acknowledge and inform you that the paper entitles:

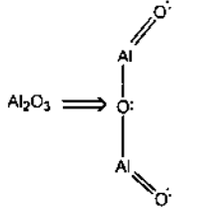
Preconcentration of Chromium(VI) at Trace Levels using Acid Alumina Resin with Column Method

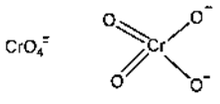
written by:

Aman Sentosa Panggabean, Subur P. Pasaribu, Bohari Yusuf, and Nurhasanah

has been reviewed and could be published in Indo. J. Chem. after major revision. The author should make some correction as follows:

Give explanation what/how is the interaction between alumina that is negative charge rich with the anion Cr[VI]





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PRECONCENTRATION OF CHROMIUM(VI) AT TRACE LEVELS USING ACID ALUMINA RESIN WITH COLUMN METHOD

ABSTRAK

Analisis runut ion Kromium(VI) menggunakan resin alumina asam sebagai material pengisi kolom dalam tahapan prakonsentrasi dengan metode off-line telah dilakukan. Resin alumina terlebih dahulu diaktivasi dengan H_2SO_4 pada pH 1 sebelum dimasukkan ke dalam kolom. Beberapa kondisi pengukuran yang optimum dalam tahapan prakonsentrasi telah dipelajari yaitu volume sampel adalah 10 mL, konsentrasi eluen NH_4OH adalah 1M dengan volume 3 mL. Hasil penelitian menunjukkan kapasitas retensi resin alumina asam adalah 3,955 mg Cr(VI)/g resin. Kinerja analitik pengukuran metode ini sangat baik, ditunjukkan dengan nilai batas deteksi adalah 3,648 µg/L. Kebolehulangan yang dinyatakan sebagai persentase koefisien variansi adalah 2,06%. Penggunaan alumina asam sebagai resin pengisi kolom dapat meningkatkan signal sebesar 15,36 kali dibandingkan dengan pengukuran ion Cr(VI) secara langsung. Akurasi metode ini sangat baik, dengan nilai persen perolehan kembali ≥ 95%, menunjukkan bahwa matriks sampel air tidak mempengaruhi hasil pengukuran, sehingga metode ini dapat digunakan untuk analisis ion Cr(VI) dalam sampel air pada tingkat runut.

Kata Kunci : Kromium(VI), Analisis runut, Prakonsentrasi, Alumina asam, Resin.

ABSTRACT

Trace analysis of Chromium(VI) ions using acid alumina resin as a filler material column in preconcentration system by off-line method has been carried out. Alumina resin was activated with H_2SO_4 at pH 1 before filled to the column. The optimal conditions of measurement in the preconcentration steps has been studied were 10 mL injection volume of waters samples, concentration of eluent NH_4OH was 1M and the volume was 3 mL. This research showed retention capacity of alumina acid resin was 3.955 mg Cr(VI)/g resin. The analytical performance of this method is good, shown with the limit of detection value was 3.648 µg/L. The reproducibility of this method shown as percentage of coefficient variance was 2.06 %. Acid alumina used as resin filler column can increase the signal up to 15.36 times for direct Cr(VI) ions measurement. The accuracy of this method is very good with the recovery percentage value > 95%, shown the matrices of water samples didn't effect the results of measurements and this method was capable to analyze Cr(VI) ions in water samples at the trace levels.

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INTRODUCTION

Chromium is a generally abundant element in the earths crust. It occurs in oxidation states ranging from Cr(II) to Cr(VI) but only Cr(III) (trivalent) and Cr(VI) (hexavalent) forms are biological significance. It has been proved that trace amounts of Cr(III) are necessary for mammalian health in order to maintain glucose, lipid and to perform protein metabolism. On the other hand, Cr(VI) can be toxic for biological systems, and water soluble Cr(VI) is extremely irritating and toxic to human body tissue owing to its high oxidizing potential and easy permeation of biological membranes [1]. Accumulation and inhalation of hexavalent chromium bearing substances lead to bronchitis, pneumonitis, asthma, nasal septum and inflammation of the larynx and liver and increased incidence of bronchogenic carcinoma. Mean-while, direct contact with these materials may cause dermatitis, dermal necrosis, skin allergies and dermal corrosion [2,3]. Cr(VI) and Cr(III) enter the environment in discharges from the steel, electroplating, leather tanning and wood-preservative industries. They may also enter the tap water supply from the corrosian inhibitors used in water pipes and containers. It is therefore important to determine the Cr(VI) quantity in environmental samples. However, Cr(VI) is normally present at very low concentrations, such as those found in natural water and seawater, where typical concentrations are in the 0.1–0.5 μg/L range [4,5].

In the analysis of trace metal ions present in various samples such as natural and waste water, biological and alloy samples, the direct determination with various instrumental methods is very difficult to be implemented, because the matrix effect and low concentration of metal ions in the sample. In trace analysis, therefore, a preconcentration and separation of trace elements from the matrix is frequently necessary to improve the detection limit and selectivity. The direct determination of chromium in water may not be possible with sufficient sensitivity by also expensive analytical methods such as inductively coupled plasma atomic emission spectrometry (ICP-AES) or electrothermal atomic absorption spectrometry (ETAAS) because of low concentrations and matrix interferences [6,7].

Preconcentration technique tools provide a solution to the limitations of the instrument in the determination of heavy metals at very low concentrations. Preconcentration steps by sorption technique does not only increases the concentration of the analyte but also can eliminate the matrix effects that can interfere in the process of analysis [8]. Preconcentration technique using cation exchange resins had advantages than other preconcentration, because the loss of analytes can be

minimized, the amount of resin used is only about 0.1 to 0.5 g, and can be regenerated so that they can be used repeatedly for the same analysis [9,10]. Preconcentration is a part of the preparation of an analysis and aims to raise the concentration of the samples in the range of the analytical measurement.

Many studies have been conducted for determination of Cr(VI) with the preconcentration technique using specific resin as a filler mini column are 1.5-diphenylcarbazone complex on amberlite XAD-16 resin [6], activated alumina for the selective species determination of Cr(III) and Cr(VI) in water samples based flow injection analysis with FAAS as a detector [11], melamine based polymeric sequestering succinic acid resin [12], Si-C_{18} [13], alumina-functionalized-isatin-thiosemicarbazone for speciation, extraction and preconcentration of Cr(III) and Cr(VI) based on dynamic and static solid phase extraction techniques [14], immobilization of 2,4-dinitrophenylhydrazine on nanoalumina coated with sodium dodecyl sulfate as a modifier material for the selective solid phase extraction of Pb(II) and Cr(III) from environmental and biological solutions [15], Microcolumn packed single-walled carbon nano-tubes were used as solid phase extraction adsorbent for chromium speciation coupled to ICP-MS for detection [16], and β-cyclodextrin-crosslinked polymer micro column for speciation of Chromium ion by using GFAAS [17], all of the method were using by on-line system. In this research, the preconcentration technique done using a column method (off-line system), has not been reported previously. This method is expected to be done in a simple laboratory because it requires only visible spectrophotometer as detector and can detect the presence of metal ions Cr(VI) at trace levels.

In this research, have been studied a several of conditions that affect the success of preconcentration Cr(VI) in a samples, are activation of pH alumina resin, retention capacity, analytical performance such as reproducibility, linearity, limit of detection and % recovery. The absorbance of Cr(VI) samples was determined by reaction with a 1.5-diphenylcarbazide (DPC) to form a red–violet complex and measured by using visible spectrophotometer as a detector.

METHODOLOGY EXPERIMENTAL METHOD

Instrumentation and Reagents

Instrumentation. Equipment used in this research are columns, glass equipment (E 'Merck), pH meter Orion model 420A, to determine the absorbance of Cr(VI) used visible spectrophotometer (Rayleigh Vis-7220G).

Reagents. The materials used in this research were Al_2O_3, $K_2Cr_2O_7$, $CrCl_3.6H_2O$, 1.5-diphenylcarbazide, H_2SO_4, HNO_3, HCl, H_3PO_4, CH_3COOH, NH_4OH, acetone, all reagents were of analytical-reagen grade (E'Merck), and aquabidest.

Effect of pH activation alumina resin

0.1 g of Al_2O_3 (alumina) soaked in the H_2SO_4 with variations of pH 1-4, and allowed for 24 hours, filtered and dried in the open air. 10 mL of Cr(VI) 0.5 mg/L is placed into a beaker glass containing acid alumina and stirred slowly, allowed for 2 hours, filtered, and then the absorbance of filtrate measured by using a visible spectrophotometer.

To determine the absorbance of Cr(VI), into the sample solution was added drops of 2N H_2SO_4 and H_3PO_4 to pH close to 1, added 1 mL of 0.1% 1.5 diphenylcarbazide. The sample solution was allowed for 10 minutes and the absorbance of sample were measured with a visible spectrophotometer at 540 nm.

Retention capacity

The batch method was used at this stage, 0.1 g of acid alumina resin soaked in 10 mL standard solution of Cr(VI) with variation in concentration of 1 - 10 mg/L at pH optimum conditions. Soaking carried out for 1 hour and measured the absorbance of Cr(VI) by using a visible spectrophotometer.

Optimization Preconcentration

Effect of eluent concentration

1 mL of Cr(VI) 1 mg/L placed into the column containing acid alumina resin. Cr(VI) ions retented were eluted with 2 mL of NH_4OH with various concentrations of 0.1 – 4.0 M. absorbance of the eluate was measured by visible spectrophotometer visible. From the measurement results will be obtained optimum concentration of NH_4OH as the eluent.

Effect of eluent volume

1 mL of Cr(VI) 1 mg/L placed into the column containing acid alumina resin. Cr(VI) retented was eluted with 2 mL of NH_4OH with variety of volumes 0.5 - 5 mL and absorbance of the eluate was measured by visible spectrophotometer.

Effect of Volume Cr(VI)

Into a column containing acid alumina, placed a standard solution of Cr(VI) 1 mg/L with a variety of volumes 1 - 10 mL. Cr(VI) retention was eluted with 2 mL NH_4OH at

optimum concentrations obtained and the absorbance was measured with visible spectrophotometer.

Analytical performance

Reproducibility

absorbance of the 25 µg/L Cr(VI) was measured as many times (n = 7) with the optimum conditions with the same procedure above.

Liniearity

absorbance of Cr(VI) in the range of variation of 10 - 300 µg/L was measured with the optimum conditions and the same procedure as above. Regression line equation was obtained by plotting absorbance vs concentration of Cr(VI).

Limit of Detection (LOD)

In this study the LOD was determined by measuring the absorbance of the concentration of Cr(VI) is the smallest that can be determined and distinguished from the blank absorbance measurements at several times. Detection limit is expressed as the ratio of the absorbance of the standard (S) against the blank (N) or (S/N) = 3.

Effect of species Cr (III)

To determine the effect of species of Cr(III) ~~to~~ on the measurement of Cr(VI), ~~made~~ measurements of a solution containing Cr(III) and Cr(VI) with a ratio of 1 : 1, the concentration of Cr(VI) is made ~~permanent~~ constant 1 mg/L and Cr(III) is ~~made~~ different from ~~the variation of~~ 1 - 5 mg/L. The mixture of species Cr(III) and Cr(VI) is passed into the column, Cr(VI) ~~retented~~ was retented at column, ~~eluted~~ was eluted with NH_4OH and the absorbance of eluats was measured using a visible spectrophotometer.

Determination of Samples

To determine the influence of matrix on the determination of Cr(VI) ions in water samples from nature, ~~done by~~ the spike method. In this method a certain ~~amount of~~ volumes of Cr(VI) were pipetted and diluted with the samples. The treatment is then performed with the optimum conditions and the absorbance was measured using a visible spectrophotometer.

RESULTS AND DISCUSSION

The determination of Cr(VI) is usually by using visible spectrophotometry after derivatisation with ~~a reagent such as~~ 1.5-diphenylcarbazide (DPC). The reaction of DPC is very selective for Cr(VI) so it can be performed directly without a separation

step. The chromate oxidizes DPC to diphenylcarbazone (DPCO) to form a soluble strongly red–violet compound with Cr(III) (Cr(III)-$DPCO^{(3-n)+}$). A large excess of DPC is essential as compounds present in the sample may consume the reagent [5].

Effect of pH activation alumina resin

Alumina is amphoteric resin, it must be activated in acidic conditions that can bind specifically to the Cr(VI) ion. Determination of optimum pH was aimed to obtain optimum conditions for the formation of chelates reaction, so the resin can thus be optimally absorb Cr(VI) ions. The result of measurements ~~are~~ is shown in Figure 1.

The measurement results show that the alumina resin can completely adsorb Cr(VI) at pH 1 and 2. It was caused by ~~the condition of~~ perfect activated ~~al~~ ion of alumina resin ~~can be perfectly,~~ so it can adsorb almost 100% Cr(VI) ion in the solution.This can be best explained by the sorption of the predominant species [$HCrO_4^-$] on the acidic alumina having a positive surface charge ~~under these conditions~~ [11]. When the pH above than 3, adsorption of Cr(VI) has not be optimal because the resin has not been activated alumina perfectly into acidic alumina.

Retention Capacity

One of the important fundamental value of which must be owned by resin is retention capacity to certain metal ion. Retention capacity is a quantity that indicates the ability of acid alumina resin to adsorb Cr(VI) ions. Determination of retention capacity of Cr(VI) performed at pH optimum with contact time during 1 hours.

Figure 2, that retention capacity obtained are 3.955 mg Cr(VI)/g alumina resin, means that for every 1 g of alumina resin can adsorb optimally 3.955 mg Cr(VI) ions. This value indicates the resin has a large adsorption capacity, so it can be used repeatedly to adsorb Cr(VI) ions and can be ~~used to~~ applied as filler material of column to preconcentration technique for determination of chromium in level trace.

Optimization Preconcentration

Effect of Eluent Concentration

Eluent is one important part in this research. Eluent is useful to remove the bound analyte on the resin. Effectiveness of the elution was affected by the type and concentration of eluent. NH_4OH was used as an eluent with a consideration of the elution process is expected that there is no damage resin in the column.

Figure 3. obtained, Cr(VI) ions completely eluted at NH_4OH concentrations above 1 M, whereas at the elution using concentration smaller than 0.5 M NH_4OH, the Cr(VI) ions retented in the column were eluted only 50%. The concentration of 1 M NH_4OH was used in the optimum concentration for further work.

Effect of Eluent Volume

The effect of the volume of NH_4OH eluent determined by varying the volume of eluent at the optimal concentration.

Figure 4. the greater the volume of eluent used to elution of the Cr(VI) ion retented in the resin, the greater the ion Cr(VI) was eluted. Elution using eluent volume above 3 mL shows the measurement results are not significantly different, this means that by using 3 mL eluent, Cr(VI) ions was completely eluted. The optimal volume of 1 M NH_4OH eluent obtained was 3 mL to be used for further work.

Effect of Cr(VI) Volume

The effect of Cr(VI) ions standard volume determined by varying the volume of standard samples whom entered to the column containing the acid alumina resin at the optimal volume and concentration of the eluent.

Figure 5. the optimum volume of the 1 mg/L Cr(VI) ion whom entered to 2 g of acid alumina resin was 10 mL. In the condition of standard samples volume above 10 mL, the resin has been saturated, Cr(VI) ions were passed into the column and not retented completely.

Analytical Performance

Reproducibility

The reproducibility of the method was examined under the optimum experimental conditions described above by using the model solution. Reproducibility level shown as percentage of the coefficient of variance (CV) value obtained from the seven measurement standard samples at the same condition. The result of measurement shows for the samples standard 25 µg/L Cr(VI), %CV value was 2.06 % . These results are good because the %CV was below 5% [18,19].

Linearity

Calibration curve was obtained by plotting concentration of Cr(VI) standard series with absorbance value. Absorbance data used for calibration curve is the absorbance of

standard solutions of Cr(VI) on preconcentration system using acid alumina resin. Based on the measurement results were obtained by the linear range at a concentration of 0.01 – 0.3 mg/L. Equation of the regression linear is y= 0.276x + 0.030 with correlation coefficient values (R) are good that is equal to 0.996.

Limit of Detection (LOD)

Detection limit is the concentration or mass minimum analyte that was detected with a high level of confidence. Detection limit is expressed as the ratio between the standard signal (S) of the blank signal (N) or S / N = 3. The result showed that preconcentration system was developed to give good results with the detection limit is 3.648 µg/L. LOD obtained in this research is good, because it is no different than using on line system using FAAS as a detector [11]. Preconcentration system developed can provide minimum mass measurements in the µg/L (ng levels).

Enrichment Factor (EF)

Enrichment factor, or often called the sensitivity of increase is done by comparing the absorbance of the ion Cr(VI) measured before and after preconcentration done. The determination of EF value is very important because it could illustrate the succes of the developed method. The greater EF value, the better of the developed method because can be used to determine samples at the trace levels. Based on the results of this research, the EF value is 15.36 times. This Mean that the developed method can increase the absorbance value 15.36 times than before preconcentration. The increase shows the Cr(VI) ion at trace concentrations can be detected using this method.

Effect of species Cr (III)

To determine the effect of species Cr(III) to the measurement of Cr(VI) was conducted by analysis of a solution containing Cr(III) and Cr(VI) with various comparisons. Table 1. shows the Cr(III) does not affect to the measurement of Cr(VI), because Cr(III) ion not retented at the acid alumina resin and directly out of the column with the carrier. Species of Cr(VI) was eluted with NH_4OH did not change significantly, it's mean acid alumina resin specific for Cr(VI).

Application to River Water Samples

The alumina acid resin has been employed for the preconcentration and analysis of Cr(VI) ion in river water samples. For that purpose, the procedure given was applied.

The result, which are shown in Table 2, have been calculated on the assumption of >95 % recovery od Cr(VI) ions. These data indicate that the accuracy of the method developed is very good and the water sample matrix does not effect on the measurement results [20].

CONCLUSION

Technique of preconcentration using acid alumina resin as a filler column for analysis of Cr(VI) ion at trace levels were obtained at the optimum condition of concentration of eluent was 1 M NH_4OH, volume eluent of NH_4OH was 3 ml, sample volume 10 mL and the retention capacity was 3.955 mg Cr(VI)/g acid alumina resin. Analytical performance obtained is very good shown with the reproducibility as percentages of coefficient variance was 2.06 %, limit of detection was 3.648 mg/L and the enrichment factor of resin was 15.36 times. Technique of preconcentration developed can be applied to determine the concentration of Cr(VI) in water samples, shown by the percentage recovery are >95%.

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Table 1. Effect of interfering Cr(III) ions

Comparisons of Cr(VI) and Cr(III) (1 mg/L)	Absorbance
1 : 1	0.296
1 : 2	0.294
1 : 3	0.294
1 : 4	0.292
1 : 5	0.291

Tabel 2. Result of determination of Cr(VI) ions in water samples

Sampel	Cr(VI), µg L^{-1}		Recovery %
	Added	Found	
R-01	0	75.36 ± 6.57	-
	100	182.24 ± 5.72	96.22 ± 0.67
R-02	0	36.44 ± 3.52	-
	25	62.18 ± 4.15	98.80 ± 0.52

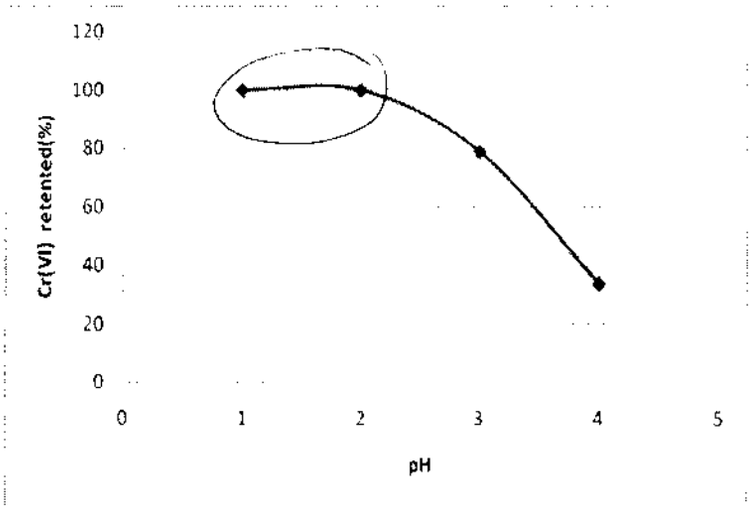

Figure 1. Effect of pH activation alumina resin

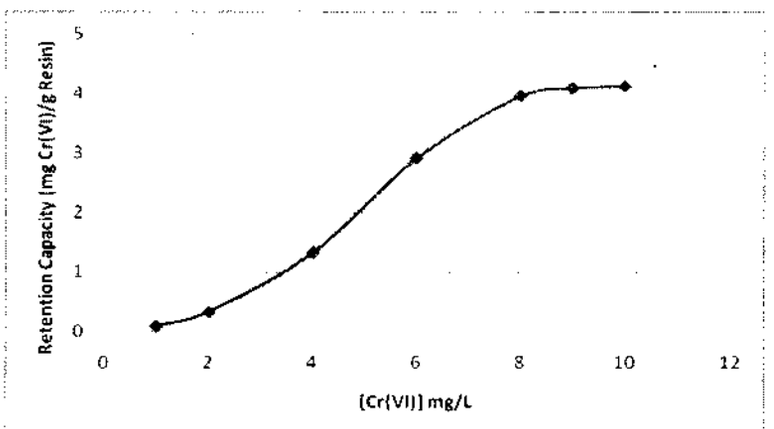

Figure 2. Retention capacity of acid alumina resin

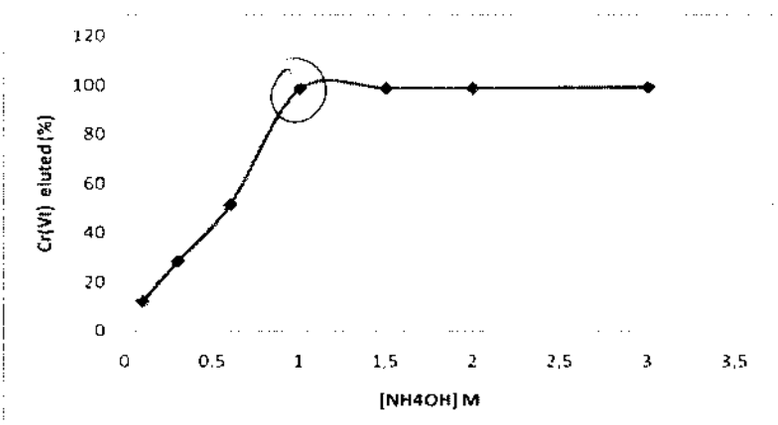

Figure 3. Effect of eluent concentration