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

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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 being filled to the column. 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 $\mu\text{g/L}$. 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.

Keywords: Chromium(VI); trace analysis; preconcentration; acid alumina; resin

ABSTRAK

Analisis runtu 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. 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 $\mu\text{g/L}$. Keboleholangan 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 runtu.

Kata Kunci: Kromium(VI); analisis runtu; prakonsentrasi; alumina asam; resin

INTRODUCTION

Chromium is a generally abundant element in the earth's 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 corrosion 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 $\mu\text{g/L}$ 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

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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 do not only increase 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-C18 [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.

EXPERIMENTAL SECTION

Materials

The materials used in this research were Al_2O_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, 1.5-diphenylcarbazide, H_2SO_4 , HNO_3 , HCl , H_3PO_4 , CH_3COOH , NH_4OH , acetone, all reagents were of analytical-reagent grade (E. Merck), and aquabidest.

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).

Procedure

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 h, 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 h, 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 2M 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 min 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 h 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

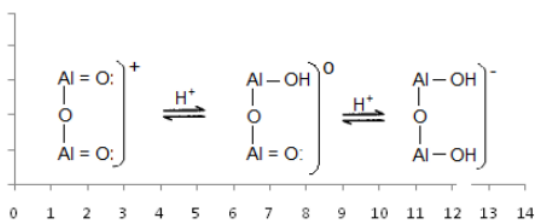


Fig 1. Surface charge of alumina in relationship to pH

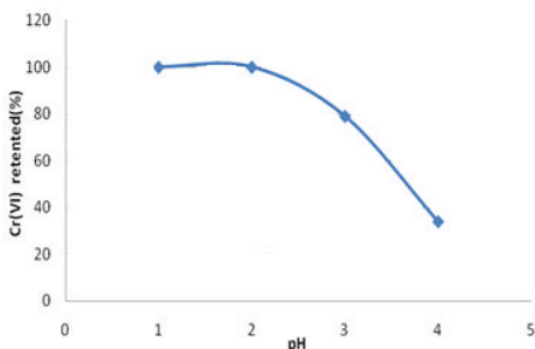


Fig 2. Effect of pH activation alumina resin

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) retained 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 $\mu\text{g/L}$ Cr(VI) was measured as many times ($n = 7$) with the optimum conditions with the same procedure above.

Linearity. Absorbance of Cr(VI) in the range of variation of 10-300 $\mu\text{g/L}$ 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) on the measurement of Cr(VI), was done measurements of a solution containing Cr(III) and Cr(VI) with a ratio of 1:1. The concentration of Cr(VI) is made constant 1 mg/L and Cr(III) is varied from the 1-5 mg/L. The mixture of species Cr(III) and Cr(VI) is passed into the column, then Cr(VI) was retained at column, was eluted with NH_4OH and the absorbance of eluates 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, the spike method was done. In this method a certain volume of Cr(VI) was pipetted and diluted with the samples. The treatment is then performed with the optimum conditions and the absorbance was measured using a visible spectrophotometer.

RESULT AND DISCUSSION

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

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. The method is based on the possibility of influencing the surface charge of activated alumina by conditioning through selection of the pH value of the buffer system (see Fig. 1). 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 is shown in Fig. 2.

The measurement results show that the alumina resin can completely adsorb Cr(VI) at pH 1 and 2. It was caused by perfect activation alumina resin, so it can adsorb almost 100% Cr(VI) ion in the solution. High adsorption of Cr(VI) at acidic pH can be explained by the species of the Cr and the adsorbent surface. At acidic pH, the predominant species of Cr are $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_4\text{O}_{13}^{2-}$ and above pH 8, only CrO_4^{2-} is stable. On the under acidic conditions, the surface of the adsorbent becomes highly protonated and

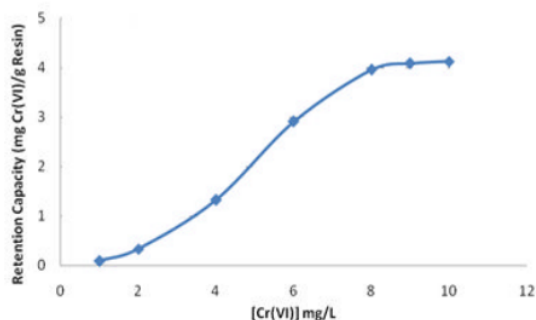


Fig 3. Retention capacity of acid alumina resin

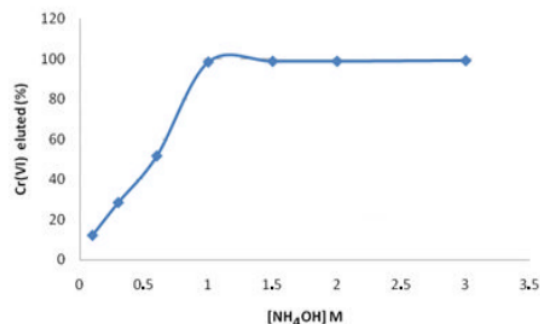


Fig 4. Effect of eluent concentration

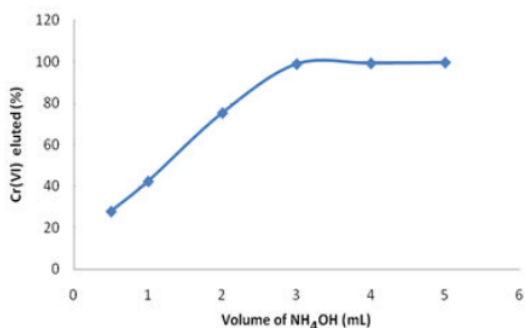


Fig 5. Effect of eluent volume

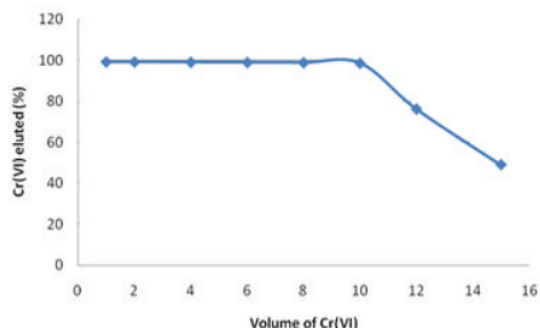


Fig 6. Effect of Cr(VI) volume

favors the uptake of Cr(VI) in the anionic form. With increase in pH, the degree of protonation of the surface reduces gradually and hence adsorption is decreased [11,18]. When the pH above than 3, adsorption of Cr(VI) has not be an optimal because the resin has not been activated 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 h.

Fig. 3, 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 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. NH₄OH was used as an eluent with a consideration of the elution process is expected that there is no damage resin in the column.

Fig. 4 obtained, Cr(VI) ions completely eluted at NH₄OH concentrations above 1 M, whereas at the elution using concentration smaller than 0.5 M NH₄OH, the Cr(VI) ions retained in the column were eluted only 50%. The concentration of 1 M NH₄OH was used in the optimum concentration for further work.

Effect of eluent volume

The effect of the volume of NH₄OH eluent determined by varying the volume of eluent at the optimal concentration.

Fig. 5 the greater the volume of eluent used to elution of the Cr(VI) ion retained in the resin, the greater the ion Cr(VI) was eluted. Elution using eluent

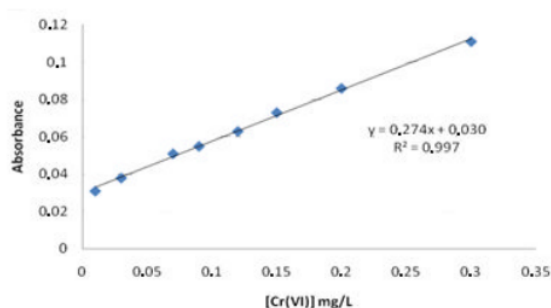


Fig 7. Calibration curve of Cr(VI)

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

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

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

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.

Fig. 6 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 retained 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 $\mu\text{g/L}$ Cr(VI), %CV value was 2.06%. These results are good because the %CV was below 5% [19-20].

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 (Fig. 7).

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 $\mu\text{g/L}$. 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 $\mu\text{g/L}$ (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 success 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 means 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 retained 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 of 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 [21].

CONCLUSION

Technique of preconcentration using acid alumina resin as a filler column for analysis of Cr(VI) ion at trace levels reached the optimum condition that are 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. The analytical performance obtained is very good shown with the reproducibility as percentages of coefficient variance that was 2.06%, limit of detection was 3.648 mg/L and the enrichment factor of resin was 15.36 times. The 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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