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The Separation and Determination of Chromium(VI) by Reducing Elution Using Anion Exchange Resin and Sodium Sulfite

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Synopsis. The reducing elution of chromium(VI) by anion exchange using sodium sulfite has been investigated. Chromium(VI) is reduced to chromium(III), which is eluted quickly and easily separated from interfering substances by colorimetry using diphenylcarbazide.

The contamination of an environment by heavy metals has become of interest in recent years. The standards of the content of total and hexavalent chromium for industrial waste water have been established by the Government.

Generally, chromium is determined by atomic absorption spectrophotometry$^{1)}$ after extraction with MIBK. A simple determination as of JIS can be carried out by spectrophotometry using diphenylcarbazide, but this method necessitates the separation of chromium (VI) to prevent the interference of some metals and that of reducing substances.

Already, several separation methods of chromium such as precipitation by oxidation in basic media$^{2)}$ and solvent extraction$^{3)}$ using diethyldithiocarbamate, have been reported. However, it is imposible to determine only chromium (VI) using diphenylcarbazide after separating chromium by these methods. Also, the separation by cation exchange using acetate as the eluent$^{4)}$ and that by anion exchange using mixed salts of thiocyanate and chloride as the eluent$^{5)}$ are known.

However, these separation methods are not suitable for spectrophotometry using diphenylcarbazide.

The present authors examined the method of the separation of chromium (VI) by ion exchange, which is suitable for spectrophotometry using diphenylcarbazide. As a consequence of their experiments, the method of ion exchange using mixed solution of sulfuric acid and sodium sulfite as the eluent was found to be suitable for this purpose.

Experimental

A column 0.8 cm in diameter and 10 cm in length was loaded with 5.0 ml of 100—200 mesh Dowex 1X8(hydroxide form).

A Hitachi model 101 spectrophotometer was used for the determination of chromium(VI).

A reagent of a special grade was used without purification.

The elution curves were made of the metal content per 10 ml fraction of the eluate, after demasking by boiling, oxidizing to chromium(VI) and coloring.

Results and Discussion

Concentration of Sulfuric Acid and Sodium Sulfite. The following experiments were performed. Chromium(VI) absorbed on the column of anion-exchange resin is eluted with the mixed solution of sulfuric acid and sodium sulfite. The excess of sulfite in the effluent is decomposed by boiling it for 20 min. The process of adding 2 or 3 drops of 0.3% potassium permanganate solution to the solution and of then boiling it for 5 min is rereated until the color of permanganate is only. After subsequent cooling, 10-ml portion of 20% urea solution is added to 100 ml of the sample solution. Then a 10% sodium nitrate solution is added to the sample solution until the color of the permanganate disappears. Finally, diphenylcarbazide is added to the solution for colorimetry.

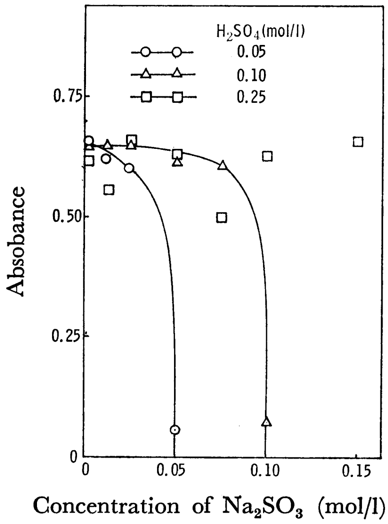

Fig. 1. Effects of concentration of H_2SO_4 and Na_2SO_3 on coloring.

In the above-mentioned experiments, we examined how the concentrations of sulfuric acid and sodium sulfite affected the absorbance. The results are shown in Fig. 1. For instance, when a mixed solution of 0.05 M sulfuric acid and 0.005 M sodium sulfite is used, the absorbance per ppm of chromium (VI) was 0.65, while in the case of 0.05 M sulfuric acid and 0.025 M sodium sulfite, the absorbance of the solution containing one ppm of chromium (VI) was 0.61. This means that, when more than 0.025 M sodium sulfite and 0.05 M sulfuric acid are used, sulfite remains after 20 minutes' boiling and so excess of permanganate has to be added in order to decompose the sulfite. As a result of this, the acidity in the sample solution falls and the absorbance lowered.

The tendency for the absorbance to be lowered is observed when more than 0.075 M sodium sulfite and 0.1 M sulfuric acid are used. Also, when more than

0.25 M sulfuric acid is used, the absorbance varies irregularly. Therefore it was concluded that the concentration of sulfuric acid should be 0.1 M while that of sodium sulfite in an eluent should be between 0.02 M and 0.005 M.

Elution of Chromium (VI) by the Mixed Solution of Sulfuric Acid and Sodium Sulfite. It was found that the direct addition of a mixed eluent leads to uncertain the elution curves, caused by foam generated by the neutralization heat which is brought about by the reaction of hydroxide in resin with sulfuric acid. Therefore, before the elution of chromium, hydroxide in resin was neutralized by introducing 0.1 M sulfuric acid, and then the chromium (VI) was eluted with a mixed solution of sulfuric acid and sulfite.

The metal content in a 10-ml fraction was determined by spectrophotometry using diphenylcarbazide after oxidation by the above-mentioned treatments. The results are shown in Fig. 2. In the first 50-ml effluent eluted by 0.1 M sulfuric acid alone, a slight amount of chromium was contained, but most of the chromium was contained in the next 200-ml fraction, obtained, using the eluent in which more than 0.01 M of sodium sulfite and more than 0.1 M of sulfuric acid were present.

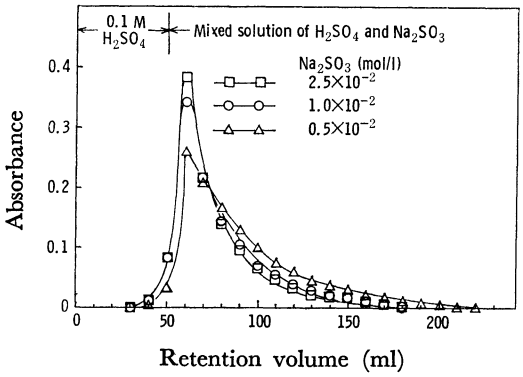

Fig. 2. Elution curves of Cr(VI), using mixed solution of H_2SO_4 and Na_2SO_3.

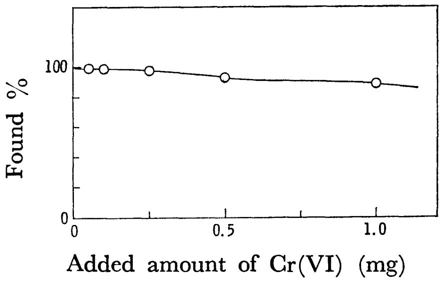

Fig. 3. Relation between found% and added amount.

Table 1. Determination of chromium(VI)[a)]

Diverse subs.	ppm of diverse subs.	Cr(VI) ppm, found[b)]	Cr(VI) ppm, found[c)]
Fe^{+++}	0.5	0.48	0.45
Fe^{+++}	5.0	0.45	0.39
Zn^{++}	0.5	0.50	0.55
Pb^{++}	0.5	0.49	0.50
Cu^{++}	0.5	0.48	0.49
Cd^{++}	0.5	0.49	0.55
HCHO	1%	0.49	0.33
waste water	BOD 50 ppm	0.49	not detected

a) 0.5 ppm Cr(VI), added. b) After the separation. c) By JIS.

When various quantities of chromium were added to the column and eluted by the same procedure, the found %, that is, the quantity of chromium in the effluent to that of the added chromium is as shown in Fig. 3. If less than 0.1 mg of chromium is used, most of the chromium is found in the first 250-ml effluent.

Effects of Diverse Substances. A 100-ml fraction of a solution containing 0.5 ppm chromium and various metals or reducing substances was introduced into the column. The chromium, separated by the above-mentioned treatment using 50 ml of sulfuric acid and 200 ml of the solution of 0.1 M sulfuric acid and 0.01 M sodium sulfite, was determined by spectrophotometry using diphenylcarbazide. The results are shown in Table 1 along with those obtained by determination by JIS. The reaction is interfered with by iron, zinc, and cadmium, and much by reducing substances. Especially, in BOD 50 ppm of industrial waste water, no chromium was detected, while chromium could be precisely analysed when this separation method was used.

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