2878 © 1980 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 53, 2878—2880 (1980) [Vol. 53, No. 10

Enrichment and Spectrophotometric Determination of a Trace Amount of Chromium(VI) as the Diphenylcarbazide Complex on a Mixed Resin Prepared from Finely Divided Anion and Cation Exchangers

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(Received April 15, 1980)

A rapid and sensitive method has been developed for the determination of a trace amount of chromium(VI). It is based on the pre-concentration of chromium(VI) as the diphenylcarbazide (DPC) complex on a mixed resin prepared from finely divided anion and cation exchangers and the subsequent measurement of absorbance of the resin phase after collection on a filter paper as a uniform thin layer. The sensitivity of the method is approximately 100 times higher than the ordinary solution method using 1-cm cell. The extraction of chromium(VI) with tributyl phosphate followed by back extraction into water is effective for reducing the influence of interfering ions.

Analytical utilization of a resin mixture of finely divided anion and cation exchangers, the diameter being smaller than 30 μm, has been reported. Rapid and selective enrichment of trace amounts of copper(II)[1)] and manganese(II)[2)] on the mixed resin were carried out by batch method in the presence of 8-hydroxy-5-quinolinesulfonate and 4-(2-pyridylazo)resorcinol, respectively. The ions on the resin were then eluted and determined by atomic absorption spectrometry.

Yoshimura *et al.* reported ion-exchanger colorimetry[3,4)] based on the pre-concentration of metal complex with negative or positive charge on respective ion exchanger ranging 200—400 mesh, and the subsequent measurement of the absorbance of the complex in the resin phase after transferring a part of the resin into a cell of 0.1 cm in thickness. The method has been successfully applied to the determination of chromium[5)] and zinc[6)] in water.

This article deals with a new method of ion-exchanger colorimetry[7)] for chromium(VI) by means of the combined use of DPC and a mixture of finely divided anion and cation exchangers. Finely divided cation exchanger collects chromium(VI)–DPC complex rapidly by the batch method in combination with anion exchanger to form a bulky material. The coagulated resin is then separated by filtration and the resulting thin layer of the colored resin on a filter paper is directly subjected to spectrophotometric measurement.

Experimental

Reagents. A stock solution of chromium(VI) (0.5 mg/ml) was prepared by dissolving 1.415 g of analytical grade potassium dichromate in one liter of water. The solution was diluted to give 0.1 μg per ml of chromium(VI) immediately before use.

Diphenylcarbazide was used in a 0.4 (w/v)% acetone–water (1 : 1) solution, a fresh solution being made each day.

Synthetic sea water was prepared according to JIS K 2510-1971.[8)]

Tributyl phosphate (TBP) saturated with 0.1 M (1 M=1 mol dm^{-3}) hydrochloric acid was used. A 150-ml portion of the ester was shaken with 50 ml of the synthetic sea water containing 0.1 M hydrochloric acid.

Ion Exchange Resin. Macroreticular type Amberlyst 15 and A-26 (both Rohm and Haas Co.) in RSO_3H and $RN(CH_3)_3Cl$ forms, respectively, were used. Suspension of the resins was prepared according to the method reported.[1)] The stock suspension was stirred immediately before being pipetted off.

General Procedure. A 100-ml aliquot of the solution containing less than 1.0 μg of chromium(VI) was taken into a separatory funnel, and then 10 ml of 0.1 M sulfuric acid, 3.0 ml of anionic resin suspension (ARS), 1.0 ml of cationic resin suspension (CRS) and finally 1.0 ml of 0.4% DPC solution were added. The mixture was then shaken for 12 min and the resulting coagulated material was collected onto a filter paper (Toyo Roshi No. 5A) placed on a holder. A disk of colored resin of 17 mm diameter and about 0.3 mm in thickness was obtained. The filter strip was dipped into a dilute acetate buffer solution of pH 4.8 for 10 s in order to stabilize the coloration. Another disk of resin was prepared without addition of chromium(VI) and used as a reference. The filter strips were fixed on the glass plate and the absorbances were measured at 550 and 700 nm, the absorption maximum lying at the former wavelength and the complex having no absorption at the latter. The net absorbance was obtained by the difference.

Results and Discussion

Determination of Exchange Capacity. The ion exchange capacity of the resin in the suspension was determined by conductometric titration. A known amount of CRS and ARS was titrated with the standard solution of sodium hydroxide and silver nitrate, respectively. In both cases inverse L-shaped titration curves were obtained. The exchange capacities were 13.3×10^{-3} meq ml^{-1} for CRS and 7.22×10^{-3} meq ml^{-1} for ARS.

Coagulation. The mutual coagulation of the finely divided anion and cation exchangers was examined according to the method reported.[1)] The 1.0-ml portion of CRS was most satisfactorily deposited from the solution with addition of 3.0 ml of ARS.

Exchange Capacity of the Coagulated Resin. The number of ion exchange sites consumed for the association of 3.0 ml of CRS with 9.0 ml of ARS was estimated by determining the hydrogen ion expelled from the cationic exchanger as a result of mutual coagulation. The proportions of the ion exchange sites taking part in coagulation to the total ion exchange sites in CRS and ARS were found to be 11.8% and 14.1%, respectively. The remaining sites are effective to fix cation or anion in the solution.

Shaking Time. During the course of shaking, the cationic chromium(VI)-DPC complex is fixed on the cationic exchanger, the latter combining with anionic exchanger to form coagulated material. A constant and maximum recovery was achieved in the shaking period of 12—16 min. With prolonged shaking, the absorbance decreased slightly.

Preparation of Thin Layer. The colored coagulated material was collected onto a filter paper placed on a holder and washed with a small amount of water. The rate of filtration was about 40 ml min^{-1} with suction. At the end of washing, the suction should be stopped in order to avoid the formation of cracks in the resin phase.

Stability of the Coloration. The resin was stored wet by dipping the end of filter paper in water. The absorbance of the complex was reduced by *ca.* 4% after 30 min. When the resin was soaked for 10 s in a dilute acetate buffer solution immediately after filtration, the coloration being stable at least for 30 min. However, in the presence of a large amount of magnesium the color based on magnesium–DPC complex developed after long immersion in the acetate buffer solution. The absorbance should be measured as soon as possible.

Absorption Measurement. The thin layers of sample and reference together with filter paper were fixed with water on a glass plate fitted directly to the window of detector. The absorbance was measured with the slit width of 2.5 mm. The chromium(VI)-DPC complex in the resin phase has the absorption maximum at 550 nm. The absorbance is given by

$$A = A_{\mathrm{RC}} + (A_{\mathrm{B,s}} - A_{\mathrm{B,r}}),$$

where A_{RC} denotes the absorbance of the complex in the resin phase and $A_{\mathrm{B,s}}$ and $A_{\mathrm{B,r}}$ denote the background absorption of the sample and reference, respectively, which are caused by the resin phase, the filter paper and the glass plate. The difference in the background absorption is estimated from the absorbance at 700 nm where the complex has no absorption. Consequently, the net absorbance of chromium(VI)–DPC complex is given by the difference in measurement at 500 nm and 700 nm.

Calibration Curve. The calibration curve deviates slightly from proportionality (Fig. 1). The relative standard deviation was 2.1% (n=6) for 1 μg of chromium(VI) and 3.3% (n=5) for 0.4 μg. The absorbance of thin layer prepared from the 100 ml of solution containing 1 μg chromium(VI) is almost the same as that for 1 ppm chromium(VI)–DPC solution in 1-cm cell. The sensitivity of the present method is approximately 100 times higher than the ordinary solution method.[9]

Sample Volume. A 1-μg portion of chromium(VI) was recovered effectively from 100—400 ml of sample solution (Fig. 2). The lower absorbance was measured with a disk prepared from 50 ml of sample solution, the reason for which is not yet clear but the result was reproducible.

Divers Ions. Effects of sodium chloride and calcium chloride examined are shown in Fig. 3. The recovery of chromium(VI)-DPC complex decreased considerably with the addition of calcium chloride, which is attributable to the competition between cations of chromium(VI)-DPC complex and calcium ion for cation exchange sites in the mixed resin. The effects of other cations are given in Table 1. Chromium-

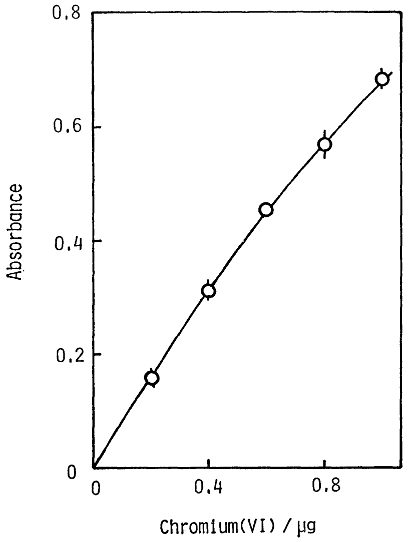

Fig. 1. Calibration curve of chromium(VI) as the complex with diphenylcarbazide. Sample volume: 100 ml. The vertical line on each plot denotes 95% confidence interval.

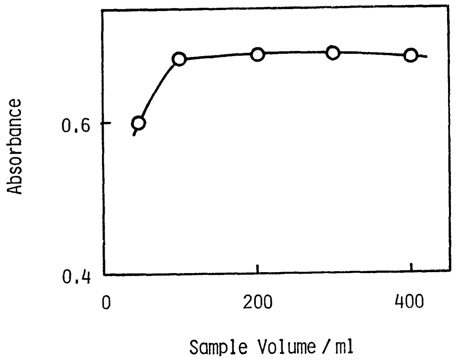

Fig. 2. The recovery of 1-μg portion of chromium(VI) from varying amounts of solution onto a coagulated resin prepared from 3.0 ml of ARS and 1.0 ml of CRS.

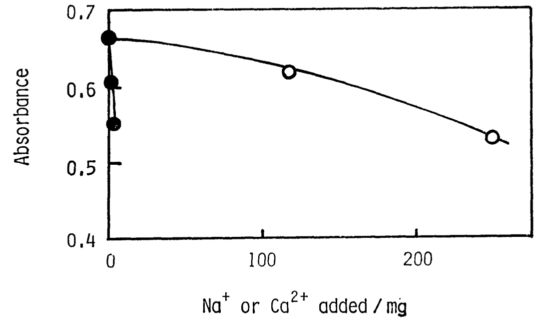

Fig. 3. Effect of sodium (○) and calcium (●) ions on the recovery of chromium(VI)-DPC complex onto a coagulated resin prepared from 3.0 ml of ARS and 1.0 ml of CRS. Amount of chromium(VI): 1.0 μg.

Table 1. Effect of foreign ions

Ions	Added as	Ratio to 0.5 μg of chromium(VI)[a]		
		40	200	400
		Relative error (%)		
Fe(III)	nitrate	−6.4	−14.5	−17.4
Cu(II)	sulfate	−8.2	−14.2	−18.6
Al(III)	nitrate	+6.8	−1.5	−11.8
Zn(II)	chloride	+7.0	+3.6	+9.4
Pb(II)	acetate	+3.1	+8.0	+9.4
Cd(II)	nitrate	+6.3	+11.6	+3.4
Cr(III)	chloride	+6.5	+14.7	+15.9

a) Sample amount: 100 ml

Table 2. Recovery of chromium(VI) from synthetic sample solution

Composition	Absorbance	r.s.d.(n) (%)	Recovery[a] (%)
A: 100 ml of saline water[b]	0.000		0.0
B: A+Cr(VI) 0.4 μg	0.298	3.1(2)	96.2
C: A+Cr(VI) 0.5 μg	0.361	3.5(4)	94.9
D: A+Cr(VI) 0.6 μg	0.428	2.0(2)	94.8
E: A+Cr(VI) 0.8 μg	0.543	1.0(3)	95.6
F: C+Cr(III) 100 μg+Zn(II) 100 μg +Al(III) 100 μg+Pb(II) 100 μg +Cd(II) 100 μg	0.375	4.8(8)	98.6
G: F+Fe(III) 50 μg+Cu(II) 20 μg	0.348	3.7(5)	91.5

a) Calculated from the calibration curve in Fig. 1.
b) The sample was prepared according to JIS K 2510-1971. The components (g/l) were: NaCl 24.54, $MgCl_2 \cdot 6H_2O$ 11.10, Na_2SO_4 4.09, $CaCl_2$ 1.16, KCl 0.69, $NaHCO_3$ 0.20, KBr 0.10, H_3BO_3 0.03, $SrCl_2 \cdot 6H_2O$ 0.04, NaF 0.003.

(III), cadmium(II), lead(II), and zinc(II) have a tendency to give a positive error, iron(III), copper(II), and aluminum(III) a negative error.

Extraction of Chromium(VI) with TBP. The extraction of chromium(VI) with tributyl phosphate[10,11] was examined with synthetic sea water. General procedure is as follows: A 100-ml portion of the synthetic sea water containing less than 1 μg of chromium(VI) was mixed with 5 ml of 2 M hydrochloric acid. The solution was then shaken with 20 ml of TBP for about 3 min. Chromium(VI) in the organic phase was stripped first with 30 ml of water for 3 min and subsequently 10 ml of water for 3 min. The two aqueous phases were combined. The final sample volume was adjusted to 100 ml by addition of water, chromium(VI) being determined by the method stated above.

Chromium(VI) was most effectively extracted from 0.06—0.14 M hydrochloric acid into TBP by shaking for 2—5 min. Rapid phase separation was attained with use of 30 ml of water for the first stripping and 10 ml of water for the second stripping. Greater amount of water has no advantage.

The TBP extraction was effective to eliminate the influence of divers ions (Table 2). About 95% of chromium(VI) is recovered by the extraction-stripping procedure.

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