Enrichment of a Trace Amount of Manganese by the Mixed Resin Prepared from Finely Divided Anion and Cation Exchangers in the Presence of 4-(2-Pyridylazo)resorcinol

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The enrichment of a trace amount of manganese(II) from sample water was carried out by the combined use of a mixture of finely divided cation and anion exchangers and 4-(2-pyridylazo)resorcinol (PAR). Manganese–PAR complex was effectively collected onto the mixed resin by batch method in the pH range 9.1—10.2. The manganese on the mixed resin was eluted into hydrochloric acid solution, extracted with 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (BMPP) into MIBK and determined by atomic absorption spectrometry. The recovery of 3 μg of manganese from the synthetic sample solution (100—500 ml) was in the range 95—97%.

Recently we reported an analytical utilization of a resin mixture of finely divided anion and cation exchangers, the diameter being smaller than 30 μm.[1] A trace amount of copper(II) in a sample water was concentrated on the mixed resin as the complex with 8-hydroxy-5-quinolinesulfonate and determined by atomic absorption spectrometry. This paper describes some preliminary results with the enrichment of manganese(II) by the combined use of the mixed resins with PAR. The compounds BMPP and 4-cinnamoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (CMPP) were examined as the reagents for the solvent extraction-atomic absorption spectrometric determination of manganese.

Experimental

Reagents. Stock solution of manganese(II) (1.0 g l^{-1}, pH=1) was prepared by dissolving the chloride into hydrochloric acid solution and its factor was determined by titration with EDTA. The Dotite PAR (Dojindo Co.) was used without further purification. Fifty milligrams of the reagent were dissolved into 3 ml of 0.1% sodium hydroxide solution and diluted to 100 ml. The reagents BMPP and CMPP were synthesized from 3-methyl-1-phenyl-5-pyrazolone and benzoyl chloride or cinnamoyl chloride (Wako Chemicals Co.) according to the method of Jensen.[2] The former BMPP was recrystallized twice from methanol. The results of elemental analysis were: Found: C, 73.1; H, 5.0; N, 10.1; O, 11.8%. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.4; H, 5.0; N, 10.1; O, 11.5%. The latter CMPP was recrystallized twice from acetone. The results of elemental analysis were: Found: C, 75.0; H, 5.2; N, 9.1; O, 10.7%. Calcd for $C_{19}H_{16}N_2O_2$: C, 75.0; H, 5.3; N, 9.2; O, 10.5%. Solutions of 5×10^{-2} M (mol dm^{-3}) BMPP and CMPP were prepared by dissolving each acid in alkaline solution, the final solution being neutral.

The resin mixture was prepared by mixing suspension of cation exchanger (CRS) with that of anion exchanger (ARS) in the volume ratio of 1 to 1.6. The exchange capacities were 0.031 meq ml^{-1} for CRS and 0.030 meq ml^{-1} for ARS as reported previously.[1]

Apparatus. A Hitachi 508 atomic absorption spectrometer with a Fe–Co–Ni–Cu–Cr–Mn multielement hollow cathode lamp was used for the determination of manganese in MIBK extract under the following conditions: wavelength 279.5 nm, lamp current 10 mA, slit width 0.18 mm, acetylene flow rate 1.5 l min^{-1} and air flow rate 13 l min^{-1}. A Toyo KG 25 filter holder (Toyo Roshi Co.) was used.

General Procedure. An aliquot of sample solution (40—500 ml) containing 3 μg of manganese(II) is taken into a separatory funnel, 1.0 ml of 0.05% PAR solution being added. The solution pH was adjusted to *ca.* 9.6 with the addition of 2 M ammonia–ammonium chloride buffer solution. A 1.0-ml portion of CRS and 1.6 ml of ARS are then added to the sample solution. After shaking for 10 min the mixture is allowed to stand for several minutes until the coagulated resin settles. The mixed resin is separated by filtration with suction from the solution onto a filter paper (Toyo Roshi No. 1). The manganese species on the resin are then eluted with 20 ml of 0.5 M hydrochloric acid into another separatory funnel. The pH of the solution being adjusted to *ca.* 7.3 with 10 ml of 1 M potassium phosphate, 2.5 ml of 0.05 M BMPP are added. The resulting manganese–BMPP complex is extracted into 5.0 ml of MIBK and the organic extract is then subjected to atomic absorption spectrometry. The absorption is corrected from the blank value observed throughout the whole procedure.

Results and Discussion

Effect of PAR. Manganese(II) reacts with PAR to form a water soluble red complex in alkaline solution.[3] The negative logarithms of acid dissociation constants of the pyridine nitrogen, *p*-hydroxyl, and *o*-hydroxyl groups in the PAR molecule are reported to be 2.3, 12.4, and 6.9, respectively.[4] In the alkaline solution, the manganese complex is expected to be present as mono- or divalent anionic species, which is fixed onto the cationic site in the mixed resin.

The effect of PAR on the recovery of manganese was studied in the presence of varying amounts of calcium and chloride ions which are most commonly present in natural water. The optimal pH range was found to be 9.1—10.2 (Fig. 1), which is comparable to the result observed in the spectrophotometric determination of manganese with PAR.[5]

In the presence of 2.3 μmol of PAR, 3 μg of manganese was effectively collected from 40 ml of a calcium chloride solution containing even 50 mg of calcium ion (Fig. 2). In the absence of PAR, the amount of non-fixed manganese increased when the amount of calcium ion increased beyond the exchange capacity of cation exchanger in the mixed resin.

Manganese on the resin was quantitatively eluted with 20 ml of 0.5 M hydrochloric acid.

Extraction of Manganese with BMPP and CMPP. Determination of manganese in the eluate was carried out by using solvent extraction followed by atomic

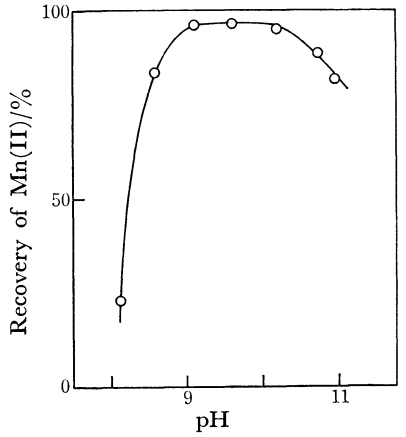

Fig. 1. Effect of pH on the recovery of 3.0 μg of manganese(II) from 40 ml of solutions containing 20 mg of calcium ion and 2.3 μmol of PAR onto the coagulated resin prepared from 1.0 ml of CRS and 1.6 ml of ARS. Buffer solution: NH_3–NH_4Cl, ionic strength: 0.1 (NaCl).

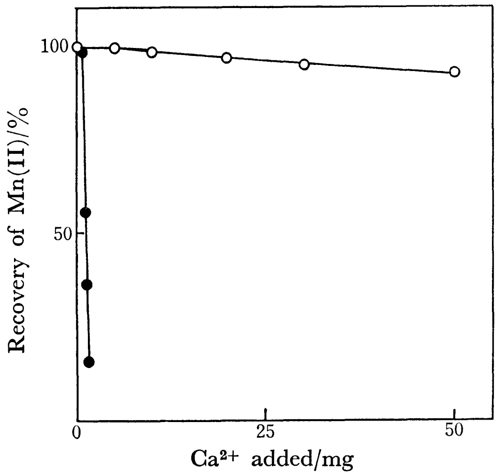

Fig. 2. Recovery of 3.0 μg of manganese(II) from 40 ml of solutions containing varying amounts of calcium chloride in the presence (○) and absence (●) of 2.3 μmol of PAR. ●: Unbuffered, ○: pH 9.6 (ammonia buffer), ionic strength 0.1 (NaCl).

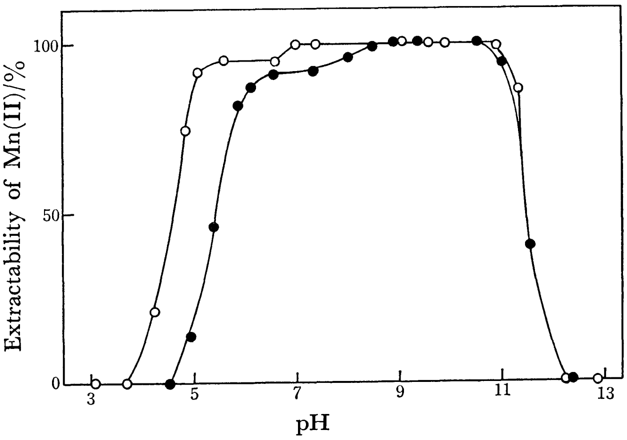

Fig. 3. Effect of pH on the extractability of manganese complex with BMPP (○) and CMPP (●) into MIBK. Solution pH is adjusted with Britton-Robinson buffer solution. Mn 3 μg, ionic strength 0.16 (NaCl), aqueous volume 50 ml, MIBK 5 ml.

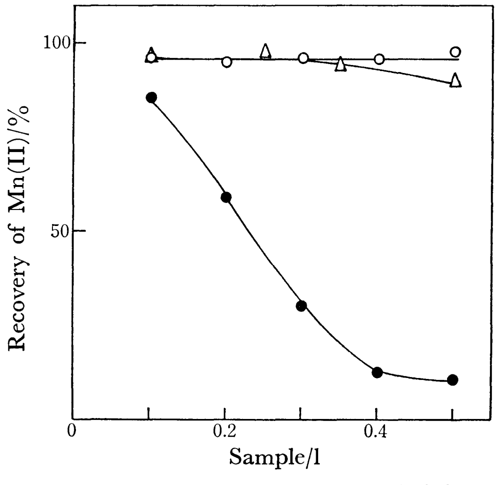

Fig. 4. Recovery of 3 μg of manganese(II) from varying amounts of synthetic sample solution (the composition is found in the text). ●: CRS 1.0 ml, ARS 1.6 ml, PAR 2.3 μmol; △: CRS 2.5 ml, ARS 4.0 ml, PAR 11.5 μmol; ○: CRS 2.5 ml, ARS 4.0 ml, PAR 46 μmol.

absorption spectrometry. The sensitivity of the AAS determination of manganese is enhanced when the organic extract is subjected to analysis.[6,7] In the preliminary tests, the methods employing ammonium 1-pyrrolidinecarbodithioate[8,9] and 8-quinolinolate[7] was examined. In the dithiocarbamate method, the back ground absorption increased with increasing amount of the reagent. On the other hand, the extraction pH higher than 10 was required in the oxinate method.

The use of BMPP and CMPP was studied. In spite of the interest in BMPP,[10] only a little information is available on the extraction of manganese complex into MIBK. The extractability of manganese BMPP complex was constant over the pH range 7.0—11.0 (Fig. 3). Manganese–CMPP complex was quantitatively extracted in the pH range 8.5—10.5. A small step was observed on the extractability-pH curves in both cases. The extraction method with BMPP was tested with the solution containing 20 ml of 0.5 M hydrochloric acid and 2.3 μmol of PAR. The solution composition is almost the same as that of the eluate from the mixed resin. The pH was adjusted by the addition of 1 M potassium phosphate. In the presence of PAR the optimal pH range became narrower in the alkaline region (pH 7.0—8.3), even larger amounts of BMPP up to 125 μmol being added. At the optimum conditions the extraction equilibrium was attained within a few minutes. The organic extract was stable at least within 30 min.

Enrichment of Manganese from Synthetic Sample Solution. The composition of the synthetic sample solution was: Na^+ 32.6, K^+ 7.8, Ca^{2+} 40.0, Mg^{2+} 12.0, Zn^{2+} 0.2, Pb^{2+} 0.005, Fe^{3+} 0.1, Cu^{2+} 0.01, Cl^- 142.22, SO_4^{2-} 58.3, SiO_2 7.5, HCO_3^- 35.4, NO_3^- 0.013, NH_4^+ 0.032 mg l^{-1}. The composition is referred to the ordinary river waters,[11] in which the concentrations of main components are fairly high. With increasing amounts of PAR and the mixed resin, the recovery of manganese was improved (Fig. 4). By combined use of 2.5 ml of CRS, 4 ml of ARS and 46 μmol of PAR, a 3-μg portion of manganese was effectively recovered from 100—500 ml of the sample solution.

References

1) M. Abe, K. Ohzeki, and T. Kambara, *Bull. Chem. Soc. Jpn.*, **51**, 1090 (1978).

2) B. S. Jensen, *Acta Chem. Scand.*, **13**, 1668 (1959).

3) R. G. Anderson and G. Nickless, *Analyst*, **92**, 207 (1967).

4) A. Corsini, I. Mai-Ling Yih, Q. Fernando, and H. Freiser, *Anal. Chem.*, **34**, 1090 (1962).

5) T. Yotsuyanagi, K. Goto, M. Nagayama, and K. Aomura, *Bunseki Kagaku*, **18**, 477 (1969).

6) F. J. Feldman, R. E. Bosshart, and G. D. Christian, *Anal. Chem.*, **39**, 1175 (1967).

7) H. T. Delves, G. Shepherd, and P. Vinter, *Analyst*, **96**, 260 (1971).

8) R. E. Mansell, *Atomic Absorption Newslett.*, **4**, 276 (1965).

9) R. E. Mansell and H. W. Emmel, *Atomic Absorption Newslett.*, **4**, 365 (1965).

10) Yu. A. Zolotov, "Extraction of Chelate Compounds," translated by J. Schmorak, Ann Arbor-Humphrey Science Publishers, London (1970), p. 91.

11) T. Hanya, "Suisitu Chosaho," (in Japanese), Maruzen, Tokyo (1960), p. 51.