Pergamon

0039-9140(94)E0005-C

Talanta, Vol. 41, No. 5, pp. 799–803, 1994
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0039-9140/94 \$7.00 + 0.00

FLOW-INJECTION SPECTROPHOTOMETRIC DETERMINATION OF CADMIUM WITH QUINOLYLAZO COMPOUND AFTER ON-LINE SEPARATION USING A SILICA GEL COLUMN

Tomosuke Ishizuki, Koji Matsumoto, Akio Yuchi, Tadao Ozawa,
Hiromichi Yamada and Hiroko Wada*
Department of Applied Chemistry, Nagoya Institute of Technology, Showa-ku, Nagoya 466, Japan

(*Received* 13 *October* 1993. *Revised* 27 *December* 1993. *Accepted* 29 *December* 1993)

Summary—2-[2-(4-Methylquinolyl)azo]-5-diethylaminophenol(QADP) reacts with cadmium in aqueous ethanol and the molar absorptivity of the QADP–cadmium complex is the highest ($1.51 \times 10^5 M^{-1}$ cm^{-1}, λ_{max} 569 nm) of the reagents reported previously. A flow-injection spectrophotometric determination of cadmium with QADP after on-line separation using silica gel column was proposed. A 450 μg/l cadmium concentration could be determined in the presence of 13 mg/l zinc, 83 mg/l lead and 11 mg/l iron.

Dithizone(diphenylthiocarbazone) has been widely used for the spectrophotometric determination of cadmium, because of its sensitivity ($\epsilon = 8.8 \times 10^4 M^{-1}$ cm^{-1}) and selectivity.[1,2] This method, however, has some drawbacks such as the necessity for multi-step extractions and the instability of the reagent itself; it is subject to oxidation by air and the purification is tedious.

Previously we synthesized a highly sensitive reagent, 2-[2-(4-methylquinolyl)azo]-5-diethylaminophenol(QADP), and applied it to the determination of nickel in the presence of cobalt.[3] It was found that QADP reacted with cadmium in 50% ethanol solution and the complex had the highest molar absorptivity ($\epsilon = 1.51 \times 10^5 M^{-1}$ cm^{-1}, $\lambda_{max} = 569$ nm) among the reagents proposed for the determination of cadmium (Table 1).[4–8] These heterocyclic azo compounds, having an ortho-hydroxy group, generally react with various metal ions. Therefore, cadmium was separated from other metals by tedious pretreatment such as precipitation, ion-exchange chromatography or extraction.

In this paper, a flow-injection system equipped with a mini silica-gel column was employed for the separation of diverse ions, and rapid spectrophotometric determination of cadmium is achieved using QADP.

EXPERIMENTAL

Reagents

QADP was prepared by the procedure described previously[3] and dissolved in ethanol to give a $5 \times 10^{-4} M$ solution. The stock solution was stable at least for two years at room temperature. Cadmium(II), lead(II) and iron(III) solutions were prepared from the nitrates. Zinc(II) and copper(II) solutions were prepared by dissolving the metals (99.99% purity) in dilute nitric acid.

The pH buffers used were $1M$ CH_3COOH–CH_3COONa (pH 3–5), $0.5M$ 3-(*N*-morpholino)ethane sulfonic acid (MES)–KOH (pH 6), $1M$ H_3PO_4–KOH (pH 6–8), $1M$ citric acid–KOH (pH 6–8), $0.5M$ 3-(*N*-morpholino)propane sulfonic acid (MOPS)–KOH (pH 6–8), $0.5M$ *N*-2-hydroxyethylpiperazine-*N*′-3-propanesulfonic acid (EPPS)–KOH (pH 8), $0.5M$ H_3BO_3–NaOH (pH 9–10) and $1M$ NH_3–NH_4Cl (pH 10).

Other chemicals were of analytical-reagent grade. Water was purified with a ultra-pure water manufacturing device (Toray Pure LV-10T).

Silica gel of chromatographic grade (Wakogel C-100) in the range of 50–80 mesh was sieved,

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*Author to whom correspondence should be addressed.

Table 1. Spectrophotometric reagents for cadmium

Reagent	Solvent	ε ($10^4 M^{-1}$ cm^{-1})	Ref.
Dithizone	Tetrachloromethane	8.8 at 520 *nm*	1,2
QADP	50% Ethanol	15.1 at 569 *nm*	3
5-Br-DMAP	3-Methyl-1-butanol	14.1 at 555 *nm*	4
5-Cl-DMAP	50% Ethanol	12.0 at 550 *nm*	5
BTADAP	*o*-Xylene	4.5 at 600 *nm*	6
2-QADNm	0.17*M* Sodium hydroxide	12.0 at 525 *nm*	7
PAR	Chloroform	5.9 at 520 *nm*	8

5-Br-DMAP: 2-[2-(5-bromopyridyl)azo]-5-dimethylaminophenol; 5-Cl-DMAP: 2-[2-(5-chloropyridyl)azo]-5-dimethylaminophenol; BTADAP: 2-(2-benzothiazolylazo)-5-dimethylaminophenol; 2-QADNm: 4-(2-quinolylazo)-1,3-dihydroxynaphthalene; PAR: 4-(2-pyridylazo)resorcinol.

digested with a double volume of hydrochloric acid (1:1) for one day, and then washed with water. Then the silica gel was dried at 110° for one day.

FIA manifold

The flow-injection system is shown in Fig. 1. A double-plunger pump (SRX-3600, Sanuki, Tokyo) was used for carrier and reagent streams, and a peristaltic pump (SA, Ismatec) for regeneration of the column filled with silica gel (streams A and B). A ceramic injector (SVM-6M2, Sanuki) with a 100 μl loop, and a spectrophotometric detector (870-UV or UV-970, Jasco, Tokyo) with a flow-through cell (volume 8 μl, light-path length 1.0 cm) were used. A mixing coil (length 20 cm, I.D. 0.5 mm) was wound around a narrow cylinder in a figure-of-eight fashion.[9] Two PTFE colums (length 25 cm, I.D. 2 mm) filled with 0.5 g of silica gel were placed in parallel and used or regenerated one after the other.

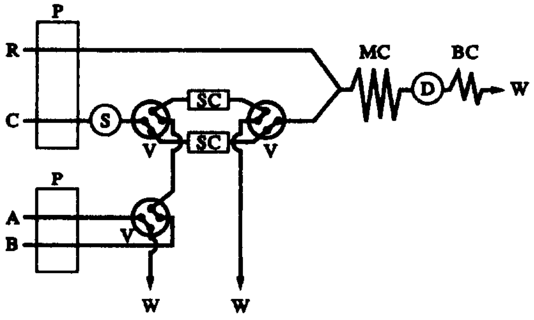

Fig. 1. Flow manifold. P, Double plunger pump; S, sample injector (100 μl); V, exchange valve; SC, silica gel column (0.5 g silica gel, 25 cm × 2 mm I.D.); MC, mixing coil (50 cm × 0.5 mm I.D.); D, detector; BC, back pressure coil (50 cm × 0.25 mm I.D.); W, waste; R, 50% aqueous ethanol containing $2.5 \times 10^{-5}M$ QADP and 0.1*M* NH_3–NH_4Cl (pH 10); C_1, 0.04*M* H_3PO_4–KOH (pH 7) and 0.42*M* KCl; C_2, $5 \times 10^{-3}M$ citrate–KOH (pH 8), $5 \times 10^{-2}M$ EPPS–KOH (pH 8) and 0.45*M* KCl; A, 2*M* HCl; B, water.

Batchwise examination of retention

Into a 50-ml centrifuge tube, 4 ml of $5 \times 10^{-4}M$ metal ion solution, 0.5 g of silica gel, buffers and various salts were added. The contents were then agitated with an electric shaker for 30 min at room temperature. The supernatant was filtered through a millipore filter. One millilitre of 1*M* HCl was added to 1 ml of the filtrate, and the solution was diluted to 10 ml. The metal concentration was determined by atomic absorption spectrometry.

Flow-injection analysis

Both the reagent solution and carrier were pumped at 0.75 ml/min. The reagent stream was 50% aqueous ethanol containing $2 \times 10^{-5}M$ QADP and 0.1*M* ammonia–ammonium chloride at pH 10. Two carrier streams examined were (C_1) 0.04*M* phosphoric acid–KOH (pH 7) + 0.42*M* KCl and (C_2) $5 \times 10^{-3}M$ citric acid, $5 \times 10^{-2}M$ EPPS–KOH (pH 8) + 0.45*M* KCl. The same buffer as used for a carrier was added to the sample solution. Precipitates were sometimes found in the phosphate system. Thus, the sample solution was filtered off with a syringe filter and 100 μl of the filtrate injected. The absorbances were monitored at 569 nm. After each measurement, a new column was introduced in the flow-path and the column once used was regenerated by passing 2*M* hydrochloric acid and water for 5 min each.

RESULTS AND DISCUSSION

Reaction of cadmium with QADP

From the results of a previous study,[3] cadmium ion reacts quantitatively with QADP at pH > 9 to form a red chelate in 50% aqueous ethanol. The chelate has the highest molar absorptivity ($1.51 \times 10^5 M^{-1}$ cm^{-1}) among the reagents recommended to date (Table 1). Thus, QADP was used for the spectrophotometric

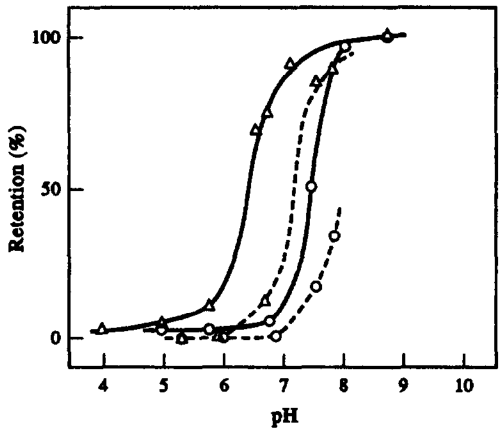

Fig. 2. Effects of pH on the retention of Cd(II) and Zn(II) to silica gel. Silica gel: 0.5 g. Metal: ○, Cd(II); △, Zn(II) (each $4 \times 10^{-5} M$). Buffer: ——, phosphate; ----, citrate.

determination of cadmium. At a pH higher than 9, however, zinc(II), copper(II) and lead(II) also react with QADP[3] and interfere with the determination of cadmium. As suitable masking agents could not be found, the separation using silica gel was studied.

Separation of metal ions with silica gel

Silica gel has been widely used for adsorption, ion-exchange and chromatography of metal ions.[10–13] Retention of metal ions on silica gel is affected by the pH of the sample solution, complexing reagents and counter cations in the sample eluent. In this study, phosphate and citrate were adopted as complexing reagents, and K^+ and Na^+ as counter cations. These factors were systematically changed to determine the optimum conditions for separation of cadmium from other metal ions.

The effects of pH on the retention of zinc and cadmium to silica gel are shown in Fig. 2. A large change in retention was found for both metal ions at pH 6–8 in both phosphate and citrate systems. At pH 7 in the phosphate system, 92% of cadmium was free from silica gel, whereas 90% of zinc was retained on silica gel. At pH 7.7 in citrate system, 82% of cadmium was free and 85% of zinc was retained.

The effects of the buffer concentration (C_{buffer}) on the retention of metal ions were studied. The results for the citrate system are shown in Fig. 3. With increase in C_{buffer}, the retention of metal ions decreased. A suitable concentration for the separation of cadmium from other metal ions was $5 \times 10^{-4} M$ at pH 6.7 (Fig. 3a) and $5 \times 10^{-3} M$ at pH 7.7 (Fig. 3b). Citrate at these concentrations did not interfere with the color-developing reaction between Cd^{2+} and QADP.

The effect of K^+ on the retention was examined under the conditions optimized above (Fig. 4). With an increase in the concentration of potassium ion, the retention of zinc, iron and lead to silica gel increased, while that of cadmium decreased. Thus separation of Cd^{2+} from other metal ions was improved by the additions of appropriate amounts of K^+ salts. Even at $0.5 M$, KCl had no effects on the cadmium–QADP complexation.

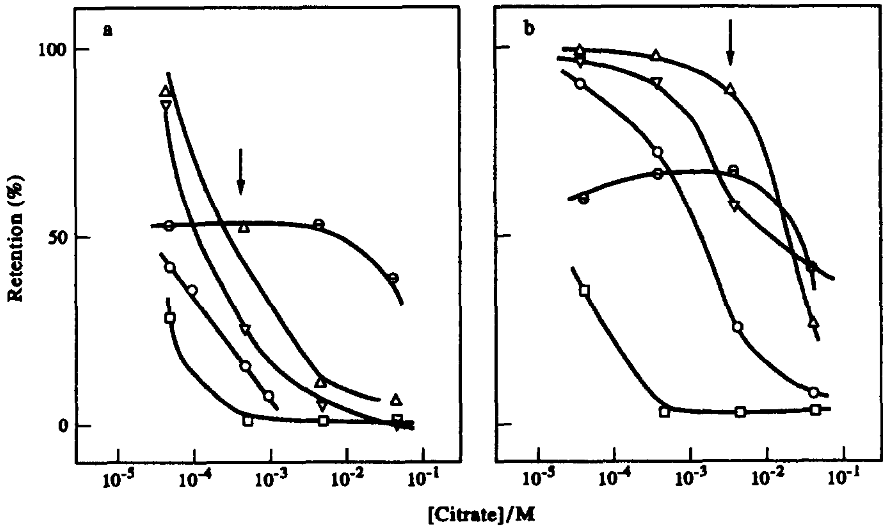

Fig. 3. Effects of citrate concentration on the retention of metal ions to silica gel. Silica gel: 0.5 g. Metal: ○, Cd(II); △, Zn(II); □, Cu(II); ▽, Pb(II); ⊖, Fe(III). pH: a, 6.7; b, 7.7.

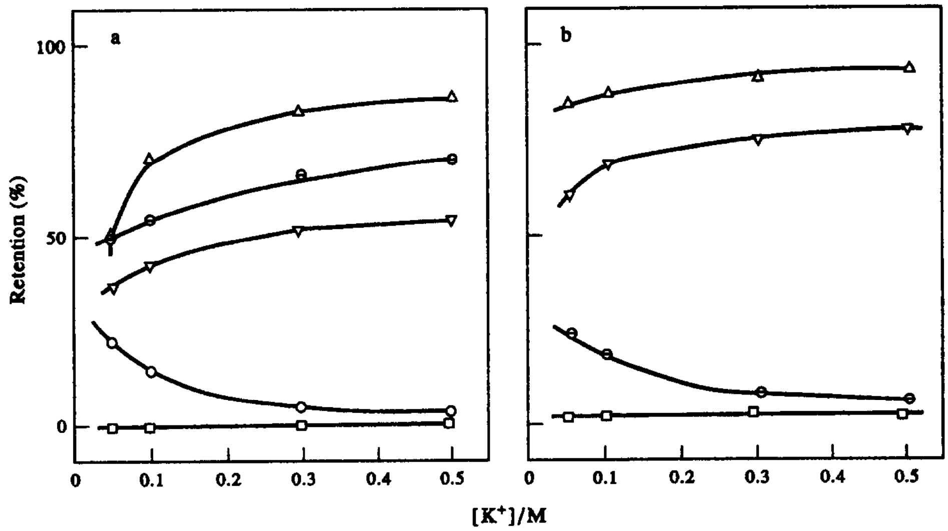

Fig. 4. Effects of K^+ concentration on the retention of metal ions to silica gel. Silica gel: 0.5 g. Metal: ○, Cd(II); △, Zn(II); □, Cu(II); ▽, Pb(II); ⊖, Fe(III) ($4 \times 10^{-5}M$). Buffer: a, $4 \times 10^{-4}M$ citrate + 0.05M MOPS–KOH (pH 6.7); b, $5 \times 10^{-2}M$ citrate + 0.05M MOPS–KOH (pH 7.7).

Determination of cadmium with flow-injection system

Cadmium could not be completely separated from other metal ions by the batchwise method with silica gel. Separation of cadmium was thus examined with a silica gel column, which was incorporated in a spectrophotometric flow-injection system with QADP.

Effects of C_{buffer} on the FIA signals for Cd ($5 \times 10^{-6}M$) and Zn ($1.5 \times 10^{-4}M$) were studied in a H_3PO_4–KOH buffer system at a fixed pH of 7. The peak for Cd increased with an increase in C_{buffer} up to 0.06M, whereas that for Zn appeared at $C_{\text{buffer}} > 0.09M$. Thus, at $C_{\text{buffer}} = 0.04M$, only Cd could be determined. At higher concentrations of phosphate buffer, both Cd and Zn peaks diminished due to the interference of phosphate with the reaction between metal ions and QADP. Similar trends were observed with other buffer systems, but peaks were broad with H_3PO_4–NaOH.

Addition of KCl enhanced the separation as in the case of batchwise experiments. When the potassium concentration in 0.02M phosphate buffer was increased from the neat value of 0.04 to 0.21M, a sharper peak for cadmium was obtained and the peak for Zn disappeared completely.

Other FIA parameters were optimized as follows: column length 25 cm; flow rate 1.5 ml/min. When a column length was fixed at 25 cm, higher flow rates gave higher peaks for Cd, but Zn was also eluted. When a flow rate was fixed at 1.5 ml/min, longer columns gauranteed better separation of Cd from Zn, but peaks for Cd were broadened.

Calibration graphs and tolerance limits

Calibration graphs were linear for both phosphate ($1–6 \times 10^{-6}M$ Cd) and citrate ($0.4–1.6 \times 10^{-6}M$ Cd) systems, respectively. In the presence of high concentrations of Fe, however, co-precipitation of Cd with Fe was observed in the phosphate system. Thus the citrate system was finally adopted. The detection limit was $1.7 \times 10^{-7}M$ (19 μg/l. Cd) at signal-to-noise ratio of 3 and a relative standard deviation of 0.7% (450 μg/l. Cd, 3 injections). The sampling throughput was 10 hr^{-1}. The tolerance limit of each metal ion, which caused a change in absorbance of ±3% for the determination of $4 \times 10^{-6}M$ Cd was as follows: $4 \times 10^{-4}M$ for Zn and Pb, $2 \times 10^{-4}M$ for Fe, and $2 \times 10^{-6}M$ for Cu. Copper(II) must be separated prior to the determination. The method was applied to the determination of cadmium in artificial samples containing $4 \times 10^{-6}M$ Cd, $2 \times 10^{-4}M$ Zn, $2 \times 10^{-4}M$ Pb and $2 \times 10^{-4}M$ Fe, and satisfactory results were obtained. If a larger amount of zinc is contained, zinc should be separated by extraction.[14] The proposed method is selective and sensitive for the determination of cadmium in the presence of medium amounts of zinc, lead and iron.

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