

# Liquid Chromatographic Behaviour of Chelates of Vanadium(V), Copper(II), Cobalt(III) and Chromium(III) With 2-(3,5-Dibromo-2-pyridylazo)diethylaminophenol

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The reversed-phase liquid chromatographic behaviour of the chelates of V<sup>V</sup>, Cu<sup>II</sup>, Co<sup>III</sup> and Cr<sup>III</sup> with 2-(3,5-dibromo-2-pyridylazo)diethylaminophenol(3,5-diBr-PADAP) was studied using a C<sub>18</sub> column, and a method for the simultaneous determination of V<sup>V</sup>, Cu<sup>II</sup>, Co<sup>III</sup> and Cr<sup>III</sup> was developed. A mobile phase of methanol-acetonitrile-water (84 + 12 + 4) containing 0.11 mmol dm<sup>-3</sup> cetyltrimethylammonium bromide and 0.1 mmol dm<sup>-3</sup> NaOAc-HCOOH(pH 3.5) was found to be the best. The chelates were detected at 590 nm. The calibration graphs were linear for 0.20–6.40 µg ml<sup>-1</sup> of V<sup>V</sup>, 0.40–12.80 µg ml<sup>-1</sup> of Cu<sup>II</sup>, 0.08–2.56 µg ml<sup>-1</sup> of Co<sup>III</sup> and 0.40–6.40 µg ml<sup>-1</sup> of Cr<sup>III</sup>. The detection limits were 0.2, 0.4, 0.04 and 0.2 ng for V<sup>V</sup>, Cu<sup>II</sup>, Co<sup>III</sup> and Cr<sup>III</sup>, respectively. The method was applied to the determination of V<sup>V</sup>, Cu<sup>II</sup>, Co<sup>III</sup> and Cr<sup>III</sup> in electroplating waste water samples.

**Keywords:** *Liquid chromatography; vanadium(V), copper(II), cobalt(III) and chromium(III) chelates; 2-(3,5-dibromo-2-pyridylazo)diethylaminophenol; electroplating waste water*

2-Pyridylazo compounds are widely used as complexing agents for the determination of metals. Reagents such as 4-(2-pyridylazo)resorcinol have been reported for the spectrophotometric determination of almost all metals except the alkali metals.<sup>1</sup> Although the reactions of these reagents with metals are highly sensitive, they generally lack selectivity; hence masking agents must be added to overcome the non-specificity of metal chelation, or prior separation of the metal ions is necessary. 2-(3,5-Dibromo-2-pyridylazo)diethylaminophenol (3,5-diBr-PADAP) is a sensitive and selective reagent that has been used as a complexing agent for the spectrophotometric determination of metal ions such as V<sup>V</sup>,<sup>2</sup> Cu<sup>II</sup>,<sup>3</sup> Co<sup>III</sup> (reference 4) and Cr<sup>III</sup>;<sup>5</sup> however, masking agents are still needed to eliminate interferences. In addition to the interferences in determining these metals individually, in the normal spectra the bands due to the four metal chelates show appreciable overlapping, which precludes their simultaneous determination. However, liquid chromatography is an alternative approach to spectrophotometry for solving the problems of interference and simultaneous determination.<sup>6</sup> Several studies of the reversed-phase liquid chromatographic behaviour of metal chelates with 2-pyridylazo complexing agents have been reported;<sup>7–10</sup> however, the reversed-phase liquid chromatographic behaviour of metal chelates with 3,5-diBr-PADAP in the presence of surfactants has not been reported.

On the other hand, it is known that the chelation of Cr<sup>III</sup> with 3,5-diBr-PADAP requires heating for at least 40 min at 100–105 °C;<sup>5</sup> the chelates of V<sup>V</sup>, Cu<sup>II</sup> and Co<sup>III</sup> with this reagent might be partly decomposed under such conditions.

In this work, the conditions for the rapid pre-column reaction of V<sup>V</sup>, Cu<sup>II</sup>, Co<sup>III</sup> and Cr<sup>III</sup> with 3,5-diBr-PADAP in the presence of sodium dodecyl sulphate and H<sub>2</sub>O<sub>2</sub> were investigated and the conditions for the separation and simultaneous determination of these metal ions by reversed-phase liquid chromatography were also studied. The proposed method was applied to the analysis of electroplating waste water samples without the need for the addition of masking agents and pre-separation. The results show good accuracy and precision.

## Experimental

### Apparatus

A Perkin-Elmer Series 3 liquid chromatograph, equipped with an LC-65T ultraviolet/visible detector, a 5 µm Nucleosil C<sub>18</sub> column (250 × 4 mm i.d.) and a Shimadzu UV-265 spectrophotometer, was used.

### Reagents

All chemicals used were of analytical-reagent grade unless stated otherwise. Doubly distilled water was used throughout.

The 3,5-diBr-PADAP was obtained from the Tianjin Institute of Chemical Reagents (China) and sodium dodecyl sulphate from the Beijing Xizhong Chemical Factory (China). Cetyltrimethylammonium bromide, sodium metavanadate hexahydrate, copper nitrate trihydrate, cobalt nitrate hexahydrate, chromium nitrate nonahydrate, methanol, acetonitrile, sodium acetate, hydrogen peroxide and formic acid were obtained from the Beijing Chemical Factory (China).

### Procedure

#### Calibration

A sample solution containing V<sup>V</sup>, Cu<sup>II</sup>, Co<sup>III</sup> and Cr<sup>III</sup> was placed in a test-tube and 1.0 ml of 0.1 mol dm<sup>-3</sup> NaOAc-HCOOH solution (pH 3.5), 1.0 ml of 1% sodium dodecyl sulphate solution, 1.2 ml of 5 mmol dm<sup>-3</sup> 3,5-diBr-PADAP solution and 3 drops of 1% H<sub>2</sub>O<sub>2</sub> were added. The solution was diluted to about 8 ml and the mixture heated in a water-bath at 98 °C for 10 min. After cooling, the solution was diluted to 10.0 ml, and 4 µl of this solution were injected into the liquid chromatograph. The chelates were detected at 590 nm. Calibration was obtained by relating the peak heights of the chelates to the concentration of the metal ions.

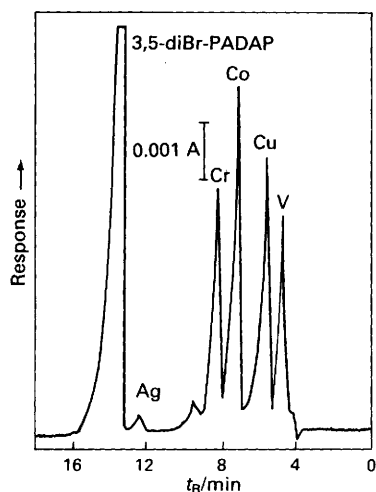
#### Analysis of electroplating waste water samples

Samples were taken from the Baoding electroplating plant. After the samples had been filtered, 5.0 ml of the filtrate were

**Table 1** Spectral properties of the metal-3,5-diBr-PDAP chelates

Metal or ligand	First peak/ nm	Second peak/ nm	Molar absorptivity (at 590 nm)*/ dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup>
V <sup>V</sup>	575	600	69 400
Cu <sup>II</sup>	540	580	68 000
Co <sup>III</sup>	575	600	239 000
Cr <sup>III</sup>	575	600	51 300
3,5-DiBr-PADAP	450	—	—

\* In the mobile phase, pH 5.5.



**Fig. 1** Separation of metal-3,5-diBr-PADAP chelates: mobile phase, methanol-acetonitrile-water (84 + 12 + 4) containing 0.1 mmol dm<sup>-3</sup> NaOAc-HCOOH and 0.11 mmol dm<sup>-3</sup> CTAB; pH, 5.5; column, 5  $\mu$ m Nucleosil C<sub>18</sub> (250  $\times$  4 mm i.d.); detector wavelength, 590 nm; flow rate, 0.5 ml min<sup>-1</sup>; and injection volume, 4  $\mu$ l. V<sup>V</sup>, 0.8 ng; Cu<sup>II</sup>, 1.6 ng; Co<sup>III</sup>, 0.32 ng; and Cr<sup>III</sup>, 1.6 ng

treated as described under Calibration. A 1  $\mu$ l aliquot of this solution was then injected into the liquid chromatograph.

## Results and Discussion

### Spectral Properties of the Metal Chelates

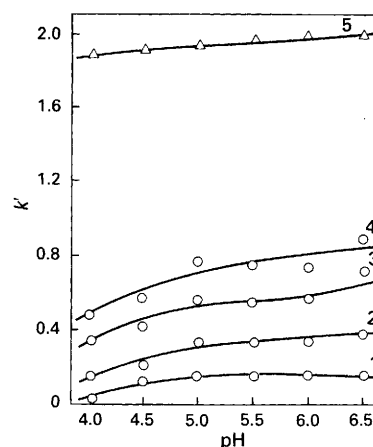
The absorption spectra of the chelates of V<sup>V</sup>, Cu<sup>II</sup>, Co<sup>III</sup> and Cr<sup>III</sup> with 3,5-diBr-PADAP and of the ligand itself were obtained in the mobile phase. The spectral properties are presented in Table 1. An investigation of the detector wavelength for the liquid chromatographic separation of the chelates was carried out in the range 540–600 nm; the optimum detector wavelength was found to be 590 nm.

The molar absorptivities of the V<sup>V</sup>, Cu<sup>II</sup>, Co<sup>III</sup> and Cr<sup>III</sup> chelates are also shown in Table 1.

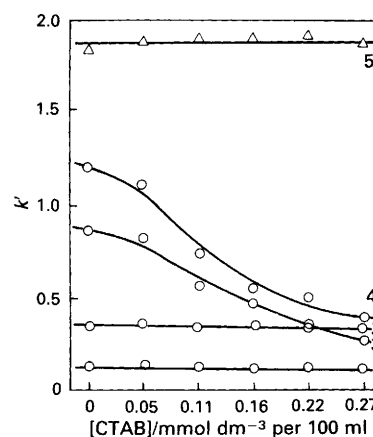
### Separation of the Chelates

A typical chromatogram for the chelates of V<sup>V</sup>, Cu<sup>II</sup>, Co<sup>III</sup> and Cr<sup>III</sup> with 3,5-diBr-PADAP is shown in Fig. 1, from which it can be seen that all the chelates are resolved.

It is known that 3,5-diBr-PADAP is a specific reagent for the spectrophotometric determination of Ag<sup>I</sup>. An attempt was made to determine Ag<sup>I</sup> by liquid chromatography; the peak of the Ag<sup>I</sup>-3,5-diBr-PADAP chelate is shown in Fig. 1. Unfortunately, this chelate was unstable in the chromatographic system used. (It is known that this chelate is decomposed in a medium in which the content of organic solvent is greater than 10%.<sup>11</sup>) No peaks were obtained for the chelates of Zn<sup>II</sup>, Mn<sup>II</sup>, Cd<sup>II</sup>, Pb<sup>II</sup>, Pd<sup>II</sup> and Hg<sup>II</sup> with 3,5-diBr-PADAP because these chelates decomposed in the mobile phase.



**Fig. 2** Variation of  $k'$  with pH of the mobile phase. 1, V<sup>V</sup>, 0.2 ng; 2, Cu<sup>II</sup>, 4 ng; 3, Co<sup>III</sup>, 0.12 ng; 4, Cr<sup>III</sup>, 4 ng; and 5, 3,5-diBr-PADAP. Other conditions as in Fig. 1 except for the pH of the mobile phase



**Fig. 3** Variation of  $k'$  with the concentration of CTAB. 1, V<sup>V</sup>; 2, Cu<sup>II</sup>; 3, Co<sup>III</sup>; 4, Cr<sup>III</sup>; and 5, 3,5-diBr-PADAP. Amounts of metal ions as in Fig. 2. Other conditions as in Fig. 1 except for the pH of the mobile phase

**Table 2** Regression analysis of calibration graphs and other quantitative data for the four metal ions studied

Parameter	V <sup>V</sup>	Cu <sup>II</sup>	Co <sup>III</sup>	Cr <sup>III</sup>
Linear range/ $\mu$ g ml <sup>-1</sup>	0.05–0.80	0.10–3.20	0.02–0.64	0.10–1.60
Detection limit*/ ng	0.2	0.4	0.04	0.2
Amount injected/ ng	0.20–3.20	0.40–12.80	0.08–2.56	0.40–6.40
Correlation coefficient	0.9974	0.9986	0.9994	0.9925
Slope†	2.44	1.26	16.10	1.27
Intercept/cm	0.27	1.49	0.64	0.42

\* Signal-to-noise ratio = 3.

† Arbitrary units.

### Effect of the pH of the Mobile Phase on the Retention of the Chelates

The mass distribution ratio (capacity factor) ( $k'$ ) of the chelates in the pH range 4.0–6.5 was investigated and the results are shown in Fig. 2. The  $k'$  values of the chelates increased in the pH range 4.5–5.0 and remained almost unchanged in the pH range 5.0–6.5. It is thought that the  $k'$  values of the chelates increase in the pH range 4.5–5.0 because of a decrease in the polarity of the chelates towards the

**Table 3** Results of the analysis of electroplating waste water samples

Sample	Metal ion	Values obtained by ICP-AES/ $\mu\text{g ml}^{-1}$	Value obtained by the proposed method/ $\mu\text{g ml}^{-1}$					SD*/ $\mu\text{g ml}^{-1}$	RSD† (%)	Recovery (%)	
			1	2	3	4	5				mean
A	V <sup>v</sup>	2.00	1.90	2.00	1.95	2.00	2.10	1.99	0.07	3.7	99.5
	Cu <sup>II</sup>	>10	32.0	31.6	32.4	32.1	31.8	32.0	0.30	0.9	—
	Co <sup>III</sup>	0.80	0.80	0.78	0.85	0.82	0.80	0.81	0.03	3.7	101.3
	Cr <sup>III</sup>	1.79	1.75	1.81	1.75	1.78	1.77	1.77	0.03	1.7	—
B‡	V <sup>v</sup>	—	—	—	—	—	—	—	—	—	—
	Cu <sup>II</sup>	—	18.0	18.8	17.6	18.5	17.9	18.2	0.48	2.7	—
	Co <sup>III</sup>	—	—	—	—	—	—	—	—	—	—
	Cr <sup>III</sup>	—	1.85	2.10	2.00	2.20	1.90	2.01	0.14	7.1	—

\* SD = standard deviation.

† RSD = relative standard deviation.

‡ Sample B was not analysed by ICP-AES.

stationary phase, caused by a decrease in the charges on the chelates as the pH increases. In order to separate the chelates completely, the pH of the mobile phase was fixed at 5.5.

#### Effect of Surfactants on the $k'$ Values of the Chelates

In order to improve the separation of the chelates, cetyltrimethylammonium bromide (CTAB) was added to the mobile phase. Fig. 3 shows the effect of CTAB on the  $k'$  values of the chelates. The Co<sup>III</sup> and Cr<sup>III</sup> chelates showed a similar and marked decrease in  $k'$  as the concentration of CTAB was varied from 0 to 2.7 mmol dm<sup>-3</sup>, whereas the  $k'$  values of the Cu<sup>II</sup> and V<sup>v</sup> chelates remained constant.

When the concentration of the added CTAB was 1.7 mmol dm<sup>-3</sup>, the Cu<sup>II</sup> and Co<sup>III</sup> chelates were not well resolved. The  $k'$  values of the Co<sup>III</sup> and Cr<sup>III</sup> chelates decreased steadily as the concentration of CTAB increased. The peak of the Co<sup>III</sup> chelate overlapped with that of the Cu<sup>II</sup> chelate when the concentration of CTAB added was 2.2 mmol dm<sup>-3</sup>. The marked effect of CTAB on the  $k'$  values of the Co<sup>III</sup> and Cr<sup>III</sup> chelates was similar to that reported recently for the Co<sup>III</sup>-5-Br-PADAP chelate.<sup>12</sup>

In addition, it was found that the peak height of the Co<sup>III</sup> chelate increased while that of the other chelates remained unchanged as the concentration of CTAB in the mobile phase increased.

#### Effect of the Methanol Content of the Mobile Phase on the $k'$ Values of the Chelates

The  $k'$  values of the chelates and of the ligand itself decreased with an increase in the methanol content of the mobile phase, particularly for the ligand. This result is consistent with the theory of reversed-phase chromatography. Relatively good resolution of all the chelates and of the ligand was obtained with a methanol content of 72% in the mobile phase.

#### Statistical Analysis

The linear range, detection limit data and regression analysis of the calibration graphs for the metal-3,5-diBr-PADAP chelates are given in Table 2.

#### Sample Analysis

The analysis of electroplating waste water samples obtained from the Baoding electroplating plant was carried out using the proposed method. Table 3 shows the results of the analysis of an electroplating waste water sample (A) spiked with V<sup>v</sup> and Co<sup>III</sup> and of another electroplating waste water sample (B). Sample A was also analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES); the results are presented in Table 3. It was found that the results obtained with the proposed method showed relatively good agreement with those obtained by ICP-AES. Sample A also contained 1.51  $\mu\text{g ml}^{-1}$  of Zn, 0.98  $\mu\text{g ml}^{-1}$  of Ni, 0.15  $\mu\text{g ml}^{-1}$  of Ti, 0.11  $\mu\text{g ml}^{-1}$  of Pb and 0.04  $\mu\text{g ml}^{-1}$  of Mo, which were determined by ICP-AES. The results showed that these metals did not interfere significantly with the determination of V<sup>v</sup>, Cu<sup>II</sup>, Co<sup>III</sup> and Cr<sup>III</sup>.

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