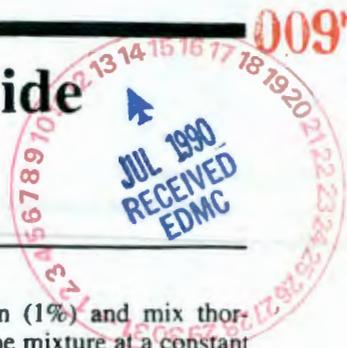


START Ion Chromatographic Analysis of Cyanide

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INTRODUCTION

It is important to analyze cyanide compounds in plating solutions and wastewaters.¹ Usually, argentometric titration is used for high concentrations of free cyanide and the zinc cyanide complex in plating solutions.² Okinaka et al.³ reported the simultaneous determination of gold (Au⁺, Au³⁺) and free cyanide in a gold plating solution by polarography. Knödler⁴ reported the determination of gold (Au⁺, Au³⁺) and free cyanide by potentiometry using a silver nitrate solution. Selig⁵ also reported the determination of free cyanide and aurocyanide, Au(CN)₂⁻, by potentiometric titration with silver ion. The author reported a coulometric determination of cyanide compounds in a silver cyanide plating solution.⁶

Haak⁷ reported the simultaneous determination of Au(CN)₂⁻ and Au(CN)₄⁻ in a gold plating solution by ion chromatography (IC). Rocklin et al.⁸ determined cyanide and metal cyanide complexes in plating wastewater by IC using an electrochemical detector. Wang et al.⁹ used potentiometric measurement with an ion selective electrode for the determination of cyanide and sulfide in plating wastewater. The author reported the determination of cyanide and metal cyanide complexes by IC using a conductivity detector.¹⁰ This method is based on the oxidation of cyanide ion to cyanate ion by sodium hypochlorite. In addition, the author reported the analytical procedure for plating solutions and wastewaters by IC.¹¹

This paper describes an IC procedure for free cyanide and metal cyanide complexes applied to plating solutions and their wastewaters.

EXPERIMENTAL

APPARATUS:

Chromatography was performed on an ion chromatograph equipped with a conductivity detector. The sample loop size was 50 μl. For the analysis of free cyanide and weak metal cyanide complexes, a separator column with one guard column and a suppressor was

used. The eluent was a solution of 2.2 mM Na₂CO₃.

For the analysis of strong metal cyanide complexes, a similar system with an eluent of a mixed solution of 2 mM tetrabutylammonium hydroxide (TBAOH), 40% acetonitrile and 0.2 mM sodium carbonate was used. The eluent flow rate was 1.5 ml/min.

REAGENTS:

All chemicals were of the highest grade commercially available. Standard cyanide solution was prepared from 1000 mg/L potassium cyanide stock solution, standardized by argentometric titration.

Standard metal cyanide complex solutions were prepared by accurate dilution of KAg(CN)₂, K₂Ni(CN)₄, K₄Fe(CN)₆, K₃Fe(CN)₆, KAu(CN)₂, KAu(CN)₄ and K₃Co(CN)₆ stock solutions (1000 mg/L). Solutions of Zn(CN)₄²⁻, Cd(CN)₄²⁻ and Cu(CN)₄³⁻ were prepared by mixing KCN and the corresponding metal cyanide complexes (Zn(CN)₂, Cd(CN)₂, KCu(CN)₂) in appropriate amounts.

PROCEDURE:

In a volumetric flask (50 ml), place an appropriate sample solution and 5 ml of sodium hydroxide solution (0.1 N) and dilute to 50 ml with deionized water. Add 50 μl of sodium hypo-

chlorite solution (1%) and mix thoroughly. Keep the mixture at a constant temperature between 20 and 80°C for 10 minutes. The flask is cooled in a water bath and an aliquot is then injected into the ion chromatograph.

RESULTS AND DISCUSSION

CHROMATOGRAM OF CYANIDE COMPOUNDS:

Usually, a separator column and fiber suppressor are used for anion analysis; however, free cyanide and metal cyanide complexes are not detected by the conventional conductivity detector due to low dissociation.

Previously, the author reported an IC procedure for free cyanide and metal cyanide complex determination with a conductivity detector.¹⁰ The method is based on the oxidation of the cyanide ion (pK=9.2) to the cyanate ion (pK=3.66) by a sodium hypochlorite solution.

The chromatograms of metal cyanide complexes by the proposed method are shown in Fig. 1.

Free cyanide and weak metal cyanide complexes such as zinc, cadmium, copper, silver and nickel were oxidized by sodium hypochlorite at 25 or 80°C, to produce cyanate ion. The retention time was 2.7 minutes; however, the strong metal cyanide complexes such as the

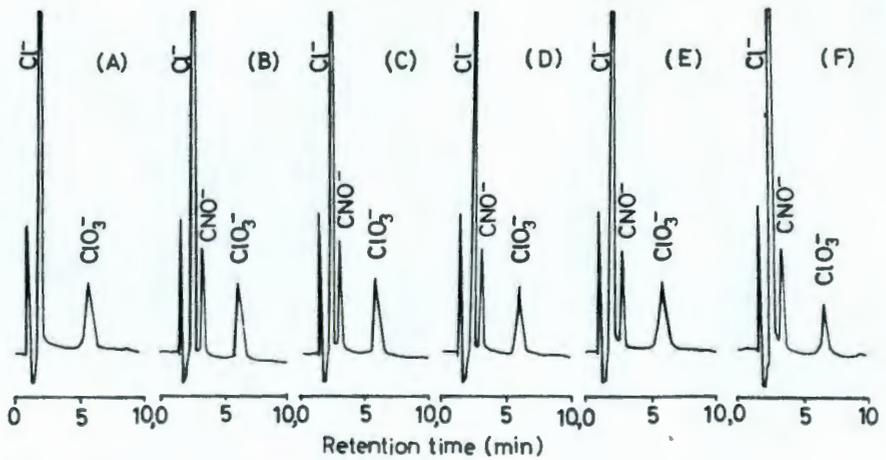


Fig. 1. Chromatograms of metal cyanide complexes. (A) Blank (water, pH 12); (B) Zn(CN)₄²⁻; (C) Cd(CN)₄²⁻; (D) Cu(CN)₄³⁻; (E) Ag(CN)₂⁻; (F) Ni(CN)₄²⁻. Pretreatment: NaClO (1%) 50 μl; 20°C (A-D); 80°C (E, F); 10 minutes. Eluent: 2.2 mM Na₂CO₃; 1.5 ml/min. Detector: Conductivity.

irons (Fe^{2+} , Fe^{3+}), golds (Au^+ , Au^{3+}) and cobalt are not oxidized by sodium hypochlorite. Almost no cyanate ion was produced even at 80°C , except for $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Au}(\text{CN})_4^-$.

A separator column and suppressor were used for the determination of metal cyanide complexes with a conductivity detector. The chromatograms of these compounds are shown in Fig. 2.

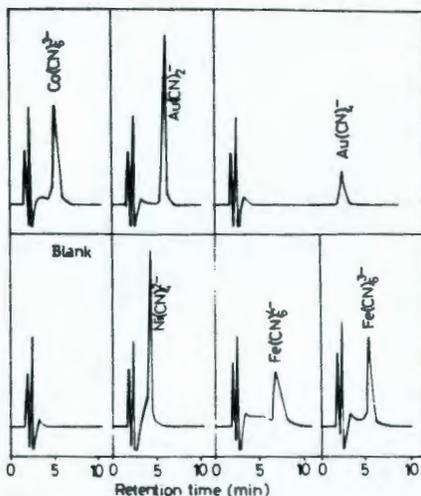


Fig. 2. Chromatograms of metal cyanide complexes.

Eluent: Mixed solution of 2 mM TBAOH, 40% CH_3CN and 0.2 mM Na_2CO_3 .
Detector: Conductivity.

The results show that the metal cyanide complexes such as the irons (Fe^{2+} , Fe^{3+}), the golds (Au^+ , Au^{3+}), cobalt and nickel can be measured. The retention times of these cyanide complexes were 6.9, 5.7, 5.9, 14.4, 5.4 and 4.4 minutes, respectively; however, the chromatograms of free cyanide and weak metal cyanide complexes such as zinc, cadmium, copper and silver did not appear.

Ion chromatographic procedures for the analysis of cyanide compounds are summarized in Table I. By combining the proposed method and the author's previous method,¹¹ a systematic analysis of cyanide compounds can be achieved.

CYANIDE IN PLATING SOLUTIONS:

The plating solutions of zinc, copper, silver and gold cyanide were diluted 1000-fold. These solutions were oxidized with sodium hypochlorite solution (1%) and controlled at 80°C for 10 minutes. The cyanate ions formed were measured. The results are shown in Fig. 3.

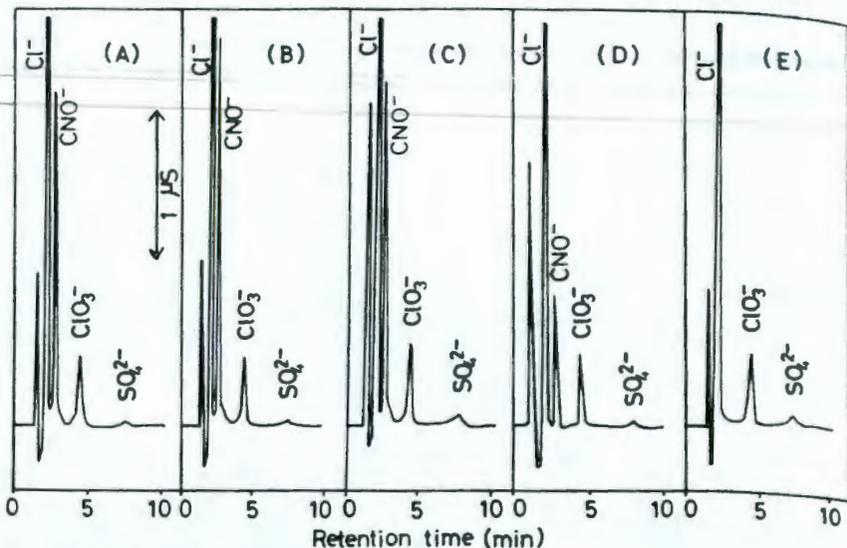


Fig. 3. Chromatograms of cyanide compounds in plating solutions. (A) Zinc cyanide; (B) Copper cyanide; (C) Silver cyanide; (D) Gold cyanide; (E) Gold citrate. Pretreatment: NaClO (1%) 50 μl ; 80°C ; 10 minutes. Eluent: 2.2 mM Na_2CO_3 ; 1.5 ml/min. Detector: Conductivity.

The results show that the sum of free cyanide and metal cyanide were measured for zinc (A), copper (B) and silver (C) cyanide plating solutions. Only free cyanide was measured for the gold cyanide plating solution (D); however, the cyanate peak did not appear from the gold citrate plating solution (E).

The gold plating solutions were diluted 100-fold. The results are shown in Fig. 4. The chromatogram of $\text{Au}(\text{CN})_2^-$ in the new gold cyanide plating solution is shown (A). The peaks of $\text{Au}(\text{CN})_2^-$ and $\text{Au}(\text{CN})_4^-$ in the used gold cyanide plating solution (B) appear; but this $\text{Au}(\text{CN})_4^-$ peak disappeared upon standing for a long time. It is thought that $\text{Au}(\text{CN})_4^-$ was reduced to $\text{Au}(\text{CN})_2^-$. This fact was also confirmed from the $\text{Au}(\text{CN})_4^-$ standard solution which formed $\text{Au}(\text{CN})_2^-$ and free cyanide ions after about two months. The peak of $\text{Au}(\text{CN})_4^-$ did not appear in the gold plating solution without the presence of free cyanide (C, D).

CYANIDE IN PLATING WASTEWATER:

The wastewater of plating solutions was analyzed with results shown in Fig. 5. The peak of the cyanate ion appeared from the wastewater by oxidizing with a sodium hypochlorite solution (1%) (A).

The plating wastewater was distilled and total cyanide determined. In the case of high concentrations of chloride and nitrite ions, the nitrite ion is decomposed with amidosulfuric acid and a distillation is performed.¹⁰ The distil-

late was oxidized with a sodium hypochlorite solution (1%) and measured (B).

The peaks of ferrocyanide and/or nickel cyanide ions from plating wastewaters were measured directly (C, D).

CONCLUSION

Cyanide compounds such as free cyanide, zinc, cadmium, copper, silver and nickel were oxidized with sodium hypochlorite to cyanate ion and measured by IC using a conductivity detector. Strong metal cyanide complexes such as the irons (Fe^{2+} , Fe^{3+}), the golds (Au^+ , Au^{3+}), cobalt (Co^{3+}) and nickel can be measured by IC directly. Both methods can be applied to cyanide compound analysis in plating solutions and their wastewaters. MF

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Table I. Systematic Analysis of Cyanide Compounds by IC

Species	Stability Const.	Proposed Method	Previous Method ¹¹
CN ⁻	9.2	O	X
Zn(CN) ₄ ²⁻	16.7	O	X
Cd(CN) ₄ ²⁻	18.8	O	X
Ag(CN) ₂ ⁻	21.2	O	X
Cu(CN) ₄ ³⁻	30.3	O	X
Ni(CN) ₄ ²⁻	31.3	O	O
Fe(CN) ₆ ⁴⁻	35	X	O
Fe(CN) ₆ ³⁻	42	X	O
Au(CN) ₂ ⁻	38.3	X	O
Au(CN) ₄ ⁻	—	X	O
Co(CN) ₆ ³⁻	64	X	O

O: Possible for analysis
X: Impossible for analysis

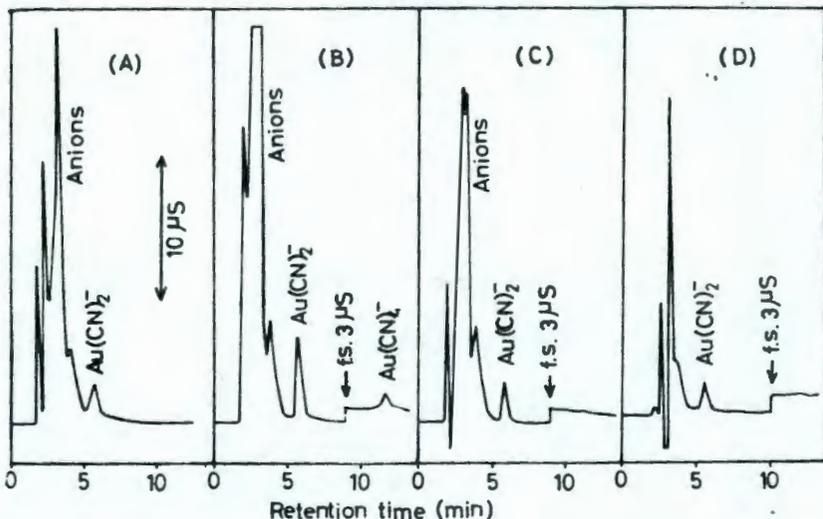


Fig. 4. Chromatograms of gold cyanide complex in gold plating solution: (A) New gold cyanide plating solution. (B) Used gold cyanide plating solution (with CN). (C) Used gold cyanide plating solution (without CN). (D) Used gold citrate plating solution (without CN). Eluent: Mixed solution of 2 mM TBAOH, 40% CH₃CN and 0.2 mM Na₂CO₃. Detector: Conductivity.

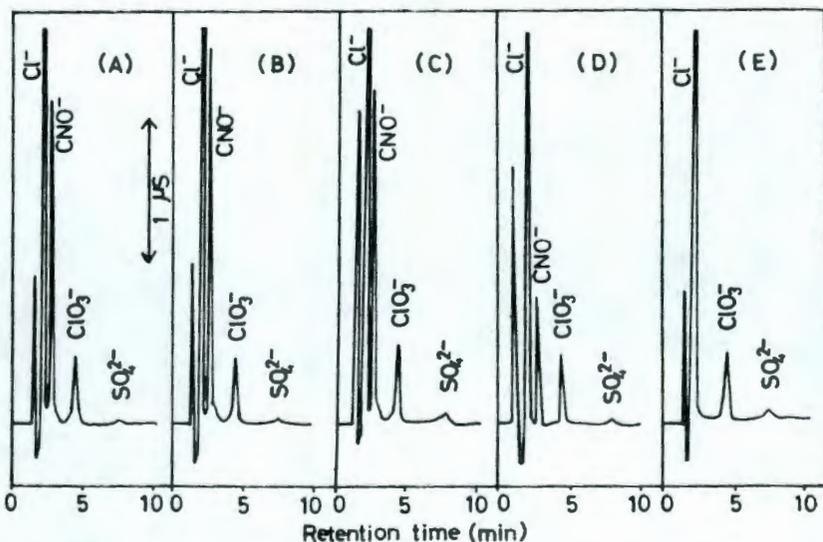


Fig. 5. Chromatograms of cyanide compounds in wastewater. (A) Plating wastewater (directly). (B) Plating wastewater (after distillation). (C) Plating wastewater (directly). (D) Plating wastewater (directly). Eluent: 2.2 mM Na₂CO₃ (A, B); Mixed solution of 2 mM TBAOH, 40% CH₃CN and 0.2 mM Na₂CO₃. Detector: Conductivity.

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