衛生化学
EISEI KAGAKU
30 (1) 7-13 (1984)

Flow Injection Analysis of Cyanide in Waste Water from Metal Plating Processes¹⁾

CHIYOMI OKUMOTO, MACHIKO NAGASHIMA, SHIGERU MIZOIRI

MASAYOSHI KAZAMA and KAZUYUKI AKIYAMA

Tokyo Metropolitan Research Laboratory of Public Health

24-1, Hyakunincho, 3 chome, Shinjuku-ku, Tokyo 160, Japan

(Received June 1, 1983)

A flow injection method for determining cyanide was applied to the screening of waste water samples from metal plating processes. A sample flowing at 1.2 ml/min was mixed with a sulfuric acid solution stream [2% (v/v), 0.4 ml/min] to adjust its pH to below 2. The acidified solution (200 μ l) was introduced into a carrier stream [10% (w/v) NaCl, 2.0 ml/min] *via* an injector valve. Hydrogen cyanide liberated was diffused into a collector stream (0.1 N NaOH, 1.2 ml/min) through a Teflon membrane in a gas diffusion cell at 40°C. The collector solution was monitored with a flow-through cyanide ion selective electrode. The apparent permeability of cyanide was calculated as 34% at the 1 μ g/ml level. A linear relationship was observed between the peak height and logarithmic concentration of cyanide in the range of 0.3–100 μ g/ml. The values determined by the present method (x) were in fair agreement with those obtained by the official method (y) for cyanide liberated at pH 5. The following correlation was obtained between the two methods; $y = 0.957x + 0.013$ ($r = 0.946$, $n = 50$). By this method, 40 samples can be analyzed in one hour.

Keywords—flow injection analysis; cyanide ion; waste water; metal plating process; gas diffusion; Teflon membrane.

A rapid and simple method for determining trace amounts of cyanide in waste water has been needed for many years. The cyanide level is regulated below 1 μ g/ml (as CN^-),²⁾ and the official pyridine-pyrazolone method³⁾ requires a tedious pretreatment. Although a cyanide ion selective electrode (ISE) can be used as a detector with high sensitivity and simple operation, a cleanup procedure is often necessary prior to the ISE analysis because of interfering species.

We recently reported a microdiffusion method combined with ISE.⁴⁾ This method is very simple, but it requires a long time for the isolation of hydrogen cyanide from waste water.

This paper deals with a flow injection analysis (FIA) method for waste water samples from metal plating processes. In the present method, hydrogen cyanide liberated from an acidified sample in a carrier solution stream is diffused into a collector solution stream through a Teflon membrane. Then, cyanide ion is measured with a flow-through ISE. By this method, 40 samples can be analyzed in one hour.

Experimental

1. Reagents—Teflon membrane (part No. 5588-0001, Bifok), three different Millipore membrane filters (Millipore Co.), Fluorinert-FG (pore size 0.2 μ m), Fluorinert-FH (0.5 μ m) and Fluori-

nert-FA (1.0 μm), Nylon-6 (thickness 25 μm , Ube Ind., Ltd.), polyethylene (20 μm , Ube Ind., Ltd.), polyester (16 μm , Ube Ind., Ltd.), polystyrene (10 μm , Ube Ind., Ltd.), polyvinylidene chloride (25 μm , Kureha Chemical Ind., Ltd.).

All reagents were of analytical grade (Wako Pure Chemical Ind., Ltd.).

Standard cyanide solution (CN^- : 1000 $\mu\text{g}/\text{ml}$; NaCN in 0.1 N NaOH) was diluted with 0.1 N sodium hydroxide solution according to the official method.⁸⁾

Carrier solution; 10% (w/v) sodium chloride solution.

Acid solution; 2% (v/v) sulfuric acid solution.

2. Apparatus—A Bifok FIA system equipped with an FIA-07 auto-sampler, FIA-08 peristaltic pump, FIA-05 main apparatus (injector and manifold), and a gas diffusion cell, was used. A glass flow cell (hand-made) was attached to a combined electrode (LT-08-SF, Ion Electrode Lab. Co.) as shown in Fig. 1. ISE potential was recorded with an ion meter (CN-1 A, Toa Electronics, Ltd.) and a pen recorder (B-181 H, Rikadenki Electronics Ltd.). A schematic diagram of the FIA is shown in Fig. 2. A Teflon tube (0.5 mm *i.d.*) was used as a connector. A flowing sample or standard solution was mixed with the acid solution stream to adjust its pH to below 2. An aliquot of the acidified solution was introduced into the carrier stream *via* the injector valve. Hydrogen cyanide liberated

Fig. 1. Electrode and Flow-through Cell
Distances in mm.

Fig. 2. Flow Diagram
Distance in mm.

was transferred into the collector stream through the Teflon membrane in the diffusion cell. The resulting cyanide ion was measured by means of ISE.

3. Analytical Conditions—The FIA parameters were as follows: Sample solution stream; 1.2 ml/min, sampling interval; 90 s, acid solution stream; 0.4 ml/min, sampling volume of the acidified sample solution; 200 μl , carrier solution stream; 2.0 ml/min, collector solution stream; 1.2 ml/min, gas diffusion cell; set at 40°C with a Teflon membrane.

Results and Discussion

1. Electrode Response and Membrane Permeability

The response of the adopted ISE reached a stable state in a short time; a lag time was observed. A small volume of cyanide solution did not give a sufficiently long contact time with the ISE in the flow cell for the response to reach the stable state (Fig. 3 A). In the stable state, a correlation was observed between the ISE response (y , mV) and the cyanide ion concentration (x , $\mu\text{g}/\text{ml}$); $y = 57.5 \log x + 60$ ($r = 0.999$, $n = 4$), in the range of $0.1 \leq x \leq 100$ (Fig. 4 a). The transient response due to a small volume of the solution was reproducible and gave a similar correlation; for example, $y = 59.0 \log x + 37$ ($r = 0.990$, $n = 4$), at the sample volume of 200 μl (Fig. 4 b). FIA is generally based on such a transient but reproducible response because of the rapid return to the base line.

In the present method, cyanide permea-

Fig. 3. Response Curves Obtained by Injecting 40 (a), 100 (b), 200 (c), 400 (d), 600 (e) and 800 (f) μl of Standard Solution (1 $\mu\text{l}/\text{ml}$) into the Stream A, B

A: Without membrane, sodium hydroxide stream.
B: With membrane, carrier stream.

Fig. 4. Calibration Curves

a: Sample volume 800 μl , without membrane.
b: Sample volume 200 μl , without membrane.
c: Sample volume 200 μl , with membrane.
In a and b, acid solution was replaced with sodium hydroxide solution.

TABLE I. Cyanide Permeability of Tested Membranes

Membrane	Origin	Type	Peak height Mean $\pm$ SD ($n=10$)
Teflon membrane	Bifok	5588-0001	1.00 ^{a)} $\pm$ 0.02
Fluorinert	Millipore	FG(0.2 $\mu\text{m}^{b)}$	0.83 $\pm$ 0.04
		FH(0.5 $\mu\text{m}^{b)}$	0.85 $\pm$ 0.01
		FA(1.0 $\mu\text{m}^{b)}$	0.91 $\pm$ 0.02
		25 $\mu\text{m}^{c)}$	0
Nylon-6	Ube	20 $\mu\text{m}^{c)}$	0
Polyethylene	Ube	16 $\mu\text{m}^{c)}$	0
Polyester	Ube	10 $\mu\text{m}^{c)}$	0
Polystyrene	Ube	25 $\mu\text{m}^{c)}$	0
Polyvinylidene chloride	Kureha Chem.		0

Standard solution (1 $\mu\text{g}/\text{ml}$) was treated under the standard analytical conditions, except that the gas diffusion membrane was changed.

a) Each value represents the relative peak height with respect to the Teflon membrane.

b) Pore size

c) Thickness

tion precedes the ISE analysis. Several membranes were checked for hydrogen cyanide permeability (Table I).

Among the tested membranes the Teflon membrane was the most permeable. The permeability of three different Millipore filters increased with increase in the pore size, but did not reach that of the Teflon membrane. The permeability of the Teflon membrane

increased with increase in temperature (Fig. 5).

Sensitive and reproducible response was observed at 40°C. However, at 50°C the peak was skewed and the base line sometimes drifted. Therefore, the diffusion cell was kept at 40°C. Under the conditions used, the following correlation was observed $y = 59.5 \log x + 10$ ($r = 0.985$, $n = 4$), in the range of $0.3 \leq x \leq$

Fig. 5. Effect of Temperature on the Cyanide Permeability of the Teflon Membrane
vertical line: Indicates mean and SD ($n=10$).

100 (Fig. 4 c). The apparent permeability⁵⁾ of cyanide was calculated as $34 \pm 0.99\%$ (mean $\pm$ S.D., $n=10$) at the $1 \mu\text{g/ml}$ level.

The sample volume was set at $200 \mu\text{l}$, because the peak height increased in the range of $40\text{--}60 \mu\text{l}$, but the return to the base

line required more than 60 s above $200 \mu\text{l}$ (Fig. 3 B).

The sampling time of 10 s was adopted, as the $200 \mu\text{l}$ sampling needed at least 6 s. The 90 s interval of the sampling was employed because at least 60 s was necessary for the return to the base line.

TABLE II. Effect of Concentration of H_2SO_4 under Continuous Flow Conditions

Concentration of H_2SO_4 % (v/v)	Peak height ^{a)}	pH of sample solution segment ^{b)}
	Mean $\pm$ SD ($n=10$)	Mean $\pm$ SD ($n=50$)
1	1.34 ± 0.03	3.4 ± 3.5
2	1.37 ± 0.03	1.1 ± 0.1
5	1.39 ± 0.03	0.8 ± 0.1
10	1.43 ± 0.04	0.4 ± 0.1

a) Peak height is given in arbitrary units. Standard solution ($1 \mu\text{g/ml}$) was treated under the standard conditions, except that the acid concentration was changed.

b) 50 actual samples were treated just as in a). The pH of the sample solution segment in the carrier stream was measured at the entrance of the gas diffusion cell.

TABLE III. Effect of Flow Rate on the Peak Height of Cyanide

Carrier stream (ml/min)	Collector stream (ml/min)					
	0.9	1.2	1.6	2.0	2.4	Mean ($n=10$)
0.9	1.0	0.8	0.6	0.4	0.6	0.6
1.2	1.1	1.0 ^{a)}		0.4	0.4	0.4
1.6	1.1	1.1	1.0	0.8	0.8	0.6
A 2.0	1.1	1.1 ^{c)}	1.0	1.0		0.6
2.4	1.2	1.0	0.8		1.0	0.4
3.0				0.8	0.6	0.8
4.0	Distorted and nonreproducible peak					

Carrier stream (ml/min)	Collector stream (ml/min)		Mean $\pm$ SD ($n=10$)
	0.9	1.2	
1.2	1.07 ± 0.02		
B 1.6	1.08 ± 0.02	1.09 ± 0.03	
2.0	1.05 ± 0.00	1.06 ± 0.03 ^{c)}	1.01 ± 0.01

Standard solution ($1 \mu\text{g/ml}$) was treated under the standard conditions, except that the flow rates of carrier and collector streams were changed. A represents the results of wide changes of flow rates, and B represents the detailed results in the favorable region.

a) Each value represents the relative peak height with respect to the indicated value.

b) Favorable region.

c) Values under the conditions employed.

2. Acid Solution and Collector Solution

In the concentration range of 2–10% (v/v), sulfuric acid solutions gave virtually the same peak height, and could control the pH of the sample solution to below 2 in 50 actual cases, when the other parameters were fixed (Table II). From these results and to avoid possible damage to the tubings, 2% (v/v) sulfuric acid was adopted.

As the collector solution, 0.1 N sodium hydroxide solution was used, because the pH of the collector stream remained above 12 and was suitable for actual ISE analysis.

The effect of the flow rates of the carrier and collector stream was investigated (Table III). Sharp and reproducible peaks were observed when the carrier flowed faster than the collector did.

Favorable conditions were 1.2–2.0 ml/min for the carrier and 0.9–1.6 ml/min for the collector: the adopted conditions were 2.0 and 1.2 ml/min, respectively. Cyanide transfer took place within 2 s under the conditions used. Faster flow regions gave small, distorted or nonreproducible peaks.

3. Carrier Solution

Salt solutions were examined as carriers of an acidified sample segment, and it was found that the peak height increased with increase of the ionic strength (Table IV).

TABLE IV. Effect of Carrier Solution on the Peak Height of Cyanide

Carrier	Peak height ^{a)} Mean $\pm$ SD ($n=10$)
H ₂ O	1.00 ^{b)} $\pm$ 0.01
Sat. Na ₂ SO ₄ soln.	1.11 $\pm$ 0.02
Sat. NaCl soln.	1.20 $\pm$ 0.04
10% (w/v) NaCl soln.	1.10 $\pm$ 0.02
1% (w/v) NaCl soln.	1.07 $\pm$ 0.04

a) Standard solution (1 μ g/ml) was treated under the standard conditions, except that the carrier solution was changed.

b) Each value represents the relative peak height with respect to H₂O.

Thus, 10% (w/v) sodium chloride solution was adopted as the carrier.

4. Calibration Curve and Detection Limit

The calibration curve was linear in the range of 0.3 to 100 μ g/ml (Fig. 4c), and the practical detection limit was 0.1 μ g/ml ($S/N=2$). A typical profile is shown in Fig. 6. Relative standard deviation at the 1 μ g/ml level was 3.4% in a day.

Fig. 6. Determination of Cyanide by Flow Injection Analysis

Standard solutions were run under the described analytical conditions.

5. Interference

Although surface-active agents were expected to affect the permeability of the membrane, Triton X-100 or sodium dodecylbenzenesulfonate did not cause any interference up to 100- or 10-fold molar ratio to cyanide ion, respectively.

Sulfur-containing compounds, sodium thiosulfate or sodium sulfite, also had no effect up to 100-fold molar ratio in the present method, though these compounds generally interfere with ISE analysis. However, a large excess of surface-active agents or these compounds should be avoided (Fig. 7).

Ethanol, sodium nitrite, potassium chro-

Fig. 7. Effect of Coexisting Substances

Sample solution containing CN^- ($1 \mu\text{g/ml}$) and a surface-active compound (a) or a sulfur-containing ion (b) was tested under the standard conditions.

DBSNa: Sodium dodecylbenzenesulfonate.

mate, or potassium dichromate had no effect.

6. Recovery from Waste Water Samples

Recoveries of cyanide from waste water samples were satisfactory and no interference was noted (Table V).

TABLE V. Recovery of Cyanide Ion from Waste Water Samples from Metal Plating Processes

Sample	Concentration of CN^- ($\mu\text{g/ml}$) Added	Found Mean $\pm$ SD ($n=10$)	Recovery (%)
A-1	0	0.0 ± 0.0	
2	1.0	1.0 ± 0.0	100.0
3	5.2	4.7 ± 0.1	90.4
4	10.4	10.2 ± 0.4	98.1
5	104	102.3 ± 3.0	98.4
B-1	0	5.3 ± 0.1	
2	1.0	6.3 ± 0.0	100.0
3	5.2	10.0 ± 0.1	90.4
4	10.4	14.7 ± 0.3	90.4
5	104	101.5 ± 4.6	92.5
C-1	0	11.9 ± 0.1	
2	1.0	12.9 ± 0.0	100.0
3	5.2	16.7 ± 0.2	92.3
4	10.4	21.5 ± 0.2	92.3
5	104	110.2 ± 4.0	94.5

Sample A is a pooled one of 20 cyanide-negative samples, B, of 25 cyanide-positive samples, and C contains NaCN , $\text{Cu}(\text{CN})_2$ and KCNS .

7. Comparison with the Official Method

A comparison between the present method and the official method was made on 50 waste water samples (with and without addition of sodium, zinc or cupric cyanide) from metal plating processes. Overall, the values determined by the present method (x) were in fair agreement with those obtained by the official method (y). The following correlation was observed between the two methods; $y = 0.957x + 0.013$ ($r = 0.946$, $n = 50$, Fig. 8).

The present method permits the rapid and sensitive determination of cyanide, and is applicable to the screening of waste water samples for cyanide liberated³⁾ at pH 5.

Fig. 8. Comparison between the Present Method and the Official Method for Determination of CN^- in Waste Water Samples (with and without Addition of Sodium, Zinc or Cupric Cyanide)

References

- 1) Presented at the 103 th Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, April 1983.
- 2) Ministerial Order concerning the Poisonous and Deleterious Substances Control Law, Paragraph 1 of Article 38.
- 3) Ministerial Order of the Ministry of Health and Welfare, No. 46, 12. 27, 1971.
- 4) K. Akiyama, M. Nagashima, C. Okumoto, K. Terashima and T. Hagiwara, *Bunseki Kagaku*, **31**, 402 (1982).
- 5) Apparent permeability (p) was calculated as follows ; $p = C_C / C_B \times 100$, where C_C is the concentration of cyanide ion obtained by the present method, and C_B is that by a modified procedure (B). In B, the acid solution was replaced with 0.1 N sodium hydroxide solution, and the flow was passed directly into the collector tube. C_C and C_B were calculated from calibration curve (b) in Fig. 3.