Kinetic-spectrophotometric determination of free cyanide by stopped-flow reversed flow injection analysis*

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Abstract— A stopped-flow reversed flow injection method for the determination of free cyanide is proposed. Pyridine-barbituric acid mixture is injected in the flow system as reagent to form the colour species with cyanide. The flow is stopped when the reagent zone comes in the flow cell, where absorbance-time data are collected at 580nm wavelength. The linear range of the determination is $0.1 - 10\mu g/ml$ CN^-. The sampling rate is $60h^{-1}$ and the relative standard deviation is 1.6% ($n = 16$) at 5.0 $\mu g/ml$ CN^{-1} level. With satisfactory results, the proposed method was applied to the determination of free cyanide in wastewater without sample pretreatment.
Keywords: kinetic analysis; stopped-flow; reversed flow injection system; free cyanide; wastewater.

1 Introduction

Being a sensitive spectrophotometric method, the pyridine-barbituric acid method was employed as a standard procedure for the determination of low levels of cyanide (APHA, 1985). A few reports on the determination of cyanide by normal flow injection analysis (nFIA) (Rios, 1984; Figuerola, 1988; Akira, 1988), or reversed flow injection analysis (rFIA) (Rios, 1984) using pyridine-barbituric acid as reagent have been published. Unfortunately they suffered from relatively narrow linearity low sensitivity and sampling rate.

In this paper, a rFIA stopped-flow system was used for kinetic-spectrophotometric determination of free cyanide. Using this system, cyanide was determined with wider linear range, higher sensitivity and sampling frequency.

2   Experimental

2.1   Reagents

All reagents used were of analytical-reagent grade and distilled water was used throughout.

Pyridine-barbituric acid reagent: place 12g of barbituric acid in a 250 ml standard flask and add water just enough to wash the walls of the flask and wet the barbituric acid. Add 60 ml of pyridine by stirring. Then, 12 ml of concentrated hydrochloric acid was added. When the mixture was cooled to room temperature, dilute it to a certain volume with water. The reagent is stable at least for 15 days at room temperature.

Chloramine-T solution: dissolved 0.6 g for chloramine-T in 100 ml of water.

Sodium dihydrogen phosphate-sodium hydroxide buffer: dissolve 78 g of $NaH_2PO_4 \cdot 2H_2O$ in one liter of water, pH was adjusted to 5.9 with sodium hydroxide.

Standard cyanide solution: cyanide standard solutions were prepared from a stock of potassium cyanide solution ($1000\mu g/ml$ CN^-, $pH = 11$) with 1 g/L sodium hydroxide.

2.2   Apparatus

A FIA star system was used. It concludes the 5020 analyzer, 5023 spectro-photo-meter, an 5022 controller. A Tecator type-III chemifold and Teflon tube (0.5 mm i. d.) was used to construct the manifold.

2.3   Procedure

Fig. 1 shows the manifold used. The sample solution, buffer, and chloramine-T solution were introduced into the system by a peristaltic pump. CNCl was formed when the cyanide sample encountered with a mixture of buffer and chloramine-T in mixing coil Cl, and CNCl reacted in coil C2 with pyridine-barbituric acid reagent injected to produce the colour species. As the reagent zone reached the flow cell, the pump was stopped for a certain period of time and the enhancement in absorbance (height of the second peak)
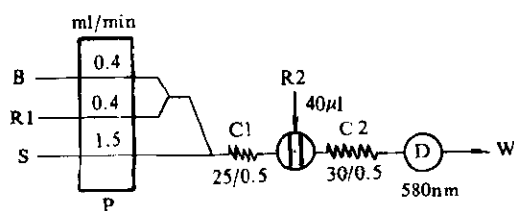
Fig. 1   Manifold used for the determination of cyanide

P: peristaltic pump; D: detector;
W: waste; Cl, C2: mixing coil;
B: 0.5mol/L NaH_2PO_4 buffer;
R1: 0.6% chloramine-T;
R2: pyridine-barbituric acid;
S: sample

at 580 nm wavelength during the stop time was collected. The flow was then restarted and the reagent zone was passed to waste. The collected data were compared with a calibration graph obtained by using standards under the identical working conditions.

3   Results and discussion

3.1   Optimization of FIA parameters

The univariate method was used to optimize the FIA parameters. The optimal flow rates, volume injected, length of reaction coils and inside diameter of tube (tube i. d.) are shown in Fig. 1.

3.2   Effect of reagent concentrations

Variations in barbituric acid concentration influence significantly the sensitivity of the system, however, changes, in concentrations of pyridine and hydrochloric acid did not. The height of the second peak increased with the concentrations of barbituric acid. Although solutions of higher concentrations of pyridine-barbituric acid reagent might be better, 4.8% (w/v) of barbituric acid was used due to its limited solubility.
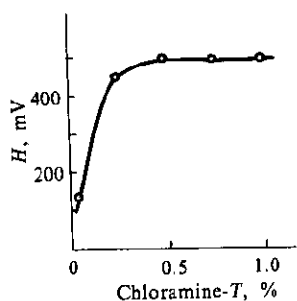

Fig. 2   Effect of chloramine-T concentration
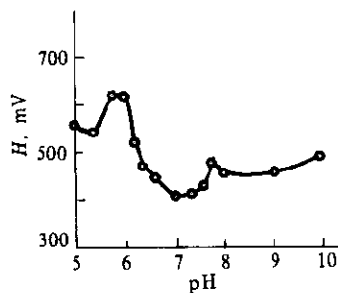   Cyanide concentration 5μg/ml

Fig. 3   Effect of pH
       Cyanide concentration 5.0μg/ml

Fig. 2 shows the effect of chloramine-T concentrations on the sensitivity of determination. Concentrations of chloramine-T more than 0.6% (w/v) did not further enhance the signal. Therefore, 0.6% (w/v) of chloramine-T was adopted in the experiments.

The concentration of buffer solution used was 0.5 mol/L NaH_2PO_4. More concentrated buffer solution was not recommended because the sensitivity decreased

with the increase of buffer concentration and precipitation might produce in the flow system if the concentration of buffer used was too high.

3.3   Effect of pH

The pH of buffer solution was optimized over the range of pH 5−10 by using standard Clark-Lubs buffer solution. The result is shown in Fig. 3 indicating that the optimum response can be obtained in the range of pH 5.8−6.0 and pH 5.9 was used in the experiments.

3.4   Effect of temperature

The effect of temperature was studied over the range 18−35 ℃ and the results are given in Fig. 4. Although increasing temperature has a positive effect on the sensitivity, 30 ℃ was chosen as an optimum working temperature, because at this temperature the reaction rate is less sensitive to temperature changes.

3.5   Effect of stop time and delay time

Using the manifold and working conditions optimized above, delay time (td) and stop time (ts) were optimized respectively. The optimum td was 13 seconds. Fig. 5 shows the signal vs. ts response curves of different cyanide concentrations. As the curves were all linear when ts ≤ 10s, so ts = 10s was used as the optimum value. What should be noted is that the signal will rise sharply at the stop time if there are unacceptable long stop time and the higher temperature and /or high cyanide concentration.
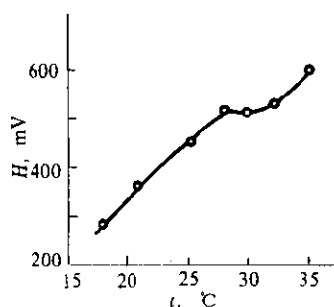

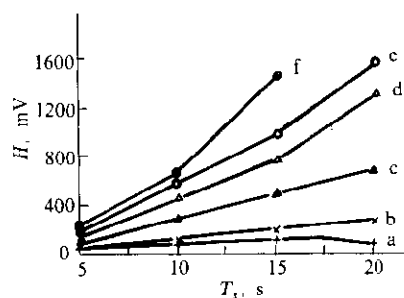Fig. 4   Effect of temperature
Cyanide concentration 5μg/ml

Fig. 5   Effect of stop-time
a. blank solution; b: 0.5; c: 2.5;
d: 5.0; e: 7.5; f: 10μg/ml cyanide

3.6   Interference study

The interference study was carried out with constant total cyanide concentration of 1μg/ml and different interferents were added at variable concentrations. In

Table 1, the results of interference study are collected. These results demonstrated that the interferences come mainly from cations, such as Ni (II) and Co (II), due to their high formation constants with cyanide. Some anions such as SCN^-, Br^- and I^- also interfered the determination of cyanide. Nevertheless, this proposed method can tolerate the relative interfering species in higher concentration.

Table 1   Interferences in the determination of cyanide with different interferents ($1\mu gml^{-1}$. CN^{-1})

Ions	Concentration, $\mu g/ml$		Recovery, %
	Interferent	Cyanide	
S^{2-}	10.0	0.91	91
SCN^-	1.00	1.04	104
Br^-	2.00	1.00	100
I^-	1.00	0.98	98
$Fe(CN)^{3-}_6$	5.00	1.09	109
$Fe(CN)^{4-}_6$	5.00	1.07	107
Phenol	10.0	1.00	100
Formaldehyde	1.00	0.64	64
Ag^+	1.00	0.91	91
Co^{2+}	1.00	0.56	56
Cu^{2+}	1.00	0.94	94
Fe^{3+}	100.0	0.96	96
Ni^{2+}	1.00	0.66	66
Hg^{2+}	1.00	0.90	90

3.7 Characteristics of the method

Fig. 6 shows the typical calibration diagrams. The calibration graph was linear over the range of $0.1 - 10\mu g/ml$ cyanide. Peak height (mV) and cyanide concentration ($\mu g/ml$) were related by regression equation $H = 74.70 \ [CN^-] + 13.40$. The correation coefficient was 0.998.

The relative standard deviation and sampling rate were 1.6% and $60h^{-1}$ respectively when a set of 16 solutions containing $5.0\mu g/ml$ CN^- were analyzed.
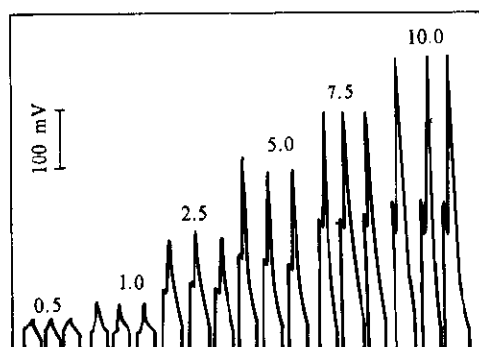

Fig. 6   Typical diagrams obtained during the determination of a calibration graph

3.8   Determination of free cyanide in wastewater samples

The proposed method was applied to determine the free cyanide in wastewater samples. The recoveries were calculated after adding 1, 2 and 4 μg/ml CN$^-$ to the wastewater samples. The results are given in Table 2.

Table 2   Determination of free cyanide in wastewater samples

Sample	Added, μg/ml CN$^-$	Found, μg/ml CN$^-$	Recovery, %
1		0.55	
	1.00	1.50	95.0
	2.00	2.52	98.5
	4.00	4.70	104
2		1.96	
	1.00	2.92	96.0
	2.00	4.03	104
	4.00	6.18	106
3		2.85	
	1.00	3.78	93.0
	2.00	4.66	90.5
	4.00	4.80	98.8

4   Conclusions

The combination of rFIA and stopped-flow technique makes the proposed flow system acquire the advantages of both rFIA and stopped-flow technique such as the minimization of reagent consumption, increase of sensitivity and eliminination of matrix interferences. Therefore, this proposed method is suitable for determining or monitoring free cyanide in wastewater, which is usually coloured or contains lag phase.

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