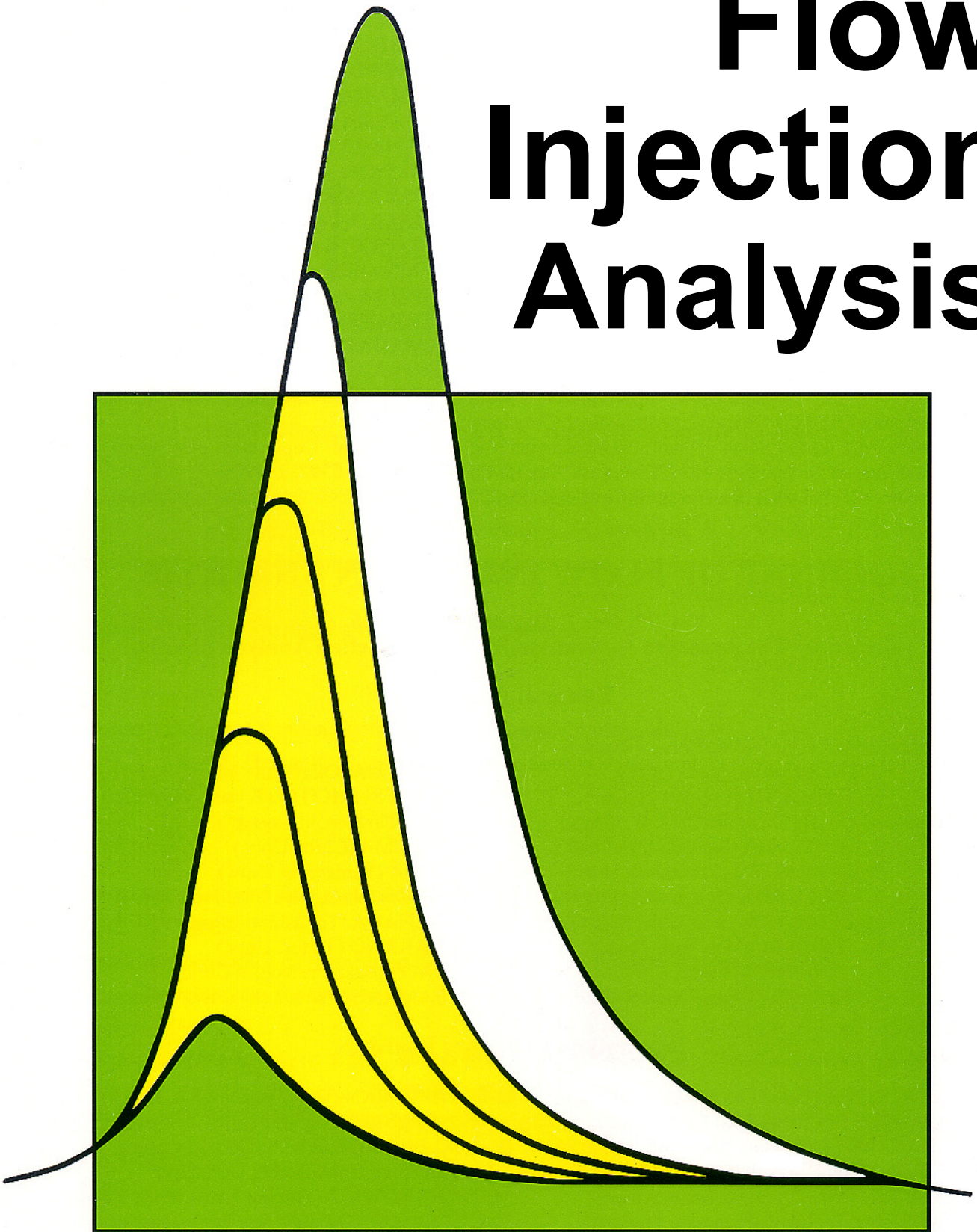


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Differential Electrolytic Potentiometric Detector in Flow Injection Analysis for Cyanide Determination

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Abstract

A simple differential electrolytic potentiometry (DEP) is coupled with the flow injection analysis (FIA) for the total cyanide determination. This simple and rapid method is based on the reaction of a silver nitrate with cyanide to form silver cyanide complex. Potassium nitrate was used as a supporting electrolyte. Platinum, gold and silver electrodes were tested and among them silver amalgam was found to be a suitable indicating system. The optimum current density for polarizing the electrodes was found to be 10–17 $\mu\text{A}/\text{cm}^2$. The sensitivity of the proposed method was further enhanced by shortening the coil length. The effect of flow rate and the volume of reagents and sample on the sensitivity of the method were also studied. The interference of chloride, iodide, sulfate, carbonate, phosphate, chromium, cobalt, nickel and cadmium were studied. Linear working range is from 1 ppm to 60 ppm. The detection limit is 0.5 ppm with a sample throughput of 10 samples / hour and the correlation coefficient is 0.999. The equation for potential measurement was: [Potential (V) = 0.241 + 0.0091 x C (ppm)]. The described FIA-DEP has the additional advantages, over the other methods, of minimizing time and amount of consumed reagents and improving the accuracy of the analysis due to computer control.

Keywords Cyanide, DEP, FIA, Silver Nitrate, Potassium Nitrate

1. Introduction

Cyanide compounds originate, in the environment, from different sources, mainly industrial sources. These sources include metal mining, metal refining, metal plating, metal cleaning and electroplating industries. For instance, potassium cyanide and sodium cyanide are frequently employed and used in mining for releasing precious metals such as gold and silver from the ore. From these sources, cyanide compounds enter the environment by different pathways. These compounds can release free CN and HCN, which are extremely toxic to animal and human. For example, cyanide at concentration as low as 50 ppb can kill brown trout. In the early 1960s, in Asia, mainly in Philippines, cyanide was used for fishing [10, 4]. Then its use spreads throughout Southeast Asia.

So, for the food industry, metal industry, industrial wastes, drinking water monitoring and environmental control, there is a strongly need for a rapid, sensitive and practicable method for cyanide determination. Generally, acid distillation is used for determination of total cyanide. It consists of two steps; the first step includes the removal of interferences and conversion of cyanide species into HCN under distillation. Then the gas is captured in an alkaline absorber solution (NaOH) [17]. Second step includes the determination which can be performed by several methods, such as titrimetric method. Although, the simplest method for direct determination is based on the ion selective electrodes, ISE may not be easily applicable due mainly to low selectivity and high interferences as well as the highly alkaline media which is needed to perform the measurements. Cyanide determination can be carried out by several methods such as, spectrophotometry [18] [15] and [6], fluorimetry [5] and [7], indirect atomic absorption spectrometry [8], polarography [16], potentiometry [13], [11] and [14], and chromatography [12] and [9]. However, their handling can be difficult. Moreover, a cheap and easy analytical method is not available so far.

The detection technique, differential electrolytic potentiometry

(DEP), consists of two polarizing identical electrodes with a heavily stabilized small direct current. The potential difference between these electrodes is measured. At the end point, this potential difference produces a symmetrical sharp peak. The tip of this peak is end point of the reaction. The technique of DEP has many advantages, e.g. polarized electrodes respond faster than zero-current electrodes. The difficulties of the salt bridge are eliminated since the technique does not require reference electrodes. The response of the electrodes is enhanced by polarization and so the equilibration takes place in a short time. Using different types of electrodes, DEP technique has been applied to various types of titrimetric reactions in aqueous and non-aqueous media [1, 19]. For acid-base reactions, redox reactions and complexation reactions, antimony electrodes, platinum electrodes and gold amalgam electrodes have been applied respectively [2, 3].

The Achilles Heel of modern analytical instrumentation is the manual handling of solutions. It has the disadvantage of being tedious, reagent consuming and time wasting. It requires a lot of manpower which generally add to overall laboratory operating cost. Currently, FIA allows automated handling of micro liters amount of sample and reagent solutions with a strict control of reaction conditions. It produces less hazardous waste. It is suitable for analysis of a large number of samples. SIA is a second generation FIA technique for automating wet chemical processes with the aid of a computer flow programming.

By coupling DEP with SIA, in this study, a new opportunity is opened for cyanide determination. In this method, two identical solid electrodes are used with a heavily stabilized small direct current. This proposed method, SIA-DEP, is based on the complete reaction of cyanide with silver nitrate to give a complex. The main potential change is found at the point where $\text{Ag}(\text{CN})_2^-$ is completely formed

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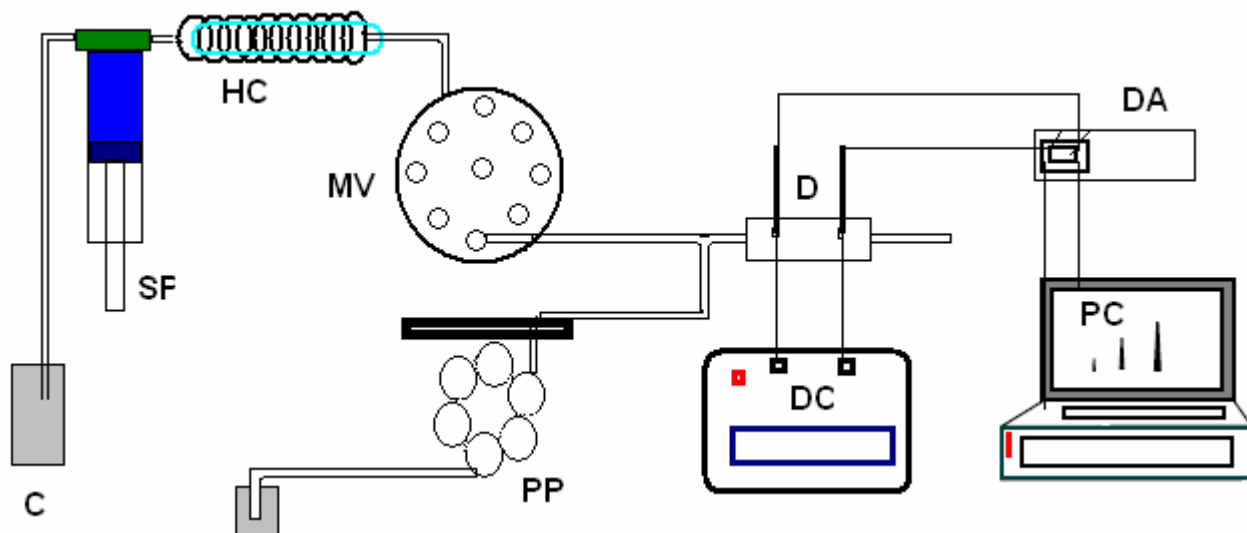


Fig. 1 Schematic diagram of the flow system. C: carrier, SP: syringe pump, HC: holding coil, PP: peristaltic pump, MV: multiselection valve, DC: direct current source, D: electrode detector, DA: digital-to-analog converter, PC: desktop computer.

2. Experimental

All reagents were prepared from analytical grade chemicals. Distilled water used was de ionized. All reagents were prepared and stored in polythene vessels.

2.1. Preparation of solutions

CAUTION: Because of toxicity of cyanide, solutions should be handled careful in the fume Hood.

- Silver nitrate solution: was prepared daily by weighing and dissolving 0.5 g of Fluka Ag NO₃ in deionized distilled water and diluted to give 200ppm.
- Potassium nitrate solution: 1.375 g of AnalR KNO₃ was dissolved in distilled water and diluted to a 500ml standard flask to produce 0.027M supporting electrolyte solution.
- Potassium cyanide: 0.25 g of Fisher KCN was weighing and dissolved in distilled water and diluted to 250ml in a standard flask. Series of standards for the experiments were prepared from this solution.
- Nitric acid solution: 6M nitric acid was prepared by carefully and gradually adding 48.8 ml of concentrated nitric acid to 51.2 ml distilled de ionized water.
- Sodium chloride: 0.125g Thorn Smith standard sodium chloride was dissolved in distilled water to 250 ml.
- Sodium iodide: 0.125 g Fluka sodium iodide was dissolved in distilled water and diluted to 250 ml.

2.2. Apparatus

The manifold used in this method consists of SIA combined with D.C. DEP. The SIA system is the Alitea USA/FIA Lab 3500 (Medina, WA USA). Silver, gold and platinum wire electrodes were used. The diameter was 0.93 mm. The purity was 99.99 %.

2.3. Method and Procedure

The following steps are applied for cyanide analysis:

- The syringe pump was filled with 2500 μ l of the supporting electrolyte by directing the tow-way valve to the in-position mode with flow rate of 200 μ l s⁻¹.
- The standard solution of silver nitrate was linked to the selector valve through valve 8.
- Cyanide solutions were linked to the selector valve through

valves 2, 3,4,5,6 and 7.

- The aspiration runs and directing the two way valve to the out position mode with flow rate of 30 μ l s⁻¹.
- A 2500 μ l volume was dispensed to the Z-flow cell passing through the reaction coil and, then, to the electrodes. Simultaneously, the 10 μ A was applied, and the difference in potential was scanned and, then, recorded.

3. Results and Discussion

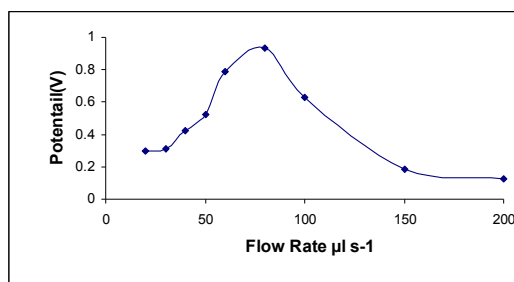
The method for cyanide determination by SIA-DEP was optimized using uni-variance approach. The parameters were optimized using standard solutions containing 25 ppm cyanide.

3.1. Coil length

The coil length, from the mixing point to the electrodes plays an important role because electrodes response to the difference in potential during the occurrence of the reaction. The coil length was varied between 10 to 90 cm. Long coil length gives rise to missing the main potential change which is found at the end point where silver cyanide complex is completely formed. The optimum coil length was 18 cm. It was found that there is no need for delay time since the reaction is fast.

3.2. Flow rate

Also, the flow rate to detector is important. Low flow rate gives much time for the reaction to take place before reaching to the detector. High flow rate causes the reagents to pass electrodes at the beginning of the reaction. The optimum flow was 80 μ l s⁻¹. This indicates that the electrodes can catch the end point.



* Average of four determinations

Fig 2. Plot of potential versus flow rate

3.3. Type of Electrodes

Three types of electrodes, silver, gold and platinum, were studied. The concentrations of standard cyanide were 0.1, 1, 10, 25, 40, 60 ppm. The platinum electrodes were cleaned with aqua regia before each experiment and rinsed with distilled water. Both silver and gold were cleaned with 6 M nitric acid and then rinsed with distilled water and then amalgam was made. The silver amalgam was having a good responds and longer-life.

3.4. Reagents and cyanide Volume

The effect of cyanide and silver volumes were studied. The cyanide volume was varied between 50 μl to 200 μl , and so for silver nitrate. As we see in tables 1 and 2, increasing the sample volume from 50 to 100 μl increases the sensitivity of this method since the analyte becomes more and so a higher potential reading. This reading stays constants up to 140 μl but the peaks become a little bit broader. Above 140 μl the reading decreases due may to high sample to reagent volume ratio. On the other hand, the low sample to reagent volume ratio is the main factor for the decreasing in potential when the volume of silver solution is more than 120 μl . The optimum volume of cyanide was 100 μl while it was 120 μl of silver nitrate.

Table 1 Effect of sample volume on the potential

Sample volume (μl)	Potential (V)
50	0.274
80	0.451
100	0.523
120	0.521
150	0.491
200	0.431

Table 2 Effect of silver volume on potential

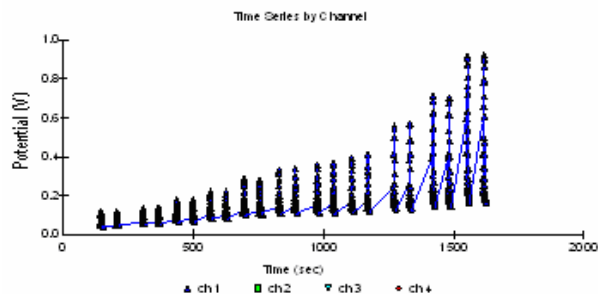
Silver volume (μl)	Potential (V)
50	0.235
80	0.377
100	0.466
120	0.546
150	0.487
200	0.325

* Average of three determinations.

3.5. Applied DC-Current

The current was varied between 0.05 and 50 μA . At the current

more than 17 μA , the peak was distributed. At current lower than 4 μA , the height of the peak was not so good comparing with that in the range 4-17 μA . Although there was lost in symmetry at 17, the best applied current was between 10 and 17 μA .



* Average of two determinations

Fig 3 Potential vs current 0.05,0.1,0.15,1,2,4,5,6,8,10, 12, 17 μA

3.6. Interference Study

Interference of added anions, chloride, iodide, sulfate, carbonate and phosphate, and some cations, chromium, cobalt and nickel, were studied using cyanide concentration of 25ppm.

3.6.1. Anions

Interference of chloride, iodide, sulfate, carbonate and phosphate, were studied by making synthetic interfering samples of known concentrations. It was found that up to 50ppm, chloride does not interfere. On the other hand, iodide has stronger interference than chloride. It was observed that the interference started at 30ppm. The interference of carbonate, sulfate and phosphate were much less than the previous anions. The interference was observed at 600ppm of both carbonate and sulfate, and 300 ppm of phosphate added.

3.6.2. Cations

Interference of Co^{+2} , Ni^{+2} and Cd^{+2} were studied by also making synthetic interfering samples of known concentrations. The order of interferences was $\text{Cr}^{+3} > \text{Ni}^{+2} > \text{Cd}^{+2}$. They interfere at concentrations higher than 20, 25, 100 ppm respectively.

3.7. Method Evaluation

3.7.1 Calibration curve

Under the optimum conditions described above, the linearity of the proposed SIA-DEP method for cyanide determination was studied. The method is linear between 1 and 60 ppm. The detection limit was 0.5 ppm. The correlation coefficient was 0.999. The equation for potential measurement was: Potential (V) = 0.24 + 0.0091 x C (ppm). A bias of 0.24 was due to the slight over-potential on the surface of the electrode.

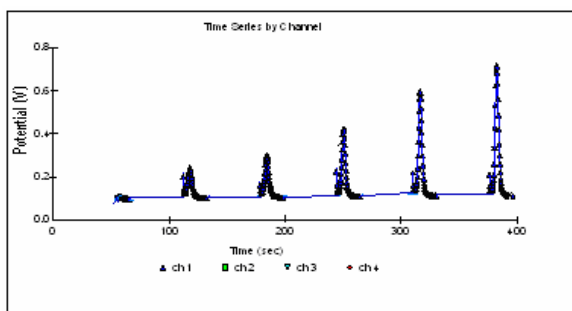


Fig 4. Potential versus run time for cyanide determination with CN = 0, 1, 10, 25, 40 and 60 ppm

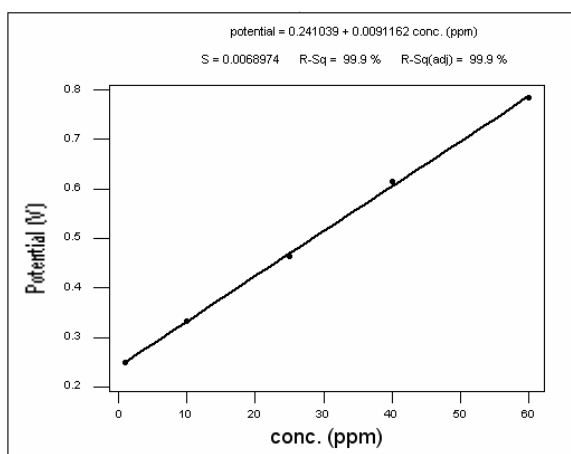


Fig 5. Calibration curve obtained for cyanide determination.

3.7.2 Comparisons of results with APHA standard method

The results obtained using the proposed method was compared with standard method APHA, American Public Health Association. The calculated t-value was 0.96 which is less than 2.776 (95% confidence level, $p=0.050$). RSD was found to be 1.43%.

Table 3 Comparisons of results with standard method

CN added (ppm)	Found (ppm)	
	Proposed method	Standard method
60	59.46 ± 0.34	60.22 ± 0.42
10	10.13 ± 0.21	9.95 ± 0.25
1	1.03 ± 0.15	1.04 ± 0.14

* Average of three determinations

t-test value = 0.96

CONCLUSION

The differential electrolytic potentiometry (DEP) coupled with the flow injection analysis (FIA) method proposed in this paper for cyanide determination is simple, precise and low-cost. It requires a simple electric circuit (DC) with only two silver wires electrodes. The sensitivity has been enhanced by shortening the coil length between the reaction point and the electrodes. The optimum flow rate was observed to be 80 $\mu\text{l s}^{-1}$ and the best applied current is 10-17 μA . The system can be applied for about 10 analyses per hour with 0.5 ppm detection limit. The equation for potential measurement is [Potential (V) = 0.24 + 0.0091x C (ppm)], and the correlation coefficient is 0.999. It has advantages of minimizing time and amount of consumed solutions.

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