

Differential Electrolytic Potentiometry: a Detector in the Flow Injection Analysis of Cyanide Using Silver Electrodes Modified with Carbon Nanotubes

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Abstract Differential electrolytic potentiometry (DEP) using silver electrodes coated with carbon nanotubes was applied as a detector in a flow injection analysis of cyanide. The direct current differential electrolytic potentiometry (dc-DEP) and the mark-space bias differential electrolytic potentiometry (m.s.b. DEP) both were applied as indicating systems. The parameters that give the best signal were investigated and optimized. A current density of $17 \mu\text{A cm}^{-2}$ and a percentage bias of 2.8% were found to be optimum in case of dc-DEP and m.s.b. DEP, respectively. The optimum flow rate of both the analyte and the supporting electrolyte was found to be of $85 \mu\text{L s}^{-1}$ using a coil length of 45 cm. In case of dc-DEP, a linear range of 1–65 ppm of KCN with a detection limit of 0.5 ppm and a relative standard deviation of 2.1% was observed. In case of m.s.b. DEP, a linear range of 1–65 ppm of KCN with a detection limit of 0.35 ppm and a relative standard deviation of 1.5% was observed. The proposed DEP-FIA methods are computer controlled, fast, sensitive, inexpensive and require low consumption of reagents.

Keywords Differential electrolytic potentiometry · Mark-space bias · Silver electrode · Carbon nanotube · Flow injection · Cyanide

1 Introduction

Cyanide (CN) refers to various specific cyanide compounds. However, cyanide itself is an organic anion which consists

of carbon and nitrogen atoms. In industry, about 1.1 million tons of cyanide is consumed annually. For example, HCN is used in the production of nylon and perspex [1]. Cyanide has attracted the attention of researchers due to its serious poisonous effects on the human beings. For instance, the chronic toxicity usually leads to cardiovascular, blood and nervous system disorders [1–3].

Different methods have been applied for the determination of cyanide in aqueous samples using chromatographic techniques [4–12]. Ion-interaction chromatography combined with fluorometry has been applied for the determination of metallic cyanides [13–15]. Various electroanalytical [1, 16–20] and spectroscopic [1, 21–26] techniques have been developed for the determination of cyanide. However, most of these methods suffer from shortcomings like lack of sensitivity, longer time of analysis and the use of expensive instruments. A sensitive, fast and inexpensive method that consumes small volumes of reagents of analysis is required.

The technique of DEP depends on polarizing two similar electrodes and measuring the potential difference between them. The response of this technique is much faster than the zero current electrodes normally used in classical potentiometry which requires a reference electrode. The problems of the salt bridge of the reference electrode are eliminated in DEP [2, 3, 13]. DEP has been used as a detection system in all types of titrimetric reactions as well as FIA [8, 26, 27].

FIA is a technique based on the injection of a liquid sample into a moving, non-segmented continuous carrier stream of a suitable mobile phase as shown in Fig. 1. The injected sample forms a zone, which is transported toward a detector that continuously records the changes in absorbance or in potential depending on the type of the detector used [26].

Coating the silver electrodes with CNTs has been found to enhance the response of these electrodes by increasing

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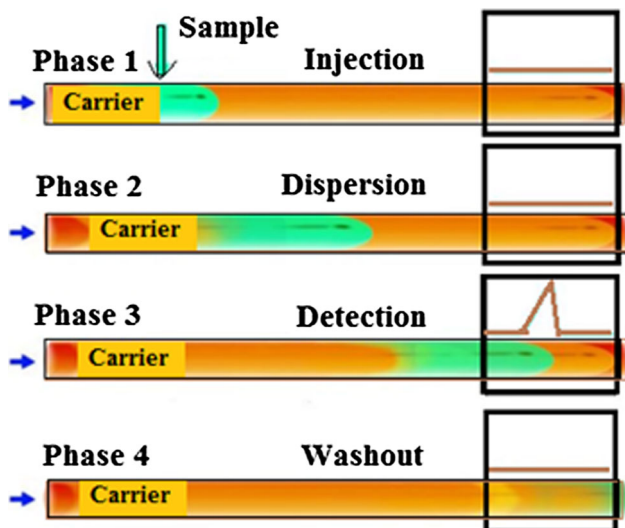


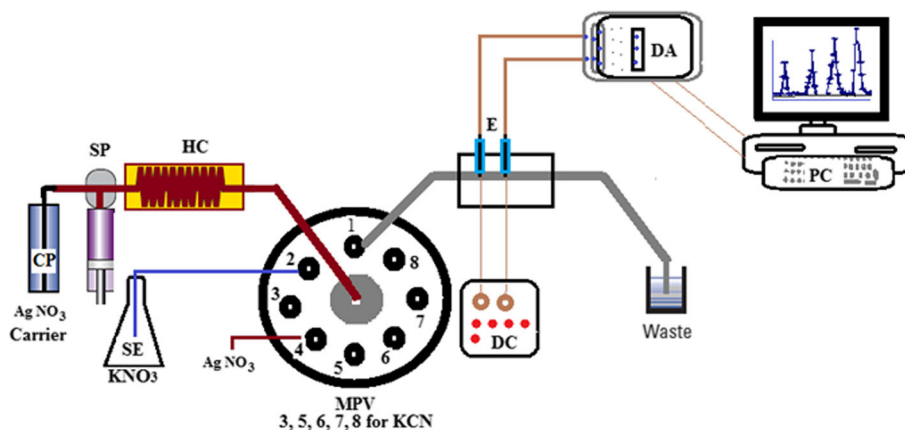
Fig. 1 Four phases of flow injection analysis

the active surface area. In addition, the modified electrodes can respond to all types of chemical reactions including ion combination and redox reactions. As a result, this analytical method is proposed for the determination of cyanide at extremely low concentrations. The DEP technique was used as a detection system for the determination of cyanide by FIA. In this method, two identical silver electrodes were modified with CNTs and polarized by either a constant current in case of dc-DEP or by a time-biased square wave in case of m.s.b. DEP. Silver nitrate was used as a reagent, and the potential difference between the two electrodes was measured. The resulting signal takes the form of a sharp symmetrical peak.

2 Experimental

Reagents of analytical grade were used in the preparation of the required solutions. Doubly distilled deionized water was used.

Fig. 2 Schematic diagram of the FIA system. CP carrier phase, SP syringe pump, HC holding coil, MPV multi-position valve, dc direct current source, E Silver modified electrodes, DA digital to analog converter. PC desktop computer)



2.1 Reagents and Solutions

The cyanide solutions were carefully prepared in a fume hood.

- Potassium cyanide (Fisher): 0.25 g of was weighed and dissolved in doubly distilled water and diluted to 250 ml in a standard flask. Series of standard solutions were prepared.
- Silver nitrate solution (Fluka) was daily prepared by weighing an amount of 0.5 g of AgNO_3 dissolved in doubly distilled water and diluted to give 200 ppm.
- Potassium nitrate solution (AnalaR): 1.375 g of KNO_3 was dissolved in doubly distilled water and diluted to a volume of 500 ml.
- A solution of 1.0 M nitric acid was prepared.

2.2 Coating Silver Electrodes with CNTs

The Ag-CNTs electrodes were prepared using the floating catalyst chemical vapor deposition (FC-CVD) method [28]. The silver electrodes each of 1 mm diameter and 2 cm length were placed in a quartz tube. Ferrocene catalyst was placed in another quartz tube. These two quartz tubes were inserted in the reactor, and the following optimum conditions were applied: a temperature of 700°C using silicon carbide and hydrogen gas as reactant and carrier at a flow rate of 25 ml/min. Acetylene gas of 99.5% purity with flow rate 75 ml/min was used as a hydrocarbon source. The reaction time was adjusted to a period of 15 minutes. Argon gas was used to flush the air from the reactor. Two of the resulting modified electrodes were cleaned with a 1.0 M HNO_3 , rinsed with deionized water and immersed in a solution of 1.0 M KNO_3 .

2.3 FIA Instrument

Alitea USA/FIA Lab 3000 (Medina, WA USA) flow injection system was used. This system is composed of a syringe pump,

a coil and a multi-position valve as shown in Fig. 2. The manifold used in this method consists of FIA combined with the detection systems dc-DEP and m.s.b. DEP.

3 Procedure

The syringe pump was filled with a volume of 2500 μL of the supporting electrolyte by directing the two-way valve to the in-position mode and adjusting the flow rate. The standard solution of silver nitrate was aspirated into the selector valve through valve 4. Cyanide solutions of different concentrations (10, 20, 30 and 65 ppm) were propelled through the selector valves 3, 5, 6, 7 and 8, respectively. An optimum dc current density of $17 \mu\text{A cm}^{-2}$ was applied in case of dc-DEP, and a percentage bias of 2.8% was applied in case of m.s.b. DEP.

4 Results and Discussion

4.1 Characterizations of the Ag-CNTs Electrodes

4.1.1 Scanning Electron Microscopy of Ag-CNTs

Scanning electron microscopy (SEM) was applied to characterize the morphology of both the bare silver electrode (Fig. 3) and the Ag-CNTs electrode (Fig. 4). It is obvious from these figures that the surface of the modified electrode

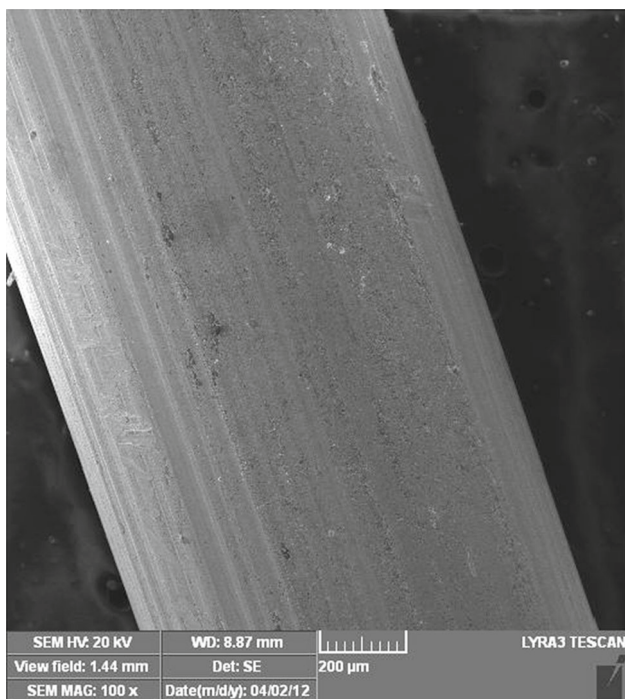


Fig. 3 SEM of bare silver electrode

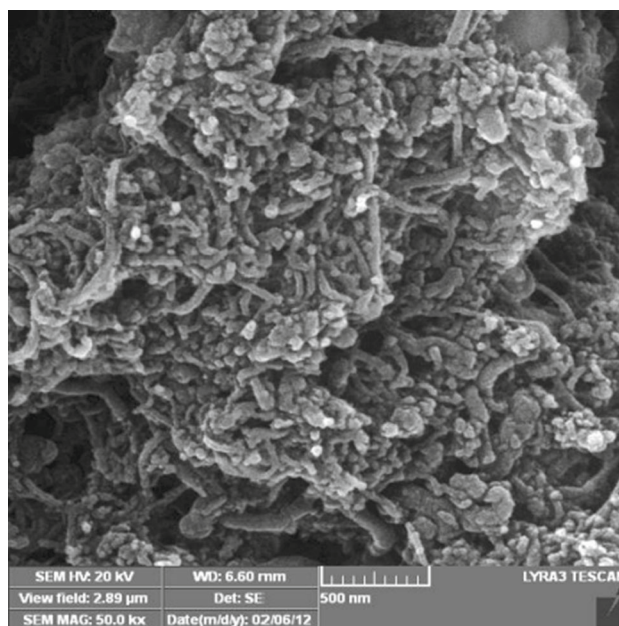


Fig. 4 SEM of Ag-CNTs electrode

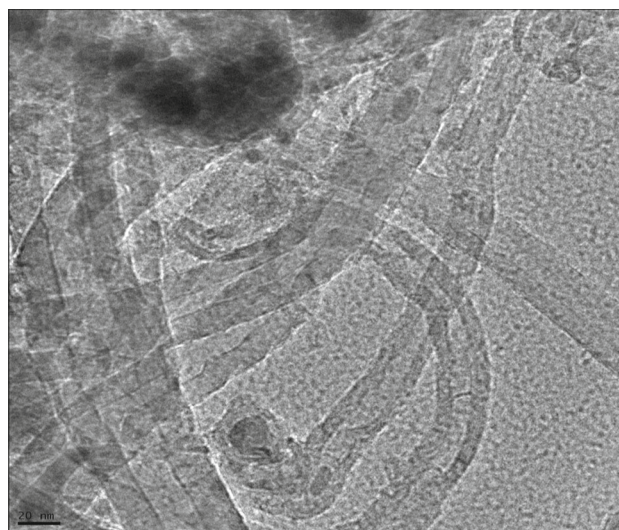


Fig. 5 TEM image of CNTs which has been grown on silver wire by CVD

is covered by the CNTs which have increased its surface area compared to the bare electrode.

4.1.2 Transmission Electron Microscopy of the Ag-CNTs

The structure of the CNTs was characterized by transmission electron microscopy (TEM). Small amount of alcohol was dropped on the CNTs films, which were transferred by means of a pair of tweezers to a carbon-coated copper grid. Figure 5 illustrates the resulting TEM images of the CNTs. These images show a small number of CNTs of hollow and tubular shape without deformity indicative of their high purity.

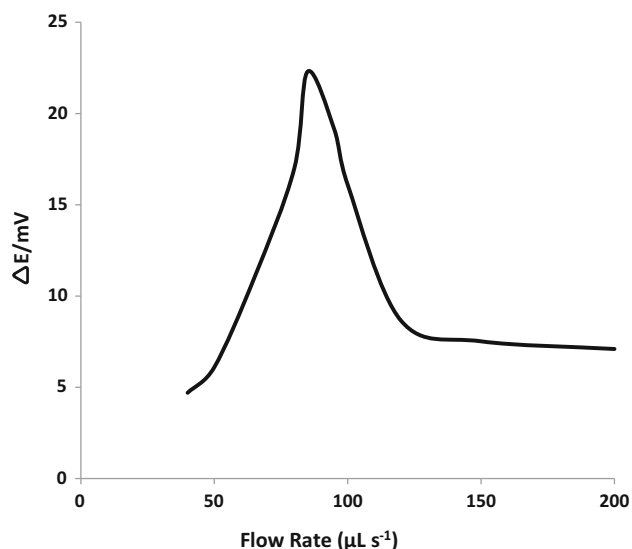


Fig. 6 The effect of flow rate of KCN and AgNO₃

4.2 Optimization of the Effective Parameters

The univariate approach was applied for the optimization of the effective parameters. These parameters include the volumes of solutions of the cyanide and the silver nitrate, in addition to the flow rate, the dc current, the percentage bias and the coil length.

A volume of 100 μL of 15 ppm potassium cyanide and 120 μL of 200 ppm of silver nitrate were allowed to react at different flow rates as shown in Fig. 6. It was found that the optimum flow rate of 85 μL s⁻¹ and a coil length of 45 cm give the best signal.

Since the reaction between cyanide and silver ions is very fast, there is no need for longer delay times. The optimum delay times that give the highest signals were 2 sec in case of dc-DEP and 5 sec in case of m.s.b. DEP. These optimum conditions were applied to establish the calibration curves shown in Fig. 7 for dc-DEP and Fig. 8 for m.s.b. DEP. Both of these curves show linear relationships between concentrations of cyanide of (1–65 ppm). However, a higher signal has resulted from the m.s.b. DEP (Fig. 8). It is evident that a concentration of 65 ppm of cyanide has given a signal of 78 mv. However, in case of m.s.b. DEP, the same concentration has given a signal of 600 mV. This can be attributed to the continuous reversal of the ac signal which keeps the electrodes more active. The dc-DEP gives a detection limit of 0.5 ppm, a correlation coefficient of 0.997 and a relative standard deviation of 2.1%. In case of m.s.b. DEP a detection limit of 0.35 ppm, a relative standard deviation of 1.5% and a correlation coefficient of 0.992 have been resulted.

The results of plotting the difference in potential versus the run time in case of dc-DEP-FIA for different KCN con-

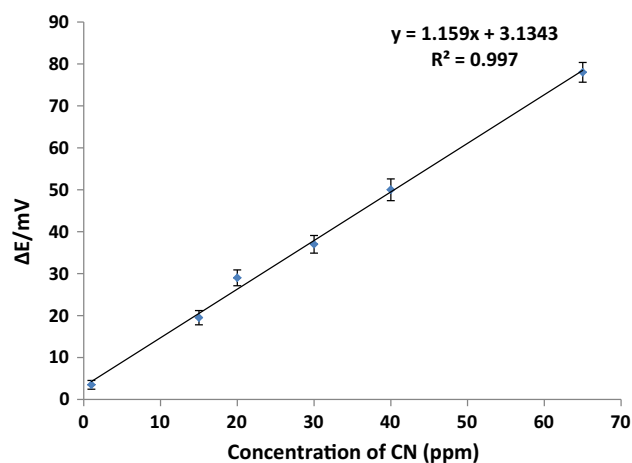


Fig. 7 Calibration curve obtained for cyanide determination using dc-DEP-FIA

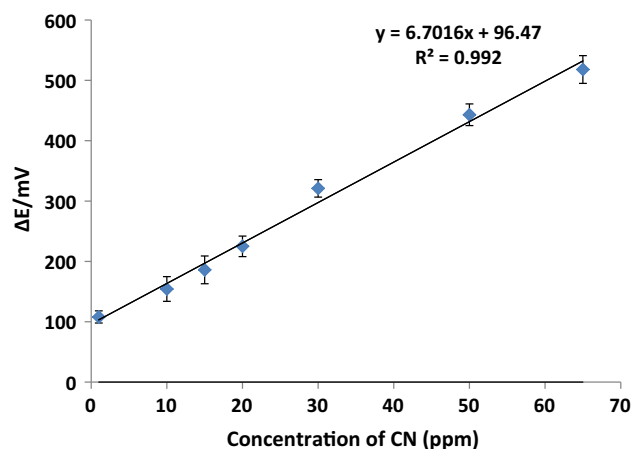


Fig. 8 Calibration curve obtained for cyanide determination using m.s.b. DEP-FIA

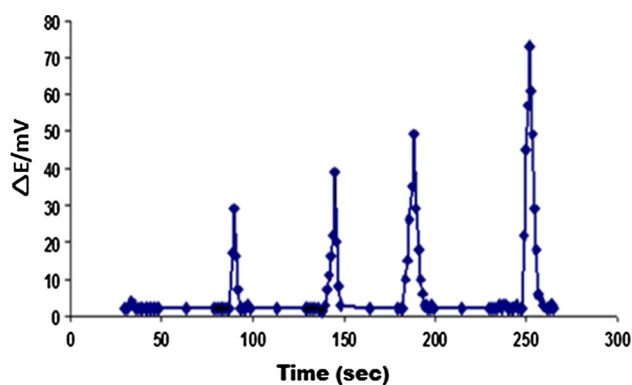


Fig. 9 ΔE versus run time for cyanide determination by dc-DEP-FIA for concentrations of KCN: 1, 20, 30, 40 and 65 ppm (left to right)

centrations of: 1, 20, 30, 40, 65 ppm are shown in Fig. 9. The repeatability of the resulting signals in each concentration (10, 20, 30 and 65 ppm of KCN) is shown in Fig. 10.

Fig. 10 The repeatability for cyanide determination by ac-FIA with 10, 20, 30 and 65 ppm KCN

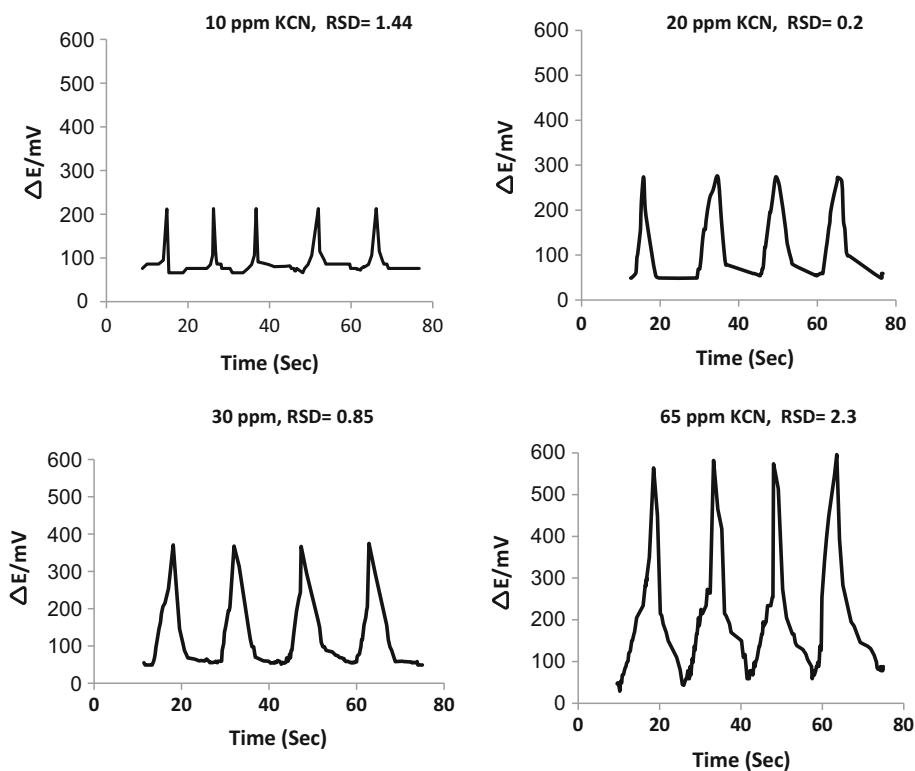


Table 1 Features of proposed method

Method case	LR (ppm)	R^2	LE	%RSDs ($n = 3$)	LODs (ppm)
dc-DEP-FIA	1–65	0.997	$y = 1.16x + 3.13$	2.1–5.2	0.50
m.s.b. DEP-FIA	1–65	0.992	$y = 6.7x + 96.5$	1.5–4.6	0.35

LR Linear range, R^2 Coefficient of determination, LE linear equation, %RSD relative standard deviation, LODs limit of detections

5 Comparison of the Analytical Performance of the Proposed Method with Other Methods

To evaluate this method, the linear range, coefficient of determination, relative standard deviation, percentage bias and LODs were investigated under the optimized condition for both cases dc-DEP and m.s.b. DEP, respectively. The results are summarized in Table 1.

Excellent linearity was observed over the concentration range of (0.5–65 ppm) for cyanide ion with favorable coefficient of determination (R^2) ranging from 0.992 to 0.997. The repeatability was studied by spiking plank samples with different concentrations of cyanide. The %RSDs were found to be between 1.5 and 5.2% ($n = 3$). The LODs, based on $S/N = 3$, range from 0.35 to 0.5 ppm. The results confirmed that the proposed method is suitable for the trace level detection of cyanide ion in water samples.

Table 2 shows a comparison between the proposed method and different reported methods available in the literature.

The developed method shows promising results compared to other methods reported for the detection of cyanide.

6 Conclusion

A simple, precise, inexpensive rapid differential electrolytic potentiometric (DEP) method for the determination of cyanide was developed. The potentiality of silver electrodes coated with CNTs as a detection system in FIA was investigated. The optimum conditions in both dc-DEP and m.s.b. DEP were elucidated.

The optimum conditions for the dc-DEP-FIA mode were found to be a flow rate of $85 \mu\text{L s}^{-1}$ and a current density of $17 \mu\text{A cm}^{-2}$. The system can handle about 45 analytical runs per hour with a detection limit of 0.5 ppm cyanide. In case of m.s.b. FIA mode, a percentage bias of 2.8% and a flow rate of $85 \mu\text{L s}^{-1}$ were found to be optimum.

Table 2 Comparison of proposed method with other reported methods for the detection of cyanide

No.	Method	Chemical system	LOD (ppm)	Comments	Refs.
1	DEP in FIA	Platinum and gold electrodes used	NA	Expensive electrodes and low responses.	[3]
2	Chromogenic	{ η^5 -(4-dimesitylboryl) indenyl}	10	Complicated synthesis, the limit of detection value is high	[29]
3	Chromogenic	Silver nanoparticles as colorimetric sensor	0.45	Multi-step procedure for nanoparticles preparation	[30]
4	UV–Vis spectroscopy	Crystal violet on triacetylcellulose	5	Good for water analysis but the detection limit is high	[31]
5	UV–Vis spectroscopy	ATP stabilized Au nanoparticles with Cu^{2+} phenanthroline	0.27	Lots of chemical reagents used with complex procedure	[32]
6	Voltammetry	Anthrone derivatives	2.86	Complex procedure, non-selective and high detection limit	[33]
7	Diffuse reflectance UV–Vis spectroscopy	Aquacyano corrinoids	1	High detection limit and used for detection of cyanide in plants and tobacco smoke	[34]
8	Electro fluorochromic	Benzothiodiazolecont-aining polymer	NA	New technique but the quantitative aspect is not available	[35]
9	Amperometry	Enzymatic sensor	0.011	Very complicated system base in biological sensor	[36]
10	Proposed method	Silver electrodes coated with CNTs.	0.35	Simple, inexpensive, easy to run with a very good detection limit, small volumes of reagents required and the analysis time is short	Current work

NA not available

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