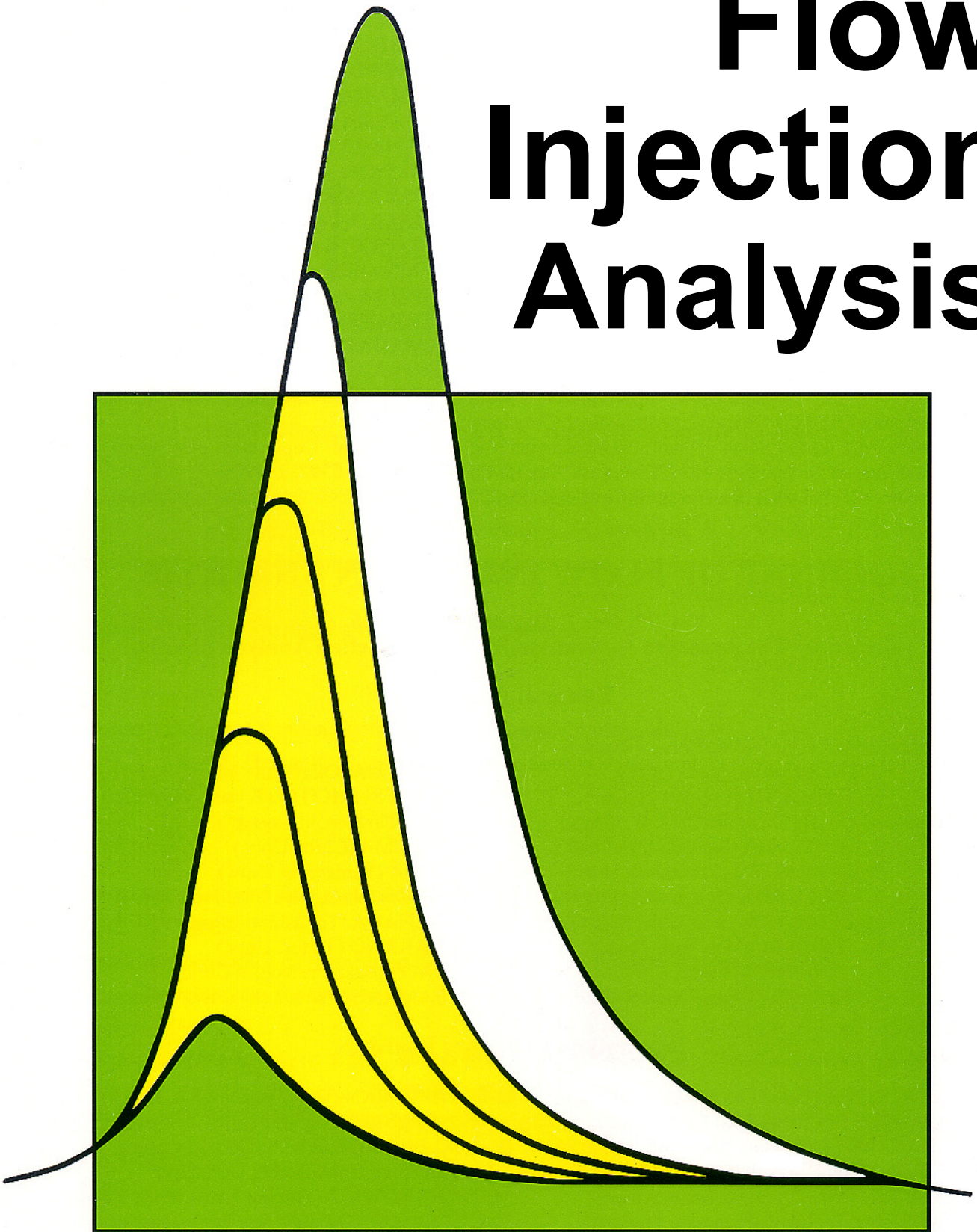


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# Sequential Injection Spectrophotometric Determination of Cyanide

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## Abstract

A simple and rapid sequential Injection spectrophotometric method for the determination of cyanide is proposed. The method is based on the reaction of cyanide with 2,2-dihydroxy-1,3-indanedione (Ninhydrin), which produces a red colored product that can be monitored at a wavelength of 600 nm. The linear range found is between 2.00 and 7.00 mg l<sup>-1</sup> with a detection limit of 0.16 mg l<sup>-1</sup>. The sampling rate was calculated to be 45 samples per hour. The proposed method has a precision and accuracy comparable with standard methods.

**Key words** Sequential injection, Cyanide, Ninhydrin.

## 1. Introduction:

Cyanide in its free and complex forms are considered as priority pollutants because of their acute toxicity to human and fish. Its determination is an important part of water quality measurements. Different methods have been developed to monitor aqueous cyanid. Those methods include chromatography [1- 9], and ion-interaction chromatography combined with fluorometry that used for the determination of metal cyanide complexes [10]. Several electroanalytical [11 – 14] and spectrophotometric [15 – 19] methods have been developed for the determination of cyanide. Flow injection with spectrophotometric detection [20] was employed for the determination of cyanide as tetracyanonickelate(II). A simple indirect spectrophotometric method for the determination of cyanide, based on the oxidation of the cyanide with chlorine (Cl<sub>2</sub>) has been described [21]. The reagent 2,2-dihydroxy-1,3-indanedione known as ninhydrin has been used for the spectrophotometric determination of cyanide in alkaline medium [22]. Most of the electrochemical methods have problems of interferences of some anions such as thiocyanate ion.

This work presents the application of sequential injection analysis for the determination of cyanide based on its modified reaction with ninhydrin in an alkaline medium, The blue colored product formed gives a maximum absorbance at a wavelength of 600 nm. The optimum conditions like the effect of reagent concentration, the volume of the reagent, the delay time and the flow rate were all investigated.

## 2. Experimental

### 2.1 Reagents and solutions

All solutions were prepared from analytical grade chemicals unless specified otherwise. All solutions used were prepared by using distilled de-ionized water.

### 2.2 Cyanide stock solution

A 1000 mg l<sup>-1</sup> standard cyanide stock solution was prepared by dissolving NaCN (Merck, Germany) in deionized water and diluting quantitatively to 1 liter with de-ionized water. Appropriate dilutions were prepared from the standard solutions.

### 2.3 Ninhydrin-solution

An amount of 0.10 g Ninhydrin (BDH) was dissolved in an appropriate volume of a 2% sodium carbonate solution.

### 2.4 Instrumentation

#### 2.4.1 SIA instrument

The manifold used in this method consists of SIA combined with a fiber optic spectrometer. The SIA system is the *FIALab 3500* (Medina, WA USA). It is composed of a syringe pump, a multi-position valve, a Z-flow cell with SMA fiber optic connectors as well as pump tubing and PC. The Syringe Pump is 24,000 steps with an optical encoder feedback and 1.5 seconds to 20 minutes per stroke of 2.5 ml size. It is > 99% accuracy at full stroke. The volume capacity of syringe is 5000 µl. The Multi-Position Valve has eight ports with a standard pressure of 250 psi (gas)/600 psi (liquid); zero dead volume; chemically inert; port selection is usually done using the software program. The Z-Flow Cell is 10 mm path length plexiglass compatible with standard SMA terminated fiber optics was used. Pump Tubing of 0.30" ID Teflon type supplied by Upchurch Scientific, Inc. (Oak Harbor, WA, USA) was used for connecting the different units; and making both the holding coil (190 cm long) and the reaction coil (190 cm long).

The fiber optic spectrometer is composed of a light source, 200 micron fiber optic connectors and a detector. The light source is LS-1 Tungsten Halogen (Ocean Optics, USA) optimized for VIS-NIR (360nm-2µm) wavelength range. The detector is USB2000 Spectrometer (Ocean Optics, USA adapted to 200-1100nm wavelength range. The SIA manifold is shown in Fig. 1 below.

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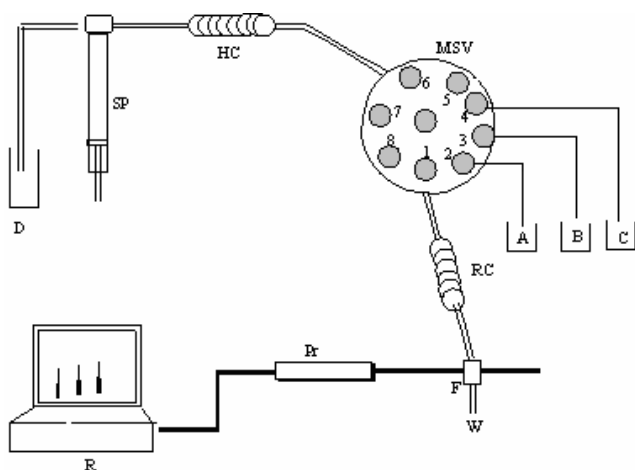


Fig.1 Manifold employed for spectrophotometric SIA determination of cyanide. Where SP = syringe pump, D = carrier, HC = Holding coil, MSV = multiselection valve, LS = light source, Pr = processor, F= flow cell, R = computer readout, A = sample, B = chromogenic reagent, C = NaOH solution.

#### 2.4.2 Software Packages

*FIALab for Windows* version 5.0 from FIALab® (Medina, WA USA) was utilized for programming, controlling the SIA manifold and data acquisition.

#### 2.4.3 UV-Visible Spectrophotometer

A perkin Elmer UV/Visible Lambda EZ210 spectrophotometer equipped with a high resolution concave diffraction grating and Seya-Mamioka mount; Stray light transmittance of 0.05% and wavelength accuracy of  $\pm 0.3$  nm. The wavelength accuracy is  $\pm 0.3$  nm ; wavelength reproducibility setting is  $\pm 0.1$  nm

### 3. Results and Discussion

Ninhydrin reacts with cyanide in aqueous medium to form hydrindatin, which decomposes in the presence of sodium carbonate to form a red-colored product. This product shows a maximum absorbance at 490 nm. However in presence of sodium hydroxide a blue colored product has been observed [22]. This product shows a strong absorption at 600 nm. Although ninhydrin reacts with amino acids and used for their determination, it can be used for selective determination of cyanide in aqueous samples that are free from amino acids like industrial wastes. Since this method is carried out in alkaline solution, the hazardous effect of hydrogen cyanide is totally avoided.

photometric accuracy (measured with NIST 930D filter) is  $\pm 0.002$  Abs (0 to 0.5 Abs) and  $\pm 0.004$  (0.5 to 1.0 Abs). The baseline flatness is  $\pm 0.002$  Abs (200 to 950 nm); Baseline stability (2 hours after power up) is within  $\pm 0.0003$  Abs/hr at 500nm; Response speed ranges from medium, fast to slow. The light source is a deuterium (D2) lamp, tungsten iodide (WI) lamp and the detector is silicon photodiode and readout is a desktop personal computer. The instrument consists of a 2 nm spectral band pass slit and a wavelength range from 190nm - 1100 nm . A 10 mm rectangular shaped cell was used for taking spectrophotometric reading.

#### 2.4.4 Method and Procedure

##### Method and Procedure for SIA method

The following steps are the protocol applied for analysis of cyanide. Working solutions of Ninhydrin, samples containing cyanide, and sodium hydroxide solution were linked to the selector valve through ports 2, 3, 4, respectively. Water as a carrier was linked to the syringe at the in-position valve. The syringe was filled with 2500  $\mu$ l of the carrier by directing the two-way valve to the (in-position) mode, with a flow rate of 100  $\mu$ l s<sup>-1</sup> the syringe pump dispensed about 800  $\mu$ l of the carrier to clear out flow cell and flush tubing . A volume of 200  $\mu$ l of Ninhydrin solution was aspirated into the holding coil and dispensed to the flow cell to flush sample tubing. A volume of 200  $\mu$ l of cyanide solution was aspirated into the holding coil and dispensed to the flow cell to flush sample tubing. Volumes of 50  $\mu$ l of Ninhydrin solution, 175  $\mu$ l of cyanide solution and 50  $\mu$ l of 0.1M sodium hydroxide were aspirated into the holding coil respectively. With a flow rate adjusted at 30  $\mu$ l s<sup>-1</sup>, a volume of 1000  $\mu$ l was dispensed to the Z-flow cell, passing through a 15-cm reaction coil to allow the zones to overlap and react. The reference and the absorbance scans both were performed simultaneously by the spectrometer at a wavelength of 600 nm and the maximum value of the monitored peak was recorded as an absorbance.

The optimum wavelength that is suitable for the quantitative determination of the cyanide ninhydrin reaction product was selected by scanning the absorbance of this product over the range of 300–700 nm. The wavelength of maximum absorbance which gives the best results was found to be 600 nm.

#### 3.1 Optimization of experimental variables

##### Effect of reagent concentration

A volume of 50  $\mu$ l of 5 ppm of cyanide solution was allowed to react with the same volume of each of Ninhydrin solutions that have different concentrations. A flow rate of 30 $\mu$ l/sec was employed and the results are shown in Fig.2.

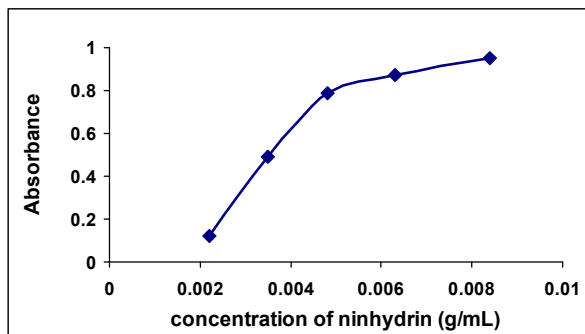


Fig.2. Effect of Ninhydrin concentration (g/ml)

#### Effect of sample volume

The effect of sample volume was studied by aspirating different volumes of cyanide solution using a volume of 50  $\mu\text{l}$  Ninhydrin solution of 0.00490 g/mL. A flow rate of 30  $\mu\text{l}/\text{sec}$  was used and the results are shown in Fig.3. As can be seen from this figure a sample volume of 175  $\mu\text{l}$  is considered to be an optimum one.

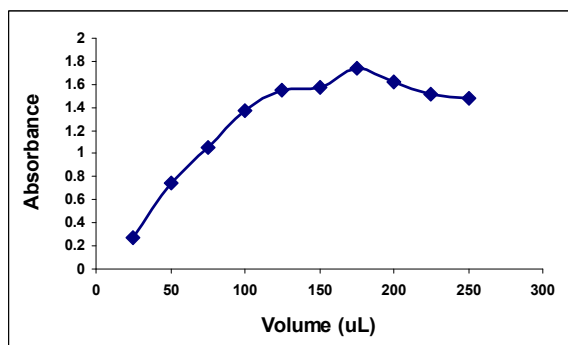


Fig.3. Effect of volume of cyanide solution ( $\mu\text{l}$ )

#### Effect of flow rate

Volumes of 50  $\mu\text{l}$  of each of 5 ppm cyanide and 0.00490 g/mL Ninhydrin solution were allowed to react at different flow rates. Fig. 4 shows that higher signal can be obtained at lower flow rates. However, at lower flow rates broad peaks were obtained. Hence it was decided to apply a value of 30  $\mu\text{l}/\text{sec}$  which was giving a symmetrical peak.

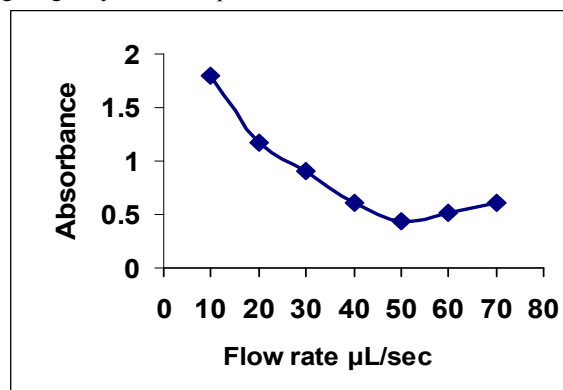


Fig.4. Effect of Flow rate  $\mu\text{l}/\text{sec}$

#### Effect of delay time

After aspirating the solutions into the holding coil as described in the above mentioned procedure, they were kept for a period of time called, the delay time, before being dispensed to the detector. As is evident from Fig.5 the delay time has no significant effect on the resulting signal.

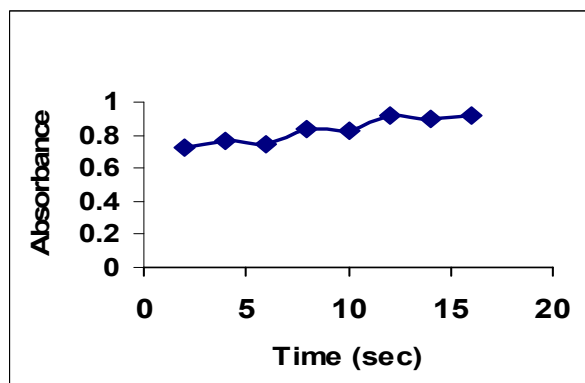


Fig.5. Effect of delay time

#### Analytical figures of merit

By adopting the above mentioned optimum condition a calibration curve was established which is depicted in Fig.6.

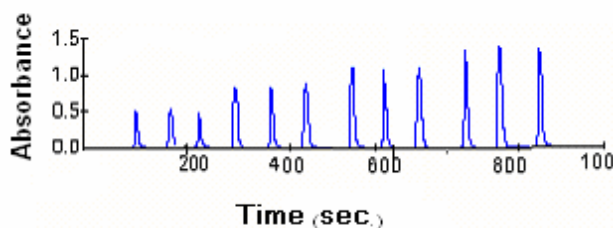


Fig.6 Typical SIA triplicates of cyanide standard solutions of (1.5, 2.0, 2.5, 3.0 ppm)

#### Linearity, accuracy, precision, detection limit and sample frequency

The regression calibration equation of the developed SIA is  $Y=0.3886+0.2389X$

where  $Y$  is the Absorbance,  $X$  the cyanide concentration in  $\text{mg l}^{-1}$ . The calibration curve is linear over the range of 2.0–7.0  $\text{mg l}^{-1}$  with a correlation coefficient ( $R^2$ ) of 0.992. The detection limit which was calculated from the following formula [23], gives an indication of the lowest concentration of cyanide that can be distinguished from the backgrounds signal with 99% certainty.

$$DL = (3\delta + \kappa)(\kappa - b)/m$$

where  $k$  is the relative peak height of the background (0.159),  $\delta$  is the standard deviation of the background (0.00358),  $b$  is the intercept of the calibration graph and  $m$  is the slope of the graph. The calculated detection limit was found to be 0.16  $\text{mg l}^{-1}$  of cyanide.

The present method provides the advantage over the conventional methods in the high sampling frequency that reaches 45 sample per hour, which makes it possible to be used in on-line monitoring of cyanide in environmental samples.

### 3.2 Interferences

The interferences of some common ions was studied using 6 ppm standard sodium cyanide solution using the optimized conditions, there were no significant interferences from

### 3.3 Method validation

In order to validate the proposed SIA method for application to real samples, cyanide was spiked to tap water and industrial effluent water samples containing cyanide. Cyanide was determined five times for both samples. The comparison was

potassium thiocyanate, sodium sulphate, sodium phosphate and sodium chloride up to 1000 ppm, ferrous and ferric ions show interferences at 400 ppm, and nickel chloride highly interfere at even 4 ppm due to the tendency of nickel to form stable complex with cyanide at the proposed conditions.

done between the proposed SIA method and the standard method to see whether the two methods give the same results at the 95% confidence level. Finally  $t_{\text{calculated}}$  was computed as  $t = (X-\mu)/s/n^{1/2}$ . The statistical results obtained by both the proposed method and standard method revealed no significant difference in the performance of the two methods regarding accuracy and precision as revealed by t-test Table (1).

Table 1 Analysis of real water samples and an industrial effluent spiked with cyanide.

Proposed SIA method			Standard method (Aldridge) [15]		$t^{\S}$	
Sample	Cyanide added ( $\mu\text{gml}^{-1}$ )	Cyanide found ±RSD	Recovery ±RSD	Cyanide found ( $\mu\text{gml}^{-1}$ )	Recovery ± RSD	
Water	5.0	4.87 *	97.4%±0.95	4.91	98.4%± 1.2	2.4
	10.0	9.75	97.5%±0.87	9.82	98.2%± 1.5	1.8
	20.0	19.67	98.4%±0.97	19.80	99.0%± 0.97	1.4
Industrial	0.0	2.6		2.5		

\* Average of five determinations.

$\S$  t (theoretical value) = 2.776 with 95% confidence

## 4. Conclusion

The robust, simple and rapid inexpensive proposed SIA system offers an important role in monitoring cyanide in aqueous media. The system is suitable to operate at a sampling throughput of 45 samples per hour in a linear range between 2.0 and 7.0  $\text{mg l}^{-1}$  with a detection limit of 0.16 ppm. The results of this proposed method and were validated with the student's t-test and are in agreement with those of standard methods.

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## 5. References

- [1] D.L. Duval, J.S. Fritz and D.T. Gjerde, *Anal. Chem.*, **54**,30, (1982).
- [2] D. F. Hilton and P.R. Haddad, *J. Chromatogr.*, **361**, 144 (1986).
- [3] M. Nonomura, *Anal. Chem.*, **59**, 2073 (1987).
- [4] B. Grigirova, S. A. Wright and M. Josephson, *J. Chromatogr.*, **410**, 419 (1987).

- [5] M. Nonomura, *Met. Finish.*, **85**, 15 (1987).
- [6] M. Nonomura and T. Hobo, *J. Chromatogr.*, **465**, 395 (1989).
- [7] L. Giroux and D. J. Barkley, *Can. J. Chem.*, **72**, 269 (1994).
- [8] Q. Huang, B. Paull and P. R. Haddad, *J. Chromatogr. A*, **770**, 329, (1997).
- [9] C. Giuriti, S. Cavalli, A. Gorni, D. Badocco and P. Pastore, *J. Chromatogr. A*, **1023** (1), 105 (2004).
- [10] E. Miralles, R. Compañó, M. Granados and M. D. Prat, *Anal. Chim. Acta*, **403**, 197 (2000).
- [11] L. S. Clesceri, A. E. Greenberg, and A. D. Eaton, "Standard Methods for the Examination of Water and Wastewater", 20<sup>th</sup> ed., **1998**, American Public Health Association, Washington, D.C.
- [12] K. Nagashima, H. Horie and S. Suzuki, *Anal. Sci.*, **2**, 271 (1986).
- [13] A. Tanaka, K. Mashiba and T. Deguchi, *Anal. Chim. Acta.*, **214**, 259 (1988).
- [14] A. Amine, M. Alafandy, J. M. Kauffmann and M. N. Pekli, *Anal. Chem.*, **67**, 28 (1995)
- [15] A. A. Schilt, *Anal. Chem.*, **30**, 1409 (1958).
- [16] J. L. Lambert and D. J. Manzo, *Anal. Chem.*, **40**, 1355 (1968).

- [17] M.W. Scoggins, *Anal. Chem.*, **44**, 1294 (1972).  
[18] J. L. Lambert, J. Ramasamy and J. V. Paukstelis, *Anal. Chem.*, **47**, 916 (1975).  
[19] J. L. Meeussen, E. M. Temminhoff, M. G. Keiser and I. Novozamsky, *Analyst*, **114**, 959 (1989).  
[20] S. Hermin, C. J. Terence and D. K. Spas, *Anal. Chim. Acta*, **214**, 259 (1988).  
[21] G. Gülçin, D. Birsen and R. Apak, *Talanta*, **53**, 305 (2000).  
[22] P. Nagaraja, M.S. H. Kumar, H.S. Yathirajan and J.S. Prakash, *Analytical Sciences*, **18**, 1027 (2002).  
[23] J.F. van Staden, L.V. Mulaudzi and R.I. Stefan, *Talanta* **64** 1196 (2004)

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