

DETERMINATION OF CYANIDE IN COKING PLANTS WASTE
WATERS USING FLOW INJECTION WITH
SPECTROPHOTOMETRIC DETECTION

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COMMUNICATION

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OZNACZANIE CYJANKÓW W ŚCIEKACH KOKSOWNICZYCH
Z ZASTOSOWANIEM PRZEPEŁYWOWEJ ANALIZY WSTRZYKOWEJ
Z DETEKcją SPEKTROFOTOMETRYCZNĄ

Cyjanki należą do silnie toksycznych substancji, a ich monitoring w ściekach przemysłowych jest obowiązkowy. Podczas oznaczania HCN był uwalniany z próbki w procesie destylacji i absorbowany w silnie zasadowym roztworze NaOH. Następnie cyjanki były oznaczane metodą FIA z detekcją spektrofotometryczną z zastosowaniem Chloraminy T, KH_2PO_4 , Na_2HPO_4 , kwasu izonikotynowego i 3-metylo-1-fenyl-2-pirazolino-5-onu, które z cyjankami tworzą czerwony związek, o maksymalnej absorpcji występującej przy $\lambda = 560$ nm. Przeprowadzono optymalizację metody i zastosowano ją do oznaczania cyjanków w ściekach koksowniczych w szerokim zakresie stężeń od $0,32 \text{ mg dm}^{-3}$ do $281,4 \text{ mg dm}^{-3}$. Przedstawiono charakterystykę metody, w zakresie: odchylenia standardowego, precyzji, granic wykrywalności i oznaczalności oraz odzysku analitu.

Summary

Cyanides are extremely hazardous substances and their monitoring in industrial waste waters is mandatory. During the determination hydrogen cyanide was liberated from the sample by distillation and collection by passing through a strongly-alkaline NaOH solution. Then cyanides were determined by flow injection analysis using spectrophotometric method with Chloramine T, KH_2PO_4 , Na_2HPO_4 , isonicotinic acid, and 3-methyl-1-phenyl-2-pyrazolin-5-one, which formed with cyanides red product with maximum absorbance at 560 nm. The method optimization was carried out and then the method was applied to the determination of cyanide in coking plants waste waters in a wide range from 0.32 mg dm^{-3} to 281.4 mg dm^{-3} . Method performances including: standard deviation, precision, limit of detection, limit of quantification and analyte recovery were carried out.

INTRODUCTION

Cyanide is used in the production of: plastics adhesives, computer electronics, cosmetics, dyes, pharmaceuticals and road salts [7]. Cyanide is also an environmental pollutant with at least three important sources: former manufactured gas plant, mining

operations and waste waters from coking plants [12]. The latter source concerns particularly industrialized regions such as Upper Silesia in Poland, where many harmful for environment coking plants are located [4].

Cyanide is a general term referring to all compounds containing the cyanide group CN^- (triple bond between carbon and nitrogen). They can be divided into four groups:

1. Hydrogen cyanide (HCN), also called hydrocyanic acid, cyanogens, or prussic acid,
2. Simple cyanides (inorganic salts such as NaCN, and KCN),
3. Metal-complexed cyanides (e.g. Fe(II)(CN)_6^{4-} , $\text{Fe(III)(CN)}_6^{3-}$, Zn(II)(CN)_6^{4-}),
4. Organic compounds such as nitriles, some pesticides with CN groups.

Toxicity of various cyanide compounds to human beings ranges from weak to extremely toxic. Free cyanides in the form of HCN or CN^- are the most toxic cyanides compounds because they are easily and rapidly absorbed through inhalation, ingestion or skin contact. Thiocyanates and iron-complexed cyanides are much less toxic than free cyanides [1]. These species must be reliably determined on suitable concentration levels owing to their toxicity.

The regulatory analysis of water samples for cyanide usually involves two steps. In the first step, the sample is digested to convert all cyanide species into gaseous HCN, which is trapped in a high pH solution. In the second step, cyanide is determined by various methods such as argentometric, and iodometric titration, fluorimetry [9], spectrophotometry [8], amperometry [3], as well as polarography and voltammetry [10]. The predominant method of cyanide determination in many laboratories is a method described by Epstein in 1947 [2].

One of the most common methods of determination of inorganic ions in water and waste waters is ion chromatography. Unfortunately, the determination of cyanide ions by ion chromatography is complicated by the fact that the sensitivity of conductivity detector, which is considered the most convenient to use, is insufficient. Moreover, the use of suppression of the conductivity of the eluent to improve the signal-to-background is precluded by a high basic nature of cyanide ions. As a result, amperometry with silver electrode is usually used as the detector in ion chromatography for the determination of cyanide [11].

Coking plants are known as sources of many hazardous compounds such as polycyclic hydrocarbons, phenols, thiocyanates and cyanides. Waste waters from coking plants belong to the most dangerous industrial wastes. The concentration of cyanides in coking waste waters can be exceeded by several hundreds mg dm^{-3} [4].

The present work describes optimization of the method described by Zhu and Fang [13] and its application for the determination of total cyanides in different types of coking waste waters. The efficiency of waste waters purification was evaluated.

MATERIALS AND METHODS

Flow Injection Analyzer system 5010 from Tecator (Hoeganaes, Sweden) consisting of FIAstar 5023 spectrophotometer, injector V-100, Chemifold II and 5017 auto sampler was used.

Analytical grades KCN, NaOH, Chloramine T, KH_2PO_4 , Na_2HPO_4 , isonicotinic acid, 3-methyl-1-phenyl-2-pyrazolin-5-one, all from Sigma Aldrich were used. Water used in the experiments was purified using Millipore equipment (Millipore, Bedford, MA, USA) and

had an electrical conductivity $< 0.05 \mu\text{S}/\text{cm}$.

A $1000 \text{ mg dm}^{-3} \text{ CN}^-$ stock standard solution was prepared by dissolving an appropriate amount of KCN in deionised water. Next, pH was adjusted to 11.5 (with 0.1 M NaOH) and solution was stored in a refrigerator at 4°C . Standard solutions of cyanide were prepared by diluting the stock standard solution to the required concentration just before use. The diagram of flow injection system used is shown in Figure 1.

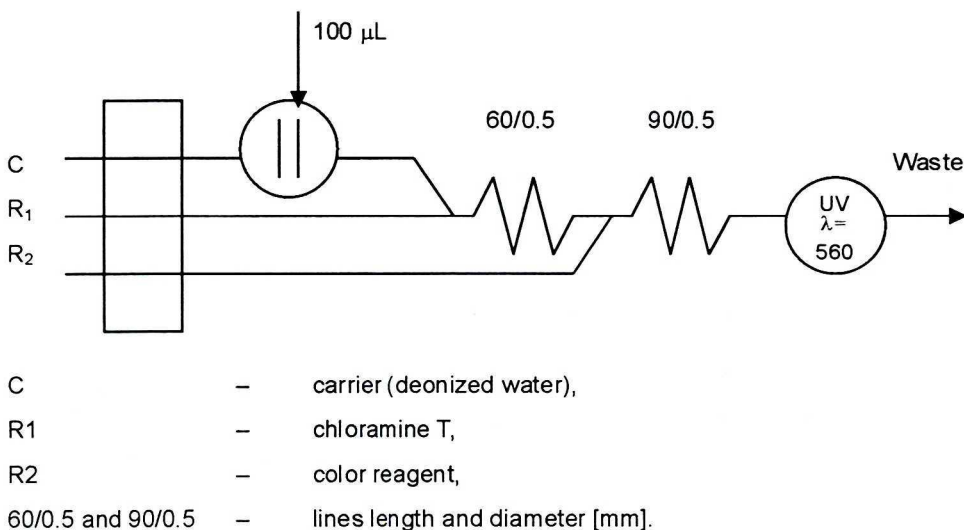


Fig. 1. The diagram of FIA system used

RESULTS AND DISCUSSION

Method optimization

100 cm^3 of each environmental sample was distilled using classical distillation procedure, as follows: cyanides as hydrocyanic acid (HCN) were released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution ($\text{pH} = 11.5$). The cyanide in the absorbing solution was then determined by spectrophotometric method described by Zhu and Fang [13].

According to that procedure cyanides are determined by flow injection analysis using following reactions: cyanides are oxidized by Chloramine T to cyanogen chloride which reacts with isonicotinic acid, and 3-methyl-1-phenyl-2-pyrazolin-5-one forming a red intermediate product with maximum absorbance at 560 nm.

Method optimization was carried out with respect to: injection volumes, concentrations of Chloramine T, and flow rates of reagents. Three injection sample loops: $40 \mu\text{L}$, $100 \mu\text{L}$ and $200 \mu\text{L}$ and four Chloramine T solutions (5.0 g dm^{-3} , 10.0 g dm^{-3} , 15.0 g dm^{-3} and 20.0 g dm^{-3}) were tested to obtain maximum signals without interferences. The important parameters in flow injection analysis are concentrations of applied chemicals and their flow rates, which are determined by using appropriate lines for chemicals mixing. In this connection several

lines for carrier and reagents mixing were used. The optimized conditions are as follows:

Flow injection analyzer	–	Tecator, model FIA 5012
Detector UV	–	$\lambda = 560 \text{ nm}$
Carrier (deionized water) (C)	–	flow rate $1.2 \text{ cm}^3 \text{ min}^{-1}$
Chloramine T (R1)	–	15.0 g dm^{-3} + buffer (KH_2PO_4 4 g dm^{-3} + Na_2HPO_4 35.5 g dm^{-3} , flow rate $0.4 \text{ cm}^3 \text{ min}^{-1}$
Color reagent (R2)	–	isonicotinic acid (73.6 g dm^{-3}) + NaOH (24 g dm^{-3}) + 3-methyl-1-phenyl-2-pyrazolin-5-one (0.52 g dm^{-3}), flow rate $1.2 \text{ cm}^3 \text{ min}^{-1}$
Injection volume	–	$100 \mu\text{L}$

Calibration and method performances

The concentrations of cyanide in wastewater from coking plant could be in the range, from limit of detection to over 500 mg dm^{-3} , thus the concentrations of cyanide in standard solutions was in the range from 0.5 to 50 mg dm^{-3} .

In order to estimate some method performances parameters, such as standard deviation, precision, limit of detection and limit of quantification, 10 calibration solutions of CN^- (0.5 ; 1.0 ; 2.5 ; 5.0 ; 7.5 ; 10.0 ; 20.0 ; 30.0 ; 40.0 and 50.0 mg dm^{-3}) were analyzed in triplicate. The obtained data are listed in Table 1.

Table 1. Method performance – selected statistical parameters

Parameter	Value
Concentration range [mg dm^{-3}]	$0.5\text{--}50.0$
Standard deviation [mg dm^{-3}]	0.02
Precision [%]	0.88
Limit of detection [mg dm^{-3}]	0.05
Limit of quantification [mg dm^{-3}]	0.15
Regression coefficient (r)	0.9987

Determination of cyanide in industrial wastewater

12 coking waste waters samples were sampled at 3 coking plants (A, B, and C) from 4 sampling points (2 raw waste waters and 2 purified waste waters).

The distillation process was carried out using classical distillation procedure, and samples were analyzed using FIA system. To check cyanide recovery, just before distillation – 0.2 cm^3 of standard stock solution ($1000 \text{ mg CN}^- \text{ dm}^{-3}$) was added to 100 cm^3 of each sample. It corresponds to 2.0 mg dm^{-3} of CN^- . The mean results (from triplicate analysis) including uncertainty of measurements calculated according to [6] are given in Table 2.

Table 2. Concentration of cyanide in wastewaters from coking plants [mg dm^{-3}]

Sample/recovery	Coking plant/sample											
	A				B				C			
	1*	2*	3**	4**	1*	2 ^{*)} *	3**	4**	1*	2*	3**	4**
Non-spiked sample	7.39 ±	18.24 ±	0.45 ±	1.37 ±	37.54 ±	28.14 ±	2.67 ±	0.32 ±	7.12 ±	33.11 ±	1.35 ±	3.47 ±
	0.58	1.51	0.11	0.24	2.65	3.71	0.24	0.04	0.64	2.21	0.11	0.33
Sample spiked with 2.0 mg dm^{-3} of CN^-	8.84 ±	20.04 ±	2.27 ±	3.12 ±	39.23 ±	28.54 ±	4.32 ±	2.17 ±	8.87 ±	34.41 ±	3.17 ±	5.21 ±
	0.72	1.94	0.17	0.37	2.73	4.84	0.31	0.36	0.93	2.48	0.15	0.72
Recovery [%]	94	99	88	95	99	94	92	94	97	98	94	95

* raw waste water

** purified waste water from sewage treatment plant

2^{*)}* sample diluted before analysis with deionized water (1:10 v/v)

CONCLUSIONS

Method performances parameters such as standard deviation, precision, limit of detection, limit of quantification and recovery show that optimized method is appropriate for the determination of cyanide in raw and purified waste waters in a wide range of concentration.

The analyzed samples originating from 3 coking plants were divided to 2 raw waste water samples, and 2 samples after purification at sewage treatment plant. The concentrations of cyanide in samples 3* and 4* (Table 2) from all coking plants are much lower than in raw waste water samples (1* and 2*), which means that purification process of waste waters is effective.

The recovery of cyanide from analyzed wastewater samples (88–99%) shows that applied method is suitable for environmental purposes.

Most of the methods used for cyanide analysis require sample distillation before final determination. Comparing to manual method, FIA is especially suitable for routine analysis in laboratories which monitored those hazardous compounds.

To check method ruggedness and flexibility, the influences of oxidizing agents present in environmental samples and certified reference materials should be tested and used in a further study.

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