International Journal of Environment, Agriculture and Biotechnology
Vol-7, Issue-4; Jul-Aug, 2022

Journal Home Page Available: https://ijeab.com/
Journal DOI: 10.22161/ijeab

Peer Reviewed

A Review on Flow Injection Analysis for Indirect Determination of Cyanide ion in Environment by Flame Atomic Absorption Spectrometer

Hawraz Sami Khalid*, Sirwan Fadhil Shawket, Nabil Adil Fakhre

Department of Chemistry, College of Education, Salahaddin University-Erbil, , Erbil, Kurdistan Region, Iraq
*Corespondance Author: hawraz.khalid@su.edu.krd

Received: 24 Jun 2022; Received in revised form: 15 Jul 2022; Accepted: 20 Jul 2022; Available online: 25 Jul 2022

Abstract**—** *Among inorganic anions, cyanide is a potent toxicant in environment. Its species are historically known as the most harmful chemical pollutants of the environment to directly affect human health and some aquatics activity, even at minimum levels. Cyanide compounds are widely available with various chemical compositions and are applied in many industrial fields. This mini-review focused on the cyanide species and their measurement utilizing several analytical techniques. Detailed information on an indirectly determined cyanide species in various environmental samples was also reviewed using a flame atomic absorption spectrometer equipped with a flow injection system (FIA-FAAS). Obtained various analytical performance properties of an indirectly measured free cyanide ion in various samples using FAAS investigated from this study.*

Keywords**— *Nonmetals, Cyanide ion, Indirect determination, FIA-FAAS.***

I. INTRODUCTION

Cyanide compounds denote any chemical compounds that have carbon and nitrogen atoms as a ($C\equiv N$) triple bonded or including (CN^-) functional group (Newhouse & Chiu, 2010). Cyanide is categorically introduced as the most harmful compounds on earth, posing a severe health hazard and direct toxic effects on humans and, more so to aquatic life even at low levels. Among inorganic anions, cyanide is a potent toxicant and one of the most harmful chemical pollutants of the environment historically known to be used as a chemical weapon (Ogbuagu, Airaodion, Okoroukwu, Ogbuagu, & Ekenjoku, 2019). This mini-review focused on the cyanide species, uses, and side effects. Several analytical techniques were mentioned to quantify cyanide species in environment. Detailed information on cyanide species' via indirect measurement in various real samples was also reviewed utilizing a flame atomic absorption spectrometer (FAAS).

1.1. Cyanide Species and their Uses

Cyanide compounds are available with various chemical compositions, physical and chemical properties (**Table 1**) (Newhouse & Chiu, 2010; Simeonova, Fishbein, & Organization, 2004). Hydrogen cyanide (HCN), potassium cyanide (KCN), and sodium cyanide (NaCN) are the most common cyanide compounds widely used in many fields (Newhouse & Chiu, 2010). Detailed information on several cyanide compounds is shown in **Table 1**. Historically, cyanide salts or agents which can form a cyanide gas when mixed with acids are lethal chemicals and broadly utilized in many industrial applications. The commonly applied cyanide species fields involve electroplating, metallurgy, chemical synthesis, agriculture, printing, tanning, photography, manufacturing of paper, and insecticides (Dobbs, 2009). Cyanide, a nitrile, is also applied in numerous industries, such as plastics, paints, mining, jewelry, pharmaceuticals, dyes, coal coking, and food processing (Sharma, Akhter, & Chatterjee, 2019).

Table 1: shows several chemical and physical properties of selected common cyanide compounds (Newhouse & Chiu, 2010; Simeonova et al., 2004).

Cyanide compounds	**CASRN**	**Synonyms**	**Formula (M.wt.) g/mole**	**Form**	**Density (g/mL)**	**MP (°C)**	**BP (°C)**	**Solubility**
Hydrogen cyanide	74-90-8	Hydrocyanic acid, Cyclone B, prussic acid	HCN (27)	Colorless gas or liquid	0.6884	-13.4	25.7	Ether, Ethanol
Potassium cyanide	151-50-8	Hydrocyanic acid, potassium salt	KCN (65)	White crystals or lumps	1.52	634.5	1,625	Water, ethanol
Sodium cyanide	143-33-9	Cyanogran, Cyanobrik, Cymag, white cyanide	$NaCN$ (49)	White (powder) crystalline	1.6	563.7	1,496	Water, ethanol
Calcium cyanide	592-01-8	Calcyanide, cyanogas, calcyan, black cyanide	$Ca(CN)_2$ (92)	White powder	1.85	640	NA	Water, ethanol, weak acid
Cyanogen	460-19-5	Dicyanogen, ethanedinitrile, oxalonitrile	$(CN)_2$ (52)	Colorless gas	0.9537	-27.9	-21.17	Water, ethanol
Potassium silver cyanide	506-61-6	Potassium dicyanoargentate	$AgK(CN)_2$ (199)	White crystals	2.36	NF	NF	Water, ethanol
Copper cyanide	54-92-3	Cupricin	$CuCN$ 89.56	Off-white powder	2.92	474	NF	Insoluble in water
Cyanogen chloride	506-77-4	Chlorine cyanide	$CNCl$ 61.47	Colorless gas	1.19	−6.55	13.8	Water & alcohol

CASRN; CAS Registry Number, BP; boiling point, MP; melting point, M.wt.; molecular weight, NA; not found, NA; not applicable

1.2. Health Hazards

Exposure to cyanides leads to severe health hazards ongoing to their empathy to metals in the presented medium. Thus, cellular respiration malfunction symptoms by inhibition of cytochrome c oxidase will occur by cyanides side effects. As a result, their compound causes convulsions, increased blood acidity (acidosis), histotoxic hypoxia, loss of consciousness, and decline in the human central nervous system's myocardial activity and functioning of the human central nervous system (Ogbuagu et al., 2019). Cyanide poisoning happens when humans or any living organisms are directly exposed to cyanide species/ions in various ways. Exposed ways can be through drinking, industrial exposure, suicidal ingestion, long-term consumption of foods containing cyanide forms, and rarely smoke inhalation (Ogbuagu et al., 2019). For these reasons, many physicochemical processes have been developed and applied to remove cyanide species from aqueous wastes from the environment. Among them includes oxidation by hydrogen peroxide, microbial cyanide degradation, ozonization, and alkaline chlorination methods (Sharma et al., 2019).

II. ANALYTICAL TECHNIQUES

Several analytical methods and techniques have been widely applied to determine cyanide species directly or indirectly in various environmental samples (Ma & Dasgupta, 2010). Among these includes spectrophotometry and colorimetry(Hao et al., 2014; Osobamiro, 2012), spectrofluorimetry(Chueachot & Chanthai, 2014; Long et al., 2019), indirect flame atomic absorption spectrometry (FAAS) (Dadfarnia, Shabani, Tamadon, & Rezaei, 2007), micro-chemiluminescence(Amjadi, Hassanzadeh, &Manzoori, 2014), room temperature phosphorimetry(Fernández-Argüelles, Costa-Fernández, Pereiro, & Sanz-Medel, 2003), gravimetric, and complexometric titrations (Breuer, Sutcliffe, & Meakin, 2011). Chromatographic techniques such as high-performance liquid chromatographic-mass spectrometry (Tracqui, Raul, Geraut, Berthelon, & Ludes, 2002), ion chromatography (Cengiz, Durak, Nilufer, & Bilgin, 2015), and gas chromatography (Sadeg & Belhadj-Tahar, 2009) have also been applied to analyze cyanide species. Many electrochemical techniques were also applied to quantify cyanide components including, voltammetry (Sousa, Godinho, & Aleixo, 1995), amperometry(Jaszczak, Ruman, Narkowicz, Namieśnik, & Polkowska, 2017), potentiometry(Amayreh & Abulkibash, 2017), and capillary electrophoresis (Jermak, Pranaitytė, & Padarauskas, 2006).

2.1 Flame Atomic Absorption Spectrometry (FAAS)

FAAS is well-known as powerful analytical techniques were broadly utilized for metal analysis. This technique is commonly applied in many science fields due to its modest setup, robustness, low costs, and suitable selectivity. Metals and metalloids can be directly quantified utilizing the AAS technique, whereas it is impossible to determine nonmetals with this technique directly. Nonmetals are difficult to directly measured by AAS due to their positioned resonance lines in the vacuum-UV range (Akman, Welz, Ozbek, & Pereira, 2015). However, nonmetals and their components (**Table 2**) can be indirectly measured and quantified in various samples utilizing their diatomic or complex molecular absorption (Akman et al., 2015; Jaszczak et al., 2017; Noroozifar, Khorasani-Motlagh, & Taheri, 2009; Yebra & Cespon, 2000).

Table 2: shows the permissible limit (mg/L) of some common non-metallic ions/compounds announced by EPA that can be quantified indirectly by FAAS.

Non-metal Ions/ Compounds	**Permissible Limits (mg/L) US EPA (EPA, 2004)**	**Documented Studies Using Indirect FAAS Technique**
Cyanide (CN^{-})	0.2	(Dadfarnia et al., 2007)
Chloride (Cl^{-})	250	(Jimenez, Gallego, & Valcárcel, 1987)
Iodide (I^{-})	0.018	(Yebra & Cespon, 2000)
Fluoride (F^{-})	2.0	(Akman et al., 2015)
Sulfide ($SO_3^{=}$)	2.0	(Zare-Dorabei, Boroun, & Noroozifar, 2018)
Nitrite (NO_2^{-})	1	(Noroozifar, Khorasani-Motlagh, Taheri, & Homayoonfard, 2007)
Nitrate (NO_3^{-})	10	(Meissam Noroozifar et al., 2007)
Sulphate ($SO_4^{=}$)	250	(Kapitány, Nagy, Posta, & Béni, 2020)
Phosphate ($PO_4^{=}$)	0.04	(Tekula-Buxbaum, 1981)
Silicate (SiO_4^{4-})	-	(Kirkbright, Smith, & West, 1967)

2.2 Flow Injection Analysis (FIA)

Flow injection analysis (FIA) methods are more popular, engaging, and applicable routine analysis systems in various fields of environment applications (Hansen & Miró, 2007). This system provides various exciting points, including ease of applicability, flexibility, reproducibility, accessibility, simplicity, an increasing sampling rate, decreasing human participation, reducing the volume of chemical consumption (samples and reagent), reduced time-wasting, and preventing lab contamination (GHOUS, 2011; Hansen & Miró, 2007). The combination of solid-phase reagents/reactors (SPR) in FIA manifolds also provided several advantages and improved this system's performances (Gomez & Calatayud, 1998; Noroozifar, Khorasani-Motlagh, Taheri, & Zare-Dorabei, 2008). The utilization of the FIA-FAAS system equipped with SPRs has been recognized and widely applied to be an effective method for automation, preparing, and analyzing various samples (Gomez & Calatayud, 1998; Kapitány et al., 2020; Noroozifar et al., 2009). This coupled instrument was well applied to enhance sensitivity and selectivity during nonmetal ions or compounds analysis. The assessment of several inorganic and organic compounds has been easily improved, utilizing SPR with FIA system. Many studies documented the application of SPRs in the FIA-FAAS system for the indirect quantification of nonmetal ions or compounds in various environmental samples (Gomez & Calatayud, 1998; Hansen & Miró, 2007; Jimenez et al., 1987; Noroozifar, Khorasani-Motlagh, & Hosseini, 2006; Zare-Dorabei et al., 2018).

III. LITERATURE REVIEW

Free cyanide and its species quantification applying FAAS was also impossible. FAAS is a powerful technique indirectly adopted to quantify cyanide species in various environment samples (Dadfarnia et al., 2007; Gürkan & Yılmaz, 2013a; Noroozifar et al., 2009). FIA equipped with the FAAS technique was a highly successful applied method to analyze free cyanide ion indirectly. This review also focused on the indirect assessment and measurement of free cyanide in many samples. Cyanide presented as a free ion, or total cyanide species were determined in many samples such as fish, cocoyam, cassava, well and dam water (Kwaansa-Ansah, Amenorfe, Armah, & Opoku, 2017), pharmaceuticals (Gomez & Calatayud, 1998), river and sea waters (Fullana-Barcedó, Bosch-Serrat, Marin-Saez, & Mauri-Aucejo, 1995), and industrial wastewaters (Noroozifar, Khorasani-Motlagh, & Hosseini, 2005). Many studies have been documented concerning the indirect analysis and quantification of cyanide species using FAAS. Detailed analytical performance properties on the indirectly used measurement of free cyanide ion by FIA-FAAS in the last and this century are shown in **Tables 3** and **4**, respectively.

For the first time, Manahan and Kunkel (1973) proposed a simple and effective AAS procedure for indirect quantification of CN^- ion based upon the solubility degree of copper carbonate ($CuCO_3$) in the sample solution and on the determination of the amount of copper attended to form a cyanide-copper complex ($Cu(CN)_3^-$) in the basic medium. They applied the proposed method to quantify low levels of cyanide at the time using the FIA system. The spiked sample was also investigated to show the quantitative recovery of cyanide (Manahan & Kunkel, 1973).

After that, Haj-Hussein, Christian, and Ruzicka (1986) proposed a novel FIA system for the indirect quantification of free CN^- ions in aqueous systems using the AAS technique. A microcolumn, which included cupric sulfide (CuS) packed column, was proposed in the on-line FIA-AAS system procedure. During analysis, aqueous cyanide solutions were inserted through an on-line CuS packed column at a pH of 11. Simultaneously, potassium hydroxide solution with a pH of 11 was utilized and passed into the system as a carrier stream. As a result, the analyte produced the cuprocyanide complex, presented in the eluent solution, and then measured by the FAAS detector. The consequences of sample volume, flow rate of the sample or used reagents and various anionic interferences during the process were examined.Various factors, such as carrier solution, injection volume, flow rate, filter selection, and AAS parameters, were investigated to optimize the flow system and obtain reproducible results. The recorded data confirmed that the sensitivity, range of linearity, and peak high could be significantly affected by the injection volume. In comparison with other methods, the selectivity, sensitivity, applicability, and detection technique applied were introduced as the novelty of the present method. **Figures 1** and **2** illustrate detailed components of the proposed microcolumn design and filter related to the on-line FIA-FAAS system (Haj-Hussein et al., 1986).

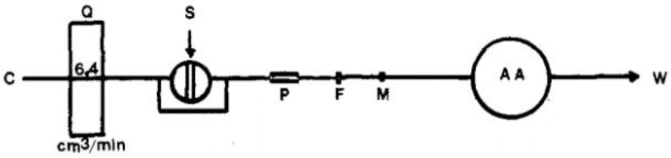

Fig.1: Illustrate the schematic diagram of FI manifold associated to FIA-AAS assessment of free CN^-, C, carrier; Q, flow rate (cm^3/min); S, point of injection; P, packed column; F, filter; M, the connection point to the nebulizer; AA, detector; W, waste (Haj-Hussein et al., 1986).

A new, sensitive, and high-speed method for extraction (**Table 3**) and indirect quantification of CN^-ion in various industrial samples by FAAS was also described in detail. This method was proposed based on the stable producing complex of CN^- ion in an alkaline medium Chattaraj and Das (1991). In the proposed method, a stable complex species of cyanide as a [Cu(BPTC)(CN)] formed in an alkaline medium (at pH 8.2) resulting from the occurring reaction by free CN^- in the sample solution with 2-benzoylpyridine thiosemicarbazone (BPTC). A mixture of isobutyl methyl ketone (IBMK) and isopentyl alcohol with different ratios (7 + 1) was used as an appropriate organic phase for extracting the stable formed complex. The analyte, which is free cyanide, converted to the stable complex [Cu(BPTC)(CN)], extracted with high efficiency, can be quantified indirectly by FAAS (Chattaraj & Das, 1991).

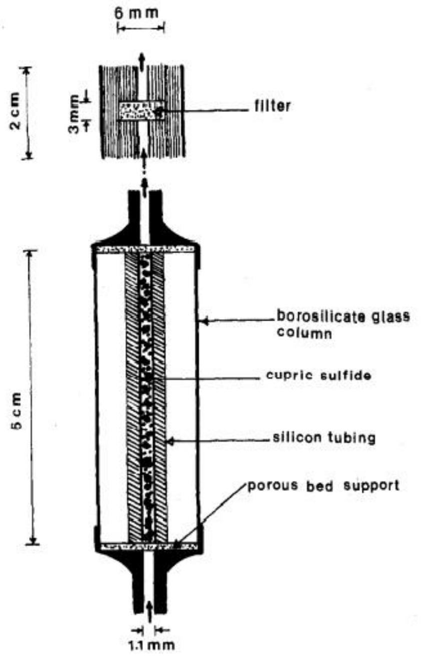

Fig.2: Shows the main components of the proposed microcolumn and filter related to the on-line FIA-FAAS structure (Haj-Hussein et al., 1986)

Esmadi, Kharoaf, and Attiyat (1993)also described and applied a new, simple, and potential FI-AAS method to determine cyanide and thiocyanate anions indirectly in aqueous systems. At first, the silver nitrate solution used as a precipitating agent passed through the flow system and precipitated the cyanide ion (analyte) in the sample solution in a Tygon tube coupled to the AAS detector. Deionized water was then used to wash the formed precipitate in the tube of the precipitating loop. Finally, NH_3 and $N_2S_2O_3$ solutions, which were used as dissolving agents, passed individually through the produced precipitated in the Tygon tube for a short period, dissolves the formed precipitate, and transfers it as a free cation content to the nebulizer of the detector. As a result, the formed cation concentration (silver ion), which is proportionally associated with the presented quantity of the examined analyte in the sample, could be measured using the AAS detector. The optimum condition was obtained due to investigate different parameters, including the concentration of the used reagents, various precipitating agents, washing time, and flow rate of the chemical solutions. Compared with other previously published methods, this method was introduced as a preferable procedure to determine cyanide ion in wastewater due to its simplicity, sensitivity, high precision, and not requiring the precipitating loop change. **Figure 3** illustrates the main components of the applied FI system in the proposed study (Esmadi et al., 1993).

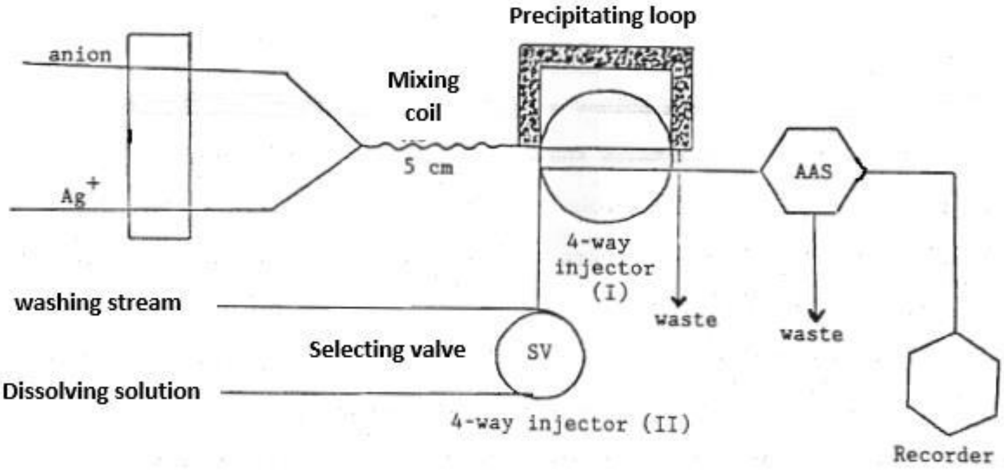

Fig.3: illustrates the principal components (schematic) of the utilized FI system to determine such as SCN^- and CN^- anions in aqueous systems (Esmadi et al., 1993).

In another study,Fullana-Barcedó et al. (1995) proposed two new, fast, and simple methods for the extraction (**Table 3**) and indirect assessment of free CN^- ion in water samples via AAS techniques. They suggested this procedure to produce a novel ion association compound of cyanide and then extraction to a new phase. The metal complexion of $Cu(CN)_3^{2-}$ or $Ag(CN)_2^-$ produced in the presence of metal ions (like Cu or Ag ion) into CN^-ion (at pH 10 or 11) in the sample solution, respectively. A new ion association compound $[C_{25}H_{46}N^+]_2[Cu(CN)_3^{2-}]$ or

$[C_{25}H_{46}N^{+}][Ag(CN)_2^{-}]$ formed from the reaction between the metal complexion with a quaternary ammonium ion (benzyldimethylhexadecylammonium ion, Cetalkonium chloride). Isomethylbutylketone (IBMK) solvent is then used as an organic phase to extract the produced ion association compounds. The AAS was used to measure the cyanide ion indirectly in the final association compound (Fullana-Barcedó et al., 1995).

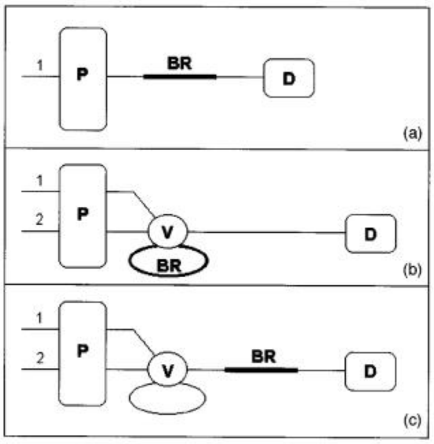

Fig.4: illustrates flow system construction: (a) preliminary experiments; (b) FIA system with the used SPR (BR) located in the loop system; and (c) suggested FIA system equipped to BR after injector part. 1, Sample; 2, carrier stream solution; P, pump; V, valves for the sample injection; BR, solid-phase reactor; and D, FAAS as a detector (Gomez & Calatayud, 1998).

In the last century, Gomez and Calatayud (1998)also suggested a new FIA procedure for indirect assessment of free cyanide in various pharmaceutical and environmental samples using FAAS. A new solid-phase reactor (SPR) filled with a homogenized mixture of immobilized silver iodide packed in polymeric resin beads was utilized during this investigation. The sample was firstly forced into a distilled water carrier, then passed throughout the proposed rector. Thus, silver cyanide complexes were produced from the direct reaction between the free silver ion in the reactor with the cyanide ion in the injected sample were finally determined by FAAS. The results verified that a good linear range (LR; 0.2 - 6.0 mg/L) was obtained. The method was successfully utilized to quantify free cyanide in different commercial samples, including industrial electrolytic baths and pharmaceutical products. This method was also preferred as a new, simple, selective, and more straightforward than other previously applied FIA methods in the literature survey. **Figure 4** illustrates the stepwise construction of the applied flow systems procedure.

In this century, Noroozifar et al. (2005) developed and alsoapplied a novel FI system to determine free CN^{-} ion in industrial wastewaters using FAAS indirectly. A novel solid-phase reactor (packed column) prepared from homogenized and immobilized cadmium carbonate ($CdCO_3$) suspended on silica gel beads was proposed in this investigation. In the proposed procedure, sodium hydroxide was utilized as the carrier stream, and aqueous cyanide solutions were forced into the prepared, packed column reactor on-line. Forming a cadmium compound as a cyanide complex resulting from the direct reaction between free cyanide and $CdCO_3$ and presented in the eluent can be determined as analyte using FAAS instrument. A pH of 10, the carrier flow rate of 3.5 mL/min, and a temperature of 20 ◦C were chosen as an optimum condition for a simple system proposition. The obtained results showed that the free CN- ion quantity directly increase the recorded absorbance in the examined sample. The recorded linear range (LR), the limit of detection, sampling rate, relative standard deviation, and recovery of the used procedure were 15 mg/L, 0.2 mg/L, 72 h^{-1}, 1.22%, and close to 100%, respectively. Several anions such as $S_2O_5^{=}$, $S_2O_8^{=}$, $CO_3^{=}$, $C_2O_4^{=}$, $B_4O_7^{=}$, $SO_3^{=}$, $SO_4^{=}$, SCN^{-}, NO_3^{-}, N_3^{-}, Cl^{-}, F^{-}, I^{-}, and CH_3COO^{-} were investigated as interferences during the reaction between free CN^{-} and $CdCO_3$. The results in the proposed FIA system showed to be new, stable, cheap, readily available in every laboratory in terms of the uses of $CdCO_3$ as the primary reagent. **Figure 5** showed detailed information on the proposed single-line flow system diagram combined with FAAS (Noroozifar et al., 2005).

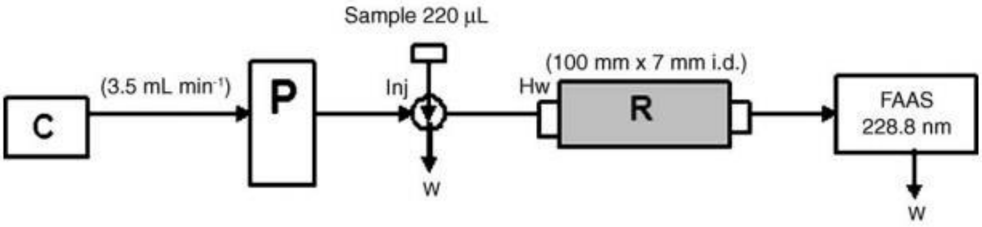

Fig.5: shows the simple components of the system combined with FAAS used to quantify free cyanide. C, carrier; P, pump; W, waste; Inj, injector; R, it is the SPR; Hw, glass wool plug and haply nut; and D, detector(Noroozifar et al., 2005).

In addition, a practical solid-phase reactor, which consists of the homogenized mixture of zinc carbonate ($ZnCO_3$) packed on silica gel beads, was also prepared and suggested for indirect cyanide investigation in industrial wastewaters using FIA-FAAS. In the proposed method, aqueous cyanide or sample solutions were inserted onto the on-line reactor, and the used carrier stream was re-distilled water. Zinc cyanide complexes, which were formed throughout the reaction between $ZnCO_3$ in the reactor and free cyanide at room temperature (pH of 6.0), were presented as a new form of analyte in the eluent and then determined by FAAS (Noroozifar et al., 2006). The measured absorbance was increased. The used $ZnCO_3$ chemical in the reactor's preparation is known as a safe, cheap, stable, and readily available reagents. The results data confirmed that the pH of 6.0, a suitable carrier flow rate (2.5 mL/min), room temperature (25°C) were selected as an optimal FIA system condition. **Figure 6** showed the proposed FIA system's simple diagram with complex components (Noroozifar et al., 2006).

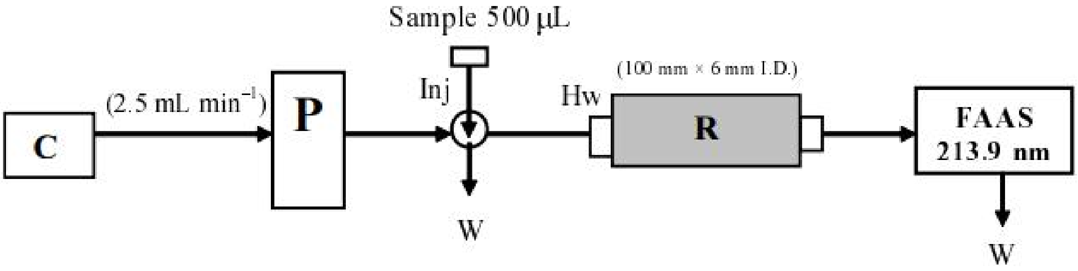

Fig.6: illustrates the main components related to the proposed flow system applied to quantify free CN^- ion. C, carrier; P, pump; Inj, injector; W, waste; Hw, glass wool plug; R is an SPR; FAAS, detector(Noroozifar et al., 2006).

Furthermore,Noroozifar, Khorasani-Motlagh, and Zare-Dorabei (2007)studied four solid-phase reactors for indirect monitoring and analyzing of free CN^- ion in various real industrial effluent using FIA-FAAS. The used solid-phase reactors were used as effectively packed columns and prepared from immobilized Ag_2X (X are $Cr_2O_7^{2-}$, CO_3^{2-}, $C_2O_4^{2-}$, and SO_3^{2-}) mixing with silica gel beads. During analysis (**Figure 7**), the sample solution, including dissolved CN^- is introduced into an on-line system, including Ag_2X with the used deionized water or NaOH as the productive carrier stream. The eluent solution includes silver cyanide complexes formed from the free silver ion's reaction with the free cyanide and can then be analyzed as a FAAS analyte. The results confirmed that the rising in the recorded absorbance is dependable on the changing anions in the Ag_2X formula and ordered as follows: $CO_3^{=} > C_2O_4^{=} > Cr_2O_7^{=} > SO_3^{=}$. The proposed method is selected as an appropriate method to determine cyanide ion due to using Ag_2X as stable, cheap reagents, and readily available as different forms in every laboratory (M Noroozifar et al., 2007).

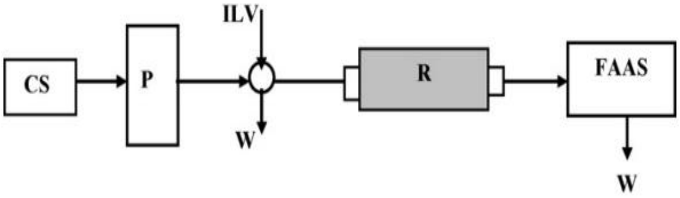

Fig.7: illustrates the main parts of FIS combined with FAAS to quantify free CN^-. CS, carrier stream; P, pump, R, solid-phase reactor; ; ILV, injector loop valve; FAAS, detector; W, residue waste (M Noroozifar et al., 2007).

Dadfarnia et al. (2007) recommended a rapid, simple, and applicable FIS for indirect quantification of cyanide by FAAS. A new microcolumn was proposed as a novel procedure for the indirect quantification of dissolved trace CN ions in different aqueous systems. The column was prepared from a mixture of Salen I on sodium dodecyl sulfate (SDS)-coated alumina saturated with Ag(I) ion. After sample injection into the microcolumn (pH 9–11), the silver solution was formed and eluted as silver-cyanide complexes and detected by FAAS. The recorded data revealed that the suggested procedure could be readily utilized in different real samples and provide a lower detection limit than previously documented FI-FAAS methods for indirect trace quantification of CN^- ion (Dadfarnia et al., 2007).

A rapid FI-FAAS was additionally proposed and improved by Noroozifar et al. (2008) for indirect quantification of dissolved cyanide in electroplating wastewater. Various solid phase reagents (SPRs) such as AgX (where X is N_3^-, Br^-, Cl^-, and I^-) were examined during analysis. In the proposed method, five SPRs, which were mixed with silica-gel beads and various AgX SPRs, were prepared for the final assessment. In a single-line FIA system (**Figure 8**), the suggested procedure was depended on CN^- ion reaction from the injected sample with immobilized AgX SPRs in the SPR, followed by silver formation cyanide complexes in a basic medium carrier stream and later analysis of the eluent by FAAS. The results revealed that the absorbance could be increased due to changes in the use of different anions as follow order: $N_3^- > I^- > Br^- > Cl^-$. Based on the results, AgN_3 is proposed as an effective SPRs for the indirect analysis of CN^- ion in many industrial residues (Noroozifar et al., 2008). Obtained results verified that the measurement of cyanide by the proposed method appeared to be acceptable and favorable relative to obtained results by the previously documented methods. This comparison is based on several factors, including the methods simplicity, sensitivity, speed, cost, the limit of quantitation (LOQ), dynamic range, and relative standard deviation (RSD %). **Figure 8** shows the simple FIA system's main components combined with FAAS (Noroozifar et al., 2008).

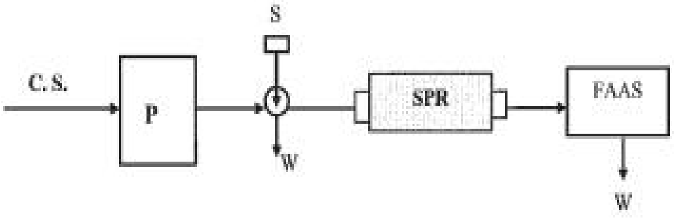

Fig.8: Shows the main parts of the FI-FAAS system for CN^- analysis (C.S., carrier stream; P, pump; S, sample; SPR, reactor; FAAS, detector; W, waste (Noroozifar et al., 2008).

In the another study, a new, cheap, simple, safe, and single-line FIA system method to indirectly quantify free cyanide in industrial wastewaters has been proposed by Noroozifar et al. (2009). The proposed method was designed and applied based on the aqueous cyanide solution through an on-line packed column (reactor), which included silver phosphate suspended on silica gel beads. The free silver ions are then reacted with the presented cyanide ion in the sample solution to form the soluble complex compound in the basic medium. The analyte, which is cyanide, can be indirectly measured utilizing the FAAS instrument. The proposed method is appropriate for quantifying cyanide in several industrial wastewater samples with a good detection limit, dynamic range, RSD, and sample flow rate (Noroozifar et al., 2009).

For the first time, a cloud point extraction (CPE) method was effectively applied for the isolation, preconcentration, and indirect measurement of CN^- ion in several water samples using FAAS (Gürkan & Yılmaz, 2013b). In the presence of CN^- ion, the reduction of Cu(II) (coming from the standard Cu(II) solution) to Cu(I) happens to produce $Cu(CN)_4^{3-}$ complex anionic ions. Then, a new ion-associate complex $[(NBO)_3Cu(CN)_4]$ is formed after the complexation reaction between the produced anionic complex with 3-amino-7-diethylamino-8,9-benzo-2-phenoxazine chloride (Nile blue, NB). Finally, the quantification analysis of cyanide is indirectly carried out by FAAS after using polyethyleneglycol mono-p-nonyl phenyl ether (PONPE 7.5). The PONPE 7.5 compound acts as an efficient extracting reagent/surfactant to the final complex at pH 5.5 medium (Gürkan & Yılmaz, 2013b).

Gürkan and Yılmaz (2013a) also developed a novel procedure for the indirect measurement of dissolved trace CN^- employing FAAS in various real waters sample. Among them includes river water, well water, hospital effluents, coking unit, and electroplating wastewater. In the proposed method, the cyanide ion presence can be efficiently quantified utilizing FAAS after separation and preconcentration with the CPE procedure. In this method, dicyanocuprate $(Cu(I)\ (CN)_2)$ complex is produced due to the reduction of Cu(II) to Cu(I) with the dissolved CN^- ion in the sample solution. At pH 4.0, a useful ion-pairing reagent (gallocyanin, GCþ) can react with the produced dicyanocuprate compound to form a new complex. The product is easily extracted by polyethyleneglycol mono-p-nonylphenylether (Ponpe 7.5), extracting surfactant, and then quantified by FAAS technique. CPE-FAAS system was introduced as an effective indirect quantification method for separation, preconcentration, and monitoring trace cyanide in various aqueous systems. This technique was well-applied due to its low cost, simplicity, wide linear range, short analysis time, reasonable accuracy and precision, broad applicability, rejection of matrix constituents, and ease of instrumentation (Gürkan & Yılmaz, 2013a, 2013b).

Detailed analytical performance properties on the indirectly used measurement of free cyanide ion by FIA-FAAS in the last and this century are shown in **Tables 3** and **4**, respectively. Analytical parameters such as methods linear range (LR), limit of methods detection (LOD), the limit of quantification (LOQ), relative standard deviation percent (RSD%), correlation coefficient (R^2), recovery, and sampling rate were shown and compared with each other(**Tables 3** and **4**). Recorded results from previous studies verified that FIA-FAAS could be applied to quantify the free cyanide in various real environmental samples (Gomez & Calatayud, 1998; Noroozifar et al., 2008). In comparison with other techniques, researchers confirmed that FIA-FAA offers promising results to quantify free cyanide in matrix samples (Dadfarnia et al., 2007). This technique is well known as simple, fast, widely applicable, more sensitive, and selective, high accurate, wide linear range, avoiding matrix constituent's methods during application based on previously documented studies. This technique also has several valuable points associated with the economy, such as its simplicity, low-cost reagents, and high analysis speed rate. This technique is preferable for the routine analytical assessments due to its simplicity and applicability.

However, this method also has some disadvantages. Several parameters have to be concerned to enhance cyanide assessment while using this technique. Among them includes controlling pH of the medium, sample or reagents flow rate, carrier stream pH, and loop volume (Dadfarnia et al., 2007). Besides, using such reagents related to toxic heavy metals can contaminate the environment (Noroozifar et al., 2005; Noroozifar et al., 2009; Noroozifar et al., 2008; M Noroozifar et al., 2007).

Table 3: shows the analytical performance properties of an indirectly measured free cyanide ion in various samples using FAAS documented from the last century

Preparation method	**Analytical method**	**LR (mg/L)**	**LOD (mg/L)**	**LOQ (mg/L)**	**R^2**	**RSD%**	**Recovery %**	**Sampling rate (sample/h)**	**Analyzed Samples**	**References**
Sample: including cyanide ion Reagents: $CuSO_4$, Na_2CO_3 Medium: a pH of 10.0 Analysis: $Cu(CN)_3^-$ ion complex	AAS /complex ion formation	0.52 – 1.1	NA	NA	NA	NA	96.7 - 103	-	Synthetic samples	(Manahan & Kunkel, 1973)
Packed column: CuS Carrier: KOH solution Medium: at the pH of 11 Analysis: cuprocyanide complex	FI-AAS	2.6 - 52	1.00	2.6	NA	2	NA	40-50	Synthetic samples	(Haj-Hussein et al., 1986)
Sample: free cyanide ion Medium: alkaline at pH 8.2 Reagents: BPTC Extraction solv.: IBMK: isopentanol Analyses: [Cu(BPTC)(CN)]	FAAS /based on extraction	0.4 - 5.7	0.005	0.026	NA	3.58	96.7 - 101	-	Industrial waste effluent	(Chattaraj & Das, 1991)
Precipitating agent: AgNO3 Washing: deionized water Dissolving agent: $NH_3/S_2O_3^=$ Analysis: liberated cation	FI-AAS Using $S_2O_3^=$ NH_3	Up to 4.4	0.078 0.13	NA	NA	1.4 1.7	NA	18 16	Synthetic samples	(Esmadi et al., 1993)
Measurement-based on extraction Metal ions; $Cu(CN)_3^{2-}$ or $Ag(CN)_2^-$ Reagent: Cetalkonium chloride Extractant: IBMK (at pH 10 or 11) Analyses:	FAAS For Cu	0 - 0.2	0.0006	NA	NA	NA	93	-	synthetic samples, drinking water, river water sea water	(Fullana-Barcedó et al., 1995)
	FAAS For Ag	0 - 0.3	0.0017	NA	NA	NA	99	-		

$[C_{25}H_{46}N^+]_2[Cu(CN)_3^{2-}]$ or $[C_{25}H_{46}N^+][Ag(CN)_2^-]$ complex										
Reactor: AgI& polymeric resin Medium: KOH solution at pH 13.7 Analysis: silver cyanide complexes	FIA-FAAS	0.2–6.0	0.1	NA	0.9974	0.8	NA	193	Pharmaceuticals, industrial electrolytic baths	(Gomez & Calatayud, 1998)

NA; none available,

Table 4: shows the analytical performance properties of an indirectly measured free cyanide ion in various samples using FAAS documented from this century

Preparation method	**Analytical method**	**LR (mg/L)**	**LOD (mg/L)**	**LOQ (mg/L)**	**R^2**	**RSD%**	**Recovery %**	**Rate (sample/h)**	**Sample matrix /application**	**References**
Analyte: sodium cyanide & sample Reactor: $CdCO_3$& silica gel beads Medium: at pH of 10.0 (20°C) Analysis: zinc cyanide complexes	FIA–FAAS	up to 15	0.2	NA	0.998	1.2	98.2 - 101	72	Industrial wastewaters	(Noroozifar et al., 2005)
Analyte: free cyanide Reactor: $ZnCO_3$& silica gel beads Medium: at pH of 6.0 (25°C) Analysis: zinc cyanide complexes	FIA-FAAS	Up to 25	0.12	NA	0.9995	1.41	98.3-101.8	65	Industrial electroplating wastewater	(Noroozifar et al., 2006)
Analyte: cyanide ion from sample Reactor: Ag_2X & silica gel bead X = $Cr_2O_7^=$, $CO_3^=$, $C_2O_4^=$, and $SO_3^=$ Medium: at pH range of 5–11 Analysis: silver cyanicde complexe	FIA-FAAS Ag_2SO_3 $Ag_2Cr_2O_7$ $Ag_2C_2O_4$ Ag_2CO_3	Up to 20 Up to 10 Up to 10 Up to 12	0.13 0.08 0.06 0.04	0.38 0.22 0.17 0.14	0.999 0.999 0.999 0.999	<1.12	98 - 100.5	180 180 180 240	Industrial electrolytic baths.	(M Noroozifar et al., 2007)
Microcolumn: Salen I on SDS-coated Al with Ag^+, pH (9–11) Analysis: silver cyanide complex	FI-FAAS	0.1–10	0.06	0.1	0.9997	4.1 – 4.7	95 - 105	-	Water and industrial wastewater	(Dadfarnia et al., 2007)
SPR: AgX (X= Cl^-, Br^-, I^- and N_3^-) Reaction: SPR with free cyanide Medium: at pH 9.0 and 11.0 for Measurement: liberated silver ions complexed by the free cyanide ion	FIA-FAAS AgCl AgBr AgI AgN_3	Up to 25 Up to 25 Up to 30 Up to 20	0.17 0.14 0.08 0.05	0.59 0.43 0.40 0.30	0.996 0.994 0.998 0.999	< 1.09	98.8-102.4	>200	Industrial electroplating wastewater	(Noroozifar et al., 2008)
Analyte: cyanide ion from sample Reactor: Ag_3PO_4& silica gel	FIA-FAAS	0.1 - 18	0.04	0.1	0.998	1.07	95 - 104.2	220	industrial wastewaters	(Noroozifar et al., 2009)

bead Analysis $Ag(CN)_2^-$ at pH of 11										
Analyte: cyanide ion Reduction: Cu(II) to Cu(I) Product: $[Cu(CN)_4]^{3-}$ complex ion Ion-pairing reagent: Nile blue Extracting agent: Ponpe 7.5 Result: complex formation (pH 5.5)	CPE/FAAS (W/ PC)	0.02–2.5	0.0038	0.012	0.9940	3.54-2.80	97.5 - 99.4	-	Environmental waters and wastwaters	(Gürkan & Yılmaz, 2013b)
	CPE/FAAS (W/O PC)	0.1–7.5	0.025	0.085	0.9968	3.45-2.50	98.3-101.4	-		
Analyte: free cyanide Reduction: Cu(II) to Cu(I) Product: Dicyanocuprate (I) Ion-pairing reagent: GCþ (pH 4.0) Extracting agent: Ponpe 7.5	CPE/FAAS (W/ PC)	0.002–1.2	0.0005	0.0015	0.9983	2.3 – 5.2	97.6 - 99.5	-	Environmental waters and wastwaters	(Gürkan & Yılmaz, 2013a)
	CPE/FAAS (W/O PC)	0.05–6.5	0.014	0.047	0.9975	2.1 – 5.0	98 - 100.6	-		

CPE; cloud point extraction, W/ PC; with preconcentration method, W/O PC; without preconcentration method, SPR: solid-phase reagents which are insoluble silver salts,

IV. CONCLUSION

Cyanide species can be indirectly and easily quantified in the routine laboratory utilizing FAAS equipped with FIA in several environmental samples. The indirect measurement of free cyanide using FAAS provides several advantages: ease of applicability, simplicity, low cost, good recovery, selectivity and sensitivity, a wide linear range, number of sample analyses, and preventing matrix components. This approach offers an appropriate alternative to the indirect quantification of cyanide species as it provides ease of availability and instrumentation in various environments.

REFERENCES

[1] Akman, S., Welz, B., Ozbek, N., & Pereira, É. R. (2015). Fluorine Determination in Milk, Tea and Water by High-Resolution, High-Temperature Molecular Absorption Spectrometry. In *Fluorine* (pp. 75-95).

[2] Amayreh, M. Y., & Abulkibash, A. M. (2017). Differential Electrolytic Potentiometry: a Detector in the Flow Injection Analysis of Cyanide Using Silver Electrodes Modified with Carbon Nanotubes. *Arabian Journal for Science and Engineering, 42*(10), 4445-4451.

[3] Amjadi, M., Hassanzadeh, J., & Manzoori, J. L. (2014). Determination of cyanide using a chemiluminescence system composed of permanganate, rhodamine B, and gold nanoparticles. *Microchimica Acta, 181*(15-16), 1851-1856.

[4] Breuer, P., Sutcliffe, C., & Meakin, R. (2011). Cyanide measurement by silver nitrate titration: Comparison of rhodanine and potentiometric end-points. *Hydrometallurgy, 106*(3-4), 135-140.

[5] Cengiz, M. F., Durak, M. Z., Nilufer, S., & Bilgin, A. K. (2015). Ion chromatographic determination of free cyanide in different classes of bottled natural mineral water consumed in Turkey. *International journal of food properties, 18*(4), 746-756.

[6] Chattaraj, S., & Das, A. K. (1991). Indirect determination of free cyanide in industrial waste effluent by atomic absorption spectrometry. *Analyst, 116*(7), 739-741.

[7] Chueachot, R., & Chanthai, S. (2014). Spectrophotometric determination of trace cyanide in fruit wines by the catalytic reaction of ninhydrin following micro-distillation. *Oriental Journal of Chemistry, 30*(1), 119-131.

[8] Dadfarnia, S., Shabani, A. M. H., Tamadon, F., & Rezaei, M. (2007). Indirect determination of free cyanide in water and industrial waste water by flow injection-atomic absorption spectrometry. *Microchimica Acta, 158*(1-2), 159-163.

[9] Dobbs, M. R. (2009). Cyanide. In *Clinical Neurotoxicology* (pp. 515-522): Elsevier.

[10] EPA, U. (2004). *Guidelines for Water Reuse, US Environmental Protection Agency*. Retrieved from

[11] Esmadi, F., Kharoaf, M., & Attiyat, A. (1993). Determination of cyanide and thiocyanate anions by flame atomic absorption spectrometry in a flow system using an on-line preconcentration technique. *JOURNAL OF FLOW INJECTION ANALYSIS, 10*, 33-33.

[12] Fernández-Argüelles, M. a. T., Costa-Fernández, J. M., Pereiro, R., & Sanz-Medel, A. (2003). Room temperature phosphorimetric determination of cyanide based on triplet state energy transfer. *Analytica chimica acta, 491*(1), 27-35.

[13] Fullana-Barcedó, B., Bosch-Serrat, F., Marin-Saez, R., & Mauri-Aucejo, A. (1995). Indirect determination of cyanide by atomic absorption spectrometry. *Polymer—Plastics Technology and Engineering, 28*(12), 2247-2258.

[14] GHOUS, T. (2011). Flow injection analysis (FIA). *Journal of the Chemical Society of Pakistan, 21*(4), 375.

[15] Gomez, A. L., & Calatayud, J. M. (1998). Determination of cyanide by a flow injection analysis-atomic absorption spectrometric method. *Analyst, 123*(10), 2103-2107.

[16] Gürkan, R., & Yılmaz, Ö. (2013a). Cloud point extraction of trace cyanide from environmental waters for indirect flame atomic absorption spectrometric determination. *Toxicological & Environmental Chemistry, 95*(9), 1455-1469.

[17] Gürkan, R., & Yılmaz, Ö. (2013b). Indirect quantification of trace levels cyanide in environmental waters through flame atomic absorption spectrometry coupled with cloud point extraction. *Journal of the Iranian Chemical Society, 10*(4), 631-642.

[18] Haj-Hussein, A. T., Christian, G. D., & Ruzicka, J. (1986). Determination of cyanide by atomic absorption using a flow injection conversion method. *Analytical Chemistry, 58*(1), 38-42.

[19] Hansen, E. H., & Miró, M. (2007). How flow-injection analysis (FIA) over the past 25 years has changed our way of performing chemical analyses. *TrAC Trends in Analytical Chemistry, 26*(1), 18-26.

[20] Hao, Y., Chen, W., Wang, L., Zhou, B., Zang, Q., Chen, S., & Liu, Y.-N. (2014). A naphthalimide-based azo colorimetric and ratiometric probe: synthesis and its application in rapid detection of cyanide anions. *Analytical Methods, 6*(8), 2478-2483.

[21] Jaszczak, E., Ruman, M., Narkowicz, S., Namieśnik, J., & Polkowska, Ż. (2017). Development of an analytical protocol for determination of cyanide in human biological samples based on application of ion chromatography with pulsed amperometric detection. *Journal of analytical methods in chemistry, 2017*.

[22] Jermak, S., Pranaitytė, B., & Padarauskas, A. (2006). Headspace single-drop microextraction with in-drop derivatization and capillary electrophoretic determination for free cyanide analysis. *Electrophoresis, 27*(22), 4538-4544.

[23] Jimenez, P. M., Gallego, M., & Valcárcel, M. (1987). Indirect atomic absorption determination of chloride by continuous precipitation of silver chloride in a flow injection system. *Journal of Analytical Atomic Spectrometry, 2*(2), 211-215.

[24] Kapitány, S., Nagy, D., Posta, J., & Béni, Á. (2020). Determination of atmospheric sulphur dioxide and sulphuric acid traces by indirect flame atomic absorption method. *Microchemical Journal*, 104853.

[25] Kirkbright, G., Smith, A., & West, T. (1967). An indirect sequential determination of phosphorus and silicon by atomic-absorption spectrophotometry. *Analyst, 92*(1096), 411-416.

[26] Kwaansa-Ansah, E. E., Amenorfe, L. P., Armah, E. K., & Opoku, F. (2017). Human health risk assessment of cyanide levels in water and tuber crops from Kenyasi, a mining community in the Brong Ahafo Region of Ghana. *International Journal of Food Contamination, 4*(1), 16.

[27] Long, L., Yuan, X., Cao, S., Han, Y., Liu, W., Chen, Q., . . . Wang, K. (2019). Determination of Cyanide in Water and Food Samples Using an Efficient Naphthalene-Based Ratiometric Fluorescent Probe. *ACS omega, 4*(6), 10784-10790.

[28] Ma, J., & Dasgupta, P. K. (2010). Recent developments in cyanide detection: a review. *Analytica chimica acta, 673*(2), 117-125.

[29] Manahan, S., & Kunkel, R. (1973). An atomic absorption analysis method for cyanide. *Analytical Letters, 6*(6), 547-553.

[30] Newhouse, K., & Chiu, N. (2010). Toxicological review of hydrogen cyanide and cyanide salts. *Washington (DC): US Environmental Protection Agency*.

[31] Noroozifar, M., Khorasani-Motlagh, M., & Hosseini, S.-N. (2005). Flow injection analysis–flame atomic absorption spectrometry system for indirect determination of cyanide using cadmium carbonate as a new solid-phase reactor. *Analytica chimica acta, 528*(2), 269-273.

[32] Noroozifar, M., Khorasani-Motlagh, M., & Hosseini, S.-N. (2006). Indirect determination of cyanide by single-line flow injection analysis-flame atomic absorption spectrometry using zinc carbonate solid-phase reactor. *Chemia analityczna, 51*(2), 285-293.

[33] Noroozifar, M., Khorasani-Motlagh, M., & Taheri, A. (2009). Indirect determination of cyanide by FIA-FAAS using Ag3PO4-packed column: suppresion of phosphate interference in FAAS determination of silver. *Chemia analityczna, 54*(5), 895-906.

[34] Noroozifar, M., Khorasani-Motlagh, M., Taheri, A., & Homayoonfard, M. (2007). Application of manganese (IV) dioxide microcolumn for determination and speciation of nitrite and nitrate using a flow injection analysis–flame atomic absorption spectrometry system. *Talanta, 71*(1), 359-364.

[35] Noroozifar, M., Khorasani-Motlagh, M., Taheri, A., & Zare-Dorabei, R. (2008). A comparative study of AgX (X= Cl-, Br-, I-and N3-) solid-phase reactors for flow-injection determination of cyanide in electroplating wastewater. *Analytical Sciences, 24*(5), 669-672.

[36] Noroozifar, M., Khorasani-Motlagh, M., & Zare-Dorabei, R. (2007). Application of Ag2X (X= SO32−, Cr2O72−, C2O42− and CO32−) solid-phase reagents for indirect determination of cyanide in the industrial effluent using FIA-FAAS system. *Talanta, 72*(5), 1773-1778.

[37] Ogbuagu, E. O., Airaodion, A. I., Okoroukwu, V. N., Ogbuagu, U., & Ekenjoku, J. A. (2019). Cyanide Toxicity: The Good, the Bad and the Ugly. *International Journal of Bio-Science and Bio-Technology (IJBSBT), 11*, 157-164.

[38] Osobamiro, M. (2012). Determination of the concentration of total cyanide in waste water of a tobacco company in Southwestern Nigeria. *Journal of Applied Sciences and Environmental Management, 16*(1), 61-63.

[39] Sadeg, N., & Belhadj-Tahar, H. (2009). Rapid and sensitive headspace gas chromatographic method for cyanide determination in whole blood. *Toxicological and Environ Chemistry, 91*(3), 419-424.

[40] Sharma, M., Akhter, Y., & Chatterjee, S. (2019). A review on remediation of cyanide containing industrial wastes using biological systems with special reference to enzymatic degradation. *World Journal of Microbiology and Biotechnology, 35*(5), 70.

[41] Simeonova, F. P., Fishbein, L., & Organization, W. H. (2004). *Hydrogen cyanide and cyanides: human health aspects*: World Health Organization.

[42] Sousa, M. d. F. B., Godinho, O. E., & Aleixo, L. M. (1995). An indirect voltammetric approach for the determination of cyanide at a chemically modified electrode. *Electroanalysis, 7*(11), 1095-1097.

[43] Tekula-Buxbaum, P. (1981). An indirect sequential determination of phosphorus and arsenic in high-purity tungsten and its compounds by atomic-absorption spectrophotometry. *Microchimica Acta, 76*(1-2), 183-190.

[44] Tracqui, A., Raul, J., Geraut, A., Berthelon, L., & Ludes, B. (2002). Determination of blood cyanide by HPLC-MS. *Journal of analytical toxicology, 26*(3), 144-148.

[45] Yebra, M., & Cespon, R. (2000). Indirect automatic determination of iodide by flame atomic absorption spectrometry. *Analytica chimica acta, 405*(1-2), 191-196.

[46] Zare-Dorabei, R., Boroun, S., & Noroozifar, M. (2018). Flow injection analysis–flame atomic absorption spectrometry system for indirect determination of sulfite after on-line reduction of solid-phase manganese (IV) dioxide reactor. *Talanta, 178*, 722-727.