


Cyanides in the environment—analysis—problems and challenges

Ewa Jaszczak¹  · Żaneta Polkowska¹ · Sylwia Narkowicz¹ · Jacek Namieśnik¹

Received: 5 January 2017 / Accepted: 21 April 2017
© The Author(s) 2017. This article is an open access publication

Abstract Cyanide toxicity and their environmental impact are well known. Nevertheless, they are still used in the mining, galvanic and chemical industries. As a result of industrial activities, cyanides are released in various forms to all elements of the environment. In a natural environment, cyanide exists as cyanogenic glycosides in plants seeds. Too much consumption can cause unpleasant side effects. However, environmental tobacco smoke (ETS) is the most common source of cyanide. Live organisms have the ability to convert cyanide into less toxic compounds excreted with physiological fluids. The aim of this paper is to review the current state of knowledge on the behaviour of cyanide in the environment and its impact on the health and human life.

Keywords Cyanides in the environment · Cyanide toxicity · Cyanide determination · Cyanide in food · Tobacco smoke · Cyanide ion

Introduction

The term “cyanides” is used to describe compounds which contain in their structure the $-C\equiv N$ group. In the environment, cyanides can be found in many different forms (Kuyucak and Akcil 2013). They occur naturally in plants and processed foods. Natural sources of cyanide ions are cyanogenic glycosides which can be found in, among others, apricot kernels, cassava roots and bamboo shoots (Jones 1998). Hydrogen cyanide and cyanides are used in various industries including the mining of silver and gold. Furthermore, they are used in plastic production of all kinds of dyes as well as in chemical laboratories (Dzombak et al. 2016). The sources of environmental pollution are, among other mines, metallurgical plants and exhaust gas from vehicles. Cyanide ions get into the environment mainly from wastewater. These compounds can also enter the environment as a result of fires at industrial workshops and houses as well as from tobacco smoke (Fig. 1) (Kuyucak and Akcil 2013; Karlsson and Botz 2004; Mudder and Botz 2000; Scheneider et al. 1997).

Their form determines their destiny within the environmental means of their transport toxicity and ecotoxicity (Fig. 2). Cyanides are present in various environmental elements such as water, soil, air exhaled, air food and biological materials like blood urine and saliva at the levels of micrograms per litre to milligrams per litre (Dzombak et al. 2016; Donald 2009). Considering the presence of cyanide in various parts of the inanimate environment and biota as well as their toxicity, there is no doubt on increasing demand for information on their prevalence in the elements of the environment or the type of material object (Dzombak et al. 2016). Based on literature data, it can distinguish a number of analytical techniques for the determination of cyanide. The most commonly used methods of cyanide ion determination are spectrophotometric techniques as well as gas and liquid chromatography (Bolstad-

Responsible editor: Philippe Garrigues

✉ Ewa Jaszczak
ewajas5@gmail.com

Żaneta Polkowska
zanpolko@pg.gda.pl

¹ Department of Analytical Chemistry, Faculty of Chemistry, Gdansk University of Technology, Narutowicza Str 11/12, Wrzeszcz, 80-952 Gdansk, Poland

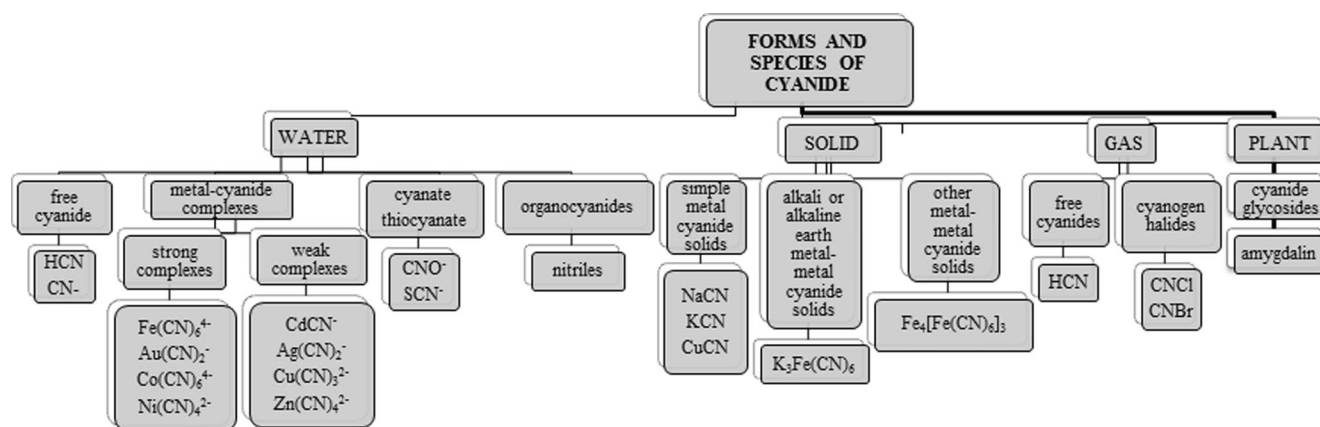


Fig. 1 Sources of cyanide in the environment

Johnson et al. 2000). This review examines the current state of knowledge on the behaviour of cyanide ion in the environment.

Cyanide occurrence in the environment

Atmosphere

In air, cyanide ions are present mainly as hydrogen cyanide (HCN). Miners, firefighters and workers of metallurgical chemical and galvanic industries are exposed largely to cyanide poisoning (Bolstad-Johnson et al. 2000). Cyanides enter into the atmosphere as a consequence of industrial processes and fires at houses and industrial halls. Hydrogen cyanide is a product of combustion of synthetic polymers, wool and silk; additionally, it is produced during the combustion of fuels in automobile engines as a result of catalytic reduction of nitrogen oxides. However, the concentration of HCN in the exhaust gas is higher only in the absence of catalyst (Karlsson and Botz 2004). Cyanide ions are generated naturally during

biogenic processes of higher plant bacteria and fungi (Mudder and Botz 2000).

Analysis of data presented in the literature leads to the conclusion that smoking and, as a result of it, tobacco smoke are the most significant source of cyanide emissions to the air (Table 1). In tobacco smoke, which is formed during smoking, two types of stream can be distinguished: the main and the side ones. Tobacco smoke has 400–500 chemical components of the gas phase and 3500 components of condensed phase. Hydrogen cyanide is a part of the biologically not indifferent substances, which account for about 22% of 500 mg of smoke inhaled from a single cigarette by the smoker (Fig. 3). Hydrogen cyanide is formed in the burning area, mainly during the pyrolysis of various nitrogen compounds, such as proteins and nitrates, at a temperature higher than 700 °C and with oxygen deficit (Borgerdinga and Klusb 2005). In the air, cyanides occur mostly in gaseous form and can be transported over long distances from the emission source (Petrova Simenova and Fishbein 2004). The duration of hydrogen cyanide in the atmosphere is estimated to be approximately 5 months (Karlsson and Botz 2004; Scheneider et al. 1997).

Fig. 2 Cyanide forms and species

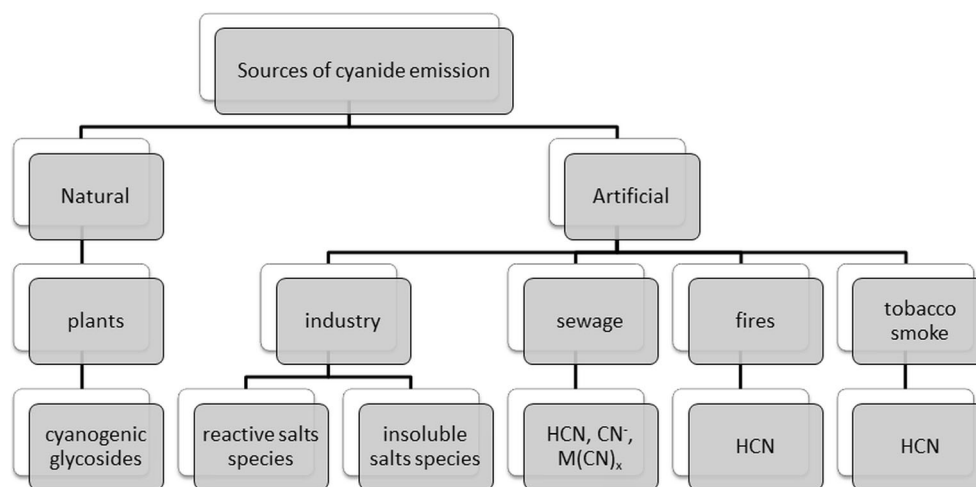


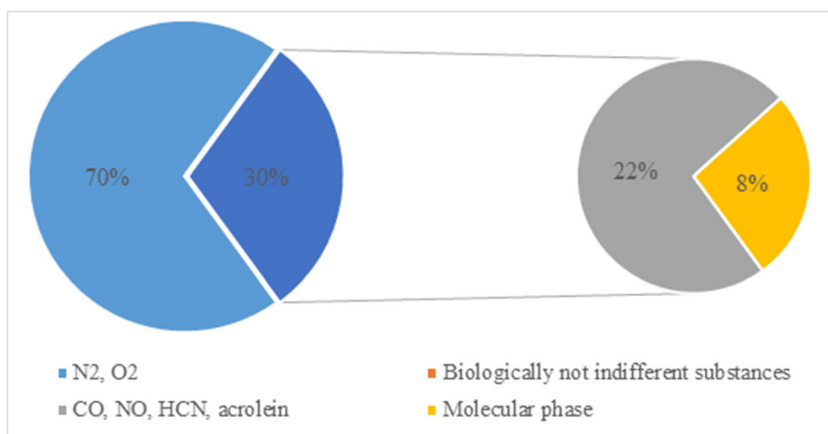
Table 1 Literature information on cyanide concentrations in different environmental samples

Type of sample	Source of sample	Concentration	References
Air			
Outdoor air	Lower atmosphere	0.36 ± 0.16 ppbv	Ambose et al. (2012)
	Atmosphere	333 ± 44 pptv (summer) 195 ± 16 pptv (winter)	Zhao et al. (2000)
	Lower stratosphere	233.5 ± 160.6 ppt 280 ± 4 pptv	Singh et al. (2003) Viggiano et al. (2003)
	Stratosphere	164 pptv	Schneider et al. (1997)
	Gold field	0.76 ppb	Orloff et al. (2006)
	Vehicular emissions	654 t/year	Moussa et al. (2016)
	Vehicular emission	0.45 mg/km	Karlsson and Botz (2004)
Indoor air	Vehicular exposure in garage	0.32 µg/m ³	Karlsson and Botz (2004)
	Air in car	14–20 ppm	Mangnusson et al. (2012)
	Fire	1.8 ± 3 mg/kg	Paton-Walsh et al. (2010)
Tobacco smoke			
Cigarette	China	125.2 µg/cig.	Zhang et al. (2011)
	Spain	6.6 µg/ cig.	Marcilla et al. (2012)
	Russia	27 µg/cig.	Ashley et al. (2014)
	CAMEL Lights	184.825 µg/cig.	Mahernia et al. (2015)
	Marlboro Gold (Germany)	165.871 µg/cig.	
	Marlboro Extra (USA)	164.309 µg/cig.	Mottier et al. (2010)
	Marlboro Lights (Switzerland)	69.344 µg/cig.	
	Winston Blue (Europe)	99.244 µg/cig.	
	Switzerland	4.1 ng/cig.	Xu et al. (2006)
	China	98.38 µg/cig.	
Water			
Surface water	Korea (Gum River)	1.01 ± 0.03 µg/L	Kang and Shin (2014)
	–	0.77 mg/L	Dadfamia et al. (2007)
	Brazil	25–50 µg/L	Frizzarin and Rocha (2013)
	China	–	Wan et al. (2015)
	Italy	5.11 µg/L	Giuriati et al. (2004)
Drinking water	USA (Sunnyvale)	<LOD	Christinson and Rohrer (2007)
	USA (San Jose)	<LOD	
	Sweden	–	Themelis et al. (2009)
Tap water	Iran	<LOD	Absalan et al. (2010)
	Iran	0.6 µg/L	Abbasi et al. (2010)
Wastewater			
	Petrochemical sludge	6.1–63.5 µg/L	Dadfamia et al. (2007)
	Electroplating waste	0.04–1.2 µg/mL	Hassan et al. (2007)
	Petrochemical sludge	4600.2 µg/L	Abbasi et al. (2010)
	Gold cyanidation solution	540 mg/L	Breuer et al. (2011)
	Industrial wastewater	–	Noroozifar et al. (2011)

Table 1 (continued)

Type of sample	Source of sample	Concentration	References
Soil			
	Japan	0.060 mg/L	Matsumura and Kojima (2003)
	Coking plant sites (Germany)	32.8 ± 1.44 mg/kg	Mansfeldt and Biernath (2000)
	Coking plant sites (France)	46.5 ± 14.5 mg/L	Manar et al. (2011)
	Goldmine (Tawurbiek, China)	70.55 µg/g	Shehong et al. (2005)
	Coking plant sites (Germany)	0.14 mg/L	Rennert and Mansfeldt (2006)
	Gold mine (Brazil)	0.83–1.44 mg/kg	Prereira and Sousa Neto (2007)
	Techatticup	<0.01 mg/kg	Sims and Francis (2008)
	Mine site (USA)		
Fresh food			
Kernel/seed	Apple	2.80 ± 0.02 mg/kg	Ma et al. (2010)
		690 ppm	Haque and Bradbury (2002)
		1–3.9 mg/g	Bolarinwa et al. (2015)
	Apricot	1.88 ± 0.07 mg/kg	Ma et al. (2010)
		785 ppm	Haque and Bradbury (2002)
		14.37 ± 0.28 mg/g	Bolarinwa et al. (2014)
	Peach	710 ppm	Haque and Bradbury (2002)
	Nectarine	196 ppm	
	Plum	696 ppm	
	Bean	1.76–1.77 mg/kg	Chove and Mamiro (2010)
	Millet	2.11–2.14 mg/kg	
	Lensed	390 ppm	Haque and Bradbury (2002)
	Rubber tree	–	Abdullah et al. (2013)
	Nuts	–	Chove and Mamiro (2010)
	Plum	247 mg/100 g	Surleva and Drochioiu (2013)
	Almond	7.4 µg/100 g	
	Apple	108 mg/100 g	
	Flax	7.3 mg/100 g	
Leaf	Sorghum	750 ppm	Haque and Bradbury (2002)
	<i>Alocasia macrorrhizos</i>	29 ppm	
	Spinach	2.51 ± 0.6 µg/g	Kuti and Konoru (2006)
		1.28 ± µg/g	
	Chokecherry	4.7–15 mg/kg	Pentore et al. (1996)
	Bamboo	1010 ppm	Haque and Bradbury (2002)
	Grapevine	123–329 mg/kg	Franks et al. (2005)
Root	Manioc	27 ppm	Haque and Bradbury (2002)
Processed food			
Liquor	Cherry	1 ng/mL	Wu et al. (2015)
Juice	Apple juice	0.003 mg/mL	Bolarinwa et al. (2015)
Marzipan		0.02 mg/g	Bolarinwa et al. (2014)
Flour	Manioc	43 ± 20 ppm	Haque and Bradbury (2002)
		232 ± 10 mg/kg	Tivana et al. (2014)
		2.3 mg/kg	Kalenga Saka and Nyirenda (2012)
	Garri	16.7 ppm	Bradbury (2009)

Fig. 3 Tobacco smoke components



Water

There are known many emission sources of cyanides to surface waters. Cyanides can contaminate the water through discharges of factory wastes and can be washed down from fields and urban areas. As a component of wastewater, they are present in the effluents from electroplating processes, gold and silver extraction and production of medicines and plastic (Table 1) (Barclay et al. 1998; Dursun and Aksu 2000).

Water containing cyanide ions is often treated with sulphur dioxide, chlorination process and/or aeration. The most efficient method uses Caro’s acid (hydroperoxysulphuric acid). Techniques based on chlorination are effective only for free cyanides and weak metal complexes. Other methods, such as ozonation or reverse osmosis, are very expensive or inefficient. Biological treatment is possible thanks to microorganisms, such as fungi (e.g. *Fusarium solani*) and bacteria (e.g. *Pseudomonas fluorescens*). In aerobic conditions and with the presence of glucose, microorganisms use ferrocyanide as a source of nitrogen and carbon. As a result of both aerobic and anaerobic biodegradability, ammonia, carbon dioxide

and formates are formed. The best conditions for maximum biodegradability of cyanide ions were observed with a glucose concentration of 0.0465 g/L and pH = 5 (Barclay et al. 1998; Dursun and Aksu 2000).

Soil

The presence of cyanide ions in the soil is primarily caused by such anthropogenic manifestation as galvanic and metallurgical industry (Table 1). The waste containing high concentrations of cyanide is produced also during the underground coal gasification. The degree of contamination of soil with cyanides depends on their amount and activity. Most of cyanides are deposited in the environment as complexes of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$. Their toxicity is low, but due to the light, they convert into highly toxic and volatile free cyanides. In soil, without the light, this process is very slow (Meeussen et al. 1995). This can be described by the following reaction:

Fig. 4 Processes of cyanide transformations occurring in water and soil

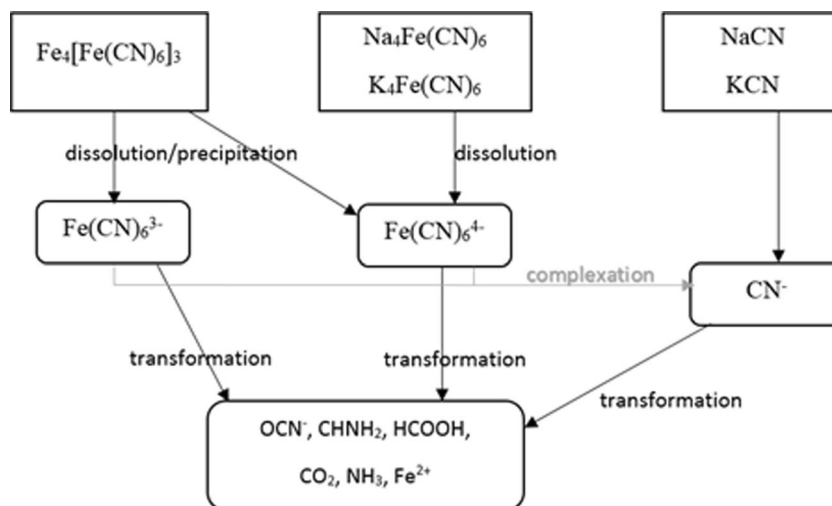


Table 3 Literature information on cyanide concentrations in biological samples

Type of sample	Source of sample	Concentration	References
Liquid			
Blood	Poisoning	2.77 mg/L	Sanchez-Verlaan et al. (2011)
	Fire victims	1.06 mg/L	McAllister et al. (2011)
	Fire victims	2.0–7.2 mg/L	Ferrari et al. (2001)
	Fire victims	1.06 mg/L	Yeoh and Braitberg (2004)
	Health volunteers	0.08 µM/mL	Kage et al. (1996)
	Fire victims	5.32 mg/L	Moriya and Hashimoto (2003)
	Post-mortem blood sample	0.03 mg/L	Felby (2009)
	Living organism	0–0.04 mg/L	
Urine	Health volunteers	0.1 mg/L	Cruz-Landeira et al. (2000)
	Death poisoning	0.15 g/mL	Liu et al. (2009a)
	Smoker	518 ± 123 nM	Zhang et al. (2015)
	Smoker	0.42 µM/L	Jermak et al. (2006)
	Non-smoker	n/a	
	Non-smoker volunteers	0.15 µg/mL	Liu et al. (2009b)
Nasal discharge	Health volunteers	0.121 mg/L	Narkowicz et al. (2013b)
Saliva	Health volunteers	0.66 ± 0.52 µM	Tsungue et al. (2000)
	Smoker	0.76 µM/L	Jermak et al. (2006)
	Non-smoker	0.38 µM/L	
Plasma	Non-smoker volunteers	11.4 µg/mL	Liu et al. (2009b)
Gastric content	Suicide victim	135 µg/mL	Minakata et al. (2009)
Gas			
Breath	Health volunteers	14 ppb	Španěl et al. (2007a)
	School students	7 ppb	Španěl et al. (2007b)
	Three volunteers	0–62 ppbv	Ma et al. (2010)
	Patients with lung disease	25.1 ppb	Dummer et al. (2013)

variety of sweet manioc is safe for direct consumption, and it is obtained after rinsing several times the bitter one. The result was the loss of water-soluble glycosides (Bradbury et al. 2011; Cumbana et al. 2007). In Italy,

cherries with pits are used for home-made tinctures (Pentore et al. 1996). In the Southeast Asia, sodium cyanide (NaCN) is still used as a method for fishing (Mak et al. 2005).

Fig. 6 Basic processes involved in the metabolism of cyanide

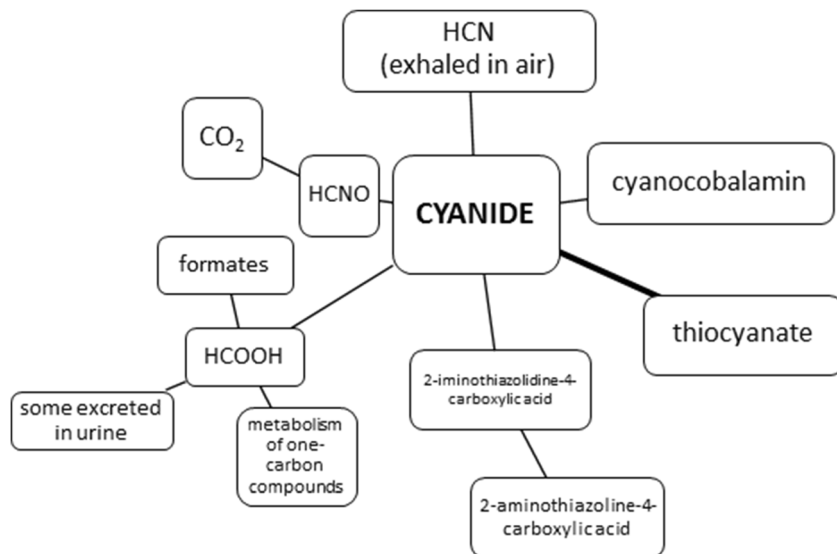
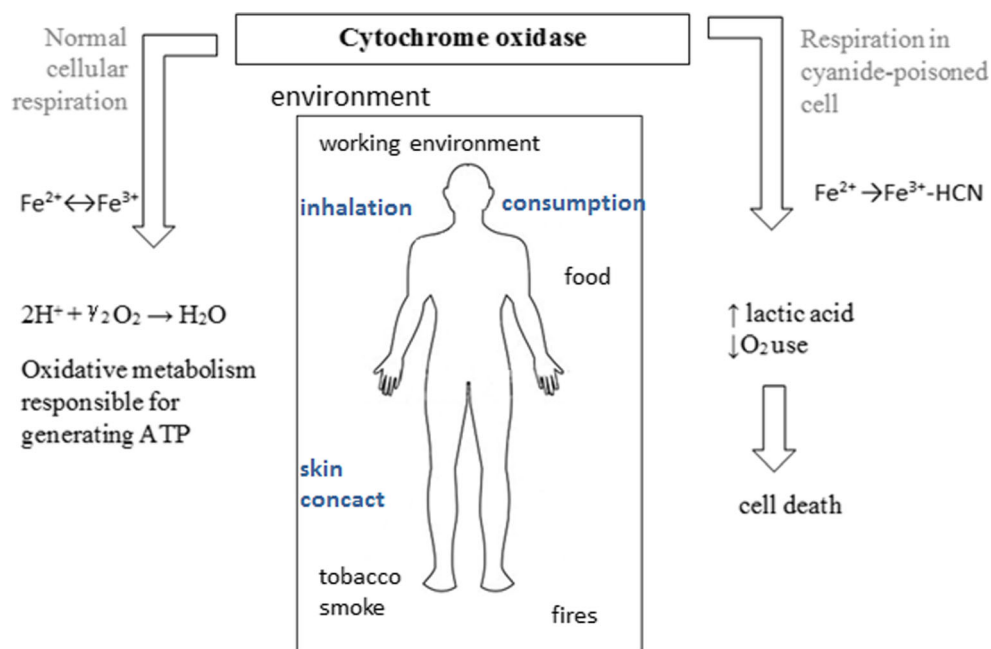


Fig. 7 Schematic representation of the impact of cyanides on the human body



In plants, metabolism of cyanides involves β -cyanoalanine formation due to reaction of hydrogen cyanide with cysteine. Then, β -cyanoalanine is transformed into asparagine (Fig. 5) (ATSDR 1997; Zagrobelny et al. 2004). An example is amygdalin—its decomposition inside the body due to enzymatic hydrolysis is initiated by the enzyme β -glucosidase, and it results in the suitable α -hydroxynitrile, which, at pH values above 6, dissociates into sugar, ketone and hydrogen cyanide (Fig. 5). At lower pH values, the reaction is catalysed by α -hydroxynitrile lyase.

Cyanides in biological materials

As a result of various industrial activities and lifestyle, cyanide ions are introduced into the human body. Biological materials are an excellent source of information on environmental pollution and its impact on human health (Ballantyne 1983).

Urine and saliva are frequently selected as biological materials for research (Table 3) due to the fact that both can be sampled in non-invasive way, and also, the size

of the sample fluid is relatively large (Sano et al. 1989a, b). Another commonly used material is blood, where cyanide determinations can be performed, as well as adducts with proteins and their metabolites. The half-life of cyanide ions in the body is about 2 h; so, to often assess the exposure on the tobacco smoke components, thiocyanate ions are used as their half-life in the body is approx. 6 days (Narkowicz et al. 2013a, 2015). Elevated concentrations of cyanides in the blood can be fatal. In case of death in fire, the results of toxicological studies of the victims, such as the level of carboxyhaemoglobin and cyanide concentration level in the blood, can be used to determine the origins and type of fire (McAllister et al. 2008).

Metabolism of cyanide

As results of pollutions, cyanides get into the environment and they can negatively affect living organisms in many ways

Fig. 8 Toxicity of cyanide forms

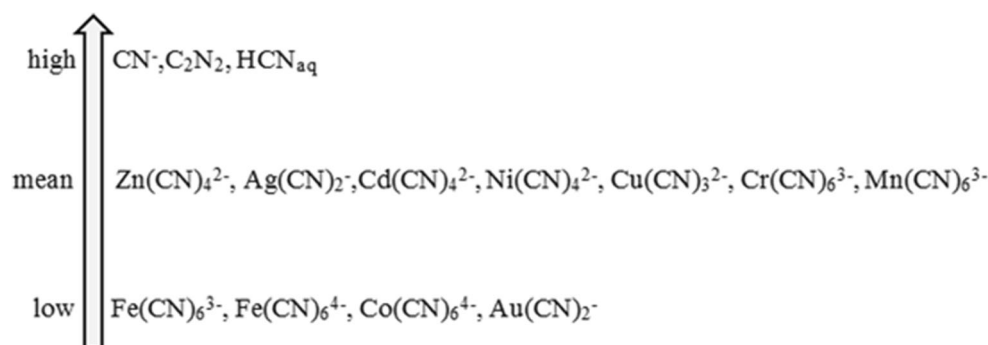


Table 4 Cyanide toxicity

Organism	Cyanide form	Parameter/exposure time	Concentration range	References	
Fish					
<i>Oncorhynchus mykiss</i>	K ₃ Co(CN) ₆	LC ₅₀ /96 h	112.9 mg/L	Little et al. (2007)	
<i>Cyprinus carpio</i>	NaCN	LC ₅₀ /96 h	1.0 mg/L	David and Kartheek (2016)	
<i>Penaeus monodon</i>	NaCN	LC ₅₀ /96 h	0.110 mg/L	Pablo et al. (1997a, b)	
	K ₃ Fe(CN) ₆		9.1 mg/L		
	K ₄ Fe(CN) ₆		60.8 mg/L		
<i>Salmo gairdneri</i>	HCN	LC ₅₀ /96 h	0.057 mg/L	McGeachy and Leduc (1988)	
<i>Cyprinus carpio</i>	NaCN	LC ₅₀ /96 h	1.0 mg/L	David et al. (2008)	
<i>Acanthopagrus butcher</i>	NaCN	LC ₅₀ /96 h	70 µg/L	Pablo et al. (1996)	
	K ₃ Fe(CN) ₆	LC ₅₀ /96 h	1730 µg/L		
	K ₄ Fe(CN) ₆	LC ₅₀ /96 h	20.5 µg/L		
<i>Carassius auratus</i>	NaCN	LC ₅₀ /96 h	318 µg/L	Cardwell et al. (2006)	
<i>Lepomis macrochirus</i>	NaCN	LC ₅₀ /96 h	134 µg/L	Kimball et al. (1978)	
	HCN	NOEC	<5 µg/L		
<i>Macquaria novemaculeata</i>	NaCN	LC ₅₀ /96 h	109 µg/L	Pablo et al. (1996)	
	K ₃ Fe(CN) ₆	LC ₅₀ /96 h	2830 µg/L		
	K ₄ Fe(CN) ₆	LC ₅₀ /96 h	285,000 µg/L		
<i>Pimephales promelas</i>	NaCN	LC ₅₀ /8 days	114 µg/L	Cardwell et al. (2006)	
<i>Pimephales promelas</i>	HCN	NOEC-LOEC/256 days	12.9–19.6 µg/L	Lind et al. (1977)	
Invertebrates					
<i>Daphnia magna</i>	NaCN	LC ₅₀ /24 h	0.171 mg/L	Jaafarzadeh et al. (2013)	
		LC ₅₀ /48 h	0.12 mg/L		
		LC ₅₀ /72 h	0.07 mg/L		
		LC ₅₀ /96 h	0.019 mg/L		
<i>Daphnia magna</i>	K ₃ Co(CN) ₆	LC ₅₀ /96 h	0.502 mg/L	Little et al. (2007)	
		LC ₅₀ /96 h	2.289 mg/L		
<i>Ceriodaphnia dubia</i>	NaCN	EC ₅₀ /48 h	0.0286 mg/L	Pablo et al. (1997a, b)	
			0.128 mg/L		
			0.686 mg/L		
<i>Asellus communis</i>	HCN	NOEC-LOEC/112 days	29–40 µg/L	Oseid and Smith (1979)	
<i>Gammarus fasciatus</i>	NaCN	LC ₅₀ /96 h	900 µg/L	Ewell et al. (1986)	
<i>Cyclops viridis</i>	NaCN	LC ₅₀ /96 h	158 µg/L	Sarkar (1990)	
Algae					
<i>Nitzschia closterium</i>	NaCN	EC ₅₀ /72 h	57 µg/L	Pablo et al. (1997a, b)	
		K ₃ Fe(CN) ₆	EC ₅₀ /72 h		127 µg/L
		K ₄ Fe(CN) ₆	EC ₅₀ /72 h		267 µg/L
<i>Scenedesmus quadricauda</i>	KCN	LOEC/8 days	30 µg/L	Bringmann and Kühn (1980)	
<i>Pseudokirchneriella subcapitata</i>	NaCN	EC ₅₀ /72 h	116 µg/L	Manar et al. (2011)	
		K ₃ Fe(CN) ₆	EC ₅₀ /72 h		158 µg/L
		K ₄ Fe(CN) ₆	EC ₅₀ /72 h		283 µg/L
Upper organism					
Mice	KCN	LD ₅₀ /24 h	8.4 mg/kg	Yamamoto (1995)	
Mice	KCN	LD ₅₀ /24 h	8.87 mg/kg	Jiang et al. (1998)	
Rat	CH ₃ CN	LD ₅₀ /24 h	>5000	Rao et al. (2013)	
			CH ₂ CHCN		95.1 mg/kg
			CH ₂ (CN) ₂		66.4 mg/kg
			CH ₃ CH ₂ CN		83.6 mg/kg
			Na ₂ [Fe(CN) ₅ NO]·2H ₂ O		83.6 mg/kg
			C ₂ H ₄ (CN) ₂		378.5 mg/kg

Table 5 Cyanide poisoning symptoms; Akintonwa et al. 1994)

	Symptoms
Nervous system	Headache, agitation, seizures, coma, mydriasis
Respiratory system	Shortness of breath, cough
Cardiovascular system	Sudden cardiac arrest, acute coronary syndrome, pulmonary oedema, supraventricular and ventricular arrhythmias
Digestive system	Abdominal pain, nausea, vomiting
Skin	Cherry-red colour of the skin, excessive sweating

(Abraham et al. 2016). The cyanide anion is absorbed easily, by the mucous membrane of the respiratory tract, through the skin especially the wet one and gastrointestinal tract. In case of animals, hydrogen cyanide reacts with methaemoglobin in the bloodstream; however, most of cyanide metabolism occurs in tissues. A substantial part (80%) of cyanides is a subject to detoxification in the liver. Responsible for it is thiosulphate sulphurtransferase enzyme present in the mitochondria of the liver. Sulphur which is required for this reaction is collected from biological compounds such as, for example, thiosulphates (Fig. 5). As a consequence of this reaction, thiocyanate ions are formed and they are approximately 200 times less toxic than cyanide excreted with body fluids. The process of cyanide metabolism in a living organism can occur in various ways (Fig. 6), among others, as a combination of cyanide with vitamin B_{12a} resulting in cyanocobalamin, i.e. vitamin B₁₂ (Petrova Simenova and Fishbein 2004). The rest of cyanides are oxidized to formate and carbon dioxide. Formates are excreted into urine while carbon dioxide, along with hydrocyanic acid, by the lungs. In the small amount, cyanides react with cysteine to form 2-iminothiazolidine-4-carboxylic acid (Petrova Simenova and Fishbein 2004).

Cyanide toxicity for a living environment

Compounds containing cyanide ions are rapidly acting poison, as they disrupt the process of cellular respiration. The basic effect of cyanide activity involves combining with trivalent iron of cytochrome oxidase, which is a key enzyme of the respiratory chain (Fig. 7). This combination results in blocking of the intracellular respiratory and increasing synthesis of lactic acid. Although the blocking of cytochrome oxidase has the most significant impact, it ought to remember that the CN⁻ ions also inhibit other enzymes: glutamate decarboxylase, xanthine oxidase, superoxide dismutase, NO synthase and nitrite reductase. Cyanide ion can cause direct damage to the nervous system by lipid peroxidation (Sun et al. 1995). Most sensitive to toxic effects of cyanides are tissues with the fastest metabolism of oxygen, so the brain and the heart muscle, but hypoxia causes the disorder of all body cells' functioning.

A toxic dose depends largely on the type of compound containing a cyanide ion. Based on the data

presented in the literature, it can be concluded that the toxicity of cyanides largely depends on the form of their occurrence (Fig. 8). The least toxic are complex cyanide compounds in contrast to free ions, which are the most toxic ones (Johnson 2015; Donato et al. 2007).

Cyanide toxicity (Table 4) is a parameter which defines the scope of their application. Numerical values for LC₅₀ and LD₅₀ are generally determined after 24-h exposure of the body to a predetermined dosage or concentration of the compound containing a cyano group. The most commonly used indicator organisms are daphnia (*Daphnia magna*) as well as fishes, mice and rats.

The estimated lethal dose for an adult human is 1.5 mg CN⁻ kg of body weight. Symptoms of severe poisoning by inhalation are observed from 53 mg HCN/m³, while the lethal dose ingested with food is approx. 200–300 mg (Oluwole et al. 2003). Prolonged exposure to cyanide can lead to body weakness and various diseases such as hypothyroidism, kidney damage and miscarriages (Table 5).

Determination of cyanide in different types of samples

Cyanide ions have a toxic effect on the health and safety of people. Biological materials collected from

Table 6 Analytical challenges in the development of new analytical procedures

Regardless of used analytical procedures
- Heterogeneity of environmental samples and biological materials
- Metabolism of cyanide depends on the age and sex of the donor
- Small volume of samples
- Losses of cyanide during sampling and sample preparation
- The use of reducing agents
- The presence of interferents
Related to the analytical procedure
- Stage of sample preparation depends on the applied analytical technique
- A complex composition of the matrix
- The ability to change the sample components while collecting, storing and transporting samples
- Low concentrations of cyanide ions
- The possibility of reaction between the compounds present in samples
- Oxidizers can co-exist with cyanide

Table 7 The composition of the matrix of environmental and biological samples

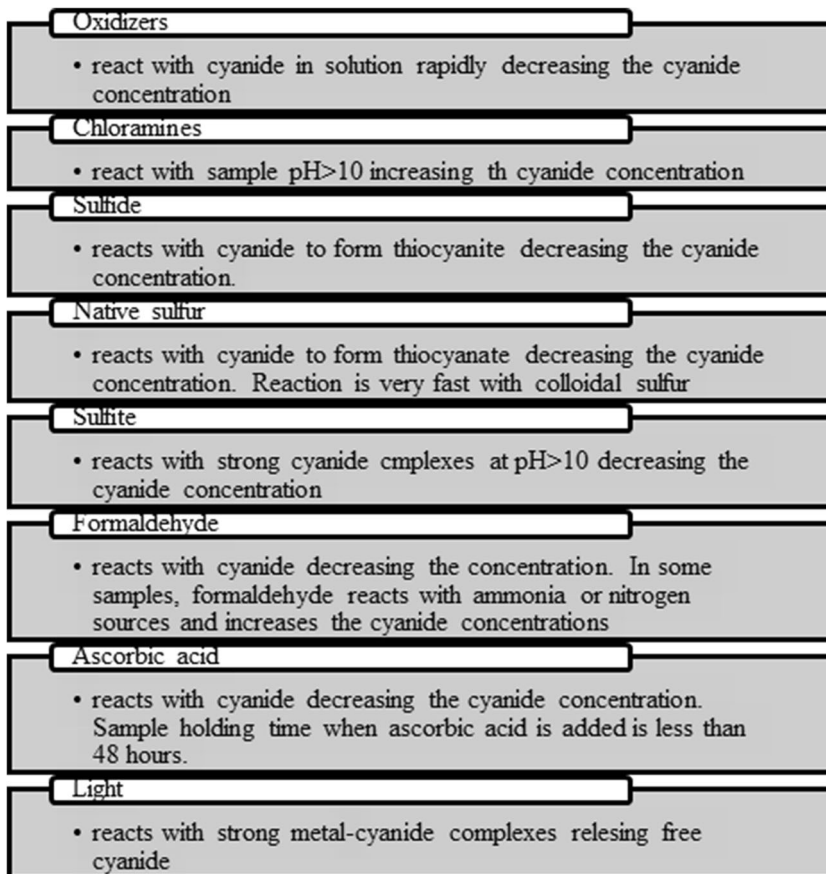
Sample	Example	Constituents of the matrix	References
Food	Almond	Linoleic acid, elaidic acid	Lin et al. (2016)
Water	Drinking water	CaCO ₃ , Ca, Cl ⁻ , PO ₄ ³⁻ , Fe ²⁺ , Mn ²⁺	Gerke et al. (2016)
Air		Benzene, CO, Pb, NO _x , PM ₁₀ , SO ₂ , VOCs	DOE (1997)
Soil	Calabria, Italy	SiO ₂ , TiO ₂ , Al ₂ O ₃ , FeO, MgO, CaO, Na ₂ O, K ₂ O, Cl ₂ O	Pelle et al. (2013)
Tobacco smoke		Benzo[a]pyrene, HCN, formaldehyde acetaldehyde, acrolein, benzene, toluene	Torikaiu et al. (2005)
Biological samples	Blood	Erythrocytes, leukocytes, protein, haemoglobin (HGB), neutrophils, blood platelets, glucose	Tong et al. (2009)
	Urine	Na ⁺ , K ⁺ , NH ₃ ⁺ , Ca ²⁺ , Mg ²⁺ , Cl ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ , water, urea, uric acid, creatinine	Yaroshenko et al. (2015)
	Saliva	Salivary amylase (ptyalin) and maltase Mucin—mucilaginous body Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , SCN ⁻ , protein, water 99.5%	Chen et al. (2015)

humans provide researchers with information regarding the health and may also be used to define the environmental pollution. Therefore, it is necessary to determine their content in representative samples taken also from inanimate objects of the environment.

Problems and challenges posed by the analysis of cyanide in environmental and biological samples

Stages of sampling, preservation and storage are crucial for the analysis of the presence of cyanide. In case of biological

Fig. 9 Interfering substances in the determination of cyanide ions



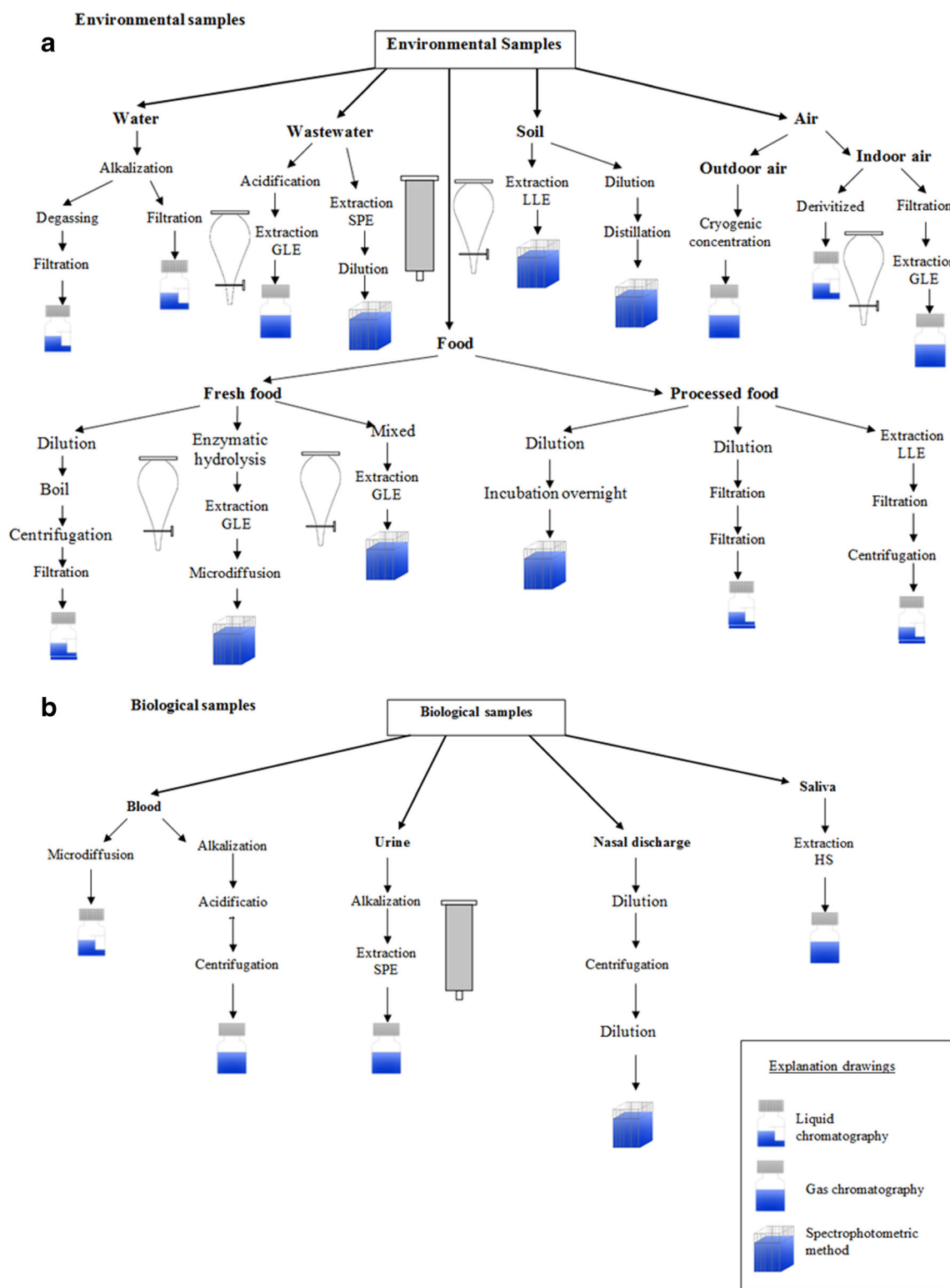
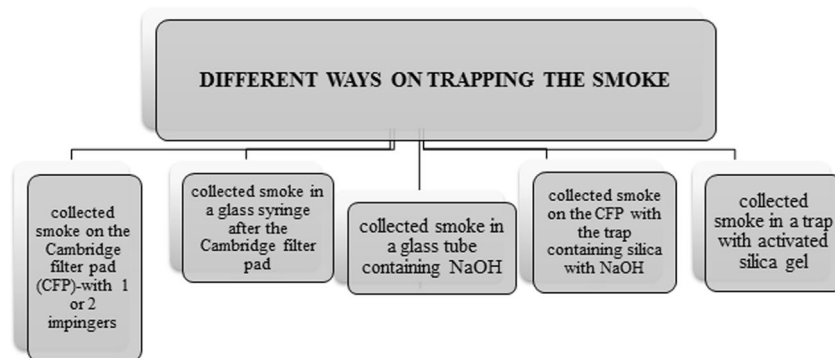


Fig. 10 a, b Sample preparation

samples, storage temperature of samples is very important as it may change the cyanide ion concentration up to 66% (Lindsay et al. 2004).

A number of analytical challenges can occur while examining environmental samples and biological materials on the amount of cyanides, and they ought to be taken into account at

Fig. 11 Information on the use of traps to trap tobacco smoke constituents



the stage of developing and implementing new analytical procedures to the current ones (Narkowicz et al. 2012) (Table 6).

Samples of biological material, wastewater and food are complex matrix ones, as they require adequate preparation for analysis (Table 7). Interferents present in the sample can react with cyanide; thus, they contribute to the errors in the results of analysis (Fig. 9). During preparation of the sample for analysis, in the extraction step beside decomposition of stable metal cyanide complexes, elimination of interfering substances occurs (Christinson and Rohrer 2007; ASTM D 7365-09a 2015).

Sample preparation stages

Preparation of the sample for analysis usually involves adding basic reagents and extracting cyanide from the sample (Fig. 10a, b). In environmental samples as well as in biological ones, it is necessary to add sodium hydroxide to stabilize the form that cyanide occurred in. The addition of NaOH results in a sample with pH above 11, and as consequence, volatile forms of cyanide are bound. Hydrogen cyanide is formed in solutions of cyanide ion complexes with metals at pH below 4. Distillation of the sample with strong acid causes the release of hydrogen cyanide but prevents determining it as free cyanide.

In order to prepare the plant samples to be analysed for the presence of cyanide, firstly, parts of plants for examination need to be thoroughly washed in distilled water and then dried for 24 h, after grinding. Later on, the extraction is carried out with NaOH or H₃PO₄. While determining cyanogenic glycosides, three gradual enzymatic biodegradations are required. For example, in case of amygdalin in the first step, it is necessary to separate it from prunasin and glucose. The second step is hydrolysis of prunasin to mandelonitrile and glucose. In the final phase of hydrolysis, mandelonitrile decomposes to benzaldehyde and hydrogen cyanide. Enzymatic hydrolysis of amygdalin to mandelonitrile usually takes place under mild acid conditions at a pH of 5–5.8, whereas the hydrolysis of mandelonitrile to benzaldehyde and HCN takes place quickly

under basic conditions (at pH10) (Ma et al. 2010; Bolarinwa et al. 2015).

In sample analysis, preparing samples is an extremely important stage, including the case of biological samples with important information, like during post-mortem examination. Looking at blood samples, it is necessary to separate cyanide ions from haemoglobin, and it can be achieved among others by microdiffusion in the Conway cell (Gambaro et al. 2007). In order to improve the efficiency and accuracy of the analytical techniques, researchers use fibre-protected headspace liquid-phase microextraction or solid-supported liquid-liquid extraction combined with capillary electrophoresis (Mak et al. 2005).

The tobacco smoke contains over 5600 compounds, which means that cyanide determination is a very complicated process (Thorne and Adamson 2013). For sampling smoke, special apparatus is used to simulate the process of cigarette smoking by man. They adjust the number of puffs per minute and puff volume. Moreover, such devices are equipped with pumps, flow meters and traps with capture solution to trap components of the tobacco smoke (Fig. 11) (Mahernia et al. 2015; Intorp et al. 2008).

Analytical techniques for determining cyanide in different samples

The most common analytical techniques used for detection and determination of cyanide in properly prepared samples of biological and environmental materials are spectrophotometric (Cruz-Landeira et al. 2000) and chromatographic (Tracqui et al. 2002) methods including gas and liquid chromatography (Table 8).

Cyanide ions in plants, water, soil and air occur in many forms of compounds. Cyanogenic glycosides can be determined by a variety of chromatographic techniques, where the main advantage is analysis of primary forms of such glycosides; however, they are relatively expensive. An indirect method of cyanogenic glycoside determination is based on the determination of hydrogen cyanide after acid or enzyme hydrolysis.

Table 8 Preparation and analytical techniques for cyanide determination

Analytical technique	Metrological parameters	Type of sample	References
IC-PAD	Linearity 0.0147–2.45 µg/mL LOD 1–3 µg/mL Recovery 94.3–101%	Mainstream smoke Drinking water Liquor	Zhang et al. (2011); Xu et al. (2006); Wu et al. (2015)
SI-GD	Linearity up to 200 g/L LOD 2.5 µg/L LOQ 7.5 µg/L	Mineral water	Themelis et al. (2009)
GC			
NPD	LOD 0.003 µg/mL–0.5 µg/L Recovery 76.8–121.5%	Petrochemical wastewater Blood	Schneider et al. (1997); Felby (2009)
FTD	MDL 0.021 ppbv	Air (lower atmosphere)	Ambose et al. (2012)
RGD	LOD 30 ppt	Air (stratosphere)	Schneider et al. (1997)
MS	LOD 0.01–0.2 µg/mL Recovery 80%	Mainstream smoke Blood	Marcilla et al. (2012); Moriya and Hashimoto (2003); Liu et al. (2009a); Tsunge et al. (2000)
µECD	Recovery 86–116% LOD 0.6 ng/mL Linearity 0.0250–15.0 ng/mL	Urine Saliva Mainstream smoke	Xu et al. (2006)
MS			
SFIT	LOD 1 ppb	Air (atmosphere) Breath	Zhao et al. (2000); Španěl et al. (2007a, b); Dummer et al. (2013)
PTR-TOF	–	Engine exhaust	Moussa et al. (2016)
MS/MS			
ESI	LOD 0.001 µg/mL Recovery 96–117% LOD 0.5 ng/mL Linearity 0.0024–0.331 ng/mL	Urine Gastric content Mainstream smoke Grapevine (leaf) Mainstream smoke	Minakata et al. (2009) Mottier et al. (2010); Franks et al. (2005) Mahemia et al. (2015)
LC	–		
Polarography	Recovery 97–109% LOD 0.007 µg/mL–0.02 mg/mL λ = 310–578 nm	Electroplating wastewater Wastewater Drinking water Soil Engine exhaust Mainstream smoke Seeds Leaf Flour Cassava pulp Blood Urine	Karlsson and Botz (2004); Ashley et al. (2014); Absalan et al. (2010); Abassi et al. (2010); Dadfamia et al. (2007); Hassan et al. (2007); (Matsumura and Kojima (2003); Mansfeldt and Biernath (2000); Manar et al. (2011); Shehong et al. (2005); Rennert and Mansfeldt (2006); Ma et al. (2010); Abdullah et al. (2013); Surleva and Drochitciu (2013); McAllister et al. (2011)
Spectrophotometric method			

Table 8 (continued)

Analytical technique	Metrological parameters	Type of sample	References
HPLC-UV	LOD 0.1 µg/mL Recovery 98%	Nasal discharge Breath Seed Blood	Bolarinwa et al. (2015); Bolarinwa et al. (2014)
Capillary electrophoresis/UV spectrometry	LOD 0.002 µg/mL Recovery 92–106% LOQ 0.10 mg/L	Urine Saliva Blood	Zhang et al. (2015); Jermak et al. (2006)
Electrochemical method			Ferrari et al. (2001)
GFIT	–	Savannah fire	Paton-Walsh et al. (2010)
The AOAC quantitative titrimetric method	–	SEED	Chove and Mamiro (2010)
Dräger gas detection tube	–	Air in car	Mangnusson et al. (2012)
CIMS	LOD 37 pptv	Air (stratosphere)	Viggiano et al. (2003)
IMRMS	–	Air (stratosphere)	Singh et al. (2003)

Beside the spectrophotometric and chromatographic techniques, chemiluminescence (Goi et al. 2007) or capillary electrophoresis is used, however not so often, in the analysis of environmental samples (Fasco et al. 2007; Sadeg and Belhadj-Tahar 2009). Mass spectrometry with ionization of selected ions in stream (SIFT-MS) is used particularly in the determination of HCN in the exhaled air. Atomic absorption spectroscopy technique cannot be directly applied to the determination of cyanide. However, after applying a microcolumn saturated with ionic silver, it was possible to use FI-FAAS techniques for analysis of cyanide in samples of wastewater (Dadfarnia et al. 2007).

In biological samples, due to the short half-life of cyanides, which ranges from several minutes to few hours at most, often their concentration is determined indirectly by determining the concentration of one of their metabolites or CN-protein adducts. Determination of cyanide ions in biological samples is possible by prior cyanide distillation or microdiffusion to solution of an absorbent material. Then, spectrophotometric methods are used for analysis of cyanide ion. The method is based on the König reaction, where the cyanide anion is oxidized with chloramine-T to cyanogen halide, which is the most accurate colorimetric method. Spectrophotometric method is a universal one; however, the limit of detection at the level of milligrams per litre (or mg/kg) narrows its usage (Goi et al. 2007).

In contrast to spectrophotometric techniques, chromatographic techniques are characterized by a low limit of detection at the level of milligrams per litre and high precision. Depending on the type of detector, gas chromatography is used to analyse various samples: neurophysiological detector (NPD) and FID for water and industrial wastewater (Wan et al. 2015), MS for biological materials (Torikaiu et al. 2005) and μ ECD for air tobacco smoke (Akintonwa et al. 1994).

However, unlike the GC-FID, analytes present in the sample are examined by a GC-NPD method and they require derivatization phase (Wan et al. 2015). Nonetheless, the widest range of concentrations (0.05–10 μ g/mL) can be attributed to gas chromatography mass spectrometry, while the lowest limit of detection is typical for capillary electrophoresis technique combined with UV detection. Electrochemical techniques and ion chromatography are characterized by high sensitivity and low detection limits (1 μ g/L). Electrochemical methods have been used for determination of HCN in exhaled breath and blood. The versatility of this method causes its extensive use (Giuriati et al. 2004; Christinson and Rohrer 2007).

Conclusions

The presence of cyanide ions in food and their use in the industry are dangerous to people's health and safety. Compounds containing cyanide ions are rapidly acting poison, which mainly interferes with the process of cellular respiration, that results in a number of ailments and illnesses and even death. Because of the cyanide ion toxicity, especially important is their determination in environmental and biological samples. The development of procedures to enable quantitation of these ions in environmental samples and in samples of biological materials allows the assessment of risks resulting from human exposure to the cyanide ions in the work environment in food and in the air.

One of the most important aspects of the cyanide ion analysis is the step focused on preparing samples for analysis. It is related to the fact that cyanide ions are not stable ones, and they occur in various forms. The presence of matrix interferences must be also considered in the preservation procedure. Sulphides and reduced sulphur compounds interfere through

Table 9 Application of analytical techniques for the determination of cyanide in various samples

Determination technique	Type of matrix					
	Water	Wastewater	Food	Air	Soil	Biological materials
Chromatography						
Gas		+		+		+
Liquid			+	+		+
Ion	+		+	+		
Spectrophotometric	+	+	+	+	+	+
Others						
SI-GD	+					
SFIT				+		
PTR-TOF				+		
ESI						+
Polarography				+		
CE						+
IMRMS				+		

formation to thiocyanate. Sulphite reacts with strong cyanide complexes at pH >10, decreasing the cyanide concentration. Oxidants such as residual chlorine or hydrogen peroxide are known to interfere. If sample contain oxidants, add a reducing agent. Sodium arsenite (NaAsO₂) and sodium thiosulphate (Na₂S₂O₃) are preferred reducing agents. Most cyanide analysis sampling protocols specify the preservation of samples at a pH of 12 or higher. During the preparation of environmental samples, extraction techniques (LLE and GLE) are used for cyanide ion determination while filtration and centrifugation are used in the case of biological samples.

Recently, in the literature, information can be found on the use of samples of biological and environmental materials in the cyanide analytics (Table 9). Especially interesting are biological materials, due to the effect of cyanide on human health and life.

When looking at information on the used analytical techniques, it can be noticed that the most interesting one became gas chromatography liquid and ion chromatography, which allow to achieve lower limits of quantification (1 µg/L); furthermore, they are characterized by good selectivity and reproducibility. In relation to the increased interest in the subject of cyanide ion analytics, researches aim to use other analytical techniques. It is, however, necessary to carry out validation on real samples.

Acknowledgements The authors would like to thank the National Science Centre in Poland (project “Iuventus Plus” project no. 0321/IP3/2015/73) for the financial support and to the project manager: Sylwia Narkowicz, PhD.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

Abbasi S, Valinezhad R, Khani H (2010) A novel kinetic spectrophotometric method for the determination of ultra-trace amount of cyanide. *Spectrochim Acta A* 77:112–116

Abdullah BM, Salimon J, Yousif E, Salih N (2013) Occurrence of cyanogenic glycoside and cyanide in the Malaysian rubber seed oil. *Journal of the Association of Arab Universities for Basic and Applied Sciences* 14:83–86

Abraham K, Buhrke T, Lampen A (2016) Bioavailability of cyanide after consumption of a single meal of foods containing high levels of cyanogenic glycosides: a crossover study in humans. *Arch Toxicol* 90:559–574

Abسالan G, Asadi M, Kamaran S, Torabi S, Sheikhan L (2010) Design of cyanide ion optode based on immobilization of a new Co(III) Schiff base complex on triacetylcellulose membrane using room temperature ionic liquids as modifiers. *Sensors Actuators B Chem* 147:31–36

Akintonwa A, Tunwashe O, Onifade A (1994) Fatal and non-fatal acute poisoning attributed to cassava-based meal. *Acta Hort* 375:285–288

Ambrose JL, Zhou Y, Haase K, Mayne HR, Talbot R, Sive BC (2012) A gas chromatographic instrument for measurement of hydrogen cyanide in the lower atmosphere. *Atmos Meas Tech* 5:1229–1240

Ashley M, Dixon M, Prasad K (2014) Relationship between cigarette format and mouth-level exposure to tar and nicotine in smokers of Russian king-size cigarettes. *Regul Toxicol Pharmacol* 70:430–437

ASTM D 7365-09a (2015) Standard practise for sampling preservation and mitigating interferences in water samples for analysis of cyanide. ASTM International West Conshohocken, PA

ATSDR (1997) Toxicological profile for cyanide. US Department of Health and Human Services Public Health Service Agency for Toxic Substances and Disease Registry, Atlanta

Ballantyne B (1983) The influence of exposure route and species on the acute lethal toxicity and tissue concentrations of cyanide. *Dev Toxicol Environ Sci* 11:583–586

Ballhorn DJ (2011) Cyanogenic glycosides in nuts and seeds nuts and seeds in health and disease prevention, vol 12. Academic, San Diego, pp 129–136

Barclay M, Hart A, Knowles CJ, Meeussen JCL, Tett VA (1998) Biodegradation of metal cyanides by mixed and pure cultures of fungi. *Enzym Microb Technol* 22:223–231

Bolarinwa IF, Orfila C, Morgan MRA (2014) Amygdalin content of seeds kernels and food products commercially—available in the UK. *Food Chem* 152:133–139

Bolarinwa IF, Orfila C, Morgan MRA (2015) Determination of amygdalin in apple seeds, fresh apples and processed apple juices. *Food Chem* 170:437–442

Bolstad-Johnson DM, Burgess JL, Crutchfield CD, Storment S, Gerkin R, Wilson JR (2000) Characterization of firefighter exposures during fire overhaul. *AIHAJ* 61:636–641

Borgerdinga M, Klus H (2005) Analysis of complex mixtures: cigarette smoke. *Exp Toxicol Pathol* 57:43–73

Bradbury JH (2009) Development of a sensitive picrate method to determine total cyanide and acetone cyanohydrin contents of garri from cassava. *Food Chem* 113:1329–1333

Bradbury JH, Cliff J, Denton IC (2011) Uptake of wetting method in Africa to reduce cyanide poisoning and konzo from cassava. *Food Chem Toxicol* 49:539–542

Breuer PL, Sutcliffe CA, Meakin RL (2011) Cyanide measurement by silver nitrate titration: comparison of rhodanine and potentiometric end-points. *Hydrometallurgy* 106:135–140

Bringmann G, Kühn R (1980) Comparison of the toxicity thresholds of water pollutants to bacteria algae and protozoa in the cell multiplication inhibition test. *Water Res* 14:231–241

Cardwell RD, Foreman DG, Payne TR, Wilbur DJ (2006) Acute toxicity of selected toxicants to six species of fish. US EPA, Duluth

Chen Z, Feng S, Pow EHN, Lam OLT, Mai S, Wang H (2015) Organic anion composition of human whole saliva as determined by ion chromatography. *Clin Chim Acta* 438:231–235

Chove BE, Mamiro PRS (2010) Effect of germination and autoclaving of sprouted finger millet and kidney beans on cyanide content. *Tanzania Journal of Health Research* 12:261–266

Christinson TT, Rohrer JS (2007) Direct determination of free cyanide in drinking water by ion chromatography with pulsed amperometric detection. *J Chromatogr A* 1155:31–39

Cruz-Landeira A, Lopez-Rivadulla M, Concheiro-Carro L, Fernandez-Gomez P, Tabernero-Duque MJ (2000) A new spectrophotometric method for the toxicological diagnosis of cyanide poisoning. *J Anal Toxicol* 24:266–270

Cumbana A, Mirione E, Cliff J, Bradbury JH (2007) Reduction of cyanide content of cassava flour in Mozambique by wetting method. *Food Chem* 101:894–897

Dadfarnia S, Shabani AMH, Tamadon F, Rezaei M (2007) Indirect determination of free cyanide in water and industrial waste water by

- flow injection-atomic absorption spectrometry. *Microchim Acta* 158:159–163
- David M, Kartheek RM (2016) In vivo studies on hepato-renal impairments in freshwater fish *Cyprinus carpio* following exposure to sublethal concentrations of sodium cyanide. *Environ Sci Pollut Res* 23:722–733
- David M, Munaswamy V, Halappa R, Marigoudar SR (2008) Impact of sodium cyanide on catalase activity in the freshwater exotic carp *Cyprinus carpio* (Linnaeus). *Pestic Biochem Phys* 92:15–18
- DOE (Department of the Environment) (1997) The United Kingdom National Air Quality Strategy. H M Stationary Office, London
- Donald GB (2009) Cyanogenic foods (cassava fruit kernels and cypad seeds). *Medical Toxicology of Natural Substances* 55:336–352
- Donato DB, Nichols O, Possingham H, More M, Ricci PF, Noller BN (2007) A critical review of the effects of gold cyanide-bearing tailings solutions on wildlife. *Environ Int* 33:974–984
- Dummer J, Storer M, Sturme S, Scott-Thomas A, Chambers S, Swanney M, Epton M (2013) Quantification of hydrogen cyanide (HCN) in breath using selected ion flow tube mass spectrometry—HCN is not a biomarker of *Pseudomonas* in chronic suppurative lung disease. *J Breath Res* 7:1–8
- Dursun AY, Aksu Z (2000) Biodegradation kinetics of ferrous(II) cyanide complex ions by immobilized *Pseudomonas fluorescens* in a packed bed column reactor. *Process Biochem* 35:615–622
- Dzombak DA, Ghosh RS, Wong-Chong GM (2016) Cyanide in water and soil: chemistry risk and management. Taylor & Francis Group, Boca Raton
- Ewell WS, Kringle RO, Gorsuch JW, Robillard KA, Spiegel RC (1986) Simultaneous evaluation of the acute effects of chemicals on seven aquatic species. *Environ Toxicol Chem* 5:831–840
- Fasco MJ, Hauer CR, Stack RF, O'Hehir C, Barr JR, Eadon GA (2007) Cyanide adducts with human plasma proteins: albumin as a potential exposure surrogate. *Chem Res Toxicol* 20:677–684
- Felby S (2009) Determination of cyanide in blood by reaction headspace gas chromatography. *Forensic Sci Med Pathol* 5:39–43
- Ferrari LA, Arado MG, Giannuzzi LG, Mastrantonino G, Guatelli MA (2001) Hydrogen cyanide and carbon monoxide in blood of convicted dead in a polyurethane combustion: a proposition for the data analysis. *Forensic Sci Int* 121:140–141
- Franks TK, Hayasaka Y, Choimes S, Van Heeswijk R (2005) Cyanogenic glucosides in grapevine: polymorphism identification and developmental patterns. *Phytochemistry* 66:165–173
- Frizzarin RM, Rocha FRP (2013) A multi-pumping flow-based procedure with improved sensitivity for the spectrophotometric determination of acid-dissociable cyanide in natural waters. *Anal Chim Acta* 758:108–113
- Gambaro V, Amoldi S, Casagni E, Dell'Acqua L, Pecoraro C, Froidi R (2007) Blood cyanide determination in two cases of fatal intoxication: comparison between headspace gas chromatography and a spectrophotometric method. *J Forensic Sci* 52:1401–1404
- Gerke TL, Little BJ, Maynard JB (2016) Manganese deposition in drinking water distribution systems. *Sci Total Environ* 541:184–193
- Giuriati C, Cavalli S, Gorni A, Badacco D, Pastore P (2004) Ion chromatographic determination of sulphide and cyanide in real matrices by using pulsed amperometric detection on a silver electrode. *J Chromatogr A* 1023:105–112
- Goi N, Takagi K, Hirai Y, Harada H, Kari A, Terashima Y, Kinai N, Hiramatsu M, Nakamura K, Ono T (2007) Effect of psychologic stress on peroxidase and thiocyanate levels in human saliva detected by ultraweak chemiluminescence. *J Health Sci* 53:161–169
- Haque MR, Bradbury JH (2002) Total cyanide detection of plants and foods using the picrate and acid hydrolysis methods. *Food Chem* 77:107–114
- Hassan SSM, Hamza MSA, Kelany AE (2007) A novel spectrophotometric method for batch and flow injection determination of cyanide in electroplating wastewater. *Talanta* 71:1088–1095
- Intorp M, Purkis S, Whittaker M, Wright W (2008) Determination of Hoffmann analytes in cigarette mainstream smoke. *Contributions to Tobacco Research* 23:161–202
- Jaafarzadeh N, Hahempour Y, Ahmadi Angali K (2013) Acute toxicity test using cyanide on *Daphnia magna* by flow-through system. *J Water Chem Techno* 35:281–286
- Jermak S, Pranaityte B, Padaruskas A (2006) Headspace single-drop microextraction with in-drop microextraction and capillary electrophoretic determination for free cyanide analysis. *Electrophoresis* 27:4538–4544
- Jiang S, Liu Z, Zhuang X (1998) Effect of procaine hydrochlorine on cyanide intoxication and its effect on neuronal calcium in mice. *Toxicol Appl Pharm* 150:32–36
- Johnson CA (2015) The fate of cyanide in leach wastes at gold mines: an environmental perspective. *Appl Geochem* 57:194–205
- Jones DA (1998) Why are so many food plants are cyanogenic? *Phytochemistry* 47:155–162
- Kage S, Nagata T, Kudo K (1996) Determination of cyanide and thiocyanate in blood by gas chromatography and gas chromatography-mass spectrometry. *J Chrom B* 675:27–32
- Kalenga Saka JD, Nyirenda KK (2012) Effect of two ethic processing technologies on reduction and composition of total and non-glucosidic cyanogens in cassava. *Food Chem* 130:605–609
- Kang HI, Shin HS (2014) Ultra-sensitive determination of cyanide in surface water by gas chromatography-tandem mass spectrometry after derivatization with 2-(dimethylamino)ethanethiol. *Anal Chim Acta* 828:168–173
- Karlsson HL, Botz M (2004) Ammonia nitrous oxide and hydrogen cyanide emissions from five passenger vehicles. *Sci Total Environ* 334-335:125–132
- Kimball GL, Smith LL Jr, Broderius SJ (1978) Chronic toxicity of hydrogen cyanide to the bluegill. *Trans Am Fish Soc* 107:341–345
- Kuti JO, Konoru HB (2006) Cyanogenic glycosides content in two edible leaves of tree spinach (*Cnidoscous* spp.) *J Food Compos Anal* 19:556–561
- Kuyucak N, Akcil A (2013) Cyanide and removal options from effluents in gold mining and metallurgical processes. *Miner Eng* 50:13–29
- Lin JT, Liu SC, Hu CC, Shyu YS, Hsu CY, Yang DJ (2016) Effects of roasting temperature and duration on fatty acid composition phenolic composition Maillard reaction degree and antioxidant attribute of almond (*Prunus dulcis*) kernel. *Food Chem* 190:520–528
- Lind DT, Smith LL Jr, Broderius SJ (1977) Chronic effects of hydrogen cyanide on the fathead minnow. *J Water Pollut Control Fed* 49:262–268
- Lindsay AE, Greenbaum AR, O'Hare D (2004) Analytical techniques for cyanide in blood and published blood cyanide concentrations from healthy subjects and fire victims. *Anal Chim Acta* 511:185–195
- Little EE, Calfee RD, Theodorakos P, Brown ZA, Johnson CA (2007) Toxicity of cobalt-complexed cyanide to *Oncorhynchus mykiss*, *Daphnia magna*, and *Ceriodaphnia dubia*. *Environ Sci Pollut Res* 14:333–337
- Liu G, Liu J, Hara K, Wang Y, Yu Y, Gao L, Li L (2009) Rapid determination of cyanide in human plasma and urine by gas chromatography-mass spectrometry with two-step derivatization. *J Chromatogr B* 877:3054–3058
- Ma J, Dasgupta PK, Blackledge W, Boss GR (2010) Combinamide-based cyanide analysis by multiwavelength spectrometry in a liquid core waveguide. *Anal Chem* 82:6244–6250
- Mahernia S, Amanlou A, Kiaee G, Amanlou M (2015) Determination of hydrogen cyanide concentration in mainstream smoke of tobacco products by polarography. *J Environ Health Sci Eng* 13:57–63
- Mak KKW, Yanase H, Renneberg R (2005) Cyanide fishing and cyanide detection in coral reef fish using chemical tests and biosensor. *Biosens Bioelectron* 20:2581–2593
- Manar R, Bonnard M, Rast C, Veber AM, Vasseur P (2011) Ecotoxicity of cyanide complexes in industrially contaminated soils. *J Hazard Mater* 197:369–377

- Mangnusson R, Nyholm S, Åstot C (2012) Analysis of hydrogen cyanide in air in a case of attempted cyanide poisoning. *Forensic Sci International* 222:7–12
- Mansfeldt T, Biernath H (2000) Determination of total cyanide in soils by micro-distillation. *Anal Chim Acta* 406:283–288
- Marcilla A, Martinez I, Berenguer D, Gomez-Siurana A, Beltran MI (2012) Comparative study of the main characteristics and composition of mainstream smoke of ten cigarette brands sold in Spain. *Food Chem Toxicol* 50:1317–1333
- Matsumura M, Kojima T (2003) Elution and decomposition of cyanide in soil contaminated with various cyanocompounds. *J Hazard Mater* B97:99–110
- McAllister JL, Roby RJ, Levine B, Purser D (2008) Stability of cyanide in cadavers and in postmortem stored tissue specimens: a review. *Journal of Analytical Toxicology* 32:612–620
- McAllister JL, Roby RJ, Levine B, Purser D (2011) The effect of sodium fluoride on the stability of cyanide in postmortem blood samples from fire victims. *Forensic Science International* 209(1-3):29–33
- McGeachy SM, Leduc G (1988) The influence of season and exercise on the lethal toxicity of cyanide to rainbow trout (*Salmo gairdneri*). *Arch Environ Contam Toxicol* 17:313–318
- Meeussen JCL, Van Riemsdijk WH, Van der Zee SEATM (1995) Transport of complexed cyanide in soil. *Geoderma* 67:73–85
- Minakata K, Nozawa H, Gonmori K, Yamagishi I, Suzuki M, Hasegawa K, Watanabe K, Suzuki O (2009) Determination of cyanide in urine and gastric content by electrospray ionization tandem mass spectrometry after direct flow injection of dicyjanogold. *Anal Chim Acta* 651:81–84
- Moriya F, Hashimoto Y (2003) Chemical factors affecting the interpretation of blood cyanide concentrations in fire victims. *Legal Med* 5: 113–117
- Mottier N, Jeanneret F, Rotach M (2010) Determination of hydrogen cyanide in cigarette mainstream smoke by LC/MS/MS. *J AOAC Int* 93:1032–1038
- Moussa SG, Leithead A, Li SM, Chan TW, Wentzell JJB, Stround C, Zhang J, Lee P, Lu G, Brook JR, Hayden K, Narayan J, Liggio J (2016) Emissions of hydrogen cyanide from on-road gasoline and diesel vehicles. *Atmos Environ* 131:185–195
- Mudder TI, Botz M (2000) A global perspective of cyanide mineral resources forum. United Nations Environment Programme
- Narkowicz S, Polkowska Ż, Namieśnik J (2012) Analysis of markers of exposure to constituents of environmental tobacco smoke (ETS). *Cr Rev Anal Chem* 42:16–23
- Narkowicz S, Polkowska Ż, Marć M, Siemonov V, Namieśnik J (2013a) Determination of thiocyanate (biomarkers of ETS) and other inorganic ions in human nasal discharge samples using ion chromatography. *Ecotox Environ Safe* 96:131–138
- Narkowicz S, Polkowska Ż, Namieśnik J (2013b) Determination of formaldehyde and cyanide ion in human nasal discharge by using simple spectrophotometric methods. *Cent Eur J Chem* 11:16–24
- Narkowicz S, Polkowska Ż, Kielbatowska B, Namieśnik J (2015) Meconium samples used to assess infant exposure to the components of ETS during pregnancy. *Int J Occup Med Env* 28:955–970
- Noroozifar M, Khorasani-Motlagh M, Taheri A (2011) Determination of cyanide in wastewaters using modified glassy carbon electrode with immobilized silver hexacyanoferrate nanoparticles on multiwall carbon nanotube. *J Hazardous Mater* 185:255–261
- Oluwole ASA, Onabolu AO, Cotgreave IA, Rosling H, Persson A, Link H (2003) Influence of endemic ataxic polyneuropathy and its relation to exposure to cyanide in a Nigerian community. *J Neurol Neurosurg Psychiatry* 74:1417–1422
- Orloff KG, Kaplan B, Kowalski P (2006) Hydrogen cyanide in ambient air near a gold heap leach field: measured vs modeled concentrations. *Atmos Environ* 40:3022–3029
- Oseid DM, Smith LL Jr (1979) The effects of hydrogen cyanide on *Asellus communis* and *Gammarus pseudolimnaeus* and changes in their competitive response when exposed simultaneously. *Bull Environ Contam Toxicol* 21:439–447
- Pablo F, Buckney RT, Lim RP (1996) Toxicity of cyanide and iron-cyanide complexes to Australian bass *Macquaria novemaculeata* and black bream *Acanthopagrus butcheri*. *Aust J Ecotoxicol* 2:75–84
- Pablo F, Buckney RT, Lim RP (1997a) Toxicity of cyanide iron-cyanide complexes and a blast furnace effluent to larvae of the doughboy scallop *Chamys asperrimus*. *Bull Environ Contam Toxicol* 58:93–100
- Pablo F, Stauber JL, Buckney RT (1997b) Toxicity of cyanide and cyanide complexes to the marine diatom *Nitzschia closterium*. *Water Res* 31:2435–2442
- Paton-Walsh C, Deutscher NM, Griffith DWT, Forgan BW, Wilson SR, Jones NB, Edwards DP (2010) Trace gas emissions from savana fires in Northern Australia. *J Geophys Res* 115:16314–16326
- Pelle T, Scarciglia F, Di Pasquale G, Allevato E, Marino D, Robustelli G, La Russa MF, Pulice I (2013) Multidisciplinary study of Holocene archeological soils in an upland Mediterranean site: natural versus anthropogenic environmental changes at Cecita Lake, Calabria, Italy. *Quat Int* 303:163–179
- Pentore R, Venneri A, Nichelli P (1996) Accidental choke-cherry poisoning: early symptoms and neurological sequel of an unusual case of cyanide intoxication. *Ital J Neurol Sci* 17:233–235
- Petrova Simenova F, Fishbein L (2004) Hydrogen cyanide and cyanides: human health aspects. WHO, Geneva
- Prereira LBF, Sousa Neto JA (2007) Cyanide distribution in the stream sediments and tailings at the bonfim (W-AU-BI-TE) mine northeastern Brazil. *Geochim Bras* 21:261–273
- Rao P, Singh P, Yadav SK, Gujar NL, Bhattacharya R (2013) Acute toxicity of some synthetic cyanogens in rats: time-dependent cyanide generation and cytochrome oxidase inhibition in soft tissues after sub-lethal oral intoxication. *Food Chem Toxicol* 59:595–609
- Rennert T, Mansfeldt T (2006) Release of trace metals sulfate and complexed cyanide from soils contaminated with gas-purifier wastes: a microcosm study. *Environ Pollut* 139:86–94
- Sadeq N, Belhadj-Tahar H (2009) Rapid and sensitive headspace gas chromatographic method for cyanide determination in whole blood. *Toxicol Environ Chem* 91:419–424
- Sanchez-Verlaan P, Geeraerts T, Buys S, Riu-Poulenc B, Cabot C, Fourcade O, Mégarbane B, Genestal M (2011) An unusual cause of severe lactic acidosis: cyanide poisoning after bitter almond ingestion. *Intensive Care Medicine* 37(1):168–169
- Sano A, Takezawa M, Takitani S (1989a) Spectrofluorometric determination of cyanide in blood and urine with naphthalene-2,3-dialdehyde and taurine. *Anal Chim Acta* 225:351–358
- Sano A, Takezawa M, Takitani S (1989b) High performance liquid chromatography determination of cyanide in urine by precolumn fluorescence derivatization. *Biomed Chromatogr* 3:209–212
- Sarkar SK (1990) Toxicity evaluation of sodium cyanide to fish and aquatic organisms: effects of temperature. *Sci Cult* 56:165–168
- Schneider J, Bürger V, Arnold F (1997) Methyl cyanide and hydrogen cyanide measurements in the lower stratosphere: implications for methyl cyanide sources and sinks. *J Geophys Res* 102:25501–25506
- Senica M, Stampar F, Veberic R, Mikulic-Petkovsek M (2016) Transition of phenolics and cyanogenic glycosides from apricot and cherry fruit into liqueur. *Food Chem* 203:483–490
- Shehong L, Baoshan Z, Jianming Z, Xiaoying Y (2005) The distribution and natural degradation of cyanide in goldmine tailings and polluted soil in arid and semiarid areas. *Environ Geol* 47:1150–1154
- Shifrin NS, Beck BD, Gauthier TD, Chapnick SD, Goodman G (1996) Chemistry toxicology and human health risk of cyanide compounds in soils at former manufactured gas plant sites. *Regul Toxicol Pharmacol* 23:106–116
- Sims DB, Francis A (2008) Mercury and cyanide used as indicator of sediment transport in ephemeral washes at the Techatticup Mine and

- Mill Site, Nelson, Nevada (USA). *International Journal of Soil Sediment and Water* 1:1–9
- Singh HB, Salas L, Herlth D, Kolyer R, Czech E, Viezee W, Li Q, Jacob DJ, Blake D, Sachse G, Harward CN, Fuelberg H, Kiley CM, Zhao Y, Kondo Y (2003) In situ measurement of HCN and CH₃CN over the Pacific Ocean: sources, sinks, and budgets. *J Geophys Res* 108: 8795–8809
- Španěl P, Dryahina K, Smith D (2007a) Acetone ammonia and hydrogen cyanide in exhaled breath of several volunteers aged 4–83 years. *J Breath Res* 1:1752–1755
- Španěl P, Dryahina K, Smith D (2007b) The concentration distributions of some metabolites in the exhaled breath of young adults. *J Breath Res* 1:260–268
- Sun P, Borowitz JL, Kanthasamy AG, Kane MD, Gunasekar PG, Isom GE (1995) Antagonism of cyanide toxicity by isosorbide dinitrate: possible role of nitric oxide. *Toxicology* 104:105–111
- Surleva A, Drochioiu G (2013) A modified micro-assay for determination of total cyanogen in plants. *Food Chem* 141:2788–2794
- Themelis DG, Karastogianni SC, Tzanavars PD (2009) Selective determination of cyanides by gas diffusion-stopped flow-sequential injection analysis and an on-line standard addition approach. *Anal Chim Acta* 632:93–100
- Thome D, Adamson J (2013) A review of invitro cigarette smoke exposure systems. *Exp Toxicol Path* 65:1183–1193
- Tivana LD, Cruz Francisco JD, Zelder F, Bergenstahl B, Dejmeck P (2014) Straightforward rapid spectrophotometric quantification of total cyanogenic glycosides in fresh and processed cassava products. *Food Chem* 158:20–27
- Tong XL, Wang L, Gao TB, Qin YG, Qi YQ, Xu YP (2009) Potential function of amniotic fluid in fetal development—novel insights by comparing the composition of human amniotic fluid with umbilical cord and maternal serum at mid and late gestation. *J Chin Med Assoc* 72:368–373
- Torikai K, Uwano Y, Nakamori T, Tarora W, Takahashi H (2005) Study on tobacco components involved in the pyrolytic generation of selected smoke constituents. *Food Chem Toxicol* 43:559–568
- Tracqui A, Raul JS, Géraut A, Berthelon L, Ludes B (2002) Determination of blood cyanide by HPLC-MS. *J Anal Toxicol* 26: 144–148
- Tsunge K, Kataoka M, Seto Y (2000) Cyanide and thiocyanate levels in blood and saliva of healthy volunteers. *J Health Sci* 46:343–350
- Vetter J (2000) Plant cyanogenic glycosides. *Toxicol* 38:11–36
- Viggiano AA, Hunton DE, Miller TM, Ballenthin JO (2003) In situ measurements of hydrogen cyanide in the upper troposphere/lower stratosphere during Arctic spring 2000. *J Geophys Res* 108:8304–8310
- Wan NW, Liu ZQ, Xue F, Zheng YG (2015) An enzymatic method for determination of azide and cyanide in aqueous phase. *J Biotechnol* 214:27–32
- Wu W, Xiao Q, Zhang P, Ye M, Wan Y, Liang H (2015) Rapid measurement of free cyanide in liquor by ion chromatography with pulsed amperometric detection. *Food Chem* 172:681–684
- Xu J, Tong H, Yan X, Du S, Yao Z, Liu S (2006) Sensitive determination of cyanide in cigarette smoke by capillary GC with a microECD. *Chromatographia* 64:609–612
- Yamamoto H (1995) Effect of alotropine on cyanide-induced acute lethality in mice. *Toxicol Lett* 80:29–33
- Yaroshenko I, Kirsanov D, Kartova L, Sidorova A, Borisova I, Legin A (2015) Determination of urine composition with potentiometric multisensor system. *Talanta* 131:556–561
- Yeoh MJ, Braitberg G (2004) Carbon monoxide and cyanide poisoning in fire related deaths in Victoria, Australia. *J Toxicol-Clin Toxic* 42: 855–863
- Zagrobelyny M, Bak S, Vinther Rasmussen A, Jørgensen B, Naumann CB, Lindberg Møller B (2004) Cyanogenic glucosides and plant-insect interactions. *Phytochemistry* 65:293–306
- Zhang ZW, Xu YB, Waang CH, Chen KB, Tong HW, Liu SM (2011) Direct determination of hydrogen cyanide in cigarette mainstream smoke by ion chromatography with pulsed amperometric detection. *J Chromatogr A* 1218:1016–1019
- Zhang Q, Maddukuri N, Gong M (2015) A direct and rapid method to determine cyanide in urine by capillary electrophoresis. *J Chromatogr A* 1414:158–162
- Zhao Y, Kondo Y, Murcray FJ, Liu X, Koike M, Irie H, Strong K, Suzuki K, Sera M, Ikegami Y (2000) Seasonal variations of HCN over northern Japan measured by ground-based infrared solar spectroscopy. *Geophys Res Lett* 27:2085–2088