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Background information and guidance on environmental cyanide analysis

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National foreword

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TECHNICAL REPORT

ISO/TR 19588

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Background information and guidance on environmental cyanide analysis

Informations et lignes directrices sur l'analyse environnementale du cyanure

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*, in cooperation with ISO/TC 147, *Water quality*.

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Introduction

Cyanide is a useful industrial chemical and its key role in the mining industry is to extract gold from its ores. Worldwide, mining uses approximately 13 % of the total production of manufactured hydrogen cyanide while the remaining 87 % is used in many other industrial processes, apart from mining. In manufacturing, cyanide is used to make paper, textiles, and plastics. It is present in the chemicals used to develop photographs. Cyanide salts are used in metallurgy for electroplating, metal cleaning, and removing gold from its ore. Cyanide gas (HCN) is used to exterminate pests and vermin in ships and buildings.

There is a large number of "official national and international methods" for the analysis of various cyanide parameters for waters, effluents, leachates, soils and wastes. This document attempts to provide background information and guidance on environmental cyanide analysis.

Cyanide can exist in many chemical forms (cyanide species) with various toxicity levels for a given mass of CN. Highest toxicity has free cyanide appearing as HCN or CN^-.

Hydrogen cyanide is a colourless, poisonous gas having an odour of bitter almonds (mp = −13,4 °C, bp = 25,6 °C, pKa = 9,36). It is readily soluble in water existing as HCN or CN^-, or both, depending on the pH conditions (Figure 1). At a pH of 7 or less in water, free cyanide is effectively present entirely as HCN; at pH 11 or greater, free cyanide is effectively present entirely as CN^-.

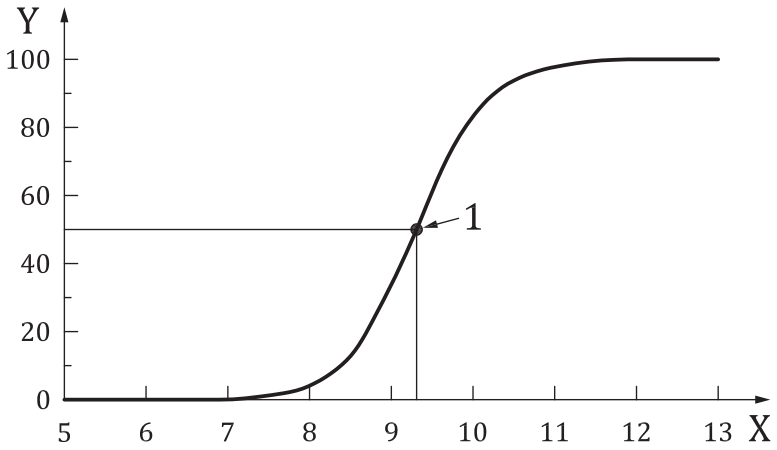

Figure 1 — Dissociation degree (%) of hydrocyanic acid (HCN) with pH

Owing to its high toxicity at low concentrations (especially to fish), "free or bioavailable cyanide" is regulated in environmental wastewater discharges and in drinking waters[1]-[7]. Cyanide is regarded as an acute rather than a chronic toxin as low levels can be metabolised. It does not bioaccumulate. The sensitivity of aquatic life to available cyanide varies with the species present and the characteristics of the water matrix. Fish and aquatic invertebrates are particularly sensitive to bioavailable cyanide exposure.

It is worth noting that the WHO guideline limit for cyanide in drinking water[6] is 70 µg/l. An allocation of 20 % of the tolerable daily intake (TDI) to drinking water is made because exposure to cyanide from other sources is normally small and because exposure from water is only intermittent. This results in the guideline value of 70 µg/l which is considered to be protective for both acute and long-term human exposure.

Hydrogen cyanide and many complexed cyanides are readily soluble in water. An overview of solubilities in water is given in Table 1.

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Table 1 — Solubility of cyanides in water[32]

Species	Solubility g/l	Temperature °C
Alkaline cyanides		
LiCN	very high	unknown
NaCN	583	20
KCN	716	25
RbCN	very high	unknown
CsCN	very high	unknown
Alkaline earth cyanides		
$Mg(CN)_2$	unstable	
$Ca(CN)_2$	unstable	
$Sr(CN)_2 4H_2O$	very high	unknown
$Ba(CN)_2$	very high	unknown
Heavy metal cyanides		
AgCN	$2{,}8 \times 10^{-5}$	18
AuCN	almost insoluble	unknown
$Pt(CN)_2$	almost insoluble	unknown
$Co(CN)_2 2H_2O$	almost insoluble	unknown
$Zn(CN)_2$	$5{,}8 \times 10^{-3}$	18
CuCN	0,014	20
$Ni(CN)_2 4H_2O$	0,0 592	18
$Cd(CN)_2$	17	15
$Hg(CN)_2$	93	14
$Pb(CN)_2$	high	unknown
$Pd(CN)_2$	high	unknown

Therefore, the majority of methods are on the analysis of soluble cyanides in water, mainly to protect the environment from toxic effects.

The toxicity of a metal cyanide complex is associated with its stability constant because the more easily dissociated cyanide species will release cyanide more readily into the environment. The more stable metal cyanide complexes are less likely to release cyanide into the environment.

The stability constants of the various relevant cyanide species is given in Table 2. Any complex with a $\log_{10}K$ > about 35 is regarded as a strong complex, with lower relative toxicity, and will generally only be detected when using a total cyanide method, often without quantitative recovery of the strong complexes. There are method recovery problems of strong complexes in most total cyanide methods. Nickel and copper cyanide complexes are considered to be in the weak acid dissociable (WAD) category due to greater relative toxicity.

Table 2 — Stability constants ($\log_{10}K$ at 25 °C) of relevant metal cyanide complexes

Metal cyanide complex	Stability constant ($\log_{10}K$ at 25 °C)	Weak or strong complex (Strong $\log_{10}K$ > 30)	Reference
$[Cd(CN)_4]^{2-}$	17,9	Weak	[10]
$[Zn(CN)_4]^{2-}$	19,6	Weak	[10]
$[Ag(CN)_2]^{-}$	20,5	Weak	[10]
$[Cu(CN)_4]^{3-}$	23,1	Weak	[10]

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Table 2 *(continued)*

Metal cyanide complex	Stability constant ($\log_{10}K$ at 25 °C)	Weak or strong complex (Strong $\log_{10}K > 30$)	Reference
$[Ni(CN)_4]^{2-}$	30,2	Weak	[10]
$Hg(CN)_2$	32,8	Weak and dissociable	ASTM D 6696
$[Fe(CN)_6]^{4-}$	35,4	Strong	[10]
$[Au(CN)_2]^-$,	37 (best estimate)	Strong	[10]
$[Pt(CN)_4]^{2-}$	40,0	Strong	[17]
$[Pd(CN)_4]^{2-}$	42,4	Strong	[10]
$[Fe(CN)_6]^{3-}$	43,6	Strong	[10]
$[Co(CN)_6]^{3-}$	64 (best estimate)	Strong	[10]

It is sometimes difficult to determine any individual species without interference from other cyanide species or interference species (thiocyanate) and some cyanide degradation products (ammonia, nitrite and nitrate) that may be present.

Thus, cyanide method parameters are empirical, where the actual method protocol often determines the result obtained. Hence, cyanide is a method defined analyte. This is especially true for samples with complex matrices. Many methods will determine the sum of a number of species with some not being quantitatively determined (i.e. incomplete breakdown). Thus, it is essential that any standard cyanide method is drafted in an unambiguous manner and the method protocol shall be closely followed to ensure consistent results are obtained within and between laboratories. Moreover, all values reported shall be attributed to the specific method applied.

A comprehensive overview of cyanide management is given in Reference [1].

It is felt that any regulatory limit legislation should specify the actual method to be used especially for "bioavailable" cyanide (e.g. free, weak and dissociable, available, weak acid dissociable or easily liberated cyanide).

NOTE The terms easily liberated cyanide and easily liberatable are both widely used and refer to the same parameter.

It is vitally important to understand how the numerous forms of cyanide are incorporated into water quality regulations for the protection of human health and the environment. In many countries, the regulatory agencies tasked with implementing regulations and the public who are ultimately affected by those regulations do not fully understand the implications of choosing one form of analysis over another upon which to base numerical water quality standards. Also the effect of matrix interferences on the results is not fully appreciated.

Methods with options (e.g. distillation versus gas membrane diffusion); or cyanide ion detection systems based upon colorimetry or amperometry may give different results owing to variation in species detection efficiencies and/or interference effects.

Even when determining "total cyanide" some species such as $[Fe(CN)_6]^{4-}$, $[Au(CN)_2]^-$, $[Pt(CN)_4]^{2-}$, $[Pd(CN)_4]^{2-}$ and $[Co(CN)_6]^{3-}$ may not be fully broken down to cyanide (or hydrogen cyanide) and some distillation methods may convert thiocyanate (SCN) to cyanide.

Another issue is that there are few reference materials for the various cyanide parameters other than for total cyanide. This is mainly due to the unstable nature of most cyanide species in environmental matrices. Thus, traceable calibration in most matrices can be very difficult to achieve.

There are also a number of significant interference effects from a range of species. Clause 9 gives guidance. More useful information is also given elsewhere[7]-[21].

There is no universal agreement on the best technique to overcome (or minimize) these interference effects. The recommended guidance given is often that the method user should demonstrate that the

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method employed should be fit for purpose in relation to the samples analysed. This can be difficult for contract laboratories which receive a wide range of unknown origin samples when using a method for which the laboratory is accredited and the method may be inappropriate for some sample matrices. It is important to appreciate that a single employed method may not be suitable for all the samples received and site specific holding time analysis studies may be required to verify stability of samples being transported to a laboratory.

A number of studies in soil samples have demonstrated that it is impossible to obtain reliable results for easily liberatable cyanide (ELC) using a manual ELC cyanide extraction/reflux method. Consequently, the current ISO 11262 standard does not include an ELC method.

Another key issue is the use of suitable interference and preservation treatments of the sample between taking and analysing the sample. The presence of sulfide drastically reduces the maximum permitted storage time from taking the sample to analysing it from 7 days to 24 hours (ISO 5667-3). See also Reference [7].

It is considered important that regulators consider the typical measurement uncertainty when setting very low regulatory cyanide limits; typical background levels of the parameter of interest and finally how to ensure there is no significant sample degradation prior to analysis. See Annex C and Reference [4].

The objective of this document is to provide a broad overview, background and guidance in the above areas. It has attempted to review this very complex topic and highlight the various problems of carrying out fit for purpose sampling and analysis for various cyanide species in a wide range of waters and soils especially at low levels. It should also be helpful as a training aid for staff involved in the analysis of cyanide. It should also be relevant to regulatory bodies involved in both setting cyanide species regulatory limits and monitoring regulatory cyanide analysis results.

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Background information and guidance on environmental cyanide analysis

1 Scope

This document provides background information on the various International (ISO), American (ASTM, EPA), and European (CEN) cyanide methods for soils, waters, effluents and wastes. It gives guidance on how to carry out fit for purpose analysis of various forms of cyanide in environmental samples, the significance of the results, how to minimize interference effects and the preservation of samples. Some information is also provided on other national and international cyanide methods.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp

See Annex A.

NOTE It is important to note that there is limited international consensus about many of these terms. The International Cyanide Management Code — under guidance of the United Nations Environmental Program (UNEP) and the International Council on Metals and the Environment (ICME) are two examples.

The International Cyanide Management Institute (ICMI) was established for the purpose of administering the "International Cyanide Management Code for the Manufacture, Transport and Use of Cyanide in the Production of Gold", and to develop and provide information on responsible cyanide management practices and other factors related to cyanide use in the gold mining industry.

ICMI's primary responsibilities are to administer the International Cyanide Management Code for gold mining, promote the Cyanide Code's adoption and implementation, evaluate its implementation, manage the certification process and to make information on the safe management practices for cyanide widely available.

The "International Cyanide Management Code For the Manufacture, Transport, and Use of Cyanide In the Production of Gold" (Code) was developed by a multi-stakeholder Steering Committee under the guidance of the United Nations Environmental Program (UNEP) and the then- International Council on Metals and the Environment (ICME).

The Code is an industry voluntary program for gold mining companies. It focuses exclusively on the safe management of cyanide and cyanidation mill tailings and leach solutions. Companies that adopt the Code shall have their mining site processing operations that use cyanide to recover gold audited by an independent third party to determine the status of Code implementation. Those operations that meet the Code requirements can be certified. A unique trademark symbol can then be utilized by the certified operation. Audit results are made public to inform stakeholders of the status of cyanide management practices at the certified operation.

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The objective of the Code is to improve the management of cyanide used in gold mining and assist in the protection of human health and the reduction of environmental impacts. ASTM International has produced a guide for selection of their cyanide methods to use with the implementation of the cyanide code: ASTM D7728 Standard Guide for Selection of ASTM Analytical Methods for Implementation of International Cyanide Management Code Guidance. Ref: http://www.cyanidecode.org/about-icmi (accessed 03.11.2016).

Moreover, in some cases, different terms are used for the same species, and sometimes the same species are named differently (see Clause 6 and Annex A).

As stated previously, cyanide analysis is empirical whereby the cyanide parameter method employed will define the result obtained for a given sample. Hence, cyanide is a method defined analyte.

4 Cyanide methods for soil, water, effluents and wastes considered for this document

Table 3 lists the analytical methods providing information on the determination of cyanide in environmental samples from soils, waters, effluents and wastes which were considered during the preparation of this document.

Table 3 — Analytical methods for the determination of cyanide in environmental samples from soils, waters, effluents and wastes

Designation	Title	Refer to
ISO 6703-1	*Water quality — Determination of cyanide — Part 1: Determination of total cyanide*	7.1.1
ISO 6703-2	*Water quality — Determination of cyanide — Part 2: Determination of easily liberatable cyanide*	7.1.1
ISO 6703-3	*Water quality — Determination of cyanide — Part 3: Determination of cyanogen chloride*	7.1.1
ISO 17690	*Water quality — Determination of available free cyanide (pH 6) using flow injection analysis (FIA), gas-diffusion and amperometric detection*	7.1.2/Annex C
ISO 14403-1	*Water quality — Determination of total cyanide and free cyanide using flow analysis (FIA and CFA) — Part 1: Method using flow injection analysis (FIA)*	7.1.3/Annex C
ISO 14403-2	*Water quality — Determination of total cyanide and free cyanide using flow analysis (FIA and CFA) — Part 2: Method using continuous flow analysis (CFA)*	7.1.4/Annex C
ISO 11262	*Soil quality — Determination of total cyanid*	7.2.1/Annex C
ISO 17380	*Soil quality — Determination of total cyanide and easily liberatable cyanide — Continuous-flow analysis method*	7.2.2/Annex C
CEN/TS 16229	*Characterization of waste — Sampling and analysis of weak acid dissociable cyanide discharged into tailings ponds*	7.3.1
USEPA Method Kelada-01	*Kelada automated test methods for total cyanide, acid dissociable cyanide, and thiocyanate*	8.2
USEPA Method 335.4	*Determination of total cyanide by semi-automated colorimetry*	8.3
USEPA Method 9012b	*Total and amenable cyanide (Automated colorimetric, with off-line distillation)*	8.4
USEPA Method 9010C	*Total and amenable cyanide: Distillation*	8.5
USGS I-2302/I-4302/I-6302	*Cyanide, calorimetric, barbituric acid, automated-segmented flow*	8.6
EPA/OIA-1677 09	*Available cyanide by flow injection, ligand exchange, and amperometry*	8.7
ASTM D2036–09	*Standard Test Methods for Cyanides in Water*	8.8/D.1

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Table 3 *(continued)*

Designation	Title	Refer to
ASTM D4282–02	*Standard Test Method for Determination of Free Cyanide in Water and Wastewater by Microdiffusion*	8.8/D.2
ASTM D4374–06	*Standard Test Methods for Cyanides in Water-Automated Methods for Total Cyanide, Weak Acid Dissociable Cyanide, and Thiocyanate*	8.8/D.3
ASTM D6888–09	*Standard Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection*	8.8/D.4
ASTM D6994–10	*Standard Test Method for Determination of Metal Cyanide Complexes in Wastewater, Surface Water, Groundwater and Drinking Water Using Anion Exchange Chromatography with UV Detection*	8.8/D.5
ASTM D7237–10	*Standard Test Method for Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection*	8.8/D.6
ASTM D7284–08	*Standard Test Method for Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection*	8.8/D.7
ASTM D7511–12	*Standard Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection*	8.8/D.8
	The Picric acid method for determining weak acid dissociable (WAD) cyanide	8.9
Standard methods for the examination of water and wastewater, Standard methods 4500	*CN- cyanide*	
Methods for the examination of waters and associated materials, standing committee of analysts (Method 235)	*The determination of cyanide and thiocyanate in soils and similar matrices*	
Methods for the Examination of Waters and Associated Materials, Standing Committee of Analysts (Method 214)	*The determination of cyanide in waters and associated materials*	
various	*Direct determination of metal cyanides by ion chromatography with UV absorbance detection*	

5 Summary of cyanide species and degradation products

5.1 Main cyanide species

5.1.1 Free cyanide

HCN(aq) and CN^-. This also includes simple fully ionised alkali and alkaline earth cyanide salts [e.g. NaCN, KCN and $Ca(CN)_2$] and a portion of the metal cyanide complexes dissociated under the testing conditions.

5.1.2 Simple (weakly complexed) cyanides

These include AgCN, $Hg(CN)_2$, $Zn(CN)_2$, CuCN, $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, $Cd(CN)_3^-$, $Ni(CN)_2$, $[Cd(CN)_4]^{2-}$, $[Zn(CN)_4]^{2-}$, $[Ag(CN)_2]^-$, $[Cu(CN)_4]^{3-}$, $[Hg(CN)_4]^{2-}$, $[Ni(CN)_4]^{2-}$.

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5.1.3 Strongly complexed cyanides

These are $[Fe(CN)_6]^{4-}$, $[Au(CN)_2]^{-}$, $[Pt(CN)_4]^{2-}$, $[Pd(CN)_4]^{2-}$, $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$.

NOTE The above cyanide complexes are in increasing stability constant order (see Table 2).

5.2 Cyanide degradation products

5.2.1 Cyanogen halides

These are CNCl and CNBr. These two species are rapidly hydrolysed in alkaline solution to cyanate. The methods outlined in this document will not detect cyanogen halides if the samples are preserved or extracted into sodium hydroxide. Cyanogen chloride hydrolyzes to cyanate at the pH used for sample preservation (pH ≥ 12) and thus will not be detected. ISO 6703-3 can be used to determine this parameter (see also 7.1, 8.9 J and 8.10 "CA").

5.2.2 Thiocyanate (SCN)

Thiocyanate is not considered to be part of the free or total cyanide. The environmental impact of thiocyanate is small compared with free (bioavailable) cyanides, and thiocyanate is normally biologically oxidized into cyanate, carbonate, sulfate and ammonia. Thiocyanate should be determined by a separate determination (see 8.9 "M", 8.10 "CA" and ASTM D4374, Annex B). However, it should be noted that upon oxidation thiocyanate can generate hydrogen cyanide under some conditions (this includes chlorination).

NOTE Some methods for total cyanide include SCN. SCN is produced during the gold leaching process for sulfidic ores and it finds its way in the tailings storage facilities (TSF) where accumulation over time can occur. The environmental impact of SCN, especially as it accumulates in the TSF and heap leach spoils is not yet clearly understood and needs to be evaluated on a site-specific basis.

5.2.3 Organic cyanides

These include substances such as cyanohydrins, cyanogenic glucosides. These are organic compounds containing a cyanide functional group. Examples of naturally occurring organic cyanides are the cyanogenic glycosides. Organic cyanides also include nitriles, which are substituted hydrocarbons such as acetonitrile (CH_3CN) or cyanobenzene (C_6H_5CN). The chemical bond to the cyanide functional group in organic cyanides is very stable. Thus, free cyanide (CN^- ion) is generally not released from organic cyanides in aqueous solution under normal ambient conditions. These are rarely encountered at significant concentrations in the vast majority of environmental samples and are not considered any further in this document. More information is given elsewhere[10].

5.2.4 Cyanates (CNO^-)

This virtually non-toxic cyanide degradation product is not determined by any cyanide method listed under Clause 4. It is not discussed any further in this document as cyanate cannot readily revert to cyanide. It is formed when cyanide is oxidized (i.e. by alkaline hypochlorite) and then hydrolyses as outlined below:

$$2CN^- + 2ClO^- = 2CNO^- + 2Cl^-$$

$$2CNO^- + 2OH^- + 3ClO^- = N_2 + 2CO_3^{2-} + 3Cl^- + H_2O$$

NOTE CNO is produced during the gold leaching process and it finds its way into the tailings storage facilities where accumulation over time can occur. CNO analysis usually forms part of "cyanide speciation" studies to determine how cyanide is consumed in the leaching process. S. *Black and R.S. Schulz*[28] have published an ion chromatographic method for cyanate.

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5.2.5 Cyanide environmental fate and degradation potential

Table 4 derived from Reference [3] attempts to summarize Environmental Fate and Degradation Potential Pathways. Formation of cyanate occurs when cyanide is in the presence of oxidising compounds such as oxygen, ozone, hydrogen peroxide, Caro's acid and hypochlorite. In soils and waters, the ultimate degradation products are likely to be mainly thiocyanate, cyanate, ammonia, formate, carbon dioxide, nitrite and nitrate.

Table 4 — Cyanide environmental fate and degradation potential

Mechanism	Pathway
Volatilisation	Free cyanide volatilisation to the atmosphere (i.e. as HCN gas) increases as the pH decreases. Thus, the proportion of HCN increases. Also, aeration increases the HCN volatilization rate: - $CN^- + H_2O \rightarrow HCN\uparrow + OH^-$
Complexation	Cyanide can potentially form complexes with a wide range of metallic elements
Adsorption	Adsorption of free and complexed cyanide forms on to solid phases
Precipitation	Cyanide complexes forming metallocyanide precipitates
Formation of thiocyanate	Reaction of cyanide with various forms of sulfur (e.g. sulfidic ores, polysulfides and thiosulfate): $Sx^{2-} + CN^- \rightarrow [S_{(x-1)}]^{2-}- + SCN^-$ and $S_2O_3^{2-} + CN^- \rightarrow SO_3^{2-} + SCN^-$
Oxidation	Oxidation to various reaction products, such as cyanate and/or cyanogens, ammonia, nitrite, nitrate and water: $2HCN + O_2 \rightarrow 2HOCN$ (hydrogen cyanate); $2CN + O_2 + \text{catalyst} \rightarrow 2OCN^-$ (cyanate ion); $2Cu^{2+} + 2CN^- \rightarrow 2Cu^+ + (CN)_2$ (cyanogen) $HCN + 0{,}5O_2 + H_2O \rightarrow CO_2 + NH_3$ $(CN)_2 + 2OH^- \rightarrow OCN^- + CN^- + H_2O$ Formation of cyanate occurs when cyanide is in the presence of strong oxidisers (e.g. ozone, hydrogen peroxide, Caro's acid and hypochlorite)
Hydrolysis	$HCN + 2H_2O \rightarrow NH_4COOH$ (ammonium formate), or $HCN + 2H_2O \rightarrow NH_3 + HCOOH$ (formic acid) Hydrolysis of cyanate: $HOCN + H_3O^+ \rightarrow NH_4^+ + CO_2$ $OCN^- + NH^{4+} = (NH_2)_2CO$
Aerobic degradation	$CN^- + HCO_3^- + NH_3 \rightarrow NO_2^- + NO_3^-$ $2HCN + O_2 + \text{enzyme} \rightarrow 2HOCN$ (hydrogen cyanate)
Anaerobic degradation	$CN^- + 2H_2S(aq) \rightarrow HCNS + H^+$ $HCN + HS^- \rightarrow HCNS + H^+$

6 Information on cyanide analysis parameters to determine various cyanide species (see also Annex B)

6.1 General

As already mentioned in Clause 3, there is limited international consensus about many of these terms. Moreover, in some cases, different terms are used for the same species, and sometimes the same species

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are named differently. Extreme care needs to be taken when comparing results obtained by different standards.

6.2 Free cyanide

Theoretically, only hydrogen cyanide and the cyanide ion in solution should be classified as free cyanide. Methods used to detect free cyanide should not alter the stability of weakly complexed cyanides as they may otherwise be included in the free cyanide result. Free cyanide includes HCN (aq) and CN^-.

6.3 Liberatable Cyanide

6.3.1 General

In practical terms, liberatable cyanide can be considered to be the forms of cyanide that are bioavailable (including free and weakly complexed) and are responsible for its acute toxic effect on organisms. Most methods for assessing acute toxicity of cyanide are based upon this parameter.

Cyanide is liberated by treatment with a weak acid and determined as CN^-. Among the standards described in this document, three terms are used: easily liberatable cyanide (ELC), weak acid dissociable (WAD) cyanide, and free cyanide.

All three terms are effectively equivalent and are actually defined by the method employed. WAD should include weak acid dissociable for the distillation methods and weak and dissociable for the ligand addition/gas diffusion methods.

6.3.2 Easily liberatable cyanide (ELC)

According to ISO 6703-2 (water analysis), easily liberatable cyanide is:

cyanide from substances with cyanide groups and a measurable hydrocyanic acid vapour pressure at pH = 4 and room temperature.

Such substances include all cyanides which will undergo chlorination, especially hydrocyanic acid, alkali- and alkaline earth metal cyanides, and complex cyanides of zinc, cadmium, silver, copper and nickel. Complex cyanides of iron and cobalt, nitriles, cyanates, thiocyanates and cyanogen chloride are not included.

6.3.3 Free cyanide (or alternatively: easily liberatable cyanide)

According to ISO 14403-1 (water analysis), free cyanide (or alternatively: easily liberatable cyanide) is:

Sum of HCN, cyanide ions and the cyanide bound in simple metal cyanides as determined in accordance with ISO 14403-1.

CAUTION — Free cyanide in this context is not equivalent to free cyanide as defined in 6.2.

6.3.4 Weak acid dissociable (WAD) cyanide

There are many definitions given for WAD cyanide in various methods. Typically, WAD cyanide includes those cyanide species liberated at pH 4,0; or 4,5; or 4,5 to 6,0; or 3,0 to 6,0 (see Annex B); or by strong acid and ligand exchange reagents through a gas permeable membrane. WAD cyanides includes: HCN(aq), CN^-, the metal bound cyanide complexes (Zn, Cd, Cu, Hg, Ni and Ag) and others with similar dissociation constants.

6.4 Total cyanide

This measurement of cyanide includes all free cyanides, all dissociable cyanides and all strong metal cyanides. Only thiocyanate is excluded from the definition of total cyanide. Total cyanide includes:
- HCN(aq), CN^-, metal bound cyanide complexes including $[Fe(CN)_6]^{-4}$, $[Fe(CN)_6]^{-3}$, a fraction of

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$[Co(CN)_6]^{-3}$, Au, Pd and Pt complex cyanides present. Most total cyanide methods do not quantitatively recover these latter four species.

6.5 Cyanide amenable to chlorination

This is based on the difference between total cyanide measurements before and after chlorination treatment. This method is used to establish the efficacy of alkaline chlorination in cyanide oxidation. The result is determined by difference: one total cyanide result from a sample without chlorination treatment and one result from a sample after chlorination treatment (using hypochlorite). The difference between the two results is cyanide amenable to chlorination.

7 Current ISO/CEN environmental cyanide standards (see also Annex C)

7.1 Water

7.1.1 ISO 6703

ISO 6703 consists of the following parts:

— Part 1: Determination of total cyanide;

— Part 2: Determination of easily liberatable cyanide;

— Part 3: Determination of cyanogen chloride.

The methods specified in ISO 6703-1, ISO 6703-2 and ISO 6703-3 are suitable for controlling the quality of water and for the examination of municipal sewage and industrial effluents (see also 7.3.1). Where significant interferences are not present, they are appropriate to the technology available for the destruction of cyanides in treatment plants, and are based on the separation of liberated hydrogen cyanide (or in the case of ISO 6703-3, for cyanogen chloride). Distillation methods at low pH have not been found to be suitable for metallurgical processing samples containing significant concentrations of thiocyanate (negative bias) or thiocyanate plus nitrate (positive bias).

ISO 6703-1 and ISO 6703-2 are still in use by small laboratories, but larger ones prefer ISO 14403-1 and ISO 14403-2.

ISO 6703-3 is applicable to the determination of cyanogen chloride in the range 0,02 mg/l to 15 mg/l. Cyanogen chloride at a solution pH of 5,4 is entrained in a current of air and absorbed into a solution of pyridine and barbituric acid and then determined photometrically. Cyanogen chloride is hydrolysed to cyanate at the pH > 12, this being the pH of preserved cyanide samples. Thus, rapid analysis is recommended for this parameter.

7.1.2 ISO 17690

ISO 17690 specifies methods for the determination of free cyanide at pH 6 in various types of water (such as ground, drinking, surface, leachate, waste water, and metallurgical processing waste water) with cyanide concentrations from 5 µg/l to 500 µg/l expressed as cyanide ions in the undiluted sample. The range of application may be changed by varying the operation conditions, e.g. by using a different injection volume.

The sample is introduced into a carrier solution of the flow injection analysis (FIA) system via an injection valve and confluence downstream with a phosphate buffer solution at pH 6 to measure free cyanide. The released hydrogen cyanide (HCN) gas diffuses through a hydrophobic gas diffusion membrane into an alkaline acceptor stream where the CN^- is captured and sent to an amperometric flow cell detector with a silver-working electrode. In the presence of cyanide, the silver electrode surface is oxidized at the applied potential. (Eapp = 0,0 V vs. the reference electrode). The anodic current measured is proportional to the concentration of cyanide in the standard or sample injected.

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7.1.3 ISO 14403-1

ISO 14403-1 specifies methods for the determination of cyanide in various types of water (such as ground, drinking, surface, leachate, and waste water) with cyanide concentrations from 2 µg/l to 500 µg/l expressed as cyanide ions in the undiluted sample. The range of application can be changed by varying the operation conditions, e.g. by diluting the original sample or using a different injection volume. In this part of ISO 14403, a typical mass concentration range from 20 µg/l to 200 µg/l is described.

Seawater can be analysed with possible changes in sensitivity and adaptation of the reagent and calibration solutions to the salinity of the samples.

This method determines total cyanide and free cyanide (easy liberated cyanide). Complex-bound cyanide is decomposed by UV light at pH 3,8. A UV-B lamp (emission maximum >310 nm to 400 nm) and a digestion coil of fluorinated ethylene propylene (FEP) or polytetrafluorethylene (PTFE) is used to block all UV light with a wavelength <290 nm thus preventing the conversion of thiocyanate into cyanide. A hydrolytic treatment in a thermoreactor (85 °C) assists the decomposition. Total and easily liberated cyanide can be directly determined. Complex cyanide can be calculated by difference. Thiocyanate will not be detected. A check is recommended that 1 000 µg/l SCN expressed as CN gives a result of ≤100 µg/l CN.

The lowest validation study concentration sample for free (easily liberated) cyanide was 63 µg/l. Thus, this method may not be suitable for monitoring discharge consents of free cyanide below 10 µg/l. See Annex C.

The method validation was carried out three years before the standard was published. In addition, this empirical method also allows amperometric detection to be used as an alternative to the photometric detection method. There does not appear to be any validation data comparing these two end point detection methods.

7.1.4 ISO 14403-2

ISO 14403-2 specifies methods for the determination of cyanide in various types of water (such as ground, drinking, surface, leachate, and waste water) with cyanide concentrations usually from 2 µg/l to 500 µg/l, expressed as cyanide ions in the undiluted sample. The range of application may be changed by varying the operation conditions, e.g. by diluting the original sample or changing the path length of the flow cell.

Sea water can be analysed with possible changes in sensitivity and adaptation of the reagent and calibration solutions to the salinity of the samples.

This method determines total cyanide and free cyanide (easy liberated cyanide) by UV digestion and distillation. Total and easily liberated cyanide can be directly determined. Complex cyanide can be calculated by difference Thiocyanate will not be detected due to the wavelength range of the UV lamp (312 nm to 420 nm). A check is recommended that 1 000 µg/l SCN expressed as CN gives a result ≤100 µg/l CN.

The lowest validation study concentration sample for free (easily liberated) cyanide was 25 µg/l. Thus, this method may not be suitable for monitoring discharge consents of free cyanide below 10 µg/l (see Annex C).

One criticism of this empirical method is that the method allows the following options:

Either distillation at 125 °C at pH 3,8 or a gas diffusion cell having a hydrophobic semi-permeable membrane at temperature of 30 °C to 40 °C can be used for separation of the hydrogen cyanide present. Data presented at the 2012 ISO/TC 147/SC 2 meeting in Paris clearly showed that loss of free cyanide occurs by reaction with sample matrix components at higher temperatures and that these two options are likely to lead to different results for real samples especially at low free cyanide (<10 µg/l levels). The method validation data carried out three years before the standard was published does not indicate which option was used. In addition, this empirical method also allows amperometric detection to be

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