TECHNICAL REPORT

ISO/TR 19588

First edition
2017-07

Background information and guidance on environmental cyanide analysis

Informations et lignes directrices sur l'analyse environnementale du cyanure

Reference number
ISO/TR 19588:2017(E)

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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*.

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^-.

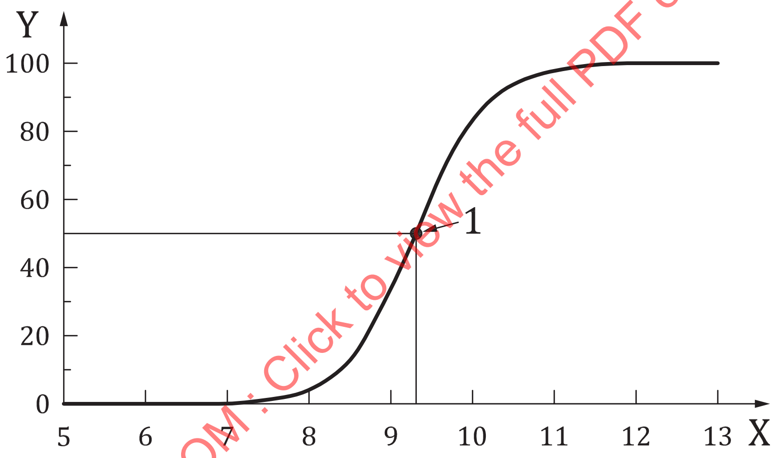

Figure 1 — Dissociation degree (%) of hydrocyanic acid (HCN) with pH

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.

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	
$Sr(CN)_24H_2O$	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
$Co(CN)_22H_2O$	almost insoluble	unknown
$Zn(CN)_2$	$5,8 \times 10^{-3}$	18
CuCN	0,014	20
$Ni(CN)_24H_2O$	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]

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 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.

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.

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

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

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.

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, poly-sulfides and thiosulfate): $S_x^{2-} + CN^- \rightarrow [S_{(x-1)}]^{2-}- + SCN^-$ 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); $2CN + O_2 +$ 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 oxi-disers (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	$CN^- + HCO_3^- + NH_3 \rightarrow NO_2^- + NO_3^-$ $2HCN + O_2 +$ 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 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

$[Co(CN)_6]^{-3}$, 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.

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 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. Thus, this method may not be suitable for monitoring regulatory discharge consents of free cyanide below 10 µg/l.

7.2 Soil

7.2.1 ISO 11262

ISO 11262 is applicable to as-received (field-moist) samples and specifies two different procedures for the liberation of cyanide from the soil:

— direct liberation of hydrogen cyanide using orthophosphoric acid distillation (normative);

— extraction with sodium hydroxide solution and subsequent liberation using orthophosphoric acid distillation (informative).

The liberated cyanide is determined either by a photometric method or a titrimetric method using an indicator. Under the conditions specified in this method the lower limit of application is 0,5 mg/kg of total cyanide (expressed on the as-received basis) for photometric determination and 10 mg/kg for titrimetric determination.

Using the alkaline extraction followed by liberation using phosphoric acid distillation, the lower limit of application is 1 mg/kg of total cyanide (expressed on the as-received basis) for photometric determination and 30 mg/kg for titrimetric determination.

7.2.2 ISO 17380

ISO 17380 specifies a method for the photometric determination of the total cyanide and easily liberatable cyanide content in soil using automated distillation-continuous flow analysis. It is applicable to all types of soil with cyanide contents above 1 mg/kg on the basis of dry matter, expressed as cyanide ion.

Sulfide concentrations in the sample higher than 40 mg/kg dry matter cause interference. This effect can be recognized by the split peaks and as a slow decrease of the detector signal and can only be prevented by diluting the sample extract.

This method is equivalent to the ISO 14403 water methods for the analytical cyanide ion detection part. It describes the sample pre-treatment procedure for the extraction of cyanide from soil. Total and easily liberatable cyanide can be directly determined. Complex cyanide can be calculated by difference.

7.3 Waste (Slurries)

7.3.1 CEN/TS 16229

CEN/TS 16229 specifies methods for sampling and analysis of weak acid dissociable cyanide discharged into tailings ponds.

CEN/TS 16229 can be used to support the requirements in the Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 on the management of waste from extractive industries.

Filtration of the sample removes the fluctuations associated with differential settling of solids. Even though weak acid dissociable cyanides are very soluble and typically do not adhere to these solids, removal of these will minimize any degradation by oxidation or other chemical reactions.

The samples can contain substances that may interfere with the determination, especially sulphides and oxidizing matter such as hydrogen peroxide. When the laboratory is off-site, oxidizing agents should be reduced prior to sending the sample to the laboratory. Before analysis, removal of sulphides is sometimes necessary. If samples are to be analysed directly after sampling the recommend procedures for sample pre-treatment can be omitted, if it has been proven that no interferences occur during the analysis time. Composite samples will require sample pre-treatment to preserve the various cyanide species.

WAD cyanides are determined by applying ISO 6703-2 or ISO 14403. When using ISO 6703-2 limited interference from thiocyanate, iron, copper, sulfate, sulfide and other compounds might occur (for details of interfering concentrations see ISO 6703-2). Application of ISO 14403-2 shows less interference but samples usually have to be diluted.

7.4 Concluding remark

Many of the above methods can be carried out on proprietary commercial equipment according to suitable methods supplied by the equipment manufacturer. However, the users will need to carry out their own method validation trials.

Annex C attempts to summarize the methodology scopes and performance characteristics of the ISO/CEN cyanide standards.

8 Other national and international cyanide standards, methodologies and guides

8.1 General

These following four organisations have all published methods for determination of cyanide and cyanide species in environmental matrices. Most of these methods are summarized below.

— The US Environmental Protection Agency (USEPA);

— The American Society for Testing and Materials (ASTM International) (see Annex D);

— Standard Methods for the Examination of Water and Wastewater (currently the 22nd Edition);

— The Environment Agency (England and Wales) Methods for the Examination of Waters and Associated Materials.

NOTE From Method 176 onward, all SCA methods are freely available on the web: http://www.environment-agency.gov.uk/research/commercial/32874.aspx (accessed 3.11.2016).

Other methods for determination of cyanide are published especially at national level. However, these were not considered in detail for the preparation of this document, due to the fact that they are not available in English.

8.2 USEPA Method Kelada-01: Kelada automated test methods for total cyanide, acid dissociable cyanide, and thiocyanate, Revision 1.2 (2001)

NOTE See http://webapp1.dlib.indiana.edu/virtual_disk_library/index.cgi/5315321/FID2672/kelada.pdf (accessed 3.11.2016).

These test methods apply to different types of water, wastewater (raw sewage, sludge, and effluent), sludge, some industrial waste, and sediments.

The methods use a combined online ultraviolet (UV) irradiation and flash distillation system in place of classical manual cyanide distillation procedures to determine total cyanide. Under irradiation in a glass coil, strongly-bound complex cyanides (excluding the majority of thiocyanate) break down into free cyanide, which is separated from the sample matrix by distillation and is detected using an online colorimeter. By omitting UV-irradiation, acid dissociable cyanide complexes are broken down and determined. By replacing the glass irradiation coil with a quartz coil, thiocyanate can then be determined.

Total cyanide is defined as: “All the acid dissociable cyanides and the strong metal-cyano-complexes, such as ferrocyanide $[Fe(CN)_6]^{4-}$, ferricyanide $[Fe(CN)_6]^{3-}$, hexacyanocolbaltate $[Co(CN)_6]^{3-}$, and those of gold and platinum.”

Acid Dissociable Cyanide is defined as: “Free cyanides as CN^- and HCN, and weak metal-cyano-complexes such as $[Cd(CN)_4]^{2-}$, $Mn(CN)_6]^{3-}$ and $[Ni(CN)_4]^{2-}$, as well as mercury cyanide $Hg(CN)_2$. Iron complexes are not included. Acid dissociable cyanide, as determined by this method, is equivalent to cyanide amenable to chlorination (CATC) and available cyanide.”

Cyanates and cyanogen halides are not detected. Cyanogen chloride hydrolyzes to cyanate at the pH of sample preservation (≥2). Most of the organo-cyano-complexes are not measured, with the exception of the weak cyanohydrins.

Thiocyanate plus nitrate is a significant interference with this method. Sulfide and nitrate plus nitrite interfere at concentrations of about 15 mg/l and higher.

NOTE The ASTM version of this method (D 4374-00) has been withdrawn by ASTM International.

8.3 USEPA Method 335.4 Determination of total cyanide by semi-automated colorimetry, Revision 1.0 (August 1993)

This method determines cyanide by manual distillation with sulfuric acid and magnesium chloride using a midi-distillation apparatus and colorimetric detection using automated pyridine-barbituric acid. It does not allow amperometric determination. The method determines total cyanides and does not use UV digestion and thiocyanate interferes. It is applicable to drinking, ground, surface and saline waters as well as domestic and industrial wastes, excluding metallurgical process or sample solutions containing significant concentrations of thiocyanate and/or thiocyanate plus nitrate. The applicable range is 5 µg/l to 500 µg/l[33].

8.4 USEPA Method 9012b Total and amenable cyanide (Automated colorimetric, with off-line distillation), Revision 2 (Nov 2004, Rev 2)

This method detects inorganic cyanides that are present as either soluble salts or complexes in wastes and leachates. It is used to determine values for both total cyanide and cyanide amenable to chlorination. The “reactive” cyanide content of a waste is not determined by this method. The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by automated UV colorimetry. The method is not suitable for metallurgical processing solutions containing significant concentrations of thiocyanate.

8.5 USEPA Method 9010C Total and amenable cyanide: Distillation (Nov 2004, Rev 3)

This method is a reflux-distillation procedure used to extract soluble cyanide salts and many insoluble cyanide complexes from wastes and leachates. It is based on the decomposition of nearly all cyanides by a reflux distillation procedure using a strong acid and a magnesium catalyst. Cyanide, in the form of hydrocyanic acid (HCN) is purged from the sample and captured into an alkaline scrubber solution. The concentration of cyanide in the scrubber solution is then determined by Method 9014 or Method 9213. This method may be used as a reflux-distillation procedure for both total cyanide and cyanide amenable to chlorination. The “reactive” cyanide content of a waste is not determined by this method. This method was designed to address the problem of “trace” analyses (<1 000 mg/l). The method is not suitable for metallurgical processing solutions containing significant concentrations of thiocyanate.

8.6 USGS I-2302/I-4302/I-6302 Cyanide, calorimetric, barbituric acid, automated-segmented flow (1989)

— Cyanide, dissolved, I-2 302-85 (mg/l as CN): 00 723

— Cyanide, total recoverable, I-4 302-85 (mg/l as CN): 00 720

— Cyanide, recoverable-from-bottom-material, dry weight, I-6 302-85 (mg/kg as CN): 00 721.

— This latter method determines thiocyanate as cyanide because of the UV lamp used emitting light at wavelengths below 290 nm.

— The method is not suitable for metallurgical processing solutions containing significant concentrations of sulphides and thiocyanate.

8.7 EPA/OIA-1677-09 Available cyanide by flow injection, ligand exchange, and amperometry

This ligand displacement method for waters and wastewaters applies manual pre-treatment of the sample with two ligands followed by gas diffusion and measurement of available cyanide with amperometric detection.

The analytical procedure employed for determination of available cyanide is divided into two parts: sample pre-treatment and cyanide detection. In the pre-treatment step, proprietary ligand exchange reagents are added at room temperature to the sample. The ligand-exchange reagents form thermodynamically stable complexes with the transition metal ions zinc, copper, cadmium, mercury nickel and silver resulting in the release of bound cyanide ion from the metal-cyano complexes.

Cyanide detection is accomplished using a flow-injection analysis (FIA) system. A 200-uL aliquot of the pre-treated sample is injected into the flow injection manifold of the system. The addition of hydrochloric acid or bismuth nitrate-sulfuric acid solution converts cyanide ion to hydrogen cyanide (HCN) that passes under a gas diffusion membrane. The HCN diffuses through the membrane into an alkaline receiving solution where it is converted back to cyanide ion. The cyanide ion is monitored amperometrically with a silver working electrode, silver/silver chloride reference electrode, and platinum/stainless steel counter electrode, at an applied potential of zero volts. The current generated is proportional to the cyanide concentration present in the original sample. Total analysis time is approximately two minutes.

Zweng et al.[16] give some further details on the use of potential non-proprietary ligand exchange reagents (tetraethylenepentamine and diphenylthiocarbazone). The goal of this very comprehensive study was to assess the method detection limits, accuracy and precision of five cyanide-species-specific and two automated-total cyanide analytical methods with a broad spectrum of contaminated water matrices such as publicly owned treatment works (POTW) influents, POTW effluents, and contaminated groundwaters from a former manufactured gas plant (MGP) site and from a waste disposal site of an aluminium smelting plant. Emphasis in the study was on performance of the methods at low (<100 µg/l) cyanide species concentrations in municipal and industrial water matrices.

8.8 ASTM International methods

Details of the eight ASTM international methods D2036, D4282, D4374, D6888, D6994, D7237, D7284 and D7511 are given in Annex D.

8.9 The Picric acid method for determining weak acid dissociable (WAD) cyanide

Picric acid can be used in a colorimetric procedure to determine the concentration of weak acid dissociable (WAD) cyanide[22]. In the presence of free cyanide, picric acid is reduced to the coloured isopurpuric acid, with the colour intensity directly proportional to the concentration of free cyanide originally present in the sample. In this procedure, cyanide that is weakly complexed with metals such as cadmium, copper, nickel and zinc is first dissociated by the addition of a chemical ligand [diethylenetriaminepentaacetic acid (DTPA)] and the resulting free cyanide is then able to react with picric acid. Cyanide bound with iron or cobalt is not measured with this method.

The method requires close control of sample pH since the intensity of colour development varies outside of the pH range of 9,0 to 9,5. Buffer solutions are prepared to provide a sample pH in this range, but samples used with the spectrophotometer should periodically be checked to ensure the pH is within this range. Information on this method is also given in Reference [1]. The method is not suitable for metallurgical processing solutions containing significant concentrations of thiocyanate.

8.10 Standard methods for the examination of water and wastewater standard methods 4500-CN$^-$ cyanide (1999)

NOTE See https://law.resource.org/pub/us/cfr/ibr/002/apha.method.4500-cn.1992.pdf (accessed 7.11.16).

The Standard Methods 4500-CN$^-$ contains methods for different cyanide species in waters and wastewaters:

A Introduction

An overview of the analysis of waters and wastewaters is given including cyanide speciation, destruction of cyanide; advice on the determination of soluble and insoluble cyanide in solid wastes; selection criteria for methods.

B Preliminary treatment of samples

This useful section highlights sample preservation and how to overcome interferences arising during sample storage.

C Total cyanide after distillation

Acid distillation with magnesium chloride. It is noted that addition of magnesium chloride is not essential for this determination. To determine cobalticyanides, UV pretreatment is needed.

D Titrimetric method

This method is applied to an alkaline distillate from option C.

E Colorimetric method

This method is applied to an alkaline distillate from option C.

F Cyanide-selective electrode method

This method is applied to an alkaline distillate from option C.

G Cyanides amenable to chlorination after distillation

After an aliquot of the water/wastewater sample is chlorinated to decompose the cyanides present, both the chlorinated and untreated sample aliquots are analysed by Method C total cyanide after distillation (see above). The difference between the untreated sample and the treated sample is cyanides amenable to chlorination after distillation.

This section notes that some unidentified organic compounds may oxidize or form breakdown products during chlorination giving higher results for cyanide after chlorination than before chlorination, thus leading to a negative value for cyanides amenable to chlorination after distillation. The method is not suitable for metallurgical processing solutions containing significant concentrations of thiocyanate.

H Cyanides amenable to chlorination without distillation (short-cut method)

This simple method covers the determination of HCN and CN$^-$ complexes that are amenable to chlorination without a distillation step; however this will also include thiocyanate. The method is not suitable for metallurgical processing solutions containing significant concentrations of thiocyanate.

I Weak acid dissociable cyanide

HCN is liberated from a slightly acidified sample (pH 4,5 to 6,0) under the prescribed distillation conditions. The method does not recover cyanide from very stable cyanide complexes that would not be amenable to oxidation by chlorine. The acetate buffer employed contains zinc salts to precipitate iron cyanide complexes.

J Cyanogen chloride

If the sample contains any detectable chlorine (detectable via starch iodide paper), sodium thiosulfate should be added to remove it. The sample pH is then adjusted to pH 8,0 to 8,5 and reaction with pyridine-barbituric acid followed by measuring the absorbance at 578 nm is used to determine cyanogen chloride.

K Spot test for sample screening

This screening spot test can be used to rapidly establish whether a sample contains more than 50 µg/l of cyanide amenable to chlorination. Formaldehyde and thiocyanate interfere.

L Cyanates

A method for determining cyanate is given with a limit of detection of 1 mg/l to 2 mg/l is given. One sample aliquot is analysed for ammonia N (B mg/l) using an ammonia selective electrode, then another aliquot is acidified with sulfuric acid to a pH of 2,0 to 2,5 and then heated to 90 to 95 °C for 30 min to hydrolyse any cyanate present to ammonia.

$$2CNO^- + 2H^+ + 4H_2O = 2NH_4^+ + 2HCO_3^-$$

After cooling, the aliquot is then analysed for ammonia (A mg/l as N). The cyanate concentration (as CNO) is then calculated as 3,0* (A-B) mg/l.

M Thiocyanate

A method for thiocyanate (0,1 mg/l to 2,0 mg/l CNS^-) is described. It uses a macroreticular resin to remove colour and interfering organic compounds without removing thiocyanate. Then the thiocyanate is determined colorimetrically after reaction with iron(III).

N Total cyanide after distillation, by flow injection analysis

This describes the determination of total cyanide with manual distillation as described above (see C above), followed by flow injection analysis with colorimetric detection.

O Total cyanide and weak acid dissociable cyanide by flow injection analysis

This describes an automated system with UV digestion and distillation, followed by colorimetric measurement. Thiocyanate is not determined and total cyanide and weak acid dissociable cyanide can be measured. For total cyanide, the sample stream is mixed with heated phosphoric acid and irradiated with UV radiation and passed over a gas permeable silicone membrane. HCN diffuses through this membrane and is detected colorimetrically. This method is similar to ISO 14403-1.

8.11 The determination of cyanide and thiocyanate in soils and similar matrices (2011). Methods for the examination of waters and associated materials, standing committee of analysts, 2011 (Method 235)

NOTE See https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/316762/Blue_Book_235_cyanide.pdf (accessed 04.11.2016).

The following seven methods are specified:

AA Determination of easily liberated cyanide by steam distillation of a buffered air-dried soil at a pH value of 4, followed by spectrophotometric determination using chloramine-T and barbituric acid.

AB Determination of easily liberated cyanide by steam distillation of a buffered “as received” soil sample at a pH value of 4, followed by spectrophotometric determination using chloramine-T, sodium isonicotinate and sodium barbiturate.

AC Determination of easily liberated cyanide by steam distillation of an alkaline extract of a soil sample at a pH value of 3,8, followed by spectrophotometric determination using chloramine-T, isonicotinic acid and 1,3-dimethylbarbituric acid.

BA Determination of total cyanide by steam distillation of an acidified air-dried soil followed by spectrophotometric determination using chloramine-T and barbituric acid.

BB Determination of total cyanide by steam distillation under acidic conditions of an alkaline extract of an “as received” soil sample, followed by spectrophotometric determination using chloramine-T, sodium isonicotinate and sodium barbiturate.

BC Determination of total cyanide by steam distillation of an alkaline extract of a sample of soil at a pH value of 3,8 after exposure to ultraviolet radiation, followed by spectrophotometric determination using chloramine-T, isonicotinic acid and 1,3-dimethylbarbituric acid.

CA Determination of thiocyanate by alkaline extraction of a soil sample, followed by spectrophotometric determination using chloramine-T, isonicotinic acid and 1,3-dimethylbarbituric acid.

8.12 The determination of cyanide in waters and associated materials (2007) Methods for the Examination of Waters and Associated Materials, Standing Committee of Analysts, 2011 (Method 214)

NOTE See https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/316795/cyanide214_1847912.pdfhttps://www.gov.uk/government/uploads/system/uploads/attachment_data/file/316795/cyanide214_1847912.pdf (accessed 04.11.2016).

The following four methods and a guidance document are described:

B Determination of “total” cyanide by reflux distillation followed by ion selective electrode potentiometry

C Determination of “total” cyanide by reflux distillation followed by colorimetric detection

D Determination of cyanide by microdiffusion

E Determination of cyanide using continuous flow measurement

F Guidance on the determination of total cyanide in the presence of strongly interfering metals and similar substances

8.13 The Direct Determination of Metal Cyanides by Ion Chromatography with UV Absorbance Detection[23]-[28]

All the methods cited in the main body of this document other than those cited in this section assess the potential toxicity due to various empirical cyanide species and directly measure only the liberated free cyanide, typically by a colorimetric reaction with a pyridine-barbituric acid reagent or amperometric detection. These other methods rely on an operational definition to distinguish between weak and strong cyanide complexes, by subjecting the sample to increasingly harsh conditions to dissociate some fraction of the cyanide complexes and liberate free cyanide. Examples include methods that measure “cyanides amenable to chlorination”, “weak acid dissociable cyanides”, “available cyanide”, “easily liberated cyanide” and “total cyanide”. The results are highly dependent on the matrix, the type of metal cyanide complexes present, and the procedure used. These methods also require time-consuming sample pre-treatment or distillation to reduce interference from sulfides, chlorine, thiosulfate, and other interfering substances. The “free cyanide” results from many interlaboratory trials are not very good for these highly empirical method defined cyanide parameters.

Ion chromatography (IC) is potentially superior to these methods because it resolves each individual metal cyanide complex into a discrete chromatographic peak. IC thus allows a precise differentiation of complexes of lesser toxicity from those of greater toxicity. However, there is the problem of obtaining fit for purpose relevant complex cyanide species reference materials for calibration. Reference [23] gives details of a method for determining metal cyanide complexes of silver, gold, copper, nickel, iron, and cobalt ($[Ag(CN)_2]^-$, $[Au(CN)_2]^-$, $[Cu(CN)_4]^{3-}$, $[Ni(CN)_4]^{2-}$, $[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$) in water and effluent samples. These ions are separated on a 2 mm IonPac® AS 11 column and quantified by measuring their absorbance at 215 nm. The main disadvantage is the relatively poor detection limits, typically at the 0,5 mg/l to 2 mg/l level.

To overcome this limitation, a further paper[24] solves the poor detection limits problem using a simple pre-concentration technique. Sensitivity for most of the metal cyanide complexes is improved by over two orders of magnitude, compared to a direct injection, by pre-concentrating metal cyanide complexes from a large sample volume onto a trap column before separation.

Another follow-on paper entitled "Determination of Metal Cyanide Complexes in Solid Wastes by Anion-Exchange Chromatography with UV Absorbance Detection" has also been published[25]. The samples were extracted in accordance with SW 846 Method 90 13A.

NOTE See https://www.epa.gov/hw-sw846/basic-information-about-how-use-sw-846 (accessed 04.11.2016).

Up to 25 g of the solid sample is combined with 500 ml of water plus 5 ml of 50 % (m/m) NaOH in a bottle and extracted by tumbling continuously for 16 h. The pH is maintained above 10 throughout the extraction step.

In addition, there is the USEPA Method 9015, Metal Cyanide Complexes by Anion Exchange Chromatography and UV Detection[26]. This test method covers the determination of metal cyanide complexes in waters and extracts of solid wastes using anion exchange chromatography and UV detection. The following analytes have been determined by this method.

Analyte	Common name
$[Ag(CN)_2]^-$	Dicyanoargentate(I)
$[Au(CN)_2]^-$	Dicyanoaurate(I)
$[Co(CN)_6]^{3-}$	Hexacyanocolbaltate(III)
$[Cu(CN)_3]^{2-}$	Tricyanocuprate(I)
$[Fe(CN)_6]^{3-}$	Hexacyanoferrate(III) (ferrocyanide)
$[Fe(CN)_6]^{4-}$	Hexacyanoferrate(II) (ferricyanide)
$[Ni(CN)_4]^{2-}$	Tetracyanonickelate(II)

Black and Schulz[27] have described a photodiode array ion chromatographic detection method as a fingerprinting tool for metal cyanide complexes in gold processing solutions.

Care shall be taken when interpreting using ion chromatographic methods that use cyanide as the eluent.

9 Sample preservation and interferences

NOTE Sample preservation for cyanide also minimizes many forms of interference relating to this complex parameter (see Annex E).

9.1 Sample preservation

Sample preservation for cyanide analysis is not necessarily compatible with preservation procedures for other determining parameters such as pH, nutrients and total metal concentrations. Hence, for the determination of parameters other than cyanide, separate sub-samples need to be taken from the original sample and need to be preserved accordingly. Details for preserving aqueous samples are available[1][7]-[12][18][19].

9.1.1 ISO 5667-3

In ISO 5667-3:2012, Table A.1, the following preservation steps are listed:

Cyanide easily liberated

Plastic or glass container; add NaOH to pH > 12. Cool to between (3 ± 2) °C. Keep samples stored in the dark or use dark-coloured bottles. Max storage 7 d or only 24 h if sulfide is present (not validated, but best practice). This also applies to ISO 14403-1 and ISO 14403-2.

Cyanide, total

Plastic or glass container; add NaOH to pH > 12. Cool to between (3 ± 2) °C. Keep samples stored in the dark or use dark-coloured bottles. Max storage 14 d or only 24 h if sulfide is present (validated). This also applies to ISO 14403-1 and ISO 14403-2.

Cyanogen chloride (cyanochloride)

Plastic container. Cool to between (3 ± 2) °C. 24 h/1 d. Best practice.

Thus, it can be seen that all water-based cyanide samples will need to be screened for the presence of sulfide, if they are to be stored for more than 24 h. The relevant ISO/CEN methods provide guidance on how this should be carried out.

9.1.2 ISO 17690

Immediately after sampling bring the pH of the water samples to 11 ± 0,1 with sodium hydroxide solutions I to III (7.2 to 7.4) such that the quantity of added alkaline yields a negligible dilution of the sample. Alternatively, bring the pH of the water samples to 11 ± 0,1 by adding sodium hydroxide pellets (1 to 2 pellets per 500 ml). Avoid excess preservation, as it can result in problems with a low recovery and/or poor peak shape of available free cyanide during analysis.

If sodium hydroxide pellets are used, take care not to raise the pH above 11,1.

If the sample appears turbid, remove the particles by filtration at 0,45 µm or by decantation at the laboratory.

Some very comprehensive data including on sample preservation and analyte stability issues was presented by the ISO/TC 147/SC 2/WG 66 technical committee in relation to ISO 17690. The purpose of this holding test was to determine how long samples with low levels of free cyanide could be stored and then tested to accurately determine the concentration of cyanide within the samples during the inter-laboratory testing of the proposed standard method. For this holding time study, samples were spiked with a known amount of cyanide, with no cyanide being added after the initial spike. Each sample was analysed for free cyanide once a week for five weeks. An initial concentration was measured on day zero, then once a week for the remaining four weeks. For the saline samples, initially 400 ppb spiked CN^- samples at concentrations of 0,1 %, 3 %, and 10 % NaCl were measured for four weeks total. A second test was performed with samples of 200 µg, 300 µg, 400 µg and 500 µg/L spiked CN^- at each NaCl concentration. The samples were analysed in replicates of 10 for the first day, then replicates of three for two weeks. For all samples, with the exception of the effluent from a biological process, a maximum holding time of six days was found to produce acceptable results.

9.1.3 Other cyanide methods

ASTM D7728-11, 6.2 of 8.1.3[11] states "Unless otherwise specified, samples must be analysed within 14 d; however, it is recommended to estimate the actual holding time for each new sample matrix as described in Practice D4841. Certain sample matrices may require immediate analysis to avoid cyanide degradation due to interferences. A holding time study is required if there is evidence that cyanide degradation occurs from interferences which would cause the holding time to be less than specified in this practice or Practice D7365".

However, USEPA Method 335.4 "Determination of Total Cyanide by Semi-Automated Colorimetry" states in 8.4 that "Samples should be analysed as soon as possible after collection. If storage is required, preserved samples are maintained at 4 °C and may be held for up to 14 days". No mention is made of the issue of samples that contain sulphide.

Two other papers provide interesting information by Delaney[29] and an application note from the company OI Analytical[30].

ISO 18512 for soil samples gives no specific guidance for cyanide species, ISO 18512:2007,11.3.4 states “Other inorganic parameters (chloride, sulfate, fluoride, cyanide, sulfide). In general, these inorganic parameters are expected to be quite stable over time. As sulfide will react with air to form sulfate, it is necessary to store samples for sulfide determination in the absence of air.” This standard implies cyanide species are stable in soil.

It also states that “a stability study has demonstrated that refrigerated soil samples are stable for at least four days”[34].

It is recommended that the assessing the effect of sulfide on the stability of relevant cyanide parameters should be carried out.

9.2 Interferences

For most groundwaters and treated (drinking) water, there are few potential interferences other than chlorine in drinking water.

For many effluents and receiving waters, as well as soils, there are a significant number of potential interference effects can affect the cyanide analytical results using methods enumerated in this document especially at low µg/l levels of cyanide. It is important that users of cyanide methods are aware of these potential interference effects and apply appropriate procedures to minimize these interference effects[7][10]-[16][18]-[21][29][30].

Interference can result from the following:

— the interfering substance or a breakdown product of it destroying cyanide;

— formation of cyanide from an interfering species or a breakdown product of it;

— interference of species with the end point detection methods commonly applied (titration; colorimetry or amperometry).

Thus, some interference effects are method dependent.

Annex E gives information on interference effects; potential sample preservation and some method modifications to overcome or minimize these interference effects.

The AMIRA project P497A, Chapter 2[31] contains detailed information from research of interferences (including salinity) and their effect on the performance of a wide range of standard cyanide methods (Free, WAD and total CN, metal cyanide speciation, SCN, CNO).

NOTE See also http://www.amira.com.au/ and http://dana6.free.fr/3%20060713%20English%20Compendium.pdf (both accessed 04.11.16).

ASTM D7365- 09A[7] entitled “Standard Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide” gives much useful guidance. This document is applicable for the collection and preservation of water samples for the analysis of cyanide and addresses the mitigation of known interferences prior to the analysis of cyanide. Responsibilities of field sampling personnel and the laboratory are indicated.

The USEPA Footnote 6 in 40 CFR, Part 136, Part 3, Table 2 “Guidelines in establishing test procedures for the analysis of pollutants under the clean water act”, 12th March 2007, also gives much useful advice on the various forms of cyanide interference and how to overcome them[8][9] (see also Annex E).

Incidentally, this footnote outlines two methods for sulfide removal:

Acidification to pH < 2 and stripping of hydrogen sulphide using a low volume of air that will fully remove sulphide, but retain over 90 % cyanide followed by adjusting the pH to > 12 or alternatively adding 1 mg of cadmium chloride per ml of sample to the sample at a pH > 12 to form cadmium sulphide. Then filtering (0,45 µm) the sample and sending both the filtered sample and the filter paper (for extraction with 5 % m/V sodium hydroxide to recover any adsorbed cyanide) to a laboratory for cyanide analysis. ASTM methods recommend the use of lead carbonate powder to remove sulphide followed by immediate filtration prior to submission of the filtered sample to the laboratory.

ASTM found that Cd causes loss of iron and mercury cyanides. Presumably by formation of insoluble metal-metal cyanide complexes. The ASTM research report also demonstrates that the volatilization methods are not very efficient. Footnote 6 in 40 CFR, Part 136, Table 2 was over ridden by a 2012 update to Part 136. The same part now refers to ASTM D7365.

Potential interferences substances are sulfide, sulfite, elemental sulfur, thiocyanate, thiosulfate, oxidising agents such as chlorine and hydrogen peroxide, ascorbic acid, nitrite, nitrate, thiocyanate, ketones and aldehydes including formaldehyde. Also, surface active agents and carbonates for methods involving a distillation step can cause foaming issues. Ultraviolet light <410 nm can also result in photodecomposition of complex cyanide species to free cyanide.

Many of these interference effects can be reduced or overcome by various method modifications usually highlighted in the relevant method. Also distillation methods, compared with lower temperature membrane diffusion methods, can be subject to enhanced decomposition of or formation of certain cyanide species.

10 Conclusions

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.

It is important to note that there is limited international consensus about the definitions of the various cyanide parameters. It is important to appreciate that all cyanide parameters are empirical, where the actual method protocol determines the result obtained (i.e. cyanide parameters are "method defined analytes"). This is especially true for samples with complex matrices and/or at very low cyanide concentrations.

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 with the absolute minimum of analyst options and the method protocol shall be closely followed to ensure consistent results are obtained within and between laboratories.

There is a very wide range of potential interference effects for the various cyanide parameters and these often significantly vary between methods and individual method options (e.g. choice of final cyanide detection method).

It is recommended that all regulatory cyanide methods are subjected to international validation using a wide range of real samples and/or synthetic matrix samples. Some international standards are considered to have insufficient validation data and/or poor validation data. More reliable measurement of uncertainty data is required, especially for the low and sub µg/l level now being required for some regulatory water samples.

Reliably monitoring free or easily liberatable cyanide in receiving waters at low µg/l levels on a long-term basis is extremely difficult. International proficiency scheme(s) are needed to assess the reliability of regulatory soil and receiving water cyanide analysis across all relevant countries. It is of little benefit bringing in regulatory limits if samples containing analyte concentrations close to these levels cannot be reliably analysed with an acceptable uncertainty.

There is need for cyanide reference materials for water and soil analysis especially for species other than total cyanide.

Annex A
(informative)

Summary of cyanide terms and definitions

The terms described in Table A.1 apply to the test solution sample prior to subjection to any analytical methodology.

Table A.1 — Summary of cyanide terms and definitions

Cyanide term	CN species included	Definition	Other information
Free cyanide	$HCN_{(aq)}$, $HCN_{(g)}$, CN^-	The uncomplexed cyanide ion (CN^-) and gaseous or aqueous hydrogen cyanide (HCN) present in solution	The proportions of HCN and CN^- in solution are according to their equilibrium equation; this is influenced by the solution pH, temperature and ionic strength. Methods used to detect free cyanide should not alter the stability of weaker cyanide complexes, as they may otherwise be included in the free cyanide result.
Weak acid dissociable (WAD) cyanide	$HCN_{(aq)}$, $HCN_{(g)}$, CN^-, cyanide complexes of Zn, Cd, Cu, Hg, Ni, Ag and others with similar dissociation constants	WAD cyanide refers to those cyanide species measured by specific analytical techniques and that are completely liberated (100 %) at pH = 4,0	Methods used to measure WAD cyanide should be free from interferences due to the presence of high concentrations of more stable cyanide complexes or other cyanide forms. If not, the interference shall be quantified and allowed for in the result.
Available cyanide or easily liberatable cyanide (ELC)	$HCN_{(aq)}$, $HCN_{(g)}$, CN^-, cyanide complexes of Zn, Cd, Cu, Hg, Ni, Ag and others depending on the analytical technique pH	Available cyanide or ELC refers to those cyanide species measured by specific analytical techniques and that are liberated at a set pH value other than pH 4,5	Each cyanide species may not be completely liberated (100 %) under the specific analytical technique used. In practical terms, ELC is the form of cyanide that is bio-available and responsible for its acute toxic effect on organisms.
Total cyanide	$HCN_{(aq)}$, $HCN_{(g)}$, CN^- cyanide complexes of all metals including Fe, Co, Cr, Pt and Au	Total cyanide includes all free cyanide, all dissociable cyanide complexes and all strong metal cyanide complexes including Fe, Co, Cr, Pt and Au. Co, Pt, and Au are only partially recovered by current Total CN methods.	Only the related or derived compounds cyanate (CNO^-) and thiocyanate (SCN^-) are excluded from the definition of total cyanide. Methods used to determine total cyanide should be shown to be capable of quantitatively determine all stable complexes of cyanide, likely to be present in the sample. If methods determine other analytes as well (e.g. SCN^-), those analytes need to be determined separately and to be deducted from the total cyanide result.
Cyanide amenable to chlorination (CATC)		Cyanide amenable to chlorination is determined by the difference from (i) one result from an untreated sample and (ii) one result from a sample after treatment with a chlorinated compound (hypochlorite)	This measurement is to establish the effectiveness of alkaline chlorination on cyanide removal.
Thiocyanate	SCN^-		Thiocyanate is produced during the cyanide leaching process of sulfidic type ores. Thiocyanate is normally biologically oxidized to carbonate, sulfate and ammonia.

Table A.1 *(continued)*

Cyanide term	CN species included	Definition	Other information
Cyanate	CNO^-		Cyanate is produced from the oxidation of cyanide and it is a by-product of cyanide destruction processes such as SO_2^- air, H_2O_2, Caro's Acid, Alkaline chlorination, Chlorine dioxide and Ozonation.
Cyanide degradation products	Mainly NH_3, NH_4^+, NO_3^- and NO_2^-		
Cyanogen halides	e.g. CNCl, CNBr		Cyanogen chloride and bromide hydrolyse to cyanate at the pH of sample preservation (pH ≥ 12) and will not be detected.
Organic cyanide	e.g. cyanohydrins, cyanogenic glucosides, acetonitrile (CH_3CN), cyanobenzene (C_6H_5CN)	Measured from organic compounds containing cyanide functional groups	Not normally present in detectable quantities in the vast majority of environmental samples. The cyanide in many of these species is not readily bioavailable.
Metal cyanide complex	$Cu(CN)_{43}^-$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Co(CN)_6^{3-}$, $Ni(CN)_4^{2-}$, $Au(CN)_2^-$, $Ag(CN)_2^-$, $Cr(CN)_6^{3-}$, etc.	Defined as a negatively charged ionic complex consisting of a number of cyanide ions bound to a single transition metal cation. General formula $[M(CN)_b]^{x-}$	Also known as metal cyano-complex.

Annex B
(informative)

Summary of cyanide analytical methods

Table B.1 — Summary of cyanide analytical methods

Cyanide parameter measured	Analytical method			
	In solution#	**Comments**	**In soil**	**Comments**
Free cyanide	APHA[a] 4500-CN^- D	Titrimetric method using $AgNO_3$		
	APHA[a] 4500-CN^- E	Colorimetric method using chloramine-T		
	APHA[a] 4500-CN^- F	Cyanide selective electrode method		
	USGS I-2302–85	Dissolved cyanide. Colorimetric, barbituric acid, automated segmented flow		
	ASTM D4282–02	Microdiffusion method		
	ASTM D7237–10	pH 6 to 8, FIA, gas diffusion and amperometric detection		
	SCA § 214 D	Microdiffusion		
	SCA § 214 E	CFA		
Weak acid dissociable (WAD) cyanide	CEN/TS 16229	pH 4; in slurry samples		
	APHA[a] 4500-CN^- I	Distillation method		
	ASTM D4374–06	Automated method		
	Picric acid method[b]			
	ASTM D2036–09, C			
Available cyanide	ISO 17690	pH 6, FIA, gas-diffusion and amperometric detection		
	EPA/OIA-1677DW	Flow injection, ligand exchange and amperometry		
	ASTM D6888–09	Ligand displacement and FIA using gas diffusion and amperometric detection		
Easily liberated cyanide (ELC)	ISO 6703-2		ISO 17380	Continuous flow, distillation
	ISO 17690	pH 6, FIA, gas-diffusion and amperometric detection	SCA § 235 A	By steam distillation at pH 4 and colorimetry
	ISO 14403-1	FIA		
	ISO 14403-2	CFA		

Table B.1 *(continued)*

Cyanide parameter measured	Analytical method			
	In solution#	Comments	In soil	Comments
Total cyanide	ISO 6703-1		ISO 11262	Cyanide liberated by (i) digestion and (ii) extraction with NaOH
			ISO 17380	Continuous flow, distillation
	ISO 14403-1	FIA	USGS I-6302–85	Recoverable total cyanide
	ISO 14403-2	CFA	SCA § 235 BA	By steam distillation and colorimetry
	APHA[a] 4500-CN- C	Distillation method	SCA § 235 BB, BC	By steam distillation of alkaline extract and colorimetry
	USEPA 335.4	Semi-automated colorimetry	SCA § 214 B	Reflux distillation and ISE potentiometry
	USEPA 9012b	Automated colorimetric with off-line distillation	SCA § 214 C	Reflux distillation and colorimetry
	USEPA 9010C	Distillation		
	USGS I-4302–85	Total recoverable. Colorimetric, barbituric acid, automated segmented flow		
	ASTM D4374–06	Automated method		
	ASTM D7284–08	Micro distillation, FIA, gas diffusion and amperometric detection		
	ASTM D7511–12	Segmented FIA, UV digestion and amperometric detection. Only partial determination of cyanide ions from Au(I), Co(III), Pd(II) and Ru(II). This is true with all total cyanide methods. The appendix in D7511 and the FI-UV Analyst paper demonstrate that distillation (EPA 335.4 and this method recover all compounds equivalently).		
	ASTM D2036–09, A	After distillation		

Table B.1 *(continued)*

Cyanide parameter measured	Analytical method			
	In solution#	**Comments**	**In soil**	**Comments**
Cyanide amenable to chlorination (CATC)	APHA[a] 4500-CN⁻ G	After distillation		
	APHA[a] 4500-CN⁻ H	Without distillation		
	USEPA 9012b	Automated colorimetric with off-line distillation		
	USEPA 9010C	Distillation		
	ASTM D2036–09, B	By difference		
	ASTM D2036-09, D	Without distillation		
Thiocyanate	APHA[a] 4500-CN⁻ M	Colorimetric method	SCA § 235 CA	By alkaline extraction and colorimetry
	Ion chromatography[d]			
	ASTM D4374–06	Automated method		
Cyanate	APHA[a] 4500-CN⁻ L	By hydrolysis to ammonia		
	Ion chromatography[c]			
Cyanide degradation products	SCN^-, CNO^-, NH_3			
Cyanogen halides	ISO 6703-3			
Cyanogen chloride	APHA[a] 4500-CN⁻ J			
Cyanogen chloride				
Metal cyanide complexes	Ion chromatography[d]	Quantification of $Cu(CN)_4^{3-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Co(CN)_6^{3-}$, $Ni(CN)_4^{2-}$, $Ag(CN)_2^-$, $Au(CN)_2^-$ and $Cr(CN)_6^{3-}$ PDAD detection	Dionex Application Note 149	Ion exchange chromategraphy and UV. See 8.12 and References [17]-[21].
	ASTM D6994–10	Complexes of Fe, Co, Ag, Au, Cu and Ni. Anion exchange chromatography with UV detection		
	Dionex Application Note 147	Ion chromatography and UV		
	Dionex Application Note 161	Ion chromatography with online sample pre-concentration and UV		
Organic cyanides	See Reference [10]			These species are not routinely analysed
Sample treatment and preservation prior to analysis	APHA[a] 4500-CN⁻ B		ISO 18512	
	ASTM D6696–10			

Table B.1 *(continued)*

Cyanide parameter measured	Analytical method			
	In solution#	Comments	In soil	Comments
	ASTM D7365–09a			
	ISO 5667-3			
Other	ASTM D7728–11	A guide to ASTM cyanide methods to be used for International cyanide management code		
	ASTM D6696–10	A guide to cyanide terminology		

Solution denotes any aqueous sample including water, waste water and sample extract

FIA – Flow injection analysis

CFA – Continuous flow analysis

PDAD – Photodiode array detection

ISE – Ion selective electrode

a APHA, Reference: American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.

b Picric acid method, Reference: Iamarino, P.F (1989), "*The direct spectrophotometric determination of cyanide with picric acid reagent*, JRGRL June 1 1989. INCO Ltd., http://www.infomine.com/library/publications/docs/CyanideMethodPicricAcid1.pdf (accessed 04.11.16)

c Ion Chromatography, Reference: S.B. Black and R.S. Schulz. *"Ion Chromatographic determination of Cyanate in saline Gold Processing Samples"*, Journal of Chromatography A, 855(1), 267–272, 1999.

d Ion Chromatography, Reference: S.B. Black and R.S. Schulz. *"Photodiode Array Detection as a Fingerprinting Tool for Metal Cyanide Complexes in Gold Processing Solutions"*, International Journal of Environmental Analytical Chemistry, 72(2), 129–136, 1998.

§ SCA – Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Methods 214 and 235. Method 214 "The determination of cyanide in waters and associated materials (2007)" (Methods B to E for easily liberated and total cyanide). Method 235 "The determination of cyanide and thiocyanate in soils and similar matrices (2011)", (Methods AA; AB; AC for easy liberated cyanide; BA; BB and BC for total cyanide and CA for thiocyanate)

See:(https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/316795/cyanide214_1847912.pdf and

https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/316762/Blue_Book_235_cyanide.pdf) (both accessed 01.11.16)

Annex C
(informative)

Summary of the methodology scopes and performance characteristics of the ISO/CEN cyanide standards

C.1 General

This annex attempts to compare and contrast the performance characteristics of the various ISO/CEN cyanide standards in a series of tables given below with respect to the following.

The method scopes including analytical concentration range and concentrations actually used in the method performance testing are summarized here. It is important that concentration levels close to any regulatory limit are tested.

Free (or easy liberatable) cyanide type methods only determine the "readily available cyanide", which in many instances is a small percentage of the total cyanide present. Thus, these are empirical methods where the extraction/liberation technique employed in the method will define the results.

In many countries, low (<10 µg/l) regulatory limits have been set for free (or easy liberatable) cyanide in effluents and/or receiving waters. Also, some low limits have been set for soil for this parameter. So it is important that any official method is thoroughly validated by assessing the method performance with a range of relevant samples. Methods that allow different options to be used should formally test all options (e.g. the ISO 14403-2 free cyanide water method allows distillation at 125 °C or gas diffusion at 30 °C to 40 °C to liberate free cyanide). These two options are likely to display different interference effects for certain parameters in the free cyanide method.

The lowest proposed predicted no-effects concentration (PNEC) derived for cyanide is 0,052 µg/l HCN for saltwater long-term[4]. This reference also states "From the literature, it can be seen that analytical methodologies provide detection limits of around 5 µg/l to 10 µg/l, which suggests that they may not be adequate to analyse cyanide for compliance with the proposed PNECs". It should also be noted that the suggested PNECs cited are also regarded as environmental quality standards (EQSs)[4]. It is considered important that regulators consider the typical measurement uncertainty when setting regulatory limits; typical background levels of the parameter of interest and finally how to ensure there is no significant sample degradation prior to analysis.

The method validation performance trial should include samples demonstrating the following:

— absence of "significant breakdown" of thiocyanate to free cyanide when determining either free or total cyanide;

— absence of "significant breakdown" of hexacyanoferrate(III) $[Fe(CN)_6]^{3-}$ to free cyanide when determining free cyanide;

— effectively quantitative recovery of cyanide from hexacyanoferrate(III) $[Fe(CN)_6]^{3-}$ when determining total cyanide.

Many regulators do not appear to understand the problems related to obtaining "fit for purpose" results for free (easily liberatable) cyanide especially at low levels (e.g. below 10 µg/l).

It is hoped that this document will help all stakeholders to appreciate the problems involved.

NOTE About the USA Approach: In general, the detection limits and limits of quantitation generated in the laboratory under optimal conditions do not reflect those obtained in the field associated with much more complicated chemical matrices. The USEPA has recognized these deficiencies and has implemented an approach to take into account inherent variability in the form of the minimum detection limit (MDL) and the minimum level (ML), also known as the practical quantitation limit. It is important to recognize that attempting to achieve extremely low cyanide reporting levels in µg/l and even sub- µg/l is not realistic on a continuous basis and frankly is no longer necessary based on decades of empirical evidence. The pursuit of this objective has led to endless confusion as to whether or not environmental impacts or permit violations have occurred. The typical outcome is litigation and turning to a judge to make the scientific determination.

Although WAD, free, easily liberated cyanide water quality standards have been applied throughout the world for protection of cold water aquatic life and sensitive salmonid species at levels between 5 µg/l to 10 µg/l in-stream, there remains the desire to fall back on the free cyanide standard of 5 µg/l which is essentially unattainable through treatment or measurement under ambient conditions. However, if the free cyanide standard is to be implemented as has been the long term goal of the USEPA, then at the moment there is only one company claiming the ability to do just that with its instrument and procedure. The EPA has approved that procedure and instrument for measurement of free cyanide at levels accurate to below 5 µg/l (see ASTM D7237). This recent development requires further consideration as the value of the other procedures and how they are best utilized.

Regardless of the accuracy and precision of a particular cyanide procedure, ultimately the reliability of the analytical result is tied to the quality of the laboratory and in particular the technician performing the analysis. There is no guarantee that the detection and quantitation limits that are in theory published will be obtained by an internal onsite or external commercial laboratory under actual ambient conditions. Again from experience, it is generally accepted that there is profound difference between the abilities of laboratories to conduct cyanide analyses. Thus, the reporting of these limits simply in a table could be misleading. ISO is a highly respected organization worldwide and it is important that ISO cyanide standards fully detail these potential problems.

C.2 Scope of ISO 14403-1:2012

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 ISO 14403-1, a suitable mass concentration range from 20 µg/l to 200 µg/l is described.

C.3 Performance data of ISO 14403-1:2012

An interlaboratory trial for flow systems as described in Clause 7 was carried out in Spring 2009. The results are shown in Table C.1.

Table C.1 — Statistical data for the determination of free cyanide by FIA (in accordance with ISO 5725-2)

Sample	Matrix[a]	l	n	o %	X µg/l	x µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
1	Drinking water	22	90	8,2	75	72,5	96,7	4,80	6,6	1,28	1,8
2	Drinking water	22	89	8,2	63	63,0	100,0	5,22	8,3	1,39	2,2
3	Surface water	22	89	12,7	113	110,6	97,9	7,26	6,6	2,00	1,8
4	Surface water	24	98	3,9	75	76,7	102,2	5,41	7,1	1,65	2,1
5	Waste water	22	89	12,7	150	143,0	95,3	9,54	6,7	2,54	1,8
6	Waste water	23	93	7,9	63	64,0	101,6	7,28	11,4	1,98	3,1

l is the number of laboratories after outlier rejection.

n is the number of individual test results after outlier rejection.

o is the percentage of outliers.

X is the assigned value.

x is the overall mean of results (without outliers).

η is the recovery rate.

s_R is the reproducibility standard deviation.

$C_{V,R}$ is the coefficient of variation of reproducibility.

s_r is the repeatability standard deviation.

$C_{V,r}$ is the coefficient of variation of repeatability.

[a] Origin of the samples:

1 an 2, spiked, City of Berlin;

3 and 4, spiked, Landwehrkanal, City of Berlin;

5 and 6, spiked, Waste Water Plant, Berlin-Ruhleben.

C.4 Scope of 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 can be changed by varying the operation conditions, e.g. by diluting the original sample or changing the pathlength of the flow cell.

In this method, a suitable mass concentration range from10 µg/l to 100 µg/l is described.

C.5 Performance data ISO 14403-2:2012

An interlaboratory trial for flow analysis systems as described in Clause 7 was carried out in spring 2009. The results are shown in ISO 14403-2:2012, Tables D.1 and D.2.

Table C.2 — Statistical data for the determination of free cyanide by CFA (in accordance with ISO 5725-2)

Sample	Matrix[a]	l	n	o %	X µg/l	x µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
1	Drinking water	21	92	1,1	30	27,9	92,9	2,21	7,9	0,45	1,6
2	Drinking water	21	93	0,0	25	25,3	101,1	2,12	8,4	0,53	2,1
3	Surface water	21	93	0,0	45	43,6	96,8	2,73	6,3	0,55	1,3
4	Surface water	20	89	4,3	30	30,8	102,6	2,32	7,5	0,45	1,5
5	Waste water	18	82	11,8	60	55,0	91,6	3,43	6,2	0,82	1,5
6	Waste water	20	90	3,2	25	24,0	96,1	2,80	11,7	0,61	2,5

l is the number of laboratories after outlier rejection.

n is the number of individual test results after outlier rejection.

o is the percentage of outliers.

X is the assigned value.

x is the overall mean of results (without outliers).

η is the recovery rate.

s_R is the reproducibility standard deviation.

$C_{V,R}$ is the coefficient of variation of reproducibility.

s_r is the repeatability standard deviation.

$C_{V,r}$ is the coefficient of variation of repeatability.

[a] Origin of the samples:

Sample 1, spiked, Metallurgical Tailings Solution, Nevada;

Sample 2, spiked, Cherry Creek, Centennial, Colorado;

Sample 3, spiked, Denver Aquifer, Parker, Colorado;

Sample 4, spiked, Heap Leach Drain Down Solution, Nevada;

Sample 5, unspiked, Laboratory Treated Metallurgical Tailings Filtrate.

C.6 Performance data ISO 14403-1:2012

For the method scope, see C.3.

Table C.3 — Statistical data for the determination of total cyanide by FIA (in accordance with ISO 5725-2)

Sample	Matrix[a]	l	n	o %	X µg/l	x µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
1	Drinking water	25	103	3,7	75	74,3	99,1	5,66	7,6	1,94	2,6
2	Drinking water	26	107	0,0	126	117,8	93,5	9,90	8,4	2,97	2,5
3	Drinking water	25	103	3,7	69	61,5	89,1	5,52	9,0	1,60	2,6
4	Surface water	26	106	3,6	113	113,0	100,0	8,41	7,4	2,63	2,3
5	Surface water	26	106	3,6	138	131,1	95,0	9,02	6,9	3,09	2,4
6	Surface water	26	107	3,6	132	118,6	89,8	10,24	8,6	2,53	2,1

For explanation of symbols, see Table C.1.

[a] Origin of the samples:

Sample 1, 2, 3, spiked, City of Berlin;

Sample 4, 5, 6, spiked, Landwehrkanal, City of Berlin.

Table C.3 *(continued)*

Sample	Matrix[a]	l	n	o %	X µg/l	x µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
7	Waste water	25	103	7,2	150	145,7	97,1	12,18	8,4	4,17	2,9
8	Waste water	27	111	0,0	157	139,5	88,9	14,96	10,7	4,11	2,9
9	Waste water	27	110	0,0	113	96,7	85,6	9,56	9,9	2,97	3,1

For explanation of symbols, see Table C.1.

[a] Origin of the samples:

Sample 1, 2, 3, spiked, City of Berlin;

Sample 4, 5, 6, spiked, Landwehrkanal, City of Berlin.

NOTE Investigations have shown that the addition of potassium hexacyanoferrate(III) to the particular waste water matrix used in the interlaboratory trial on total cyanide was not fully recovered. The recovery actually achieved depends on the time delay between preparation of the spiked solution and the moment of analysis. The samples for the total cyanide test were spiked with hexacyanoferrate(III). It is assumed that a part of this reagent was reduced by components of the matrix and that therefore a negative bias could have arisen.

This finding explains the lower recovery of total cyanide in waste water samples 8 and 9 as observed in the interlaboratory trial by several participants. Nevertheless this effect is highly reproducible as shown by the absence of outliers.

These observations are expected to be of minor importance for practical purposes, because usually waste water does not contain hexacyanoferrate(III) in measurable concentrations. It can also be assumed that the possible reduction of hexacyanoferrate(III) by components of the waste water has finished when the sample is taken.

C.7 Performance data ISO 14403-2:2012

For the method scope, see C.4.

Table C.4 — Statistical data for the determination of total cyanide by CFA (in accordance with ISO 5725-2)

Sample	Matrix[a]	l	n	o %	X µg/l	x µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
1	Drinking water	21	93	9,7	30	28,8	96,1	1,64	5,7	0,57	2,0
2	Drinking water	20	91	13,3	50	47,5	94,9	2,32	4,9	0,78	1,6
3	Drinking water	20	91	9,9	28	25,8	92,3	2,00	7,7	0,50	1,9
4	Surface water	18	86	14,9	45	45,2	100,4	1,72	3,8	0,62	1,4
5	Surface water	21	96	7,7	55	52,9	96,2	2,65	5,0	1,05	2,0
6	Surface water	19	88	16,2	53	48,9	92,3	3,75	7,7	0,69	1,4

For explanation of symbols, see Table C.1.

[a] Origin of the samples:

Sample 1, 2, 3, spiked, City of Berlin;

Sample 4, 5, 6, spiked, Landwehrkanal, City of Berlin.

Table C.4 *(continued)*

Sample	Matrix[a]	l	n	o %	X µg/l	x µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
7	Waste water	18	84	20,0	60	57,7	96,1	3,00	5,2	0,68	1,2
8	Waste water	19	88	16,2	63	55,9	88,7	4,09	7,3	0,67	1,2
9	Waste water	20	93	11,4	45	39,9	88,7	4,14	10,4	0,75	1,9

For explanation of symbols, see Table C.1.

[a] Origin of the samples:

Sample 1, 2, 3, spiked, City of Berlin;

Sample 4, 5, 6, spiked, Landwehrkanal, City of Berlin.

NOTE Investigations have shown that the addition of potassium hexacyanoferrate(III) to the particular waste water matrix used in the interlaboratory trial on *total cyanide* was not fully recovered. The recovery actually achieved depends on the time delay between preparation of the spiked solution and the moment of analysis. The samples for the total cyanide test were spiked with hexacyanoferrate(III). It is assumed that a part of this reagent was reduced by components of the matrix and that therefore a negative bias could have arisen.

This finding explains the lower recovery of total cyanide in waste water samples 8 and 9 as observed in the interlaboratory trial by several participants.

These observations are expected to be of minor importance for practical purposes, because usually waste water does not contain hexacyanoferrate(III) in measurable concentrations. It can be also assumed that the possible reduction of hexacyanoferrate(III) by components of the waste water has finished when the sample is taken.

C.8 Scope of 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.

In ISO 17690, two suitable mass concentration ranges from 5 µg/l to 50 µg/l and from 50 µg/l to 500 µg/l are described.

For a given aquatic environment and given cyanide speciation, the extent of HCN(aq) formation is mainly dependent on the pH and to a lesser degree on temperature. The flow injection manifold described in this method can effectively account for both of these parameters. The aquatic “free” cyanide determined with this procedure should be similar to the actual levels of HCN(aq) in the original aquatic environment. This in turn may give a reliable index of toxicity to aquatic organisms.

Extensive species and concentration dependent cyanide recovery studies were carried out using this method for determination of aquatic free cyanide in water and wastewater samples.

Previous research has shown that no method can measure the true free cyanide levels. In that respect, the method developed in this study is no different. However, this novel method has significant advantages over the classical procedures:

— better sensitivity and lower limit of detection;

— better selectivity (interferences: EPA OIA-1677 and D6888);

— analysis time is 70 seconds (compared to 4 h to 8 h for ASTM diffusion method and 2 h to 3 h for CATC method);

— method mimics the condition of aquatic environment (pH and temperature) in relations to the actual formation of free cyanide;

— since no distillation is required, the method is easy to use in the field as well as to automate.

Cyanide recoveries from Zn, Cd, Hg, Cu and Ag cyano species are independent of the reaction time as long as at least 30 cm × 0,5 mm i.d. mixing coil was utilized.

Except for dicyanoargentate(I) species, the change in temperature had no effect on the cyanide recoveries.

pH of the reagent (buffer) solution utilized has the most profound effect on the cyanide recoveries from cyano complexes of intermediary stability (Cu, Ag, Ni cyano species); the lower the pH of the buffer, the higher the cyanide recovery.

Comprehensive sample stability tests have been carried out down to 50 µg/l free cyanide.

C.9 Performance data of ISO 17690:2015

Table C.5 — Statistical data for the determination of free cyanide by FIA (in accordance with ISO 5725-2)

Sample	Matrix[a]	l	n	o %	X µg/l	x µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
1	Drinking water	11	22	8,33	822	815	99,1	60,9	7,47	8,30	1,02
2	Surface water	11	22	8,33	409	398	97,3	32,5	8,16	6,16	1,55
3	Portable water	11	22	8,33	195	202	104	16,0	7,92	1,76	0,87
4	Leach solution	11	22	8,33	167	179	93,3	12,8	7,15	2,28	1,27
5	Effluent	11	22	8,33	9,4	8,00	85,0	2,95	36,9	0,51	6,38

l is the number of laboratories after outlier rejection.

n is the number of individual test results after outlier rejection.

o is the percentage of outliers.

X is the assigned value.

x is the overall mean of results (without outliers).

η is the recovery rate.

s_R is the reproducibility standard deviation.

$C_{V,R}$ is the coefficient of variation of reproducibility.

s_r is the repeatability standard deviation.

$C_{V,r}$ is the coefficient of variation of repeatability.

[a] Origin of the samples:

Sample 1, spiked, Metallurgical Tailings Solution, Nevada;

Sample 2, spiked, Cherry Creek, Centennial, Colorado;

Sample 3, spiked, Denver Aquifer, Parker, Colorado;

Sample 4, spiked, Heap Leach Drain Down Solution, Nevada;

Sample 5, unspiked, Laboratory Treated Metallurgical Tailings Filtrate.

C.10 Scope of ISO 11262

ISO 11262 is applicable to as-received (field-moist) samples and specifies two different procedures for the liberation of cyanide from the soil:

— direct liberation of hydrogen cyanide using orthophosphoric acid (normative);

— extraction with sodium hydroxide solution and subsequent liberation using orthophosphoric acid (informative).

The liberated cyanide is determined either by a photometric method or a titrimetric method using an indicator. The method is applicable to all types of soil.

Under the conditions specified in ISO 11262 , the lower limit of application is 0,5 mg/kg of total cyanide (expressed on the as-received basis) for photometric determination and 10 mg/kg for titrimetric determination.

NOTE Using the alkaline extraction followed by liberation using phosphoric acid, the lower limit of application is 1 mg/kg of total cyanide (expressed on the as-received basis) for photometric determination and 30 mg/kg for titrimetric determination.

C.11 Performance data ISO 11262: 2011

An interlaboratory trial was conducted to test the procedures specified in ISO 11262. In this trial, the amount of total cyanide was determined by a number of laboratories on a number of soils. The repeatability (*r*) and reproducibility (*R*) of the results of these analyses are given in Table C.5. The values have been calculated according to ISO 5725-2.

Table C.6 — Validation data of the 15th BAM interlaboratory comparison "Contaminated soil", September 2009 — Samples 1 to 3: contaminated soil from former gasworks sites in the area of Berlin (Germany)

Sample	N_L	N_A	N	X_{mean} mg/kg	s_r mg/kg	V_r %	s_R mg/kg	V_R %	r mg/kg	R mg/kg
Soil 1	26	25	50	107,0	5,0	4,7	19,5	18,3	13,8	54,1
Soil 2	19	18	36	76,2	2,4	3,2	11,8	15,5	6,7	32,7
Soil 3	21	20	40	48,2	1,3	2,6	6,6	13,6	3,5	18,2

N_L is the number of laboratories.

N_A is the number of accepted laboratories.

N is the number of accepted single values.

X_{mean} is the mean value.

s_r is the repeatability standard deviation.

V_r is the relative repeatability standard deviation.

s_R is the reproducibility standard deviation.

V_R is the relative reproducibility standard deviation.

r is the repeatability limit.

R is the reproducibility limit.

NOTE The reproducibility limit (*R*) is the value less than or equal to which the absolute difference between two results, obtained under reproducibility conditions, may be expected to be with a probability of 95 %, i.e. for soil 1, 107,0 mg/kg ± 54,1 mg/kg.

C.12 Scope of ISO 17380

ISO 17380 specifies a method for the photometric determination of the total cyanide and easily-liberatable cyanide content in soil using automated distillation-continuous flow analysis. ISO 17380 applies to all types of soil with cyanide contents above 1 mg/kg on the basis of dry matter, expressed as cyanide ion.

NOTE Sulfide concentrations in the sample higher than 40 mg/kg dry matter cause interference. This effect can be recognized by the split peaks and as a slow decrease of the detector signal and can only be prevented by diluting the sample extract.

C.13 Performance data for ISO 17380:2013

In an interlaboratory trial, the following validation data were obtained using the method described in ISO 17380. Data are calculated according to ISO 5725-2.

Table C.7 — Validation data — Easily released cyanide

Easily released cyanide									
Sample	N	N	$\bar{X}$	S_r	S_R	$C_{V,r}$	$C_{V,R}$	r	R
		Measurements	mg/kg	mg/kg	mg/kg	%	%	mg/kg	mg/kg
Soil I	12 (0)	24	1,70	0,150	0,609	8,8	35,8	0,42	1,65
Soil II	12 (0)	24	5,18	0,409	1,40	7,9	27,1	1,15	3,93
Soil III	12 (0)	24	16,3	1,19	3,91	7,3	24,0	3,36	11,0
Standard	11 (1)	22	24,1	0,530	1,13	2,2	4,7	1,45	3,18

Table C.8 — Validation data — Total cyanide

Total cyanide									
Sample	N	N	$\bar{X}$	S_r	S_R	$C_{V,r}$	$C_{V,R}$	r	R
		Measurements	mg/kg	mg/kg	mg/kg	%	%	mg/kg	mg/kg
Soil I	14 (0)	28	7,73	0,356	1,03	4,6	13,3	0,99	2,89
Soil II	14 (0)	28	31,8	0,795	3,34	2,5	10,5	2,21	9,35
Soil III	13 (1)	26	193	5,98	20,8	3,1	10,8	16,8	58,2
Standard	12 (2)	24	63,8	1,21	6,12	1,9	9,6	3,18	1,72

N is the number of laboratories left over after rejection of statistical outliers according to ISO 5725-2.

() is the number of rejected results.

$\bar{X}$ is the mean value, in milligrams per kilogram (mg/kg).

S_r is the repeatability standard deviation, in milligrams per kilogram (mg/kg).

$C_{V,r}$ is the relative repeatability standard deviation, in per cent (%).

S_R is the reproducibility standard deviation, in milligrams per kilogram (mg/kg).

$C_{V,R}$ is the relative reproducibility standard deviation, in per cent (%).

r is the repeatability, in milligrams per kilogram (mg/kg).

R is the reproducibility, in milligrams per kilogram (mg/kg).

NOTE The reproducibility limit (R) is the value less than or equal to which the absolute difference between two results, obtained under reproducibility conditions, may be expected to be with a probability of 95 %, i.e. for soil III, 16,3 mg/kg ± 11,0 mg/kg for easily liberatable (free) cyanide and 193 mg/kg ± 58,2 mg/kg for total cyanide.

Annex D
(informative)

Summary of ASTM international cyanide methods

D.1 ASTM D2036-09

D.1.1 General

Test Method D is applicable for natural water and clean metal finishing or heat treatment effluents. It may be used for process control in wastewater treatment facilities providing its applicability has been validated by Test Method B or C.

The spot test outlined in ASTM D2036 09, A.1 can be used to detect cyanide and thiocyanate in water or wastewater, and to indicate its approximate concentration.

D.1.2 Scope

These test methods cover the determination of cyanides in water. The following test methods are included:

	Sections
Test Method A - Total Cyanides after Distillation	12 to 18
Test Method B - Cyanides Amenable to Chlorination by Difference	19 to 25
Test Method C - Weak Acid Dissociable Cyanides	26 to 32
Test Method D - Cyanides Amenable to Chlorination without Distillation (Short-Cut Method)	33 to 39

Cyanogen halides may be determined separately.

NOTE 1 Cyanogen chloride is the most common of the cyanogen halide complexes as it is a reaction product and is usually present when chlorinating cyanide-containing industrial waste water. For the presence or absence of CNCl, the spot test method given in ASTM D2036 09, A.1 can be used.

These test methods do not distinguish between cyanide ions and metallocyanide compounds and complexes. Furthermore, they do not detect the cyanates. Cyanates can be determined using ion chromatography without digestion.

NOTE 2 The cyanate complexes are decomposed when the sample is acidified in the distillation procedure.

The cyanide in cyanocomplexes of gold, platinum, cobalt and some other transition metals is not completely recovered by these test methods. Refer to Test Method D6994 for the determination of cyanometal complexes.

Cyanide from only a few organic cyanides are recovered and those only to a minor extent.

Part or all of these test methods have been used successfully with reagent (laboratory) water and various waste waters. It is the user's responsibility to ensure the validity of the test method for the water matrix being tested.

This document does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this document to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific hazard statements are given in ASTM D2036 09, 5.1, 8.8, 8.18, 9, 11.3, and 16.1.9.

Test method A — Total cyanides after distillation

This test method covers the determination of cyanides in water, including the iron cyanide complexes (total cyanide).

The cyanide in some cyano complexes of transition metals, for example, cobalt, gold, platinum, etc. is not determined.

The cyanide concentration can be determined with titration, IC-PAD, colorimetric, selective ion electrode procedure, or flow injection analysis with gas diffusion separation and amperometric detection as described in Test Method D6888.

This test method has been used successfully on reagent (laboratory), and surface water as well as coke plant, refinery, and sanitary waste waters. It is the user's responsibility to ensure the validity of the test method for the water matrix being tested.

Because of the sample preservation, certain suspended and/or colloidal forms of metal cyanide complexes such as those from iron and copper will dissolve prior to the distillation step. The recovery of this cyanide may depend on solution parameters such as the cyanide concentration in suspended solids, ionic strength of the sample, sample temperature, acid digestion times, and so forth.

Test method B — Cyanides amenable to chlorination by difference

This test method covers the determination of cyanides amenable to chlorination in water.

Iron cyanides are the most commonly encountered compounds not amenable to chlorination.

This test method has been used on reagent (laboratory), surface, and industrial waste waters. It is the user's responsibility to ensure the validity of the test method for the water matrix being tested.

Test method C — Weak acid Dissociable cyanides

This test method covers the determination of cyanide compounds and weak acid dissociable complexes in water.

The thiocyanate content of a sample usually does not cause interference.

Any of the three procedures, titration, colorimetric, or selective ion electrode, can be used to determine the cyanide content of the absorption solution. The lower limits of detectability are the same as for Test Method A.

This test method has been used successfully on reagent (laboratory) and surface water and coke plant, refinery and sanitary waste waters. It is the user's responsibility to ensure the validity of the test method for the water matrix being tested.

Test method D — Cyanides amenable to chlorination without distillation (Short-cut method)

This test method covers the determination of free cyanide and cyanide complexes that are amenable to chlorination in water. The procedure does not measure cyanates nor iron cyanide complexes. It does, however, determine cyanogen chloride and thiocyanate.

Modification is outlined for its use in the presence of thiocyanate.

