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Background information and guidance on environmental cyanide analysis

National foreword

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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).

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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^-.

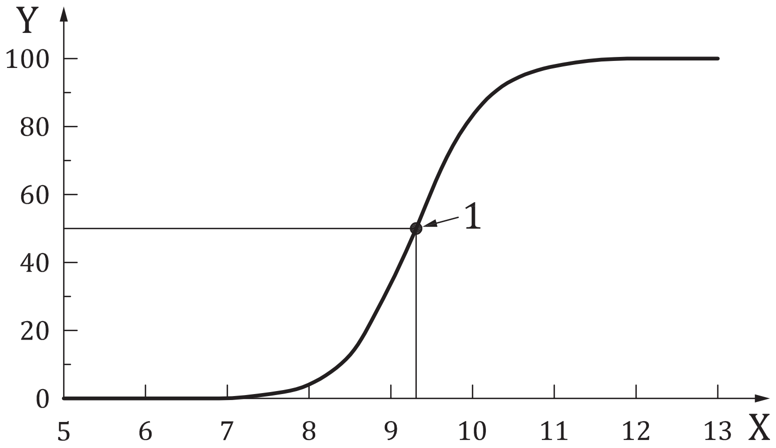

Figure 1 — Dissociation degree (%) of hydrocyanic acid (HCN) with pH

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.

