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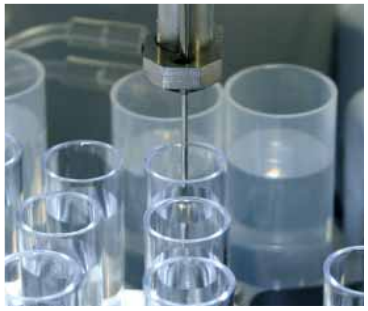
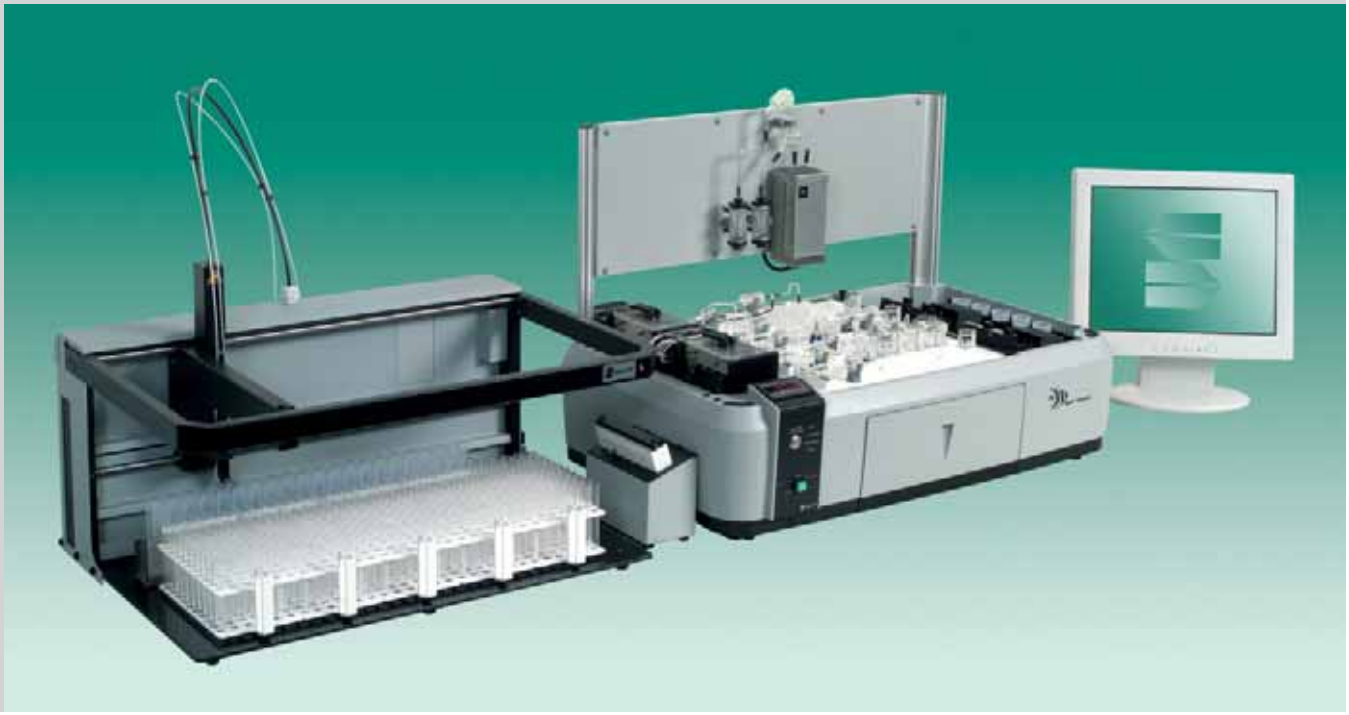
Cyanide Analysis



The San^{++} Analyzer for Cyanide Determination



Introduction

Cyanide can be present as a contaminant of water and soil. Cyanides are introduced in the environment from several sources. They are produced by a wide variety of micro organisms including fungi, bacteria and algae. Furthermore 800 species of plants are known to synthesize cyanide, mainly in the form of cyanogenic glucosides. Also in kernels of almonds, cherry, apple, peach and apricot, cyanide will be found.

In the mining industry cyanide is used to extract gold from ore. A sodium cyanide solution is mixed with finely-ground rock that is proven to contain gold and/or silver, and is then separated from the ground rock as gold cyanide and/or silver cyanide solution. Zinc is added to recover gold from this solution as precipitate.

In the electroplating industry cyanide is used in plating baths. Another source of introducing cyanide into the environment was the former production of coal gas. This gas was produced by the destructive distillation of coal and contained up to 0.15% of $HCN_{(g)}$. Prior to distribution the HCN was removed by filtration through iron-bearing soil. So called Prussian blue was formed. When the material was saturated, it contained up to 10-15% of cyanide. First it was sold as a raw material to the dying industry but later it ended up as waste material discarded in the vicinity of the gas plants.

The risk for the occurrence of adverse effects on human health and the environment strongly depends on the form in which cyanide is present [1]. With only a few exceptions cyanides are rapidly acting poisons, both by mouth and inhalation, which can also be absorbed through the skin [2]. The ratio between CN- /HCN is strongly depending on pH: at pH=8 the ratio is 100% for HCN and at pH=10 CN^- is 100%. (So it is always important to keep the pH >10 for aqueous samples so no HCN will be produced)

Summary of Cyanide Species

Cyanides species

1. Free Cyanide as $HCN_{(aq)}$, $HCN_{(g)}$ and CN^-.
2. Simple Cyanides as f.e. KCN, AgCN, NaCN, $Ca(CN)_2$, $Hg(CN)_2$, $Zn(CN)_2$, CuCN, $Ni(CN)_2$
3. Complex Cyanides as $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{2-}$, $[Zn(CN)_4]^{2-}$
4. Organic Cyanides as Cyanohydrins, Cyanogenic glucosides
5. Thiocyanates as $-SCN^-$
6. Cyanates and cyanogen halides as CNO^- and CNCl, CNBr, CNF.

From these groups the free cyanides are considered to be the most toxic. The toxicity of the other groups mainly depends on the possibility of dissociation to free cyanide and varies from equally toxic (simple cyanides) to slightly toxic (complex cyanides).

Free Cyanide

Only hydrogen cyanide and the cyanide ion in solution can be classified as free cyanide. 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. Free cyanide includes: $HCN_{(aq)}$, $HCN_{(g)}$ and CN^-.

Weak Acid Dissociable (WAD) Cyanide

WAD cyanides refers to those cyanide species measured by specific analytical techniques. WAD cyanide includes those cyanides species liberated at pH=4.5. WAD cyanides includes: $HCN_{(aq)}$, CN-, the metal bound cyanide complexes (Zn, Cd, Cu, Hg, Ni and Ag) and others with similar dissociation constants [3].

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 ferro-cyanide $[Fe(CN)_6]^{-4}$, ferri-cyanide $[Fe(CN)_6]^{-3}$, parts of $[Co(CN)_6]^{-3}$ and $Au(CN)^{2-}$.

Cyanide Amenable to Chlorination (CATC)

This measurement is to establish the effectivity of chlorination on cyanide removal. The results is determined by difference: one result from a sample without treatment with a chlorinated compound and one result from a sample after treatment with a chlorinated compound (hypochlorite). The remainder is cyanide amenable to chlorination.

Thiocyanate

Thiocyanate is not considered to be part of the total cyanide. The environmental impact is very small compared to free cyanides. Thiocyanate can be determined by a separate determination or by calculation with determinations of different cyanide species.

Cyanates and cyanogen halides

Within this article the methods discussed will not detect cyanates and cyanogens halides. Cyanogen chloride hydrolyzes to cyanate at the pH of sample preservation (pH ≥ 12) and will not be detected.

Standards and Methodologies

A vast amount of different analytical techniques is used to determine cyanide in different types of sample. The different Environmental Protection Agency's, the International Organization for Standardization ISO, the American Society for Testing and Materials ASTM and Standard Methods have published methods for determination of cyanide and cyanide species. A list of the different methods is given below.

USEPA Method Kelada – 01

This method, named to his inventor Dr. Kelada, is determining acid dissociable (WAD) cyanides, total cyanide and thiocyanate. The last one by subtraction: first analyze total cyanide with thiocyanate and then subtracted total cyanide without thiocyanate[4].

Skalar Method 297 with on-line digestion (quartz + borosilicate glass) and on-line distillation;
for total cyanide, WAD cyanide, thiocyanate (by difference)

USEPA Method 335.3

This method determines total cyanide with a standard UV lamp (optimum 254 nm) and automatic distillation, followed by colorimetric detection. By choice of this UV-lamp, thiocyanate will be determined. This method is withdrawn[5].

Skalar Method 293 with on-line digestion (quartz) and on-line distillation;
for total cyanide, WAD cyanide. (thiocyanate is included)

USEPA Method 335.4

This method defines cyanide analyses with manual distillation and automated detection by a gas diffusion cell with ampèrometric detection. The method determines total cyanides and does not use UV digestion.

Skalar Method 296, with manual digestion/distillation;
for total cyanide (no UV digestion)

USGS I-2302/I-4302/I-6302

These methods describes the determination of dissolved cyanide (I-2302), total recoverable cyanide (I-4302) and cyanide recoverable–from-bottom-material (I-6302). The method determines thiocyanate as cyanide because of the used UV lamp[6].

Skalar Method 293 with on-line digestion (quartz) and on-line distillation;
for total cyanide, WAD cyanide. (thiocyanate is included)

EPA/OIA-1677

This methods applies manual pretreatment of the sample with a ligand followed by gas dialyses and measurement of available cyanide with ampèrometric detection.

Skalar Method 296 with gas dialyses and ampèrometric detection;
for total cyanide and available cyanide.

ISO 14403:2002

This methods determines free cyanide, complex cyanide and total cyanide by UV digestion and distillation. Thiocyanate will not be detected due to the chosen wavelength of the UV lamp (312 - 420 nm)[7].

Skalar Method 295 with on-line UV digestion (borosilicate glass) and on-line distillation;
for total cyanide, free cyanide. (thiocyanate is excluded)

ISO 17380: 2004

This method is equal to ISO 14403 for the analytical part. It describes the sample pretreatment procedure for the extraction of cyanide from soil. Easily released cyanide, complex cyanide and total cyanide can be determined[7].

Skalar Method 295 with on-line UV digestion (borosilicate glass) and on-line distillation;
for total cyanide, free cyanide. (thiocyanate is excluded)

ASTM D4374-06

This method determines total cyanide, acid dissociable cyanide and thiocyanate. The last one by calculation. An automated system is described with UV-digestion, distillation and colorimetric determination. By choice of the UV coil, it can be determined that thiocyanate will not be measured as cyanide[8].

Skalar Method 293 with on-line digestion (quartz) and on-line distillation;
for total cyanide, WAD cyanide. (thiocyanate can be measured by changing the UV digestion coil into borosilicate glass)

ASTM Method D6888-04

This method equals method OIA-1677 completely: pretreatment with a ligand followed by gas dialyses and measurement of available cyanide with ampèrometric detection[8].

Skalar Method 296 with gas dialyses and ampèrometric detection;
for total cyanide and available cyanide.

ASTM Method D7284-08

In this method a manual distillation is used prior to the determination of released cyanide by gas diffusion and ampèrometric detection. Total cyanide will be measured[8].

Skalar Method 296 with gas dialyses and ampèrometric detection;
for total cyanide and available cyanide.

Standard Methods 4500-CN-

The Standard Methods 4500-CN- contains methods for different cyanide species. Only the relevant (semi)automated methods are described here. Method 4500-CN- N is describing the determination of total cyanide and weak acid dissociable cyanide with manual distillation, followed by colorimetry. Method 4500-CN- O 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[9].

Skalar Method 295 with on-line UV digestion (borosilicate glass) and on-line distillation;
for total cyanide, free cyanide. (thiocyanate is excluded)

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Total Cyanide in Water and Soil according to EPA

With the Kelada-01 method (approved and adapted to the U.S.A. Federal Register Volume 72, No. 47, Monday, March 12, 2007, Part III, EPA 40 CFR Parts 122 & 136) there are several possibilities of determining different species of cyanide.

The Kelada-01 method uses a combined on-line UV irradiation and flash distillation system to automatically determine cyanide. The reactor combines UV irradiation together with the distillation. The system can be equipped with a borosilicate coil to determine total cyanide excluding thiocyanate. But, equipped with a quartz coil, you will determine total cyanide including thiocyanate. By subtraction of both figures, the concentration of thiocyanate is calculated. By omitting UV radiation, weak acid dissociable (WAD) cyanides are broken down to free cyanide and determined.

A flash distillation is included in the system which makes it very convenient for cyanide analysis without any manual pretreatment at all. As an option, it is also possible to determine free cyanide with the system.

The system is suitable to analyze drinking water, surface water, waste water and soil extracts.

The Skalar-Kelada Reactor

Total Cyanide in Water and Soil according to ISO

According to ISO 14403 and ISO 17380, free and total cyanide can be completely automated with the Skalar San^{++} analyzer. The built in UV digestion is omitting thiocyanate conversion. The borosilicate glass coil from the UV digestion, passes only light above 300 nm; this light will not decompose thiocyanate to cyanide. The completely closed thin film distillation system avoids loss of cyanide vapors and because of that safe to the user. No thermal decomposition of thiocyanate takes place in this unique in-line distillation. The detection is colorimetric (Skalar method 295).

Instead of distillation the ISO methods gives the possibility of using a gas diffusion cell, followed by ampèrometric detection (Skalar method 296).

No manual treatment of the water sample other than conservation is necessary. Soil samples are analyzed on the same system after extraction with sodium hydroxide. Other types of sample can also be analyzed, such as wine, food, solid waste, etc.

With a multi channel analyzer, it is possible to measure free cyanide, total cyanide and thiocyanate simultaneously. The San^{++} system for cyanide is ideal for combinations with other parameters. A widely used combination for instance in waste water analysis is the combination with phenol index and/or Methylene Blue Active Substances (MBAS).

Two continuous thin film distillation set-ups

Contact Skalar

Skalar's Headquarters

Skalar Analytical B.V.
Tinstraat 12
4823 AA Breda
The Netherlands
Tel. +31 (0)76 5486 486
Fax. +31 (0)76 5486 400
Email: info@skalar.com
Internet: www.skalar.com

USA Headquarters
Skalar, Inc.
5012 Bristol Industrial Way,
Suite 107, Buford, GA 30518
Tel. + 1 770 416 6717
Toll Free: 1 800 782 4994
Fax. + 1 770 416 6718
Email: info.usa@skalar.com

United Kingdom
Skalar (UK) Ltd.
Breda House,
Millfield Industrial Estate
Wheldrake, York , YO19 6NA
Tel. + 44 (0)1904 444800
Fax. + 44 (0)1904 444820
Email: info.uk@skalar.com

Belgium
Skalar Belgium bvba
Antwerpsestraat 126
2850 Boom
Tel. + 32 (0)3888 9672
Fax. + 32 (0)3844 3441
Email: info.belgium@skalar.com

Germany
Skalar Analytic GmbH
Gewerbestraße Süd 63
41812 Erkelenz
Germany
Tel. + 49 (0)2431 96190
Fax. + 49 (0)2431 961970
Email: info.germany@skalar.com

Austria
Skalar Analytic GmbH
Am Anger 22
A-7451 Oberloisdorf
Austria
Tel. + 43 (0)2611 2023411
Fax. + 43 (0)2611 2023412
Email: info.austria@skalar.com

France
Skalar Analytique S.A.R.L.
79, Avenue Aristide Briand
94110 Arcueil
Tel. + 33 (0)1 4665 9700
Fax. + 33 (0)1 4665 9506
Email: info.france@skalar.com

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For more information please contact your local Skalar agent or Skalar's headquarters in the Netherlands

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