



Designation: D4374 – 06

Standard Test Methods for Cyanides in Water—Automated Methods for Total Cyanide, Weak Acid Dissociable Cyanide, and Thiocyanate¹

This standard is issued under the fixed designation D4374; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the determination of different species of cyanides and thiocyanate in water and waste water, namely weak acid dissociable cyanide, total cyanide, and thiocyanate **(1)**.²

1.1.1 *Total Cyanide*— This test method determines all the weak acid dissociable cyanides and the strong metal-cyano-complexes, such as ferrocyanide $[\text{Fe}(\text{CN})_6]^{4-}$, ferricyanide $[\text{Fe}(\text{CN})_6]^{3-}$, hexacyanocobaltate $[\text{Co}(\text{CN})_6]^{3-}$, and those of gold and platinum.

1.1.2 *Weak Acid Dissociable Cyanide*—This test method basically determines free cyanides, as CN^- and HCN , and weak metal-cyano-complexes such as $[\text{Cd}(\text{CN})_4]^{2-}$ and $[\text{Mn}(\text{CN})_6]^{3-}$. Iron complexes are not included.

1.1.3 Strong cyanide complexes, like those of iron, cobalt, etc., can be determined by difference, that is, cyanide complexes = total cyanides – weak acid dissociable cyanides.

1.1.4 *Thiocyanate*— This test method determines the thiocyanate as the difference between another measurement that includes total cyanide plus thiocyanate and the value of total cyanide, that is, thiocyanate = total cyanide plus thiocyanate – total cyanide.

1.2 Cyanates and cyanogen halides are not detected. Cyanogen chloride hydrolyzes to cyanate at the pH of sample preservation (≥ 12).

1.3 Most of the organo-cyano-complexes are not measured, with the exception of the weak cyanohydrins.

1.4 These test methods apply to different types of water, waste water (raw sewage, sludge, and effluent), sludge, some industrial waste, and sediments. Sample matrixes should be evaluated by the user. The reported precision and bias (see Section 16) may not apply to all samples.

1.5 The values stated in SI units are to be regarded as the standard.

1.6 *This standard 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 standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards*:³

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

D2036 Test Methods for Cyanides in Water

D3370 Practices for Sampling Water from Closed Conduits

D3864 Guide for Continual On-Line Monitoring Systems for Water Analysis

D4193 Test Method for Thiocyanate in Water

D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

D6696 Guide for Understanding Cyanide Species

3. Terminology

3.1 *Definitions*—For definition of terms relating to water, refer to Terminology D1129.

3.1.1 For definitions related to cyanide terminologies, refer to Guide D6696.

3.2 *Definitions of Terms Specific to This Standard*:

3.2.1 *distillation ratio*,

$$\% = \frac{\text{volume of distilled portion of sample}}{\text{total volume of acidified sample}} \times 100$$

4. Summary of Test Method

4.1 Some automated continuous flow modules are used (see Guide D3864) in addition to the newly developed on-line thin film distillation **(2)** and ultraviolet (UV) irradiation **(3)**.

¹ These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

Current edition approved July 1, 2006. Published July 2006. Originally approved in 1984. Last previous edition approved in 2000 as D4374 – 00. DOI: 10.1520/D4374-06.

² The boldface numbers in parentheses refer to the list of references at the end of the text.

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.