

**ENVIRONMENTAL PROTECTION AGENCY**

**40 CFR Part 136**

[FRL-5206-8]

**Guidelines Establishing Test Procedures for the Analysis of Pollutants; Total Kjeldahl Nitrogen**

**AGENCY:** Environmental Protection Agency (EPA).

**ACTION:** Proposed rule and request for comment.

**SUMMARY:** This proposed amendment would approve the use of three additional test procedures at Part 136 for the determination of Total Kjeldahl Nitrogen (TKN) in wastewater. Use of approved test procedures is required whenever the waste constituent specified is required to be measured for: an NPDES permit application; discharge monitoring reports; state certification; and other requests from the permitting authority for quantitative or qualitative effluent data. Use of approved test procedures is also required for the expression of pollutant amounts, characteristics, or properties in effluent limitations guidelines and standards of performance and pretreatment standards, unless otherwise specifically noted or defined.

**DATES:** Comments on this proposal will be accepted until June 16, 1995.

**ADDRESSES:** Send comments to: James E. Longbottom, Environmental Monitoring Systems Laboratory-Cincinnati, U.S. Environmental Protection Agency, Cincinnati, OH 45268-0525. The comments should be labeled as "Guidelines Establishing Test Procedures for the Analyses of Pollutants Under the Clean Water Act—Total Kjeldahl Nitrogen."

The record and all supporting information on this proposal is available to the public for inspection or copying during normal business hours at the Cincinnati Laboratory. The public should contact James E. Longbottom at (513-569-7308) for access. A complete copy of the record and supporting information is also available to the public for inspection and copying at the Water Docket, U.S. Environmental Protection Agency, 401 M Street, SW., Washington, DC 20460. For access to Water Docket materials, call (202) 260-3027 between 9 am and 3:30 pm for an appointment. For information about materials in the docket see

**SUPPLEMENTARY INFORMATION.**

**FOR FURTHER INFORMATION CONTACT:** Mr. James E. Longbottom, Environmental Monitoring Systems Laboratory, Office

of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268. Telephone number: (513) 569-7308.

**SUPPLEMENTARY INFORMATION:**

**Docket Materials**

Materials in the public docket include the following:

- Copy of the proposed procedures and performance data.
- Technical reviews of the proposed analytical techniques.
- Statistical reviews of the performance data.
- Recommendations for Nationwide Approval from the Director, Environmental Monitoring Systems Laboratory-Cincinnati.

**I. Authority**

This proposed regulation is issued under authority of sections 301, 304(h) and 501(a) of the Clean Water Act, 33 U.S.C. 1251 *et seq.* (the Federal Water Pollution Control Act Amendments of 1972 as amended) (the "Act"). Section 301 of the Act forbids the discharge of any pollutant into navigable waters unless the discharge complies with a National Pollutant Discharge Elimination System (NPDES) permit, issued under section 402. Section 304(h) of the Act requires the Administrator of the EPA to "promulgate guidelines establishing test procedures for the analysis of pollutants that shall include the factors which must be provided in any certification pursuant to section 401 of this Act or permit application pursuant to section 402 of this Act". Section 501(a) of the Act authorizes the Administrator to "prescribe such regulations as are necessary to carry out his functions under this Act".

**II. Regulatory Background**

The CWA establishes two principal bases for effluent limitations. First, existing discharges are required to meet technology-based effluent limitations. New source discharges must meet new source performance standards based on the best demonstrated technology-based controls. Second, where necessary, additional requirements are imposed to assure attainment and maintenance of water quality standards established by the States under Section 303 of the CWA. In establishing or reviewing NPDES permit limits, EPA must ensure that permitted discharges will not cause or contribute to a violation of water quality standards, including designated water uses.

For use in permit applications, discharge monitoring reports, and state certification and to ensure compliance with effluent limitations, standards of

performance, and pretreatment standards, EPA has promulgated regulations providing nationally-approved testing procedures at 40 CFR Part 136. Test procedures have previously been approved for 262 different parameters. Those procedures apply to the analysis of inorganic (metal, non-metal, mineral) and organic (chemical, radiological, bacteriological, nutrient, demand, residue, and physical) parameters.

Additionally, some particular industries may discharge pollutants for which test procedures have not been proposed and approved under 40 CFR Part 136. Under 40 CFR Part 122.41 permit writers may impose monitoring requirements and establish test methods for pollutants for which no approved Part 136 method exists. 40 CFR 122.41(j)(4). EPA may also approve additional test procedures when establishing industry-wide technology-based effluent limitations guidelines and standards as described at 40 CFR 401.13.

The procedures for approval of alternate test procedures (ATPs) are described at 40 CFR 136.4 and 136.5. Under these procedures the Administrator may approve alternate test procedures for nationwide use which are developed and proposed by any person. 40 CFR 136.4 (a). Under 136.4 (d), dischargers seeking to use such alternate procedures on a limited basis (e.g. for their own discharge) must apply to the State or Regional EPA office in which the discharge occurs. As specified below, today's proposed rule would approve optional nationwide alternate procedures for the determination of TKN in wastewater test samples.

**III. The Total Kjeldahl Nitrogen (TKN) Test Procedures**

The Perstorp Analytical Corporation, in accordance with the regulations published at 40 CFR 136.5, applied for nationwide approval of three alternate procedures for the determination of TKN in wastewater.

**A. Scope of the Procedures**

The applicable ranges for the titrimetric method (PAI-DK01) and colorimetric method (PAI-DK02) are 0.4 to 10 mg/L, when analyzing a 100 mL sample. The applicable range for the gas diffusion method (PAI-DK03) is 0.2 to 10 mg/L when analyzing a 200 µL sample. The method detection limit has been determined to be 0.15 mg/L for the titrimetric and the colorimetric methods and 0.02 mg/L for the gas diffusion method. These methods would not be available for use to determine TKN concentrations greater than 10 mg/L

unless one of the following two requirements are met:

a. Dilution of the TKN concentration of a sample to a level less than, or equal to 10 mg/L, before the initiation of the analysis, multiplication of the TKN concentration observed in the digested, diluted sample by the appropriate dilution factor, and demonstration of acceptable accuracy (percent recovery) as required in the Quality Control section of the method.

b. Demonstration of the applicability of a specific scope extension by demonstrating calibration range linearity, laboratory performance, and analyte percent recovery, particularly in fortified samples, as outlined in the Quality Control section.

#### B. Summary of the Methods

TKN is defined as the sum of free ammonia and organic nitrogen compounds which are converted to ammonium sulfate under the conditions described. The procedures convert nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.

For all three methods, the sample is heated in a block digester with concentrated sulfuric acid, potassium sulfate and copper sulfate and evaporated until the solution becomes colorless or pale yellow. The block-digested sample is cooled and diluted to volume. For the colorimetric and titrimetric methods the cooled, diluted solution is made alkaline with a hydroxide-thiosulfate solution and distilled in an automated distillation system. In the colorimetric method (Method PAI-DK01) the ammonia in the alkaline digestate is measured at 400–425 nm after reaction with Nessler reagent. In Method PAI-DK02, the ammonia is distilled into a boric acid receiving solution and is measured by automated or manual titration with 0.02 N H<sub>2</sub>SO<sub>4</sub> to a bromocresol green methyl red indicator endpoint. In the FIA system (Method PAI-DK03), a 200-μL aliquot of the digested and diluted sample is injected into the flow injection manifold. The subsequent addition of NaOH releases the ammonia from the ammonium sulfate originally present in the digested sample. The released ammonia passes through a gas diffusion membrane into an indicator receiving solution which is monitored at 590 nm. The extent of indicator color change is proportional to the

concentration of TKN present in the sample.

#### C. Technical Justification for Proposed Procedures

The recommendations for approval of these procedures are based on the data packages submitted by the applicant, Perstorp Analytical. EPA is proposing to approve the methods based on the method descriptions in EPA's Environmental Monitoring Management Council format, comparative analyses using the proposed and approved procedures, and EPA's technical and statistical reviews of each data package.

Perstorp Analytical provided test data comparing the three proposed procedures with an appropriate approved procedure. All three proposed methods were compared to the approved EPA Ion Selective Electrode Method 351.4; EPA statisticians and chemists conducted independent reviews of the data. The submitted recovery data for both the approved and proposed methods were also compared to the recovery acceptance criteria derived from results for block digester analyses (EPA Method 351.4) in EPA's Performance Evaluation Studies WP 18 through 23.

The Agency has judged the block digester electrode procedure (EPA Method 351.3), utilized as the reference approved method by the applicant to be applicable in the evaluation of the three proposed procedures. EPA's Environmental Monitoring Systems Laboratory in Cincinnati, Ohio (EMSL-Cincinnati), thoroughly reviewed and evaluated the supporting data submitted by Perstorp. The reviews indicated that the analyses afforded comparable recovery and precision in the recommended concentration ranges for TKN. EPA is proposing approval of the TKN procedures and is seeking public comment on the suitability of these three methods as alternate procedures for use in the determination of TKN. The administrative record is on file at EMSL-Cincinnati, 26 W. Martin Luther King Dr., Cincinnati, Ohio 45268. The record is available for public inspection. Descriptions of the proposed procedures are also available from Perstorp Analytical Company, 1256 Stockton, St. Helena, CA 94574.

Based on EMSL-Cincinnati's review, and pursuant to 40 CFR Section 136.5, EPA proposes to approve the Perstorp titrimetric, colorimetric, and FIA gas diffusion methods for TKN as acceptable alternative test procedures for nationwide use. Specifically, the methods exhibit sufficient precision and recovery to establish (1) their acceptability under Part 136 and (2)

their comparability to other approved procedures for analysis of TKN. As approved alternate test procedures, these methods are acceptable for use by any person required to test for TKN.

Public comment is requested concerning the suitability of these methods for the determination of TKN in wastewater.

#### IV. Regulatory Requirements

##### A. Executive Order 12866

Under Executive Order 12866, EPA must judge whether a regulation is "major" and, therefore, requires a regulatory impact analysis. EPA has determined that this regulation is not major as it will not result in an effect on the economy of \$100 million or more, a significant increase in cost or prices, or any of the effects described in the Executive Order. This proposed rule would simply specify alternate analytical methods which may be used by laboratories in measuring concentrations of TKN and, therefore, would have no adverse economic impacts. The Office of Management and Budget (OMB) has waived Executive Order 12866 review of the proposal.

##### B. Regulatory Flexibility Act

This proposed rulemaking is consistent with the objectives of the Regulatory Flexibility Act (5 U.S.C. 602 et seq.) because it will not have a significant economic impact on a substantial number of small entities. The procedure included in this rule gives all laboratories the flexibility to use these alternate methods or not to use them.

##### C. Paperwork Reduction Act

This rule contains no requests for information activities and, therefore, no information collection request (ICR) was submitted to OMB for review in compliance with the Paperwork Reduction Act, (44 U.S.C. 3501 et seq.).

#### List of Subjects in 40 CFR Part 136

Environmental protection, Incorporation by reference, Water pollution control.

Dated: May 8, 1995.

**Carol M. Browner,**  
Administrator.

For the reasons set out in the preamble, part 136 of title 40 of the Code of Federal Regulations is proposed to be amended as follows:

#### PART 136—[AMENDED]

1. The authority citation for part 136 continues to read as follows:

**Authority:** Secs. 301, 304(h), 307, and 501(a) Public Law 95–217, Stat. 1566, et seq.

(33 U.S.C. 1251 *et seq.*) (the Federal Water Pollution Control Act Amendments of 1972 as amended by the Clean Water Act of 1977).

2. Section 136.3 is proposed to be amended as follows:

a. In Table IB in paragraph (a), by revising entry 31 and by adding notes 39 through 41.

b. By adding paragraphs (b)(35) through (b)(37).

The revision and additions read as follows:

**§ 136.3 Identification of test procedures.**  
(a) \* \* \*

TABLE 1B.—LIST OF APPROVED INORGANIC TEST PROCEDURES

Parameter, units and method	Reference (method number of page)				
	EPA <sup>1, 35</sup>	Std. Methods 18th ed.	ASTM	USGS <sup>2</sup>	Other
31. Kjeldahl Nitrogen—Total, (as N), mg/L; Digestion and distillation followed by: .....	351.3	4500-NH <sub>3</sub> B or C.	D3590-89(A)		
Titration .....	351.3	4500-NH <sub>3</sub> E	3590-89(A)		<sup>3</sup> 973.48
Nesslerization .....	351.3	4500-NH <sub>3</sub> C	3590-89(A)		
Electrode .....	351.3	4500-NH <sub>3</sub> F or G.			
Automated phenate colorimetric .....	351.1			<sup>8</sup> I-4551-78	
Semi-automated block digester colorimetric .....	351.2		D3590-89(B)		
Manual or block digester potentiometric .....	351.4		D3590-89(A)		
Block Digester, followed by:					
Auto distillation and Titration, or .....					Note 39
Nesslerization .....					Note 40
Flow injection gas diffusion .....					Note 41

Table 1B Notes:

<sup>1</sup> "Methods for Chemical Analysis of Water and Wastes", Environmental Protection Agency, Environmental Monitoring Systems Laboratory-Cincinnati (EMSL-CI), EPA-600/4-79-020, Revised March 1983 and 1979 where applicable.

<sup>2</sup> Fishman, M. J., et al, "Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments," U.S. Department of the Interior, Techniques of Water—Resource Investigations of the U.S. Geological Survey, Denver, CO, Revised 1989, unless otherwise stated.

<sup>3</sup> "Official Methods of Analysis of the Association of Official Analytical Chemists," methods manual, 15th ed. (1990).

<sup>8</sup> The approved method is that cited in "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments", USGS TWRI, Book 5, Chapter A1 (1979).

<sup>35</sup> Precision and recovery statements for the atomic absorption direct aspiration and graphite furnace methods, and for the spectrophotometric SDDC method for arsenic are provided in Appendix D of this part titled, "Precision and Recovery Statements for Methods for Measuring Metals".

<sup>39</sup> Nitrogen, Total Kjeldahl, Method PAI-DK01 (Block Digestion, Steam Distillation, Titrimetric Detection), revised 12/22/94, Perstop Analytical.

<sup>40</sup> Nitrogen, Total Kjeldahl, Method PAI-DK02 (Block Digestion, Steam Distillation, Colorimetric Detection), revised 12/22/94, Perstop Analytical.

<sup>41</sup> Nitrogen, Total Kjeldahl, Method PAI-DK03 (Block Digestion, Automated FIA Gas Diffusion), revised 12/22/94, Perstop Analytical.

(b) \* \* \*

References, Sources, Costs, and Table Citations:

<sup>35</sup> "Nitrogen, Total Kjeldahl, Method PAI-DK01 (Block Digestion, Steam Distillation, Titrimetric Detection)", revised 12/22/94, Perstop Analytical. Method available from Perstop Analytical Corporation, 1256 Stockton, St. Helena, CA 94574. Table 1B, Note 39.

<sup>36</sup> "Nitrogen, Total Kjeldahl, Method PAI-DK02 (Block Digestion, Steam Distillation, Colorimetric Detection)", revised 12/22/94, Perstop Analytical. Method available from Perstop Analytical Corporation, 1256 Stockton, St. Helena, CA 94574. Table 1B, Note 40.

<sup>37</sup> "Nitrogen, Total Kjeldahl, Method PAI-DK03 (Block Digestion, Automated FIA Gas Diffusion)", revised 12/22/94, Perstop Analytical. Method available from Perstop Analytical Corporation, 1256 Stockton, St. Helena, CA 94574. Table 1B, Note 41.